ANNUAL REPORTS ON NMR SPECTROSCOPY

Volume 5A

E. F. Mooney

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NMR SPECTROSCOPY

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NMR SPECTROSCOPY

Edited by

E. F. MOONEY

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PREFACE

The ever-growing use of NMR in chemistry is again clearly reflected in the amount of data presented in the chapters. However, anticipating a recent comment about the price of these volumes, it has been decided to split this volume into two parts. Volume 5B is more specific, dealing with the NMR parameters of phosphorus compounds, and as such has appeal to those who might not normally be interested in the general aspects of these series.

It will be appreciated on examination of the first two chapters, dealing with ^{1}H and ^{19}F NMR respectively, that these two authors have made a really fine job of a very difficult task. The next two chapters update earlier contributions by these two authors who are acknowledged experts in their own fields. The fifth chapter updates an earlier chapter on nitrogen NMR written by different authors, while the sixth, on gallium and aluminium, completes the available information on the Group III elements. Finally, the last chapter deals with Fourier Transform Spectroscopy, which will answer the questions of chemists regarding this latest "answer to everything" in NMR Spectroscopy.

I am ever grateful to all the very helpful comments sent to me by readers of this series and to their very encouraging remarks as to the usefulness of these works; this is sufficient reward to the contributors and myself for the effort which goes into preparing these volumes.

Finally, I would express my gratitude to all the authors of this volume for their assistance, patience and the care with which they have prepared their manuscripts.

ERIC F. MOONEY

Anacon (Instruments) Ltd,
Buckinghamshire,
July, 1972

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THE CHEMICAL SHIFT SCALES

Readers are reminded of the convention for the presentation of chemical shift data introduced into Volume Three of this series. This self-consistent convention has now been used for some two years in various places and is gradually being universally accepted.

Convention adopted for Chemical Shift Scales

1. All shifts will be denoted by the delta scale, low-field shifts being shown as positive and high-field shifts as negative values. In all cases the standard will take the reference shift of δ 0·0.
2. No other symbols to denote shifts at infinite dilution will be used.

General Review of Proton Magnetic Resonance

T. N. HUCKERBY

Department of Chemistry, The University, Bailrigg, Lancaster, England

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I. INTRODUCTION

THIS REVIEW represents an attempt to present for the non-specialist a survey of some of the current uses which are being made of proton magnetic resonance spectroscopy and to collate scattered and potentially

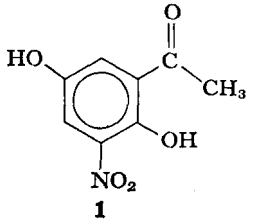
useful data or methods which may be of general value or provoke thought. In view of the breadth of topics embraced by current chemical science and the rapid growth in routine use of proton NMR (the references cited below were selected from some 1250 relevant papers in the 1970 literature) the author apologises in advance for the omission of much excellent material and also for any ignorance of earlier findings here cited as being apparently novel.

The Review is organised in a similar manner to a previous report[1] in this series which summarised the literature for 1968, and as before most of the information here presented has been abstracted directly from the original publications. Defined topics such as Carbohydrate Spectroscopy, the study of fluorine-containing molecules and conformational analysis, which are regularly covered in other chapters, are again only given brief attention.

II. EXPERIMENTAL TECHNIQUES

A. The sample

Two cautionary notes have been published concerning the use of dimethyl sulphoxide, with regard to its extreme hygroscopic properties. A routine spectrum of the acetophenone derivative (**1**) in DMSO-d_6 showed no sharp acetyl singlet, and investigation showed that deuterium exchange took place, *via* the traces of D_2O present in the solvent.[2] A report[3] that the tetrazole (**2**) existed in the amino form (**2a**), based on its NMR spectrum in DMSO-d_6 has been modified[4] by the observation that, with carefully dried solvent, a signal for the form (**2b**) can also be detected; addition of traces of water produced the spectrum reported earlier.[3] Caution in the interpretation of spectra from samples containing potentially labile protons is advised, if DMSO is used as solvent.



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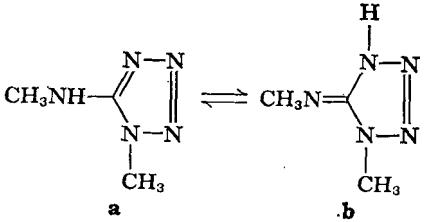


a **b**

2

Although liquid sulphur dioxide is widely used as a co-solvent in studies using strong acid media its potential as a solvent for more straightforward spectroscopic investigations has perhaps been neglected. In a study of the dimers of coumarin and *N*-methyl carbostyril,[5] it was

found that although these materials were poorly soluble in organic solvents, and showed almost equivalent cyclobutane protons, the use of liquid SO_2 as solvent gave good spectra and allowed complete analyses of the cyclobutane 4-spin systems in terms of geometrical configurations.

The novel use of a molten organic salt as NMR solvent has recently been described.[6] Using pyridinium hydrochloride as solvent, chemical shift measurements for varying concentrations of cetyldimethylbenzylammonium chloride showed a discontinuity at 0·06 mole kg^{-1} which correlated well with other physicochemical data, indicating the onset of micellation.

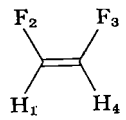
A simple and convenient method for the removal of dissolved oxygen from NMR samples has been given[7] in which the charged sample tube is sealed with a serum cap and attached to a water pump *via* a small gauge hypodermic needle while heated in warm air.

The accurate calibration of NMR sample temperatures has been discussed in two papers. In the first, standard samples have been calibrated against known reference points which were identified by the appearance of signals from solids upon melting, the references being contained in the inner chamber of a standard coaxial tube.[8] The other describes a study of the methanol "thermometer" down to its melting point.[9] Sharp lines were induced at all temperatures by the addition of a trace (0·03%) of HCl, and a quadratic equation was derived which fitted the data (measured using a static thermistor probe and a spinning tube) between 175 and 330°K. Convenient graphs are obtainable from the author for this and also for the ethylene glycol "thermometer". Both publications stressed that makers' calibrations were in error by up to 5°K.

B. Specialised solvent systems

1. *Nematic phase liquid crystals*

The study of solute molecules partially oriented in the nematic phase of liquid crystals in order to determine anisotropies of spectral parameters and to measure relative molecular dimensions is now being actively pursued. The current commercial availability of liquid crystals which exist in the nematic mesophase at normal NMR probe temperatures should now make further studies experimentally much easier.



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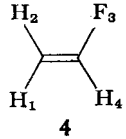

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Geometries have been obtained[10] for *cis*-1,2-difluoroethylene (**3**) and

vinyl fluoride (**4**). In the former compound the ratio r_{FF}/r_{HH} was found to be 1·080 which compares well with the microwave value of 1·079. For r_{14}/r_{12} the value was 1·218 which shows a 2·4% error with respect to the microwave ratio of 1·248. This may indicate an anisotropy in J (FH-*gem*) or J (FH-*trans*) but it should be noted that for this molecule, and for vinyl fluoride, the influences both of anisotropy and of molecular vibrations have been neglected. For the latter compound, with C_s symmetry it was necessary to assume two parameters (r_{12} and r_{13}—from microwave studies) in order to calculate bond distances and angles. The derived parameters are summarised in Table I.

TABLE I

Molecular dimensions for vinyl fluoride (4)

Parameter	Found	Microwave
α(∡ 1–2–4)	53·49 ±0·13°	..
β(∡ 3–2–4)	40·34 ±0·08°	..
r_{13}	3·304±0·005 Å	3·302 Å
r_{14}	2·484±0·002 Å	2·402 Å
r_{24}	3·090±0·005 Å	3·061 Å
r_{34}	2·014±0·003 Å	2·077 Å

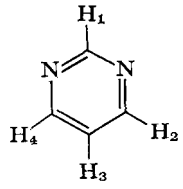
Liquid crystal techniques have been applied in the study of both cyclobutane[11] and bicyclobutane.[12] The monocyclic compound, analysed by a method which included the observation of ^{13}C satellites by spectrum accumulation, was found to be bent; the symmetry was D_{2d} with the molecule oscillating between the two equivalent bent conformers giving a spin Hamiltonian of D_{4h} symmetry. As part of a full isotropic analysis of bicyclobutane the values of D_{ij} between the *exo* pair and *endo* pair of protons were determined from a nematic phase spectrum in order to obtain an unambiguous assignment of chemical shifts for these nuclei.

The spectrum of oriented 2,2′-di(trideuteromethyl)-1,3-dioxolane has been discussed[13] in terms of its geometry and of dipolar couplings between hydrogen and deuterium. The molecular dimensions derived for pyrimidine[14] (**5**) are summarised in Table II, and differ significantly from those determined in an earlier partial microwave study. Although these deviations may be due to molecular vibrations a more complete microwave analysis should perhaps be made.

The nematic phase spectrum of 2,6-dichlorotoluene has been described[15] and an expression for the direct coupling between methyl protons and a proton positioned off the rotational axis given for the free

TABLE II

Molecular dimensions for pyrimidine



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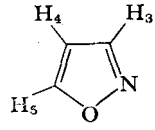
Parameter	Found	Microwave
r_{24}/r_{13}	1·706 ± 0·004 Å	1·712 Å
r_{13}/r_{23}	1·90 ± 0·02 Å	1·979 Å
r_{12}/r_{23}	1·62 ± 0·01 Å	1·695 Å

rotation situation. Similar results have been given for 3,5-dichlorotoluene,[16] and it was shown that NMR studies should in principle allow the determination of the positions of minimal energy of the rotational potential as well as approximate barrier heights, if the problem is sufficiently overdetermined and the precision of measurement is high.

Orientation parameters have been calculated[17] for $C_6H_5SiD_3$, $C_6H_5PD_2$ and C_6H_5SD in liquid crystal solutions, and the same authors have demonstrated that in phosphine the H–P–H angle is 95·3 ± 1°. When the nematic phase spectrum of bullvalene was measured at 130°, a symmetrical binomial ten-line multiplet was observed.[18] The linewidths were much larger than is normal but the spectrum was unmistakably characteristic of an oriented system containing ten equivalent nuclei. A consistent picture from the *spectroscopic* point of view is that the bullvalene remains in a single orientation while the proton spins are permuted rapidly over the surface of the molecule. The result is a single H–H coupling, being a statistically weighted average of the 12 independent couplings in the static molecule. The orientation parameter $|S|$ of 0·054 is surprisingly high, since the expected gross shape anisotropy is small.



6

The proton resonance and double resonance spectra of oriented isoxazole (**6**) are reported[19] in a paper which illustrates how the "spin-tickling" technique can be used to analyse complicated liquid crystal spectra. With this particular unsymmetrical molecule it is not possible to

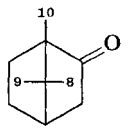
obtain a unique solution from line positions and intensities alone. The extra information needed to identify individual transitions was readily obtained *via* spin tickling, and afforded the dipolar couplings $D_{35} = -64 \pm 2$; $D_{45} = -300 \pm 2$; $D_{34} = -487 \pm 2$ for the experimental conditions used.

The spectra from partially ordered $^{13}CH_3F$ have been used to measure the anisotropies and absolute signs of the indirect coupling constants,[20] and the chemical shift anisotropy for a solute molecule in two completely different ordering media has been studied.[21] Very similar values were obtained for *p,p'*-di-*n*-hexyloxy-azoxybenzene and a lyotropic mesophase (D_2O—$C_{10}H_{21}SO_4Na$–$C_{10}H_{21}OH$–Na_2SO_4) as liquid crystal phases. Methane was found to be preferable as a reference standard—tetramethylsilane must exhibit shift anisotropy since multiplet structure is observed.

2. *Lanthanide shift reagents*

The observation by Professor Hinckley in 1969 that the bis-pyridine complex of tris(dipivalomethanato) europium(III) dissolved in organic solvents could induce "contact shifts" in suitable solute molecules while not adversely affecting spectral linewidths has prompted a flood of publications on this effect. The complex appeared to interact with basic sites and the influence of the paramagnetic nucleus on shifts dropped markedly with increasing separation of the protons from the position of interaction. Hinckley has himself[22] used the complex [abbreviated $Eu(dpm)_3.py_2$] to further illustrate its power, by separating the three different methyl singlets of camphor (**7**), and deduced that $\delta(9) > \delta(10) > \delta(8)$. Consequently it was used also[23] to distinguish between *exo*, *exo*-(**8a**) and *endo*,*exo*-3-acetoxy-5-chloronortricyclene (**8b**). The C*H*OAc and C*H*Cl signals moved smoothly downfield on sequential addition of $Eu(dpm)_3.py_2$. In both (**8a**) and (**8b**) the former signal moved by equal amounts, while the latter moved downfield three times as quickly in (**8b**).

An important improvement to the technique was contributed by Sanders and Williams[24] who demonstrated that the pyridine free deriva-



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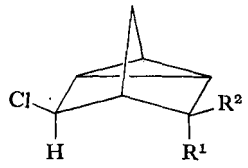


8a $R^1 = H$, $R^2 = OAc$
b $R^1 = OAc$, $R^2 = H$

tive $Eu(dpm)_3$ was more effective. This compound is very soluble in CCl_4 and introduces no interfering signals between δ0 to 16; it will complex with alcohols, ketones, esters, ethers, amines and other basic groups. The remarkable shift power is illustrated by the production of a first-order spectrum for *n*-hexane, which is reproduced in Fig. 1.

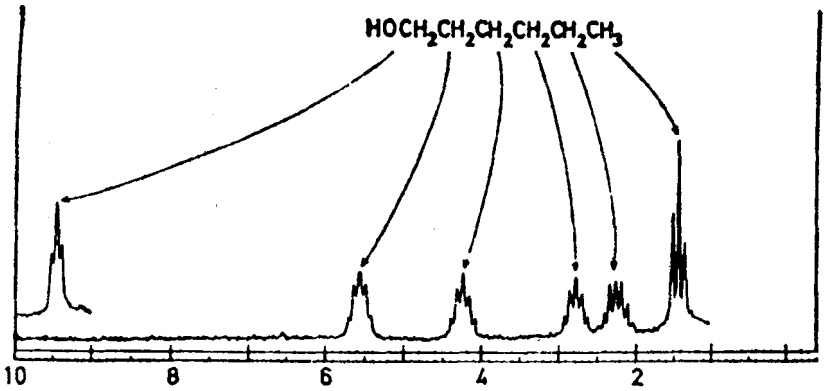


FIG. 1. 100 MHz ^1H NMR spectrum of *n*-hexanol in CCl_4 after the addition of $Eu(DMP)_3$ (0·29 moles). Superimposed trace offset 1 ppm. Chemical shifts in δ units (ppm) relative to internal Me_4Si. (From Sanders and Williams.[24])

Subsequently the power of other tris(dipivalomethanato) lanthanides as paramagnetic "shift reagents" was investigated.[25,26] The most important discovery was that the analogous praseodymium derivative, $Pr(dpm)_3$, also induced shifts without bad line broadening, but in the *opposite* direction. This means that a specific peak lying under an envelope otherwise composed of weakly affected protons may be displaced to which ever side of the band is most convenient. The relative shift powers for a series of lanthanides are summarised in Table III.

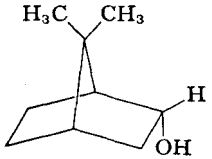
TABLE III

Relative powers of some tris(dipivalomethanato) lanthanides as "shift reagents"

Metal	Approx. power relative to $Eu(dpm)_3$[a]	Broadening effect (Hz/Hz of shift)
Pr	−1·1	0·05
Sm	−0·2	0·02
Eu	+1·0	0·003
Tb	−5·5	0·1
Ho	−7	0·02
Yb	+4	0·02

a. Negative values imply upfield shifts.

In several publications attempts have been made to quantify the induced shifts. The change in shift for all protons in an affected molecule is directly proportional to the mole fraction of complex present.[27,28] From a study of the rigid molecule borneol (**9**) using $Pr(dpm)_3$ com-



9

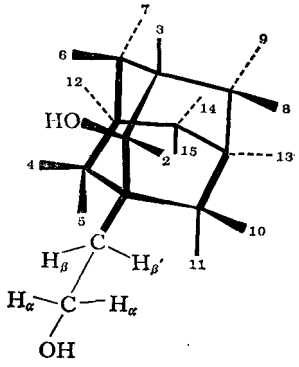
parisons were made between induced shifts and molecular dimensions in the assumed complex and a strong dependence was found upon the (O–Pr–H) internuclear angle.[27] From the interaction of a series of molar ratios (m) of $Eu(dpm)_3$ with borneol and other rigid alcohols[28] and extrapolation to values of the shifts for $m=0$ and $m=1$ paramagnetic induced shifts

$$\Delta_{Eu} = \delta_{CDCl_3} - \delta^{m=1}_{Eu(dpm)_3}$$

were calculated. From a plot on logarithmic axes of Δ_{Eu} *vs.* vector distances R (the distance between the hydroxyl oxygen and the proton(s) in question) an unexpected linear correlation with $(1/R)^{2\cdot2}$ was obtained. This value could be due to the neglect of angular variations mentioned above.

In the study of adamantan -1-ol and -2-ol evidence was shown[29] for the involvement of "through space" *and* "through bond" effects in the mechanism of deshielding in the presence of $Eu(dpm)_3$. The former appeared more important when four or more bonds were involved, if close approach of Eu and the proton involved was likely. In a separate investigation[30] adamantan-2-ol was studied, together with a series of 1-R-adamantanes [$R=(CH_2)_nOH$; $n=1$, 2, 3] and the conclusion was drawn that the direct effect was dominant for all protons. A plot of shifts *vs.* molar ratio of $Eu(dpm)_3$ gave a series of slopes "S", the "Europium shift parameter", and a satisfactory plot of these S values against r^{-2} (measured from molecular models) was obtained, i.e. similar to the relationship found[28] with borneol. This r/S relationship was then applied[31] to the molecule (**10**) which contains two potential binding sites. The shifts induced were consistent with a model in which the Eu atom was not chelating, but lay on a line connecting the two OH functions and was much closer to the primary site.

Although it thus does not yet appear wise to rigorously pursue a



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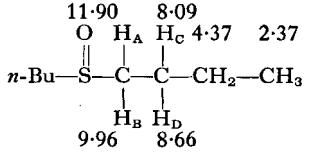
quantitative analysis of "shift reagent" data the technique has already been used to grossly simplify several otherwise unanalysable spectra. Williams *et al.*[32] have illustrated several ways in which the organic chemist may benefit. The substituent pattern up to 6 or 7 carbon atoms removed from an NH_2 or OH group may often be easily revealed in acyclic systems, and the "expanded" spectra are susceptible to double resonance. Aromatic systems give first-order spectra which enable the rapid location of non-complexing substituents. A spectacular simplification of the proton NMR spectra of carbohydrate derivatives has also been reported.[33]

The reagents accentuate formal magnetic non-equivalence[32,34] and a most striking example is that of dibutyl sulphoxide (**11**) where the

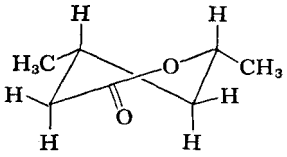


Shifts are given for a molar ratio of Eu(dpm)$_3$.
$J_{AB} = -13{\cdot}6$ Hz, $J_{CD} = -14{\cdot}0$ Hz.

11

diastereotopic nature of the β-protons is clearly revealed;[34] it has been possible to assign configurations to three rigid sulphoxides.[35] Proof for the proposed half chair conformations of the diastereomeric δ-lactones (**12**) and (**13**) has been sought by a study of their spectra in the presence of Eu(dpm)$_3$.[36]

The shift reagents are becoming of importance in the study of biologically important molecules. The NMR analysis of the hydrocarbon-like steroids and terpenoids has been severely limited by insufficient resolution of chemical shifts which is only partially overcome in 220-MHz studies. In a 100-MHz study[37] of 5α-androstan-2β-ol in the



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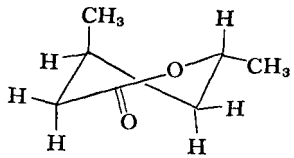

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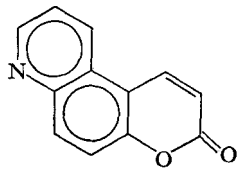
presence of $Eu(dpm)_3$ aided by decoupling experiments it was possible to unambiguously assign all ring-A protons, and some information was also obtained for those in ring B. The Lanthanide cations have been shown to act as excellent NMR probes for their immediate coordinated neighbours, and of their environment in enzymes including more distant molecules such as bound substrates.[38]

$Eu(dpm)_3$ has been used[39] to characterise a quinoline derivative as (**14**) rather than the isomeric structure (**15**).



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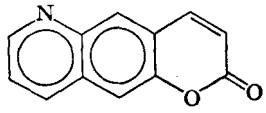

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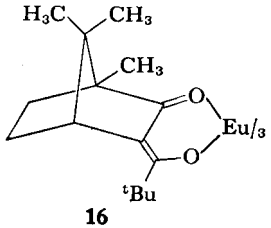
In order to obtain optimum results[32,33] it should be noted that the complexes slowly absorb water, and that reproducible results are most easily gained from freshly sublimed material and dry substrates. Some concentrations of the reagents may produce accidental shift equivalences as signals cross; sequential addition facilitates the location of optimal shifts for clarity of the spectrum.

Although the lanthanide complexes provide the neatest ways of inducing shifts, with minimal line-broadening it must be remembered that similar effects can be obtained with other paramagnetic species, albeit with much greater loss of signal resolution. Three papers have been published describing the use of Co(II)[40,41] and Ni(III)[41,42] acetylacetonates as shift reagents, and their use in preference to the lanthanides might possibly be justified on grounds of economy! The Co(II) derivative was used to distinguish between *cis* and *trans* cyclic diols[40] and in conjunction with the Ni(II) analogue in an investigation of the conformation of some substituted aniline derivatives.[41] The latter reagent also facilitated the assignment of protons in some ethylene episulphoxides.[42]

A lanthanide derivative for determining enantiomeric purity, tris

3-(*tert*-butylhydroxymethylene)-*d*-camphorato europium(III) (**16**) has been described.[43] Its properties are similar to $Eu(dpm)_3$ except that it is appreciably more soluble in non-polar solvents and it has signals located in the range $\delta = +2$ to -1. Examination of the proton NMR spectra of polar chiral substrates in optically active solvents has been previously described and the small shifts induced have proved a valuable method for the determination of enantiomeric purity. The derivative (**16**) allows the observation of relatively *large* shift differences between resonances of enantiomeric substrates dissolved in *achiral* solvents.



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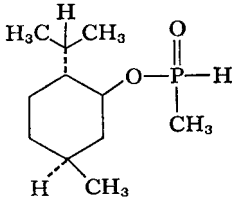
3. *Chiral systems*

A correlation of the NMR sense of non-equivalence of (−)-α-phenylethylamine salts of chiral phosphorus thioacids has been correlated with their absolute configurations.[44] However, a warning has been given[45] that, because of chemical shift perturbations by ion-pair aggregation, the sense of spectral non-equivalence for diastereomeric salts may not be readily correlated with the relative (or absolute) configurations of the diastereomers. Thus, although this correlation technique has proved reliable for diastereomeric solvates formed by enantiomeric solutes in chiral solvents, caution should be exercised in the study of diastereomeric salts.

The principle of diastereoisomerism is being used extensively for the identification and quantitative estimation of epimers and a few examples are given below. NMR has been used to check the optical purity of an epimer of the menthyl methylphosphinate (**17**),[46] and measurements at elevated temperatures were used[47] to determine the optical purity of



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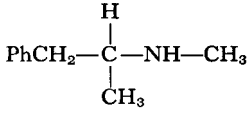

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(+)-(*S*)-deoxyephedrine (**18**) in order to remove torsional diastereomerism and leave only intrinsic effects. The technique has been used also to determine the absolute configurations of some diastereomeric Co(III) complexes of optically active amino acids[48] and terpenes[49] and in an absolute geometrical study of Pt(IV) propylene-diamine coordination complexes.[50]

4. *Miscellaneous studies*

The *anhydrous* salts $NiCl_2$ and $CoCl_2$ have been found to dissolve in organic solvents containing the trialkyl phosphites $P(OR)_3$ ($R = CH_3$, C_2H_5) with the spectroscopically observable formation of complexed species.[51] The effect of this complex formation is to cause relaxation of the phosphorus nucleus such that it is effectively decoupled from protons which previously showed a P–H coupling. Figure 2 illustrates the effect on $P(OEt)_3$ where the methylene group is reduced to a quartet.

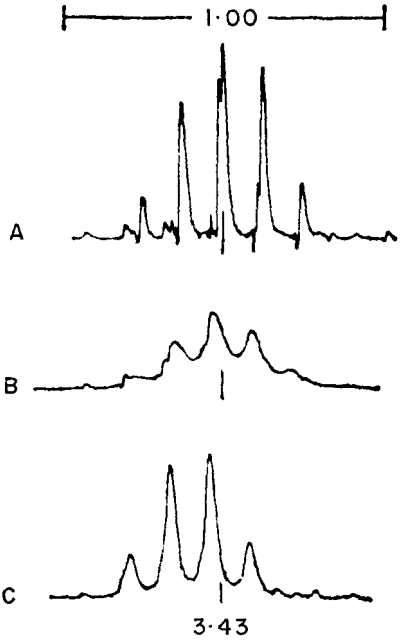


FIG. 2. A—1·2 M-triethyl phosphite in benzene; B—1·55 M-triethyl phosphite, 1·91 10^{-2} M-$NiCl_2$ in benzene; C—$7{\cdot}92 \times 10^{-1}$ M-triethyl phosphite, $4{\cdot}33 \times 10^{-2}$ M-$NiCl_2$ in benzene. Positions given in ppm upfield from benzene. (From Engel.[51])

Several studies have been reported on bulk and complexed ions associated with suspensions of ion-exchange resins. The proton NMR spectra of some cross-linked cation exchange resins in ther $H^{\oplus}$, $Li^{\oplus}$,

$Na^{\oplus}$, $K^{\oplus}$, $Rb^{\oplus}$, $Cs^{\oplus}$ and $NH_4^{\oplus}$ forms have been recorded[52] and the molar chemical shifts $\delta^0_{M\oplus}$ summarised. These shifts were very similar to those obtained in the corresponding aqueous systems indicating similar interactions. The temperature-dependent chemical shifts between resin-phase and bulk water in aqueous suspensions of ion exchange resins has been used to estimate the hydration number of a number of resin-phase counter-ions.[53]

The rate of free exchange of water protons between the interior and exterior regions of an ion exchange bed has been determined by a double resonance method[54] which also afforded values for the longitudinal relaxation times of the different protons. A mixture of cation exchange resins in two different forms will, when in physical contact, undergo ion scrambling. The variation in chemical shifts was used to investigate this process,[55] and the NMR method is free of ion selectivity and co-ion effects.

C. Instrumental methods

1. *The nuclear Overhauser effect (NOE)*

This technique has now become an important method for gaining information on the spatial proximity of protons or groups of protons and has been the subject of a short review showing typical applications.[56] It has proved possible to quantitatively relate the signal enhancements observed in NOE experiments to the internuclear distances between the protons involved.[57,58] A relationship of

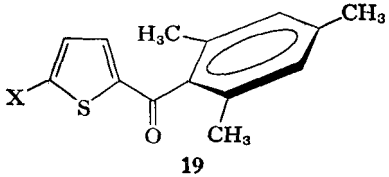
$$\frac{1}{\%\ \text{NOE enhancement}} = A(r_{AB})^6$$

was found where r_{AB} is the internuclear distance between two protons (or a proton and the centre of the circle described by a rotating methyl group), with $A = 1{\cdot}8 \times 10^{-2}$ (H–H) or $0{\cdot}8 \times 10^{-2}$ (H–CH_3).

Overhauser enhancements at the formyl proton of dimethylformamide have been measured at and above room temperature.[59] At 90°, separate irradiation of the two methyl singlets resulted in equal enhancements although the system was well below the coalescence temperature. This was explained in terms of differing time scales for the NOE (related to the relaxation time T_1 of the methyl groups) and the coalescence process (dependent on the signal frequency separation). The point was made that the mere occurrence of an NOE in an unknown compound is *not* sufficient evidence for the time *in*dependent close proximity of the nuclei; the sole inference from single temperature studies must be that two nuclei (or groups of nuclei) can be located in each other's neighbourhood for some period of time. A further paper has also appeared on the correlation

of NOE's with conformational preferences in a series of amides.[60] By using NOE to make resonance assignments in some benzamides,[61] tertiary amides[62] and thioamides[62] several inaccuracies in previous literature reports have been brought to light. Shift arguments alone should not therefore be used as an unambiguous method.

The NOE is an excellent tool for the investigation of molecular configurations and preferred configurations. For example 2-thienyl carbonyl derivatives [e.g. (**19**)] have been shown to exist exclusively in the *s-trans* conformation[63] and the observation of signal enhancements has allowed configurations to be assigned for some substituted 1,3-dioxanes[64] and β-lactams.[65] The preferred orientation of 9-alkyl groups in a series of 9-alkyl-9,10-dihydroanthracenes was shown[66] to be pseudo-axial as in (**20**) by NOE observations, and this was confirmed by the observation of long-range ^5J homoallylic couplings. Configurational assignments made[67] for the dibenzthiepin sulphoxide (**21**) reverse tentative arguments previously suggested.



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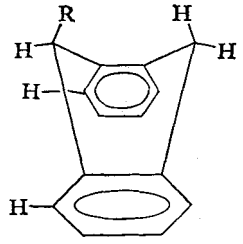

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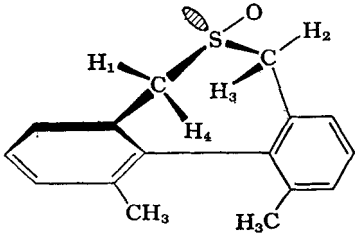
NOE measurements have proved an excellent way of determining the 3-dimensional skeletal arrangements of a wide variety of natural products and their derivatives. For example, irradiation of the N-CH_3 group in ring B of geneserine[68] has shown the absolute configuration to be (**22**). It should be mentioned that an identical conclusion was reached from a variable temperature study of the nitrogen inversion process in this compound.[69] A Japanese group has successfully applied Overhauser



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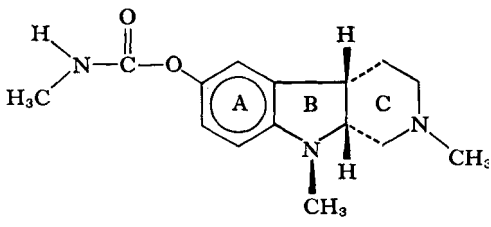

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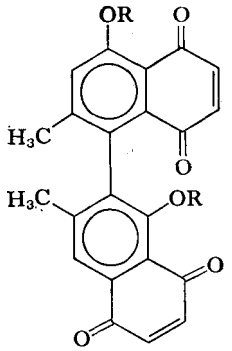
studies in a study of the stereochemistry of a series of furan sesquiterpenes.[70 to 72] Enhancements induced by irradiation of the methyl and methoxyl signals in the dimethyl ether of isodiospyrin (**23**) disclosed the relative positions of these on the aromatic rings.[73] Structural proof was based on NMR analysis including the observation of an Overhauser enhancement for a series of 6-thiasteroids,[74] including 8-*H*-iso-6-thiaestrone (**24**).



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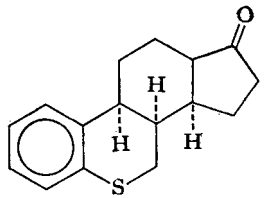

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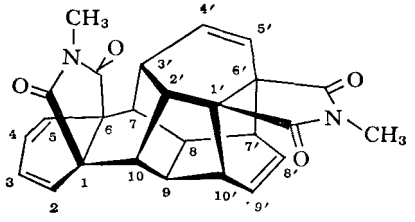
The observation of Overhauser effects in some penicillin sulphoxide[75] and cephalosporin[76] derivatives has allowed configurational and conformational assignments to be made. It seems that NOE measurements may be of some considerable value in the study of biochemical interactions; evidence for the intercalation of purine between the bases of single stranded nucleic acids has been obtained.[77] Strong irradiation of H(3′) H(5′) and H(5″) ribose protons gave purine signal enhancements which suggested a complex oriented so that the purine H(6) or H(8) protons were close to the ribose.

Large enhancements have been observed between ^{1}H and ^{19}F in a series of fluoroaromatic derivatives.[78] This heteronuclear effect implies that it should be possible to use the halogen atom(s) in such compounds as fluoro-steroids in order to gain conformational and configurational information.

2. *Other double resonance techniques*

The INDOR technique provides a useful way of discovering the nature of resonances hidden in an unresolved signal envelope if other nuclei to which they are coupled can be clearly observed. A simple modification has been described[79] which allows a Varian HA-100 spectrometer to be used routinely for ^{1}H–^{1}H internuclear double resonance (INDOR) experiments, and several examples shown illustrating

its value in the carbohydrate field. This technique has also been applied[80] in a precise determination of the frequencies of hidden lines (leading to values of chemical shifts and coupling constants for these protons) in the spectrum of a propellane dimer, allowing its structure to be defined as (25). A combination of partial decoupling and INDOR has been used[81]



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to measure splittings small enough to be obscured by magnetic field inhomogeneities. In this way a coupling of $0{\cdot}10 \pm 0{\cdot}01$ Hz was discerned in 2,3-dibromopropene. A detailed study of the ring A nuclei in 2α-fluoro-cholestan-3-one has been made which illustrates the potential both of a proton-proton INDOR technique (to probe beneath the methylene envelope) and of proton-fluorine heteronuclear decoupling experiments.[82] Specific details have been given for the design of an inexpensive heteronuclear decoupler for the HA-100[83] together with suggestions for suitable sources of AF noise,[83,84] which should make heteronuclear decoupling more widely available at the "application" rather than the "research" level. Relatively modest modifications for a routine 60-MHz proton NMR spectrometer have been described which afford excellent spectra of "other nuclei" which are coupled to protons.[85]

3. *Chemically induced dynamic nuclear polarisation* (*CIDNP*)

The presence of free radicals produced by a reacting chemical system under study in an NMR spectrometer can be detected by the observation of lines showing enhanced absorption or emission of RF energy. A theory which satisfactorily explains the observed spectra from various systems has been developed by Closs.[86 to 88] A *caveat* in the interpretation of CIDNP emission signals has been presented[89] following the observation of such bands in the thermal rearrangement of benzyl toluene-*p*-sulphenate to benzyl-*p*-tolylsulphoxide, which could not have arisen as a result of the reaction itself. It is probable that the emission signal was an artefact from the homolytic cleavage of the rapidly produced product.

Emission bands have been observed during the rearrangement of some nitrogen[90,91] and sulphur[92] ylides. Evidence has been reported[93] for radical character in the reactions of simple alkyl Grignard reagents with

alkyl bromides and iodides; systems in which there has been speculation as to the degree of radical and ionic character for many years.

The mechanism of reaction between *N,N*-dimethylaniline oxide and acetic anhydride to yield *o*-acetoxy-*N,N*-dimethyl-aniline has been a subject of controversy. Under no circumstances was it possible to observe CIDNP spectra for the main reaction products[94] therefore it appears that a free radical pair is not involved as an intermediate. A related reaction mechanism, between 2-picoline *N*-oxide and acetic anhydride has similarly been clarified.[95]

CIDNP studies have been made of some photo-induced reactions, in order to identify the species involved. The photo-induced decomposition of methyldiazoacetate ($N_2CHCO_2CH_3$) in chloro-substituted methanes appears to involve a radical chain mechanism as derived from spectra recorded during and immediately after UV irradiation.[96] A relaxation time of *ca.* 70 seconds indicated that products must still be forming in the post-irradiation period. Photolysis of benzaldehyde in solution was shown to involve a radical pair as one of the intermediates.[97]

4. *Spectra at 220 MHz and higher frequencies*

The high field strengths afforded by superconducting magnets are being put to great chemical use. Instruments producing proton NMR spectra at 220 MHz are now widely used both in the induction of first-order spectra for small molecules and for the extraction of previously obscured information from both synthetic and biological high polymers. The feasibility of producing 300-MHz spectra has been demonstrated in the past year.

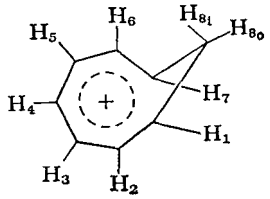
A few selected studies made possible by ultra-high field instruments are outlined below.

At $-50°$ the 220-MHz NMR spectrum of the complex $H_2Fe[P(OEt)_3]_4$ showed a triplet of doublets, which, by comparison with a simple quintet observed at $+50°$ afforded the first unambiguous example of stereochemically non-rigid behaviour in 6-coordinate complexes.[98]

The enhanced shift separation can often reveal previously hidden magnetic non-equivalence. Such an effect has been observed in high-field spectra of some Group VIB alkyls.[99] The results are consistent with steric hindrance to rotation about C–M bonds. Spectra obtained at 220 MHz can provide useful initial parameters for the complete solution of high-resolution spectra obtained at lower frequencies in terms of accurate shifts, couplings and relative signs. Such an approach has been used in a study of the conformation of 3,4-cyclopropylproline.[100]

Proton spectra obtained at 251 MHz have been used[101] for a study into the nature of the monohomotropylium ion (**26**), and afforded a complete

assignment of all signals. A combination of 100- and 251-MHz NMR spectra for *trans, trans*-1,4-bis-(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene show no evidence for valence tautomerism.[102]



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A conformational analysis of some cannabinoids has been facilitated by the use of high-field studies.[103] Cellulose derivatives have been used[104] as examples to show how 220-MHz spectroscopy may be applied in structural studies of polysaccharides, in order to distinguish between hexoses and pentoses, to discern the nature of the glycosidic bond, etc. The characteristic features in the 220-MHz spectra of heparins have suggested[105] a rather different proportion of D-glucopyranosyluronic residues to that previously proposed. It has been possible with the aid of spectral accumulation[106] to observe resonances for the NH protons of the tryptophan residues in myoglobin and oxomyoglobin.

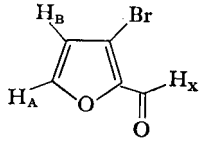
5. *Other techniques*

The observation of double-quantum transitions in second-order spectra recorded under high-power levels can provide extra information which aids their interpretation. Most DQT studies reported have been for 3-spin systems. The method has been extended[107] to include some types of larger molecules, where it is possible to isolate a 3-spin sub-system by spin decoupling. The allyl cyanide and 3-methyl thiophene spectra were taken as examples. In the assignments of DQT's, spin tickling experiments involving these transitions proved useful, and can provide a very accurate way of assigning the frequencies of the double-quantum transitions.[108]

In a study of conformational changes in trisalicylides involving line shape studies, it was emphasised that low RF power levels (0·015 to 0·02 mG) were used in order to obtain steady-state spectra.[109]

Fourier transformation techniques are being reviewed separately (see p. 557), but it should be mentioned that this pulsed NMR experiment can overcome line broadness arising from a failure to satisfy "slow passage" conditions. By this means, for example, values for long-range

couplings can be obtained[110] which would be very difficult to resolve using conventional systems, as is seen for instance in (**27**) where $J_{BX} = 0{\cdot}05$ Hz.



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The Los Alamos Scientific Laboratory has described[111] a wide-line NMR system which can take an NMR spectrum from a whole living animal. Protons in water, proteins and lipids display characteristically different signal widths, and the system seems potentially valuable for quantitative *in vivo* determinations both for protons and other nuclei.

D. Computational methods

Haigh[112] has published full details of his modified notational method for the description of spin systems in NMR spectroscopy. The above system will be used where appropriate in this Review and is briefly described here. It presents a more economical way of indicating that a similar group of nuclei is repeated one or more times in a molecule than is allowed by the use of primes. It is stated that "square brackets (with subscript numbers) shall be used to indicate repeated symmetry related magnetically non-equivalent groups of nuclei. All strictly isochronous nuclei *within* a square bracket are to be considered magnetically equivalent unless the contrary is specified by the use of further square brackets. In the same way, the square bracket (without a subscript) shall be used to denote the magnetic equivalence of isochronous nuclei inside it." Thus each square bracket implies a specific symmetry operation (or set of operations). In cases of ambiguity which can arise where three-fold or higher symmetry axes may be possible, the relevant point group must be appended in round brackets. For example, cyclobutene is represented as $[[A_2]X]_2$ where the inner brackets represent the ring plane, the outer brackets the perpendicular plane. Others are listed below:

ortho Dichlorobenzene	$[AB]_2$
Sulphur tetrafluoride	$[A_2B_2]$
Pyridine	$[AB]_2C$
1,3,5-trifluorobenzene	$[AX]_3$ (C_{3v})
Biphenyl	$[[AB]_2C]_2$ (D_{2d}, rot.)

Accidental shift equalities, not related to symmetry, are specifically excluded from consideration.

The properties of NMR spectra arising from three protons have been explored in two papers. In the case of two isochronous nuclei[113] (labelled AA'B or AA'X to denote the absence of a *symmetry* equivalence) the experimental occurrence was discussed, and the proton NMR spectrum of $CH_2BrCHDCl$ analysed as an example containing an aa'b subspectrum. In a detailed analysis of the vinyl protons in methyl acrylate, two exact solutions were found for both the 60- and 100-MHz spectra, which gave identical transition energies and assignments,[114] even though the molecular parameters obtained differed considerably. The two solutions at 100 MHz yielded couplings of differing signs, but could not be differentiated by tickling experiments. The reasons, and the general problem of determinacy in the analysis of NMR spectra, were discussed.

Problems in the unambiguous analysis of spectra with $[AB]_2$ symmetry have been discussed in two papers. One method of solution is based on a simultaneous treatment of resonance frequencies obtained when the chosen spectrum is measured at two or more differing field strengths.[115] In the other, a previously published scheme[116] was modified[117] by the introduction of a revised criterion Δ_1' which always appears to be a minimum for the correct assignment and is related to various transition energies in the spectrum. A theory[118] has been developed relating the vicinal coupling relationships L $(=J-J')$ and N $(=J+J')$ in $[AB]_2$ spectra of disubstituted ethanes in terms of rotational averaging and potential function characteristics which allows the determination of physical parameters.

The quantitative analysis for parameters describing rate processes and energy barriers by the simulation of NMR spectral line shapes is becoming an important technique. Binsch[119] has published the formalism involved in his highly sophisticated computer program DNMR3 which can be used for the quantitative study of complicated exchange-broadened NMR spectra, and has illustrated some of its uses. A method has been developed[120] for the complete digital analysis of NMR line shapes, using a small instrument computer, and illustrations are given of the determination of exchange rates in a variety of systems.

It has been concluded[121] that systematic correlations between experimental and theoretically derived chemical shifts can be reliably made only when the measured shifts have been obtained by the iterative second-order analysis of spectra obtained at or near infinite dilution in a common isotropic solvent. It is now widely recognised that spectra calculated from parameters assumed in terms of a model geometry can be valuable in ascertaining stereochemistry. This method has been used, for

example, in a study of the ring fusion in some 3-oxabicyclo -octanes and -nonanes.[122] In iterative analyses of complicated spectra it should be noted that there could be signal regions involving many overlapped lines such that insufficient single transitions are observable to enable a computation to converge.[123]

III. CHEMICAL SHIFTS

A. Semi-empirical considerations

The twentieth anniversary of the discovery of the chemical shift phenomenon has been (belatedly) commemorated in a short historical review[124] which also focused attention on the variety of chemical shift definitions currently used. Differences and inconsistencies were discussed, and a self-consistent set of shift definitions was proposed.

The McWeeny "ring current" theory has been critically evaluated[125] against a set of consistent accurately determined chemical shifts for protons in planar unsubstituted condensed hydrocarbons and gave a good account of values for non-hindered positions. This approach was successfully extended[126] to shifts observed for all the known planar hexacyclic condensed hydrocarbons. This method has also been used[127] to show that the assumption of equal ring currents in 5- and 6- membered rings is not valid; the former appear to be much smaller.

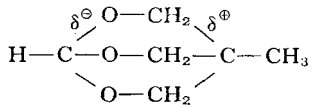
Some proton chemical shifts have been calculated[128] using Ramsey's equation for the nuclear shielding constant. Satisfactory agreement with experiment was found for acetylene. Electron charge densities have been calculated[129] for several substituted benzenes using the parametric approach proposed by Del Re. The charge density at positions *ortho* to substituents gave a good linear correlation with observed shifts. Spectral parameters have been reported[130] for the isomeric trithienyl carbonium ions which indicate a linear correlation between shifts and π-charge densities, the proportionality constant being higher than that found for benzene derivatives. A correlation between the shifts of non-angular protons and the corresponding partial rate factors of various electrophilic and other reactions has been observed.[131] A good linear correlation was noted[132] between π-electron densities determined by the SCF method and proton chemical shifts in a series of ten cyano-substituted pyridines.

An approach to the calculation of NMR solvent anisotropy shifts for non-polar solutes in benzene has been given in which the hard sphere and hard disc model is modified to take account of attractive Van der Waals forces, and in which non-polar solutes of arbitrary shape can be considered.[133] An alternative model which is simple, but with apparent accuracy has also been proposed.[134]

B. Shifts induced by aromatic solvents

The stoicheiometry of association between benzene and several polar solvents has been determined from the solvent shifts at various concentrations,[135] and it is suggested that there is a continuum of behaviour. For instance, chloroform forms 1:1 complexes while ketones only associate randomly with benzene.

The use of hexafluorobenzene for inducing aromatic solvent shifts has been investigated,[136] and its inertness and lack of protons would appear to make it a useful alternative to chloroform. Unusual solvent effects due to benzene and hexafluorobenzene in aromatic shift effect studies on molecules such as (**28**) have been reported.[137] In benzene, strong downfield shifts are observed for the proton at the negative end, whereas with C_6F_6 a new aromatic shift phenomenon is seen in which the same proton signal is displaced upfield. The results are interpreted in terms of a solvent cluster model, as indicated in (**29**) for benzene and (**30**) for C_6F_6. When 1-methylnaphthalene was used as an alternative solvent for a study of the geometry of cyclic ketones,[138] it was found that a big increase in the aromatic solvent induced shift occurred, relative to that observed with benzene.



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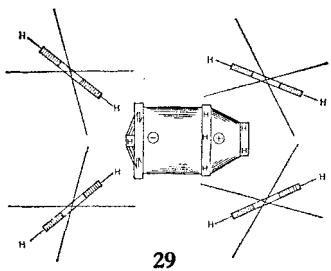

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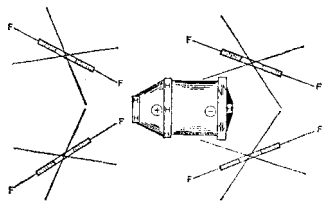
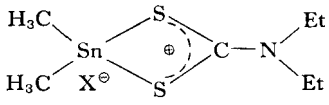


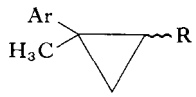
30

In changing from carbon disulphide to benzene as solvent for some compounds of type (**31**) the chemical shifts of the *N*-ethyl groups were found to move upfield by 0·4 to 0·6 p.p.m.[139] This could possibly arise from stereospecific solvation of the planar dithiocarbamate group by benzene, placing the *N*-alkyl protons in the diamagnetic region of the benzene ring.



X = Cl, Br, I, S·CS·NEt$_2$

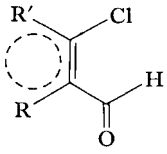
31



R = CN, CONH$_2$, CO$_2$H

32

Aromatic solvent-induced shift (ASIS) studies have been used to assign specific structures to the stereoisomeric derivatives (**32**) of cyclopropane,[140] and for an assignment of geometry to some β-chlorovinyl aldehydes[141] and chloro- or dichloro- olefins.[142,143] With the aldehydes, the benzene associated in such a way that it was remote both from the halogen and the negative end of the C=O dipole, as in (**33 a** and **b**). For the chloro- or dichloro- olefins it was observed that protons or methyl groups *trans* to chlorine in a vinylic system experienced a greater solvent shift than when in a *cis* position.



a

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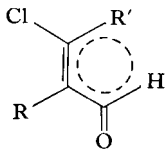
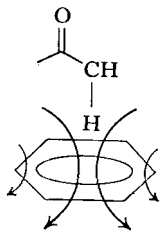


b

The shifts induced by aromatic solvents in a series of polar compounds bearing acidic hydrogens have been determined.[144] Those activated by electron withdrawing groups showed large upfield shifts, and the values could be interpreted successfully in terms of a model involving C–H$_\pi$ hydrogen bonding, as in (**34**). The values of $\Delta\delta$ [$=\delta(CCl_4)-\delta(C_6H_6)$] measured for a series of substituted 1,3-dioxanes[145,146] have proved valuable in the assignments of some signals and for confirming molecular geometry.



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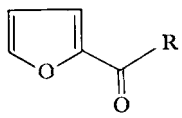
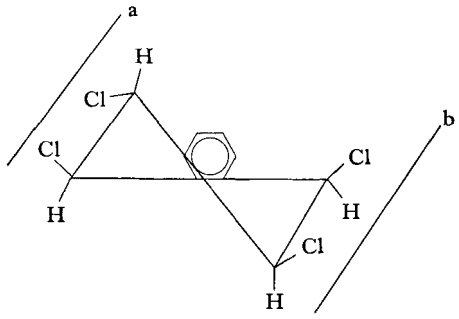


35

For saturated and unsaturated ketones it is already known that ASIS values are positive for protons lying behind a reference plane through the

carbonyl carbon atom perpendicular to the C–O bond, and negative otherwise. This relationship has been used[147] in a study of 2-carbonyl furans together with anisotropy considerations using the new model of ApSimon (see p. 32) in order to confirm that the most abundant rotational isomer is indeed (**35**), as was predicted by long-range couplings and Overhauser studies.[63] For lactones it has been shown that ASIS parameters are in general positive, but much smaller, for protons in front of the reference plane than for those behind it.[148]

From benzene solvent shift measurements on a series of polysubstituted benzene derivatives (with respect to values in cyclohexane as a reference solvent) an additivity effect was observed involving the Taft substituent constants σ_m° and σ_p°.[149] It was suggested that charge effects were much more important than steric effects in determining both the magnitude and sign of $\Delta\delta$. In a study of the dehydrochlorination of some naphthalene tetrachlorides[150] it was found that the reactions were substantially dependent on the solvent in a way which indicated complex formation. It was possible to correlate these observations with aromatic solvent shifts of the protons of the alicyclic group; one probable interaction is shown in (**36**).



36
a, b are aromatic solvent molecules

For a series of substituted biphenyls ASIS values were observed[151] which could be divided into two contributions; one arising from a benzene solvent molecule coordinated with the substituent, and the other from benzene solvent molecule(s) weakly associated with the rest of the solute.

Solvent-induced shifts can be of value in assigning the configurations and conformations of natural products and their derivatives. Examples of this are to be found in the analysis of benzene- and pyridine- induced

shifts for some derivatives of santonene,[152] and in the pyridine ASIS values reported for some beyerine alcohols.[153]

C. Other medium effects

Using a coaxial sample technique[154] the shifts of non-polar solutes in a range of solvents have been measured relative to hexamethyldisiloxane, and the factors contributing to the solvent shifts deduced from a graphical analysis. Gas-phase shifts of non-polar molecules could also be estimated from the graphs. A new technique for measuring bulk susceptibility differences, and obtaining reference independent NMR solvent shifts has been described[155] which also uses coaxial samples, and takes advantage of the different magnetic field geometry between conventional and superconducting magnet spectrometers. A new procedure, based on an external referencing method which largely accommodates screening effects of the media, has been described for the investigation of molecular interactions in a two-component solution.[156] It was incidentally demonstrated that the shift position of cyclohexane is inert to benzene, while TMS interacts strongly. A study has been made[157] of the variation of "neighbour anisotropy" screening with mixture composition, in which it was proposed that this variation was a function of the "degree of perfection" of the mixture. The authors suggest that this technique might afford a simple means of determining whether a mixture is perfect, for such mixtures give linear plots of anisotropy against mole fraction of one of the solutes.

The proton chemical shift measurements on water-solubilised benzene have been extended[158] to include an anionic and a neutral surfactant. Such measurements can be used to estimate Z, the character of the medium (where $Z=0$ for pure water, and 1 for pure saturated hydrocarbon).

Three papers have discussed systems in which solvent reaction field effects are seen to be important. Solvent effects on the spectrum of pyridine have been proven to be dominated by reaction fields[159] and in a study of the solvent dependence of shifts and couplings in the 1,2-dichlorofluoroethylenes it was concluded[160] that the dominant factor operating was the reaction field of the solvent.

A study of solvent effects on the internal chemical shifts of six aromatic molecules C_6H_5X ($X=NO_2$, NH_2, F, Cl, Br and I) showed a good linear relationship with the dielectric function formulated by the reaction field theory over a wide range of dielectric constant.[161]

The importance of site factors in NMR solvent effects arising from interactions between different types of molecules has been discussed, and the site factors illustrated graphically.[162]

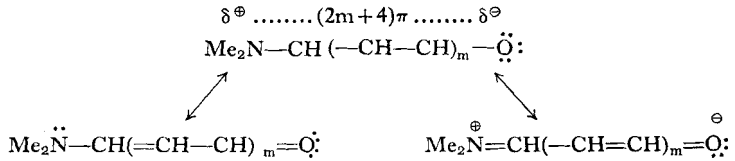
The proton NMR spectra of some amino- and hydroxy- pyrimidines have been measured in the four solvents: trifluoroacetic acid (TFA), TFA–SO_2, FSO_3H and FSO_3H–SbF_5–SO_2 at 27° and −55°.[163] The structures of the mono- or di- protonated species could be derived from the chemical shifts. All signals could be assigned, and this approach was also recommended for the structural determination of other heterocyclic compounds.

Some NMR chemical shift studies have been described in which spectral parameters are used to determine basicities. Using the non-aqueous solvents TFA–H_2SO_4 and TFA–CF_3SO_3H a value[164] of pK = −10·2 was obtained for acetaldehyde, indicating that it is less basic than expected. This approach has been extended to a determination of ketone basicity and allows the use of ketones as indicators for evaluations of medium acidity.[165] It has the advantage of being rapid, and has no colour purity requirement. A similar basicity study of some aliphatic ketones in sulphuric acid has also been described.[166] An arbitrary acidity scale has been proposed for peptide hydrogens using kinetic data obtained *via* NMR shift studies.[167]

On the basis of NMR shift measurements for a variety of hydrocarbons and their organo-lithium derivatives a simple method for determining quantitatively the acidity of weak carbon acids has been proposed.[168]

On the basis of the small shift changes observed between spectra obtained in DMSO and in CH_2Cl_2 or CCl_4 for a series of alkenyltin compounds it has been concluded[169] that there are no significant π-interactions between the *d*-orbitals of tin and the olefinic π-systems.

As shown by UV and NMR investigations, simple merocyanine dyes exhibit a polyene-like electron structure in non-polar solvents, while showing a polymethine state in polar solution.[170] The resonance contributors are shown in (**37**).



37

D. Substituent effects

The chemical shifts due to the bromomethine proton in a series of conformationally constrained α-bromo- and α,α′-dibromo- cyclohexanones have been given,[171] and are found to be a remarkably reliable

index of the axial or equatorial nature of the protons in question. Additive diamagnetic shifts for xanthones with *o*- *m*- and *p*- OH, OR and R substituents have been determined empirically; the predicted and experimentally observed shifts agree well providing that allowance is made for steric hindrance.[172] In an attempt[173] to shed further light on the effect of polyatomic highly polar substituents on methine chemical shifts, the proton shifts of some benzhydryl compounds have been determined. These cannot be predicted satisfactorily by Shoolery's rules, and do not correlate with shifts for the methylene protons in the corresponding benzyl compounds; this could be on account of a deviation from sp^3 hybridisation in benzhydryl groups.

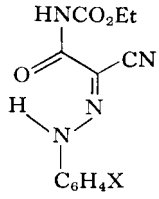
Substituent chemical shifts have been determined for some quinolines,[174,175] quinoxalines[175] and naphthalenes.[175] The effects parallel those in benzene derivatives except that these shifts are modified by partial bond fixation, steric hindrance or other effects which are at least qualitatively understood.

The NMR spectra of some methylpolygermanes have been measured at 220 MHz, and differences of chemical shift sufficient to allow structural assignments were found.[176] The δ-values generally fell in the order $Me_3Ge < Me_2Ge < MeGe$, as has already been found for poly- silanes and -stannanes. However, in the linear compound (**38**) the central Me_2Ge resonance is to high field of the flanking Me_2Ge groups, contrary to the situation found for the Si analogue.

$(Me_3Ge.GeMe_2)_2GeMe_2$

38

In several publications covering a wide range of structural types, Hammett-type correlations have been reported involving chemical shifts. In aryl thioureas[177] the aromatic shifts agreed well with calculated values if a substituent constant of −0·03 p.p.m. was assumed for the –NH·CS·HN– group, while the NH chemical shifts were correlated with Hammett substituent constants for the *para* positions. A similar correlation for NH shifts was found in a series of hydrazo compounds of type (**39**).[178] Measurements of the acetyl chemical shifts for a range of

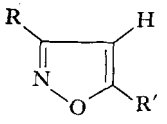


39

substituted acetophenones[179] demonstrated that although the extreme $\delta(COCH_3)$ values for *m*- and *p*- substituted derivatives differed by only 0·2 p.p.m., the individual shifts were linearly correlated with the corresponding Hammett σ values; no such relationship held for *o*-substituents.

The Hammett treatment of shifts for aromatic side-chain protons has not always proved successful. This failure has been ascribed to the neglect of long-range magnetic effects and when corrections[180] were made, both for ring current diminution because of polar canonicals and for substituent magnetic anisotropy, an excellent equation was obtained relating *meta*-substituted aromatic side-chain protons to Hammett constants.

The structures of disubstituted isoxazoles of type (**40**), where R and R′ are aryl groups, can be very difficult to determine. However, shift studies have now shown[181] that this problem can be overcome. The shift of H(4) appears to be essentially insensitive to *m*- or *p*- substituents on the C(3) aryl group, while showing a quantitatively predictable change when the aryl group at C(5) is substituted. Using Hammett σ values, $\delta[H(4)] = 0{\cdot}30\sigma + 6{\cdot}79$.



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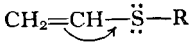
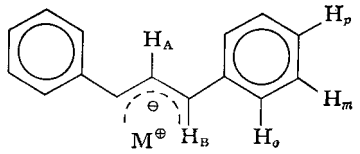


41

The significance of resonance effects in determining chemical shifts has been considered for some olefinic and aromatic systems. In an investigation of some alkyl vinyl sulphides,[182] differences compared with the corresponding ethers have been explained by a mesomeric interaction (**41**) involving the ability of sulphur to accommodate a decet of electrons in its valence shell.

In a study on $(p\text{–}d)\pi$ bonding, in silicon-substituted furans,[183] it was clearly established that, for the trimethyl-silyl group, simultaneously operative yet opposing +I and −M forces are present. The significance of the resonance effect in determining ring proton shifts in substituted benzenes and pyridines has been discussed[184] in the light of pure field and resonance parameters recently derived from Hammett constants. The pure resonance term was shown to be dominant.

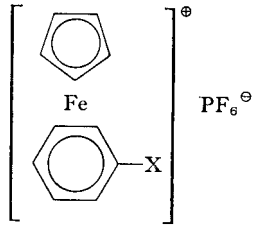
Evidence for ion-pairing in alkali-metal salts of 1,3-diphenylpropene (**42**) has been obtained from shift studies using different alkali metals.[185] Except for Li, increasing atomic weight moves the spectrum to higher field, and it is suggested that for Na, K and Cs, ion pairs dominate although exchange is rapid.



M = Li, Na, K, Cs

42

From a study of the chemical shifts for some 1′-substituted and 2-substituted 1-methyl ferrocenes,[186] the transmission coefficient of the electronic effect through the ferrocene nucleus was calculated to be 0·28. The NMR spectra of a series of arenecyclopentadienyliron compounds, e.g. (**43**), containing a range of substituents have been studied,[187] and the shifts correlate well with Hammett-Taft σ parameters. For (**43**), the cyclopentadienyl ring shift $\delta(\text{cp}) = -0{\cdot}484\sigma_p^{\circ} + 0{\cdot}04$, where σ_p° is the Taft constant. In the organometallic derivatives (**44**) and (**45**) (M = Pd,Ni; X = halogen, NO_2, CN, NCO, NCS), protons on the hydrocarbon ligands



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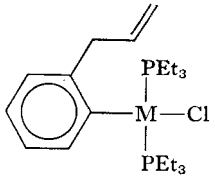

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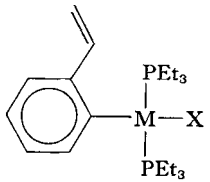


45

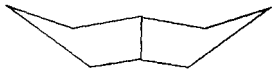
in close proximity to the metal have been found[188] to exhibit low-field shifts relative to the corresponding protons of the parent hydrocarbons. This has been explained in terms of the paramagnetic anisotropy of the substituent transition metal ion. In a series of *p*-substituted benzonitrile complexes of the type $C_5H_5Mn(CO)_2(NCC_6H_4X)$ a linear correspondence was observed between the Hammett σ_p values and a range of spectroscopic parameters including the shift of the cyclopentadienyl ring protons.[189]

Using the example of acidolysis of tetramethyllead with acetic acid-d_4 it has been shown[190] that the concentrations of several reacting species in a competitive consecutive reaction system can be determined simultaneously with high precision.

A method of unequivocally assigning structures for symmetrically disubstituted diastereomeric 1,2-glycols and 1,3-dioxolanes has been given. The *meso* derivatives give rise to AB spectra for the methylene group at C(2) while the *dl*- racemates shown an A_2 singlet,[191] because of molecular symmetry.

E. Shielding effects

The chemical shifts for the proton α- to OH or OAc in the *exo*- and *endo*- *cis*-bicyclo[3.3.0]oct -2-yl and -3-yl alcohols and their acetates have been measured.[192] The *endo*-2 proton was more shielded than the *exo*-2 as expected but, contrary to previous predictions, the *exo*-3 proton was considerably more shielded than the *endo*-3. Calculations based on probable conformations suggested that the observed shifts could be rationalised by assuming a W skeleton as in (**46**).



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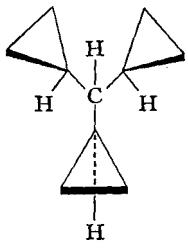


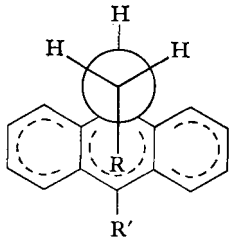
47

NMR data have been given[193] for some D-homo steroids which should be useful reference compounds; there is a close correspondence of ring D shifts with those caused in ring A of normal steroids by adjacent methyl groups, etc. A large temperature-dependent shielding effect has been observed for the central methine proton in tricyclopropyl-methane (**47**).[194] The signal moves upfield, to a value $\delta = -0{\cdot}5$ p.p.m. at $-83°$ which is apparently not a maximum. This probably arises from an averaged diamagnetic shielding effect and suggests that the conformation in (**47**) cannot be an accurate description of its shape at room temperature.

In a study of some styrene, stilbene and stilbazole oxides, it has been observed that the shifts of some oxirane protons are higher in *cis*- than in *trans*- isomers.[195] This has been explained in terms of the electric dipole moment of one CH bond causing polarisation at the other CH bond.

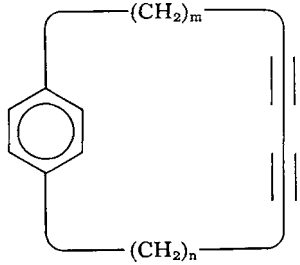
An upfield shift is also found for ring protons *cis* to the anisotropic *N*-alkyl bond in aziridines.[196] This upfield shift decreases markedly with increasing bulk of the substituent and a dispersion-induced deshielding *and* shielding (DIDS) effect has been invoked in explanation.

An unusually strong shielding for the CH_3CH_2 group in the 9*H*$^{\oplus}$-9-ethyl-10-methylanthracenium ion has been observed[197] and can be accounted for if conformation **48** is assumed to be highly preferred. The *syn-* and *anti-* isomers of tricyclo [3.2.2.0^{2,4}] non-6-ene have proved useful in affording an empirical "map" of anisotropy for the double bond.[198] For example $\delta = -0{\cdot}1$ for the H(3,3′) (cyclopropyl methylene) protons in the *syn* isomer, while $\delta = 0{\cdot}85$, 0·53 p.p.m. in the *anti*-compound. Long-range shieldings on olefinic protons by cyclopropyl rings



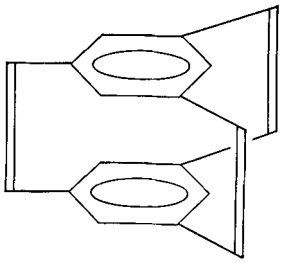
R = R′ = CH_3

48



49

in some homobarrelenes and bullvalenes have allowed the assignment of configurations.[199] Spectral parameters for four paracyclophadiynes (**49**) have been reported.[200]As the bridge becomes shorter the aromatic shift moves slightly downfield, which must be attributed to long-range shielding of the diacetylene, since deformation should induce a high-field shift. In the tris-bridged cyclophane (**50**) the aromatic protons were shifted upfield as expected, but an unusual downfield vinyl shift was



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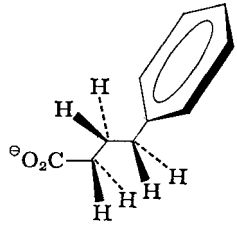
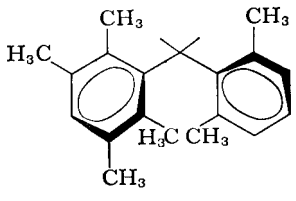


51

observed, presumably related to the unusual strain in the rigid molecule.[201]

Ring current shielding and deshielding effects often provide a useful method for investigating molecular conformations. For example, phenyl shielding values indicate that (**51**) is the favoured conformer of 4-phenylbutyrate salts[202] and have made possible the estimation of dihedral angles between the plane of the phenyl ring and the polycyclic ring in some phenylphenanthrenes.[203] Shielding studies on some methyl substituted diphenylmethanes[204] have suggested that the twisted form as in (**52**) dominates. The shift of H_x in the newly isolated *trans*-15,16-dihydropyrene (**53**) at $\delta - 5{\cdot}49$ gives proof of a strong diamagnetic ring



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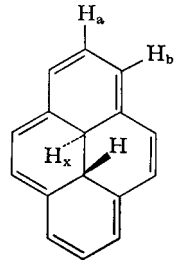
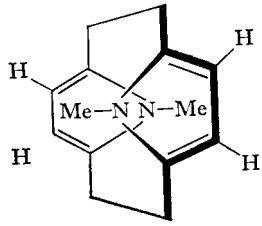


53

current and hence aromatic character.[205] Extreme structure perturbation was detected by IR and UV spectroscopy in some poly-*tert*-butyl naphthalenes.[206] *Peri*-crowded groups suffered an upfield shift, presumably because these were twisted out of the mean plane of the ring and therefore out of the zone of maximum deshielding. The β-protons in *N*,*N*′-dimethyl[2,2](2,5)-pyrrolophane[207] show an unexceptional shift ($\delta = 6{\cdot}1$ p.p.m.), which suggests that the compound has the *anti*-configuration (**54**), in which there is a minimum of transannular shielding.



54

ApSimon *et al.*[208] have extended their calculations of chemical shift

values to include a derivation of the shielding effect of the ketonic carbonyl group which includes both magnetic anisotropy and electric field screening. As previously for the carbon-carbon double bond, the results necessitate a substantial modification of the popular picture for a shielding cone round the carbonyl group and the modified shielding patterns for both the C=C and C=O groups are shown in Fig. 3. The general validity of these models has been illustrated by their application to a variety of substances; it must be noted that, contrary to previous thought, it can no longer be assumed a general rule that a proton situated in the plane of a C=O or C=C bond is always deshielded.

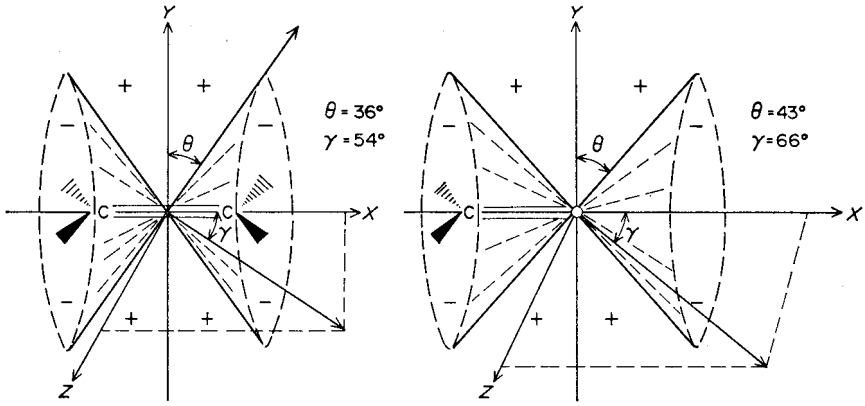
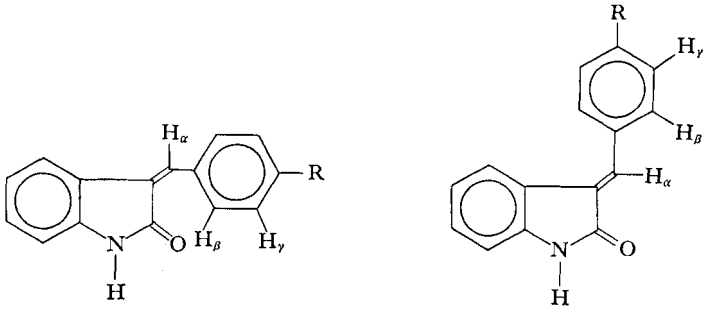


FIG. 3. Shielding cones for C=C and C=O groups. (From ApSimon *et al.*[208])

In a discussion on the origin of the chemical shift from hindered rotation in *N*,*N*-dimethylformamide[209] emphasis was placed upon the parallel importance of electric fields as well as the more usually considered magnetic fields in determining shielding parameters. Using a point dipole model it was shown that a satisfactory approximation could be made to the observed line separation.

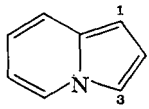
The anisotropic shielding in a molecule caused by the presence of a carbonyl group can often provide an insight into molecular geometry. The preferred conformations of some labile alkyl substituted α,β-unsaturated ketones have been determined in this way,[210] and the degree of non-planarity arising from steric crowding estimated. The carbonyl anisotropy allowed an assignment of geometry[211] to pairs of benzylideneoxindoles (**55**). In some mono- and di- acyl mesitylenes, the ring methyl shifts showed that there was a steep effective conformational angle for the carbonyl functions relative to the aryl moiety,[212] and in some mono-



a **b**

55

acylferrocenophanes, deshielding by an α-acyl group causes the individual bridge methylene proton closest to the substituent to be deshielded by 0·8 p.p.m., while a β-acyl group has no effect.[213] It was possible to readily distinguish αα′, αβ′ and ββ′ substitution patterns in the corresponding diacyl derivatives.



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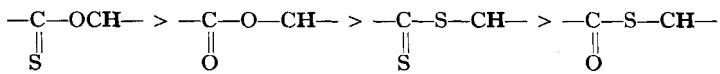
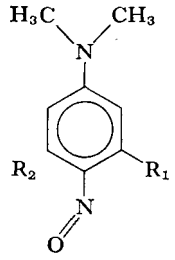
A few reports have appeared concerning shielding caused by thiocarbonyl functions. It was found possible to prepare[214] some indolizines (**56**) substituted at the 1- or 3- position with stable thioaldehyde groups. The –CHS protons appear at *ca.* 0·8 p.p.m. to lower field than the corresponding aldehydes, and the group exerts a much greater anisotropic deshielding effect upon the H(8) or H(5) neighbour than does the oxygen analogue. The anisotropy of the thioketone group in adamantanethione has been investigated,[215] and a deshielding effect observed for the anomeric proton of a number of thionucleosides has been ascribed to the anisotropic effect of a thione group;[216] this provides a new method for the structural assignment of certain isomeric thionucleosides. A strong anisotropic deshielding effect has been noted for the highly polarised thiocarbonyl group in some thioesters[217] and decreased in the following order:



A model of anisotropy, rather similar to that of the carbonyl group,[208] has been proposed for the *C*-nitroso moiety, involving the N=O bond.[218] The anisotropic effect of such a group has been demonstrated to extend even as far as to the *N*-methyl groups in (**57**).[219]



57

A calculation of screening effects for chlorine in 1,8-diaminoperchloronaphthalene has produced a shielding parameter for the difference between this and the corresponding 1,8-diaminonaphthalene which correlates quite well with the experimentally observed difference.[220]

F. Hydride shifts

Many values of chemical shifts for hydride protons in organometallic compounds have been presented and discussed in the recent literature. A few of these results are presented below in the hope that they may be of some interest.

Anionic organozinc hydride complexes of the type $MH(ZnR_2)_n$ ($M = Li$, Na; $n = 1,2$) have been studied in detail.[221] For a given organozinc, stoichiometry of the product depends on the activity of the metal hydride and nature of the solvent, and NMR spectra demonstrate a mobile equilibrium $MHZnR_2 + ZnR_2 \rightleftharpoons MH(ZnR_2)_2$ for alkylzinc systems. If dialkylzinc is present in excess the single hydride signal is found at the remarkably low field value of $\delta = 7$ p.p.m.

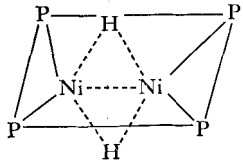
A binuclear dihydride of iron, $H_2Fe_2(CO)_6[P(CF_3)_2]_2$, showed, in the NMR spectrum in $Fe(CO)_5$, two triplet signals at $\delta = -5{\cdot}60$ and $-5{\cdot}82$ which were assigned to the *cis*- and *trans*- isomers (**58a** and **b**).[222] Some

a **b**

Unmarked P ligands are to CF_3

58

interest has been taken in nickel hydride complexes. For example, the 5-coordinate square pyramidal $HNi[P(OEt)_3]_4^{\oplus}X^-$ species[223] probably have the proton in an apical position, where it has a shift of $\delta - 14{\cdot}3$. The typical hydride shift of *ca.* $\delta - 12{\cdot}5$ is observed for the stable complexes $[(Ph_2P{-}CH_2{-}PPh_2)_2NiH]^{\oplus}X^-$,[224] while a novel hydrogen bonded structure has been proposed for the dinickel dihydrides (**59**) where two equivalent protons are seen ($n=2$, $\delta = -11{\cdot}4$; $n=4$, $\delta = -10{\cdot}4$).[225]



The P–P ligand is $P(C_6H_{11})_2(CH_2)_nP(C_6H_{11})_2$

59

A series of rhodium hydride shifts have been summarised[226] including a value of $\delta - 15{\cdot}4$ for the sparingly soluble $(Ph_3P)_2RhH(GeEt_3)Cl$.[227] The tertiary phosphine and arsine complexes of W(IV) halides were found to show single methyl signals at abnormal shifts ($\delta = -26$) owing to contact and/or pseudo-contact interactions of the unpaired electrons.[228] Structural details have also been given in the literature, with the aid of hydride shift data, for complexes or Ir,[229 to 231] Ru,[231] Os,[231] Pd [232, 233] and Pt,[233] amongst others.

G. Solvation

A solvation study has been made[234] of Li and Na ions in DMSO and 1-methyl-2-pyrrolidone, where a shift *vs.* mole ratio plot shows breaks corresponding to solvation number of 6 and 4 respectively for $Na^{\oplus}$. The observation[235] that the OH resonance from methanol molecules bound to $Mg^{2\oplus}$ [in $MgBr_2$, $Mg(NO_3)_2$ and $Mg(ClO_4)_2$] shifts with concentration in a way very similar to the OH in bulk solvent has been interpreted in terms of a purely statistical interaction between the protons of $Mg(MeOH)_6^{2\oplus}$ and the anions. In the light of the biochemical significance of Mg(II)–N coordination the primary solvation number of Mg(II) in anhydrous liquid ammonia has been reinvestigated by an improved procedure[236] and was found to be 6 rather than 5.

A proton NMR study has been made of Al(III) chloride in water-DMSO solvent mixtures.[237] At mole fractions of water greater than 0·8, the Al(III) ion was preferentially solvated by water, while below a mole fraction of 0·75 DMSO was favoured; rate measurements and mechanisms are discussed. A study of Al(III) chloride in acetonitrile has confirmed[238]

an apparent solvation number of 1·5; for perchlorate, as the anion, the average solvation number was 2·9 and several species were observed. (See also p. 487.)

A study of the complexes formed by Co(II) with imidazole, pyridine, 4-methylpyridine, pyrimidine and purine in water/acetone solvent[239] has allowed the assignment of structures to the dominant species. In a mixture containing both imidazole and pyrimidine, the only observable complex was $Co(Im)_6^{2\oplus}$. PMR investigations of $Zn(NO_3)_2$ in anhydrous methanol have led to the conclusion[240] that above $-30°$, the $Zn^{2\oplus}$ and NO_3^- ions can form ion pairs; below $-30°$ they are solvent separated. The solvation number apparently decreases with increasing concentration and an interpretation of this effect is given. For $Zn(ClO_4)_2$ in water-acetone the observed hydration number of 6 reflects the lack of complex formation with ClO_4^-—a fact consistently noted in PMR studies of this anion.[241] A similar situation was noted[241] also with $UO_2(ClO_4)_2$, which shows a hydration number of 4.

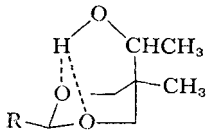
A magnetic resonance coordination number study has been reported for the gallium halides[242, 243] and the nitrate and perchlorate[243] in acetone-water mixtures, and the results discussed in terms of ion-pairing. (See also p. 477.) Direct integration studies indicated[244] an average cation solvation number of *ca.* 2 for both $SnCl_4$ and $SnBr_4$ in the same medium as above. This was interpreted to indicate the presence of $Sn(H_2O)_6^{4\oplus}$ and SnX_6^{2-} as the dominant species. In a hydration study of $Y^{3\oplus}$, $Th^{4\oplus}$ and $Sc^{3\oplus}$, as their nitrates,[245] it was observed that in the presence of perchloric acid the $Sc^{3\oplus}$ value increased from 3·9 to 5·1—a clear indication of a hydrolysis process—while the other values remained constant.

Methylene chloride has been used as an inert probe in aqueous solutions of paramagnetic ions,[246] in order to study the effect of second coordination sphere solvent ordering; for a series of $Cr^{3\oplus}$ complexes it was found that cations ordered the second sphere of coordination more effectively than anions.

H. Hydrogen bonding

The chemical shifts induced by hydrogen bonding of thiocyanic, cyanic and hydrazoic acids to a selection of Lewis bases have been examined[247] in relation to the enthalpy of association and $\Delta\nu$, the change in N–H stretching frequency. Individual correlations are distinguished for each acid and have been discussed in terms of anisotropic shieldings. In a study of solvent effects on hydrogen bonding in methanol[248] it was noted that there was a hydrogen-bonded interaction between methanol and CCl_4 and that, for solutions in cyclopentane and cyclohexane, the results were best fitted by a monomer-tetramer model. A general NMR

method has been described[249] for the evaluation of chemical shifts of weak 1:1 complexes and their equilibrium quotients of formation, and it was applied to hydrogen bonding interactions between phenyl-acetylene and a series of ethers and thioethers in carbon tetrachloride solution. Unequivocal proof for the structures of *cis*- and *trans*- isomers of some 2-substituted 5-(α-hydroxyethyl)-5-methyl-1,3-dioxans was obtained by spectroscopic observation of hydrogen bonding with the *cis*-isomers, as in (**60**).[250] The shift value of δ 9·74 observed[251] for the SH proton of dithiotropolone (**61**) shows it to be markedly deshielded, indicating the presence of a hydrogen bonded chelate ring. On the basis of NMR and electronic spectra observed for an *O*-alkylated derivative, the structure of the green form of dithizone existing in neutral solutions has been postulated[252] as the hydrogen bonded species (**62**).



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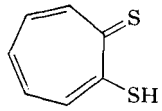

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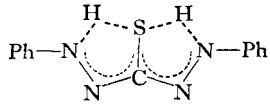
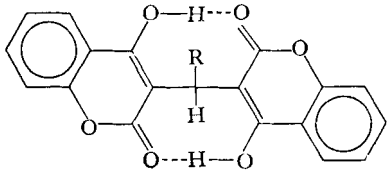


62

In a dynamic study of several dicoumarol derivatives[253] it was found that there was a doubly restricted rotation from hydrogen bonding, as shown in (**63**). Proton NMR investigations have been reported[254] of self-association of phenol in CCl_4 and cyclohexane, and of hydrogen bonding between phenol and some carboxyl and phosphoryl compounds. A summary has been given[255] of the OH shifts for a large number of aromatic hydroxyl compounds measured on dilute solutions in



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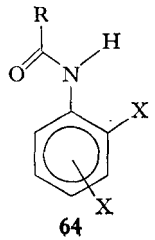
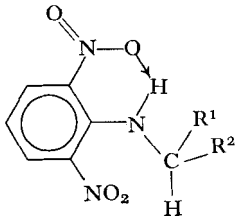


64

CCl_4 and DMSO. An excellent linear correlation was found between pK_a and δ(DMSO), in which

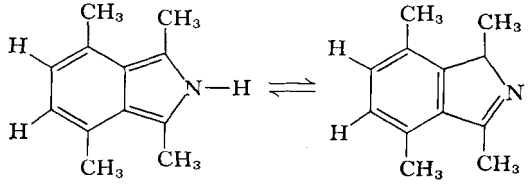
$$\delta(\text{DMSO}) = -0{\cdot}640\ pK_a + 15{\cdot}56;$$

shifts in this solvent were virtually independent of concentration. The chemical shift changes induced at H(6) in some *ortho*-substituted anilines (**64**) upon *N*-acylation correlate well with Hammett substituent constants, and are ascribed to the presence of intramolecular hydrogen bonding between the amide proton and the *ortho*-substituent.[256] The influence of two *ortho*-nitrosubstituents on the chemical shift of the N–C–**H** proton in (**65**) has been investigated and discussed in terms of the



65

interaction shown.[257] The magnetic non-equivalence of methyl groups in some *para*-substituted dimethylbenzamides has been demonstrated to depend on both solvent and substituent.[258] Rotation about the C–N bond was found to be progressively more hindered with increasing solvent polarity, and even more so by the ability of the solvent to form hydrogen bonds. The tautomeric equilibrium in (**66**) has been investigated in a variety of solvents by NMR.[259] The N–H form is stabilised in solvents which are able to provide lone-pair hydrogen bonding (e.g. pyridine) while the other form is predominant in those (e.g. methanol) which act as H-donors in hydrogen bonding.



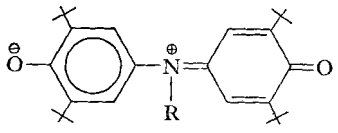
66

I. Miscellaneous

A graphical method, based on NMR measurements, has been developed[260] which allows the calculation of the association constant and

the chemical shift of the 1:1 molecular complex in binary mixtures. Results for chloroform in a variety of proton-acceptor solvents have been presented and discussed. A tabulation has been published of chemical shift data for 344 steroids in the androstane, pregnane and oestrane series which have been prepared by microbiological hydroxylation reactions.[261]

NMR evidence has been presented[262] for the existence of the trichlorosilyl anion from experiments in which tri-*n*-propylamine was added to an acetonitrile solution of trichlorosilane. The sharp singlet ($\delta = 6{\cdot}25$) of the latter broadened and diminished while a new signal appeared at $\delta = 11{\cdot}03$, assignable to the tri-*n*-propyl-ammonium ion. The Forsen-Hoffman spin saturation technique showed that these two signals were connected by exchanging protons.



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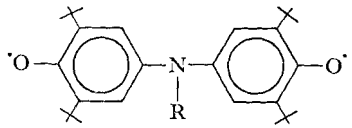
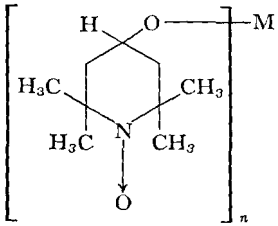


68

Several papers have described NMR studies of systems involving radical species. For example the kinetics of equilibria between the zwitterion (**67**) and its related biradical (**68**) have been investigated by use of observations made over a wide range of temperatures.[263] Paramagnetic shifts measured for stable free radicals have the advantage of affording not only the magnitude but also the sign of electron-proton coupling constants. This technique has been used in a study of some polynitroxide radicals of type (**69**), and the derived parameters were used in the estimation of exchange integrals.[264]



a $n = 3$, M = P
b $n = 4$, M = Si

69

Magnetic susceptibilities play an important part in NMR spectroscopy, but their values are not always known. A method has been given[265] for the measurement of paramagnetic susceptibilities, and an explanation

offered for the linear dependence of magnetic susceptibility *vs.* observed shift.

IV. COUPLING CONSTANTS

A. Proton-proton coupling

1. *Theoretical and general considerations*

Self-consistent field calculations using the INDO molecular orbital approximation have been applied[266] to the calculation of geminal ^2J(H–H) couplings for some substituted methanes and ethylenes, assuming a Fermi contact mechanism, and the derived values showed in general the experimentally correct trends for substituent and structural effects. This theoretical approach has also proved capable of reproducing several important experimental trends for ^3J(H–H) couplings.[267] These include dependence on the HCCH dihedral angle, the relationship to hybridisation of the connecting carbon atoms, and has also been used to account for many of the dominant patterns of H–H coupling constants observed in benzene and substituted benzenes.[268]

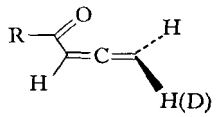
Values of π-electron contributions have been calculated[269] for a variety of unsaturated hydrocarbons using a range of methods, and predictions made for several molecules for which no experimental values have been reported. Extended Hückel theory calculations have been applied[270] to a study of the ^3J(H–H) couplings in fluoroethane as a function of dihedral angle, demonstrating the effect of an electronegative substituent. A small phase shift was observed, and the calculated angles could be given by an equation of the type:

$$J_{AB} = A + B\cos\phi + C\cos 2\phi + D\sin\phi + E\sin 2\phi$$

where $A = 3{\cdot}68$, $B = -1{\cdot}21$, $C = 3{\cdot}35$, $D = -0{\cdot}20$ and $E = 1{\cdot}12$, with an error of 0·1 Hz.

Two papers have discussed anisotropy of spin-spin couplings.[271,272] By using equations, derived by Ramsey for nuclear spin-spin coupling, to obtain general expressions for the anisotropy of the electron coupled interaction[272] it was suggested that, since the calculated values of ΔJ were far too small, discrepancies between molecular parameters derived from microwave and from nematic phase NMR studies probably do *not* originate from a coupling anisotropy.

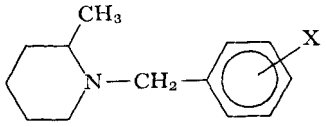
A significant solvent dependence for ^2J(H–H) in allenic derivatives has been observed *via* ^2J(H–D).[273] For a series of allenic ketones (**70**), $|^2J$(H–H)| increased with dielectric constant of the solvent. This coupling is negative, and the experimental changes satisfied the correlations of solvent effects on direction and sign of coupling.



70

2. *Geminal and vicinal couplings*

The ^2J(H–H) couplings between the non-equivalent benzylic protons in a series of *meta-* and *para-* substituted *N*-benzyl-2-methylpiperidines (**71**) were shown[274] to be proportional to the Hammett σ-constants of the substituents. An experimental curve has been obtained relating the



71

magnitude of the HCH geminal coupling constant with the dihedral angle of a β-substituent.[275] The curve is reproduced in Fig. 4, and has been used to modify the structure earlier proposed for the bromination product of 2α-methylcholestan-3-one. Values of the observed *J*(*gem*) between the non-equivalent C(21) protons in a series of 21-substituted 20-oxo-steroids have been used[276] to calculate rotamer populations about the C(20)–C(21) bond.

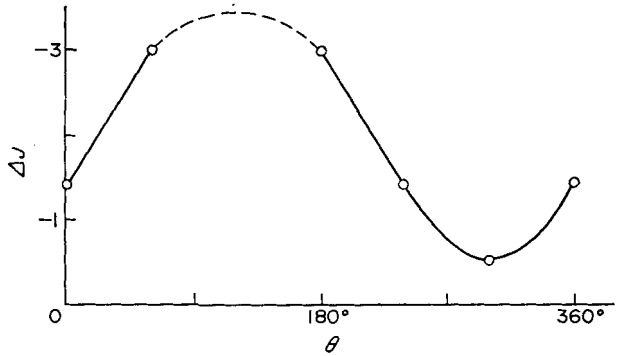


FIG. 4. Perturbation of *J*(*gem*) with dihedral angle of a β-bromo-substituent. (From Hudec.[275])

As part of a series of studies on compounds with bridgehead nitrogen atoms, the published data for $J(CH_2)$ in N–CH_2–N groups have been summarised.[277] This coupling varies according to the projected angle (θ) between the CH_2 group and the adjacent lone pair orbital and the

plotted values (Fig. 5) seem to indicate a smooth relation between J and θ. This curve should, however, be treated as speculative and applied with

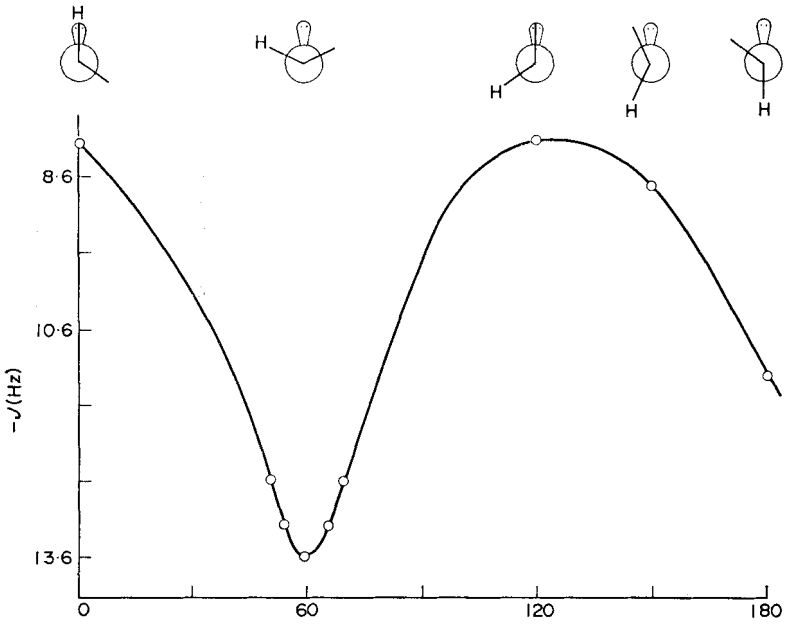
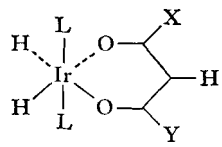


FIG. 5. Variation of J of methylene group protons with dihedral angle θ with one adjacent N lone pair orbital. (From Chivers and Crabb.[277])

extreme care to conformational problems. The influence of axial or equatorial β-substituents on the $^2J(OCH_2O)$ coupling in some 1,3-dioxanes has been investigated. Composite influences were found, but in suitable cases (e.g. *p*-substituted phenyl groups) a numerical decrease with increasing electron donating power was observed, which was more pronounced for axial substituents.[278]

The stereochemistry of some β-diketonate hydrides of iridium have been assigned as (**72**) on the basis of IR and NMR spectra.[279] For the trifluoracetyl derivatives, AB groups were observed for the meridional protons, with $^2J(H\text{–}Ir\text{–}H) \approx 8$ Hz. Some values of J(HCMH) and J(HMAsH) (M = Si, Ge) have been tabulated[280] for some silyl and germyl arsines.

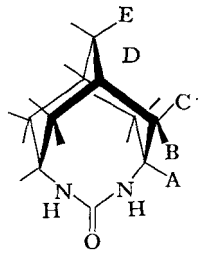
The difference between the two vicinal couplings J(AC) and J(CD) (7·5 and 4·0 Hz respectively) in (**73**) clearly indicates a difference in dihedral angle between the pairs of C–H bonds, which can be calculated as 90°(AB) and 20°(AC) by the Karplus equation.[281] This suggests a



L = Ph_3P or Ph_3As

	X	Y
a	CH_3	CH_3
b	CH_3	CF_3
c	CF_3	CF_3

72

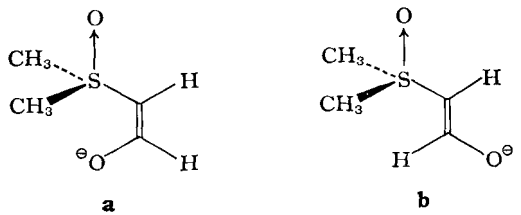


73

flattened chair conformation for the two 6-membered rings in this strained molecule.

From newly determined accurate data for the magnitudes of *cis*-vinyl ^3J(H–H) couplings in *cis*-dialkylethylenes and cycloalkenes it has proved possible to make a critical determination of the correlation between ^3J(H–H) and C=C–H bond angles in ethylenic systems.[282] It appears that it is possible to obtain accurate estimates of bond angles using these couplings, though more experimental data will be needed to confirm this proposal. Further studies have been made on the effect upon coupling constants of steric compression.[283] The observed values may be satisfactorily explained on the basis of in-plane strain relieving bending for some 1,4-disubstituted naphthalenes and for benzo[*c*]phenanthrene. NMR analyses have been performed[284] on a specifically deuterated cyclohexane and some deuterated methylcyclohexanes. The observed couplings indicate that no ring distortion is caused by the equatorial methyl group. For *cis*-dihydrodecadeuterocyclohexane, the $^3J(ae)$ at $-90°$ was found to be 3·56 Hz.

A detailed investigation of 2-fluoroethanol and ethylene glycol has confirmed that in the former the *gauche* isomer is strongly favoured.[285] The solvent and temperature dependence of vicinal couplings in the glycol have indicated, however, that this compound does not—as fre-



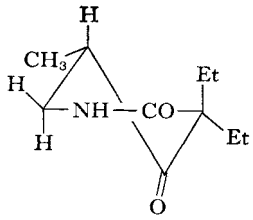
a **b**

74

quently suggested—exist solely as the *gauche* conformer but, in solvents of low dielectric constant, contains up to 20% of the *trans* isomer.

NMR evidence has been obtained for the existence of two rotational isomers of the ylide (**74a** and **b**) in solution.[286] Two ^3J vicinal couplings were observed, of magnitude 2·5 and 10 Hz for (**74a**) and (**74b**), which did not coalesce in the temperature range -50 to $+70°$. Vicinal couplings in a series of isomeric trithienyl carbonium ions were found[130] to be in satisfactory agreement with the corresponding calculated π-bond order.

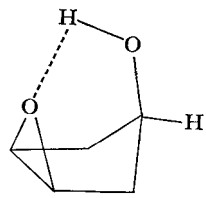
The first observation of coupling by amino protons in strongly basic amines has been reported.[287] Samples were carefully dried over NaK alloy, and afforded the following ^3J(HNCH) values: *N*-methylaniline 5·21 Hz, dimethylamine 6·11 Hz and diethylamine ~6·8 Hz. It thus appears that ^3J(HNCH) is dependent upon the electron releasing ability of the organic groups attached to nitrogen; $J(Et_2NH) > J(Me_2NH) > J$(MeHNPh). The observation of a 5·3 Hz stereospecific ^3J(HNCH) coupling between H(6-quasiaxial) and the NH proton in (**75**) indicates the presence of the half-chair form shown.[288]



75

3. *Specific hydroxyl coupling*

Several mono-, di- and tri- hydroxyderivatives of cyclopentane and -ene have been studied by NMR. Chemical shifts and couplings for the OH protons in DMSO solution were correlated with structure.[289] Some stereospecific interactions were proposed, e.g. for the epoxide (**76**) with $^3J(HCOH) = 7·8$ Hz. Conformational properties of the sugar-ring OH protons of some common nucleosides have been explored.[290] It was

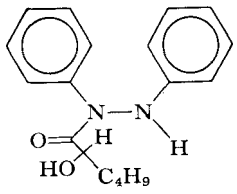


76

concluded that C'_3–OH groups in ribose moieties prefere a *gauche* conformation relative to the C'_3–H bond from a Karplus-type study of ^3J(HCOH) values.

Intramolecular O–H····N hydrogen bonding in (**77**) has permitted the observation of ^3J(HCOH) is most solvents.[291] Solvent effects on this coupling have been discussed and the H–C–O–H dihedral angle was calculated to be 145°.

A detailed IR and NMR study[292] has confirmed the absolute configurational assignments of diastereomeric β-hydroxy (and acetoxy) episulphides. The strong ^3J(HCOH) for the *threo* isomer at all concentrations (9·0 ± 0·2 Hz) contrasted with the smaller (2 to 3 Hz) value for the *erythro* isomer observed only at low concentration. The probable structures of the *threo* form is shown in (**78**).



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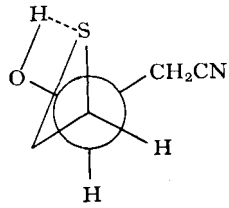
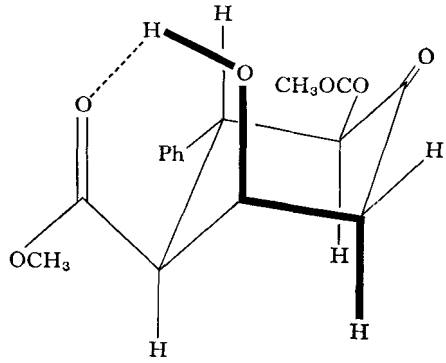


78

In a study of the condensation products formed between benzaldehyde and acetoacetic ester a product was isolated which showed a large four-bond coupling to a hydroxyl proton.[293] This was attributed to a preferential hydrogen-bonded conformation (**79**) which holds the coupled protons in a W orientation.



79

4. *Long-range coupling*

A ^5J coupling has been observed through saturated bonds in a series of *cis*-2-methyl-1-oxa-5-oxy substituted cyclopentanes.[294] Analogous 6-membered ring compounds do not show this splitting of 0·35 to 0·4 Hz, which involves the C(5) proton. This phenomenon has been used for the determination of anomeric configuration in some furanoses.

The observed trends of the olefinic, vicinal and allylic couplings in a series of *cis*/*trans* pairs of 1,2-disubstituted olefins have been discussed in terms of rehybridisation at the sp^2 carbon atoms.[295] It was noted that, contrary to a previous theoretical prediction, *trans*-allylic couplings were generally more negative than the corresponding *cis* interactions. Steric hindrance was cited as the probable origin of this and related trends. The spectra of two penta-1,3-diene isomers and of three hexa-2,4-dienes have been fully analysed, and appreciable values for long-range coupling involving CH_3 groups were found[296] including a ^7J coupling of *ca.* 0·5 Hz. The mechanism of coupling in butadienes was discussed in terms of σ and π contributions and values were suggested for the magnitude of the π contribution to ^4J and ^5J interactions.

The variation of $|^4J(\mathrm{ab})|$ with structure has been examined for a series of aldimines of the type $PCH_a=N-CH_bQR$, and evidence was observed for conformational effects similar to those for allylic coupling.[297]

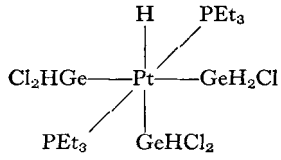
The observation of long-range couplings for silyl germyl-sulphide and selenide[298] completes the series of values summarised in Table IV. The

TABLE IV

Long-range coupling constants in some SiH_3XMH_3 derivatives

X = S		X = Se	
M	$\lvert^4J\rvert$ (Hz)	M	$\lvert^4J\rvert$ (Hz)
C	0·45	Si	0·63
Si	0·70	Ge	0·73
Ge	0·80		

trend in the sulphides appears to extend also to the selenides and is offered to the theoreticians for rationalisation. Analyses have been reported of the NMR spectra for a series of bis(triethylphosphine) tris(halogermyl) platinum hydrides.[299] These exhibited some large couplings involving the hydride proton; for example in (**80**) ^3J(HPtGeH-*trans*) = 23 Hz, while ^4J(HGePtGeH-*trans*) = 4·5 Hz.



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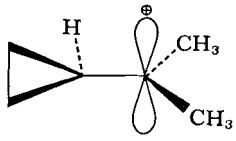
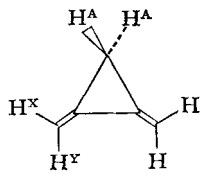


81

Evidence has been offered[300] that the most stable form of the dimethylcyclopropylcarbinyl cation is (**81**). The $^4J(CH_3–CH_3)$ coupling of 1·2 Hz indicates that the positive charge is delocalised into the ring. Spectra at $-65°$ indicate also that only one CH_3 couples to the tertiary hydrogen [$^4J(HCCCH_3) = 0{\cdot}9$ Hz]. The long-range couplings in vinylcyclopropane have been discussed[301] in terms of the π-character of a cyclopropyl group and also in relation to the dihedral angles involved.

Dimethylenecyclopropane (**82**) has been analysed as an $A_2[XY]_2$ system.[302] The magnitudes of ^4J(AX) and ^4J(AY) (1·7 and 2·6 Hz respectively) indicate a large σ-π overlap and therefore a large external H(A)–C–H(A) angle. Spectral analyses and structural correlations have been reported for all the epihalohydrins.[303, 304] Extensive spin tickling



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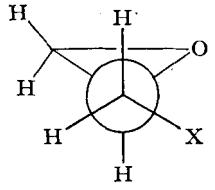
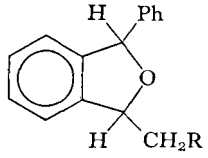


83

experiments have shown the ^4J *cisoid* couplings to be negative, while the corresponding *transoid* interactions are positive. Conformational factors obscured any possible relationship between substituent electronegativity and long-range couplings; (**83**) was suggested as a major conformer.

In a stereochemical study of some 1,3-disubstituted phthalans[305] (**84**) a substantial ^4J coupling of *ca.* 2 Hz through the H–C–O–C–H system was reported for *both* geometrical isomers. It has been observed[306] that in general for lactones of type (**85**), *trans*-derivatives have larger $|^4J|$



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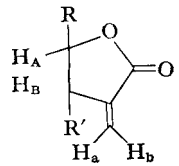
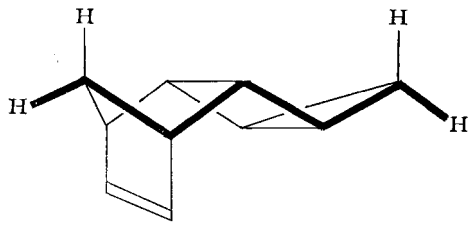


85

couplings than *cis*-compounds, and that $|^4J(b,A)| \geqslant 3$ Hz $\geqslant |^4J(a,A)|$. These allylic couplings can therefore act as an additional source of geometrical information.

There has been some controversy as to the true shape of cyclohexa-1,4-diene. From a study of 1,4-dihydrobenzoic acid and a deuterated derivative, values were obtained for ^5J homoallylic couplings which allowed the conclusion that both the acid and its parent diene were in a boat conformation.[307] In the Diels-Alder adduct (**86**) an unprecedented ^6J coupling of 1 Hz was observed over a zig-zag path of saturated bonds.[308]

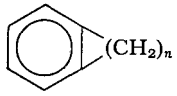


86

A study of some deuterated naphthalenes, and related compounds, demonstrated that a linear relationship existed between 4- and 5- bond couplings:

$$^4J = -0{\cdot}86\ ^5J + 1{\cdot}83$$

and the ^5J coupling was related to the MO–π-bond order, where $^5J = 7{\cdot}82P^2 - 0{\cdot}23$ ($P = \pi$-bond order).[309] The aromatic ring ^4J and ^5J couplings have been measured for some strained benzocycloalkenes (**87**).[310] The ^4J coupling decreased sharply with increased strain, while

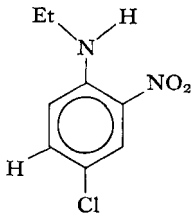


$n = 1$ to 3

87

the *para* ^5J interaction increased appreciably. The reasons for these effects were discussed in terms of empirical relationships, and of an extended Hückel MO treatment. Values for the signs of inter-methyl couplings in some *o*-, *m*- and *p*- xylenes have been observed[311] to be in agreement with the predictions of theories based upon σ–π interactions [$^5J(o) = +0{\cdot}40$, $^6J(m) = -0{\cdot}19$, $^7J(p) = +0{\cdot}62$].

In the *N*-substituted aniline (**88**) a ^5J coupling was observed between the N*H* and a *meta*-proton which showed the stereospecificity expected

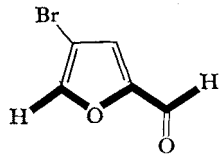


^5J = 0·67 Hz

88

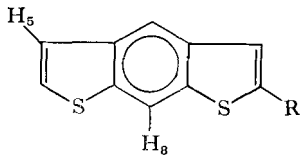
from the zig-zag rule;[312] a similar effect was observed in 2-acetyl-4-nitro-*N*-methylaniline.[313] Double and triple resonance techniques have been used[314] to determine the magnitudes of long-range couplings in monosubstituted aldehydo and methyl pyridines, together with some relative sign information. NMR studies have been reported[315] for some 2-pyridones, thiones and 2-thioalkylpyridines. The $^4J(3,5)$ coupling is the same in both the ketones and thiones, while $^4J(4,6)$ is 0·45 Hz less in the thiones. This suggests that the latter change may arise from the increased positive charge on nitrogen in the more polar thiones.

For some time there has been confusion as to whether in compounds of the furan-2-aldehyde type the dominant conformer is the *s-cis* or the *s-trans* form. If the former is correct, then this is contrary to the accepted rule for the observation of long-range couplings which would require a planar W conformation. Evidence for the presence of a favoured *s-trans* form has been cited already, from NOE studies (p. 13) and in the light of solvent shifts (p. 24). A combination of X-ray and low-temperature NMR studies has now shown that the favoured form of 4-bromo-furan-2-aldehyde (70% at −91°) is indeed the *s-trans* system (**89**) with $^5J(H_5\text{–}CHO) = 1$ Hz.[316] It has also been demonstrated that, for some furan and



89

thiophene 3-aldehydes, the *s-trans* structure is usually dominant, as indicated by ^5J couplings.[317] In the benzodithiophens (**90**) a $^5J(5,8)$ of 1·0 (R = H) and 1·5 Hz ($R = CH_3$) has been reported,[318] while in (**91**) a $^5J(H_6\text{–}CHO)$ coupling of 0·6 Hz has been recorded.[319] It is of interest to note that in both (**92**)[319] and (**93**)[320] no such long-range couplings have



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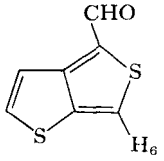

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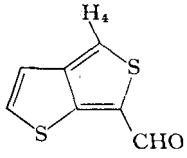

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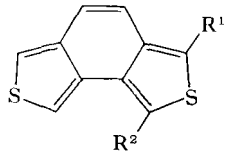
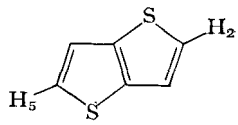


a R^1 = H, R^2 = CHO
b R^2 = H, R^1 = CHO

93

been observed. It would therefore, in the light of the conformational data described earlier, seem reasonable to suggest that *s-cis*-structures are dominant for both (**92**) and (**93**).

The cross-ring coupling constants in thieno[2,3-*b*]thiophene, a number of bromo-substituted thieno[2,3-*b*]thiophenes and thieno[3,2-*b*]-thiophenes have been determined.[321] The largest couplings involve protons separated by a ^6J straight zig-zag path, for example $^6J(2,5)$ in (**94**) is +1·55 Hz.



94

5. *Erythro-threo correlations*

A method for the assignment of *erythro* and *threo* configurations to the diastereomeric 1-(4-methoxyphenyl)-1-methoxy-2-aminopropanes and related compounds based on NMR spectra has been presented and discussed.[322] Similarly the configurations of the amino-alcohols formed by reduction of α-asymmetric β-amino propiophenones have been obtained from spectral data, which also afforded their preferred conformations.[323]

A study of a series of diols bearing various alkyl substituents has shown[324] that increasing substituent size results in generally increasing coupling constants in *erythro* isomers, while diminishing values are found in the *threo* isomers. The preferred conformations of *threo*- and

erythro- phenyl(1,1-dioxy-2-thiolanyl) carbinol have been deduced from a study of the vicinal coupling constants.[325]

It has been shown [326] that the generalisations proposed to deduce the stereochemistry of 1,2-disubstituted indans on the basis of NMR spectra are an oversimplification. It would seem that for this type of compound it is advisable to examine spectra of *both* isomers before assigning stereochemical information.

B. Proton-heteroatom coupling

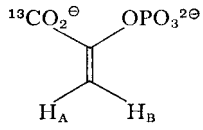
1. *Carbon-13*

The approximate self-consistent M.O. theory of nuclear spin coupling has been applied [327] to the ^1J(CH) system and good agreement, with experimental trends, was found for $-I^{\oplus}$ substituents (F, OR, NR_2, etc.) but not with $-I^{\ominus}$ substituents (CF_3, NO_2, etc.). When this method was applied, to ^1J(CH) couplings in small ring compounds, promising correlations were found with experimental data.[328] Molecular orbital correlations have been successfully extended to the ^2J(CCH) system where signs and relative magnitudes of this coupling could be correctly predicted.[329]

The variable temperature spectra of normal and ^{13}CN enriched $(CH_3)_3SiCN$ and $(CH_3)_3SiNC$ have been reported.[330] The data are consistent with rapid exchange of CN groups between –SiCN and –SiNC derivatives. In a mixture, a single line is always observed, and no long-range $^3J(HCSi^{13}C)$ coupling is observed, even though in $(CH_3)_3CCN$, the corresponding $^3J(HCC^{13}C)$ is 5·4 Hz. The relative reactivities of CH bonds, in some alkyl chlorosilanes, have been shown[331] to correlate with the ^1J(CH) values. The Hammett-Taft equation applies to the correlations, and new ^{13}C–H couplings are tabulated for several silanes. The ^1J(CH) couplings have been reported for a series of trimethylsilyl-substituted methanes.[332] Increasing substitution gives a progressive, but *non*-additive decrease for this parameter, and the deviation is suggested to arise from sterically induced rehybridisation in the more congested compound which induces higher *p*-character in the CH bonds.

Several papers have reported ^1J(CH) couplings in methyl groups, which can be related to their molecular environment. In a series of group IV and V amines, (e.g. Me_2NPMe_2) the dimethyl series shows ^1J(CH) couplings in the order $P > N \geqslant As$, while for tris(methyl) compounds the order is $P > As > Sb$.[333] The value $P > N$ must be interpreted as indicative of π-interaction between N and P. The comparison of ^1J(CH) in trimethylstibine sulphide (Me_3SbS) with values for related compounds leads to the conclusion that the semipolar $Me_3Sb^{\oplus}$–$S^{\ominus}$ bond

can be considered to be present, although some contribution from d_π–p_π bonding may be involved.[334] Two papers have reported and discussed ^1J(CH) couplings in dimethylgold(III) compounds.[335,336] Spectroscopic studies on the Me_2In(III) cation showed no obvious correlation between ^1J(CH) and substituent electronegativities.[337]



$^3J_{AC}$ = 3·1 Hz

$^3J_{BC}$ = 9·2 Hz

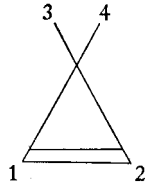
95

From a study of the NMR spectra of phosphoenolpyruvate and its $^{13}CO_2^-$ analogue (**95**), it was concluded that the downfield proton was *trans* to the phosphate.[338] A study of the ^{13}C satellite lines in the PMR spectrum of *trans*, *trans*-1,4-bis(dicarbonyl-π-cyclopentadienyliron)-buta-1,3-diene and its dimethyl derivative has indicated that the fluxional process in these molecules involves mainly 1,3-shifts of the metal-carbon bonds.[339] The linear relation between ^1J(CH) and ^2J(CCH) couplings in acetylenes has also been shown to hold for the four halogenoacetylenes.[340] These values also correlate well with Pauling electronegativity, e.g.:

$$^1J(X\text{–}C{\equiv}{}^{13}C\text{–}H) = (208{\cdot}4 \pm 4{\cdot}7) + (17{\cdot}4 \pm 1{\cdot}8)E_x$$

The ^1J(CH) couplings in some platinum acetylene complexes have been correlated with the reduction in bond order on coordination.[341]

Excellent multiple regression correlations have been obtained between the ^2J(CCH) and the various J(HH) couplings in a series of monosubstituted cyclopropanes ($R = 0{\cdot}973 - 0{\cdot}998$).[342] The spectrum of cyclopropene (**96**) has been described, and showed a $|J(1,2)|$ of 1·3, and $^1J(^{13}CH)$ of +226 Hz, which indicates 45% *s*-character.[343] This corre-



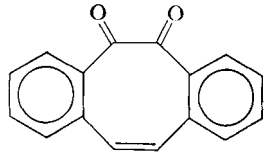
96

lates well with the 44% *s*-character deduced for di- and tri- chlorocyclopropene from the ^1J(CH) parameters.[344] The J(CH) parameters have

also been reported[345] for three salts of the cyclopropenyl cation and suggest 53% *s*-character. The ^2J(CCH) of 50 Hz is very similar to that observed for the ethynyl proton in propyne (50·8 Hz). A complete PMR analysis, including all observable $J(^{13}C-H)$ couplings, has been reported[346] for phenylcyclobutadiene-iron tricarbonyl. The results are discussed in terms of molecular structure and bonding properties and exclude the possibility of a cyclic diene with alternating double and single bonds.

The ^{13}C-satellite lines for *p*-dithiene and *p*-dithiin have been analysed and the results discussed in relation to those for thiophene, in terms of electronic effects.[347] The coupling constants, obtained from the satellite lines, of benzodioxan show that the heterocyclic ring exists in two rapidly inverting half-chair conformations;[348] a 2-substituent prefers the pseudo-axial position. Some ^{13}C–H coupling parameters have been reported[349] for a series of twelve monosubstituted thiophenes. It seems a general rule that ^1J(CH) at the α-position is consistently *ca.* 15 Hz greater than for a β-proton.

The effect of steric hindrance on some ^1J(CH) methyl couplings in aromatic compounds has been studied.[350] The reduction in coupling observed may be explained by steric inhibition of resonance interactions. IR and NMR studies have shown that the eight-membered ring of (**97**)



97

is not aromatic;[351] J(HH) for the olefinic protons is 12·8 Hz, while ^1J(CH) = 160 Hz. An NMR study of [1-^{13}C]-labelled naphthalene, before and after an attempted automerisation with aluminium chloride, has shown that scrambling of carbon atoms does *not* occur under the conditions described in the literature.[352]

The observation of ^{13}C satellite lines on PMR spectra has been used to determine the sites of incorporation of ^{13}C-methyl labelled propionates in the biosynthesis of the naturally occurring insecticide Piericidin-A, and affords direct information on the biological origin of the methyl groups in the antibiotic.[353]

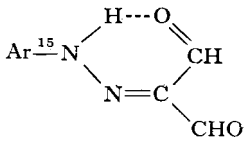
2. *Nitrogen-14 and -15*

Further evidence has been produced for the dependence of $^1J(^{15}NH)$ on the hybridization of nitrogen.[354] The $^1J(^{15}NH)$ coupling constants in some aminophosphines, aminoarsines and sulphenamides have been

determined and the 2*s*-character in the nitrogen bonding orbitals derived.[355] In a study of the barrier to internal rotation in formamide the use of a ^{15}N-enriched sample avoided the broadening of the proton resonances normally observed,[356] and kinetic parameters were obtained by analysing the line shapes at various temperatures for the resultant ABCX system.

A series of ^{15}N enriched amino acids have been studied, and it has been possible to deduce that a fairly shallow and somewhat skewed Karplus relationship holds for the angular dependence of $^3J(^{15}NCCH)$ coupling.[357] It has been found that with several ^{15}N-labelled amino acids the observed line broadening at high pH in their ^{14}N analogues can in fact be attributed to a change in $^1J(NH)$.[358]

Spectroscopic measurements on ^{15}N labelled arylazomalondialdehydes have shown that in solution these exist as hydrogen-bonded mesoxaldialdehyde-2-phenyl-hydrazones (**98**).[359] The ^1J (^{15}NH) coupling of 96 ± 1 Hz shows sp^2 hybridisation at the nitrogen.



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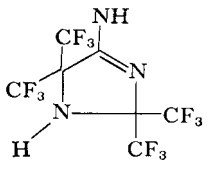
Stereospecific couplings to ^{15}N have been observed in 2-(α-naphthyl)-aziridine which are all of the same sign.[360] A solvent dependence was observed arising from differences in NH populations in various media. Dependence of $J(^{14}NH)$ on the conformation of the nitrogen lone-pair has also been observed, in a study of 1-chloro- and 1-amino- aziridines.[361] Stereospecificity of ^{15}NH coupling constants has allowed the assignment of geometry to non-inverting oxaziridines.[362]

The PMR spectrum of amino-labelled (**99**) has shown that it exists primarily as the amino tautomer, and indicates restricted rotation for the amino group probably arising from the contribution of the ionic form (**100**).[363]



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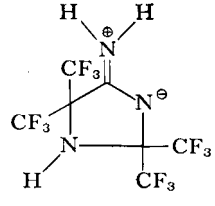


100

Analyses of the 100 MHz spectra of ^{15}N-pyrrole have allowed a complete and accurate determination of all the coupling constants.[364] (^1J(NH) = −96·537 ± 0·010; ^2J(NH) = −4·520 ± 0·009; ^3J(NH) = −5·398 ± 0·09 Hz). Double resonance experiments have also shown that in ^{15}N-2,5-di-*t*-butylpyrrole the ^1J and ^3J(NH) couplings are of like sign;[365] the ^1J(NH) value, −91·5 Hz, is a little lower than in the parent compound. A double resonance study of the ^{14}N-broadened AB spectra in 2-bromo-thiazole and 2,3,4-trichloronitrobenzene has allowed the measurement of proton relaxation times and of the ^{14}N–H couplings in these compounds.[366]

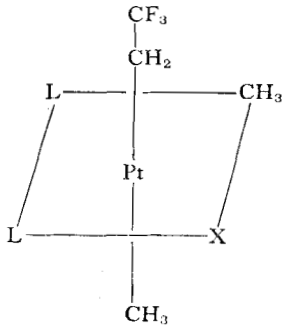
3. *Fluorine-19*

The NMR spectra from a series of fluorine-substituted bicyclic compounds have revealed that vicinal ^3J(HF) coupling constants are extremely sensitive to substituent electronegativity, with ^3J(HF)-*trans* exhibiting a forty-fold change.[367] The magnitude of the substituent effect varies with dihedral angle and is largest for $\phi = 0$, 180°. Limited data indicate that this ^3J coupling may be estimated from Karplus-type expressions of the form A $\cos^2\phi$ ($0° \leqslant \phi \leqslant 90°$); B $\cos^2\phi$ ($90° \leqslant \phi \leqslant 180°$); where A and B are inversely proportional to the sum of substituent electronegativities. The J(HF) values have been documented for some fluorinated furans, and it was noted that ^3J and ^4J couplings were of opposite sign.[368] In a study of mono- and di- fluorinated pyridines, and the corresponding pyridinium ions, the magnitudes and signs of the J(HF)'s were generally in accord with analogous J(HH) values, but with an exaggerated range.[369] In the α-fluoropyridines, the *o*-HF couplings appeared to be negative; the heteroatom therefore reduces (makes more negative) this three bond coupling by 11·5 Hz compared with the same coupling in fluorobenzene.

Substituent effects on long-range couplings in some substituted benzotrifluorides have been investigated.[370] These appear to be little affected, in analogy with similar H–H couplings in toluenes, and thus support theories that these couplings are transmitted by a σ–π exchange polarisation mechanism.

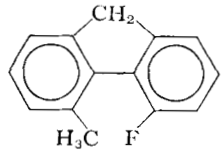
Several papers have recorded long-range proton-fluorine couplings. For example, in $CH_3N(PF_2)_2$, ^4J(HF) = 1·6 Hz,[371] while for $(CH_3)_2NPF_2$, ^4J(HF) = 4·0 Hz,[372] and with $(CH_3)_2NP(CF_3)_2$ a ^5J(FCNPCH) of 0·5 Hz has been observed.[372] In the NMR spectrum of the platinum complexes (**101**) a 1·1 Hz quartet was observed which could only be explained in terms of a ^5J(FCCPtCH_3) interaction.[373]

Two publications have provided compelling evidence for through-space H–F interaction. In the bridged biphenyl (**102**) steric crowding



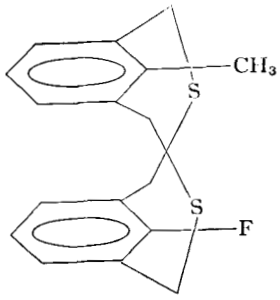
L = $AsMe_2Ph$

101



102

leads to the largest six-bond H–F coupling yet observed;[374] $^6J(F,CH_3) = 8{\cdot}3$ Hz. With the metacyclophane (**103**), in the *Z* conformation, a through-space coupling constant $^9J(HF)$ of 2·5 Hz is found between the methyl of one ring and the fluorine in the other![375]



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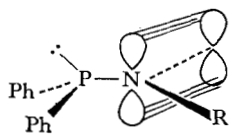
4. *Phosphorus-31*

The effect of the phosphorus lone-pair orientation on $^3J(PNCH)$ couplings has been discussed.[376] It would appear that this coupling is remarkably sensitive to the nature of the nitrogen substituents as well as the lone-pair orientation, and that π-bonding as in (**104**) is an important factor. Although these couplings are normally 8 to 19 Hz, a value which



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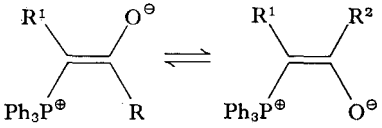
is both abnormally low and temperature dependent has been reported (1·4 Hz at 20°) for $PhCH_2NPh \cdot PPh_2$. This has been explained by conformer population effects.[377] A discrepancy between predicted and experimental ^3J(POCH) in trimethyl phosphite has prompted a precise measurement of this parameter for various acyclic phosphites and phosphates.[378] It is suggested that such couplings involving $P^{\overline{V}}$ may be explained approximately by the same mechanisms as for vicinal H–H interactions.

NMR shifts and couplings have been discussed[379] for adducts of alkyl and aralkyl phosphines with In^{III} halides. The $^2J(PCH_3)$ couplings increase markedly on complex formation, indicating an increase in the *s*-character of the P bonding orbitals.

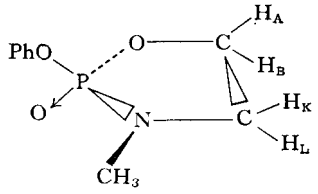
A spectroscopic interest has been taken in keto- and formyl methylenetriphenyl phosphoranes.[380 to 383] These appear to be best described by the equilibrium (**105**) ($R^2 = H$ or alkoxy); the individual conformers are



105

observable for the aldehyde ($R^1, R^2 = H$) and structures have been unambiguously assigned from J(PH) values and a $\Delta G^{\ddagger}$ of 17·6 ± 0·5 kcal/mole measured by variable temperature studies. Non-ester keto phosphoranes appear to be uniformly *cisoid* in structure.

^3J(PNCH) couplings have been recorded[384] for some phosphorylated aziridines and for some oxazaphospholanes,[385] e.g. (**106**), where both



106

^3J(POCH) and ^3J(PNCH) couplings to protons *trans* oriented to the P–O bond were of larger magnitude than the *cis* interactions. A use of the ^2J(PCH) geometrical dependence for stereochemical assignment in the phospholene series has been illustrated.[386] The ^4J(HCPCH) coupling in these compounds is sensitive to the orientation of the P substituent,

being larger when both protons are *cis* to each other and to the lone-pair. A study of some bicyclo[2.2.1]heptyl phosphonates has confirmed[387] that ^3J(PCCH) couplings exhibit a Karplus-type conformational dependence similar to that of ^3J(HCCH).

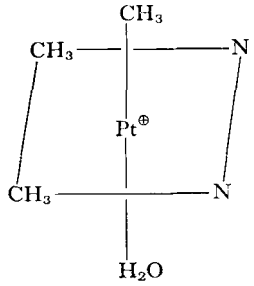
Three papers have discussed the NMR spectra of 2- and 3- furyl and -thienylphosphines and some derivatives.[388 to 390] In all cases the ^{1}H–^{31}P as well as the ^{1}H–^{1}H couplings have the same sign except for $^5J(PCH_3)$ in methyl[tri-(5-methyl-2-furyl)]phosphonium iodide and tri-(5-methyl-2-furyl)phosphine sulphide.

^{1}H–^{31}P coupling constants in some 2-pyridylphosphine derivatives have also been reported by two groups,[391, 392] where ^4J(P–H(6)) was found to be opposite in sign to the other values. It is of interest to note[393] a coupling between the π-cyclopentadienyl ring protons and phosphorus of 1 to 1·5 Hz in complexes of the type $Cp–V(CO)_3PR_3$.

Several papers[394 to 398] have reported the use of proton NMR studies to determine not only P–H couplings but also P–P interactions. This can involve the use of INDOR techniques where appropriate and the analysis of $[AX_n]_2$ spectral systems which directly give this parameter. In order to interpret a novel 5-line pattern observed in the NMR spectra of some *trans*-bis(di-*t*-butylphosphine)-metal complexes, ways of analysing the $[AMX_n]_2$ spin system were devised[399] and afforded values for ^2J(PMP), together with ^1J, ^3J and ^5J(PH) coupling constants.

5. *Platinum-195*

Several papers have used observed ^{195}Pt–H satellite spectra for the elucidation of chemical structures, and a few examples are given here. In a series of platinum hydride complexes of general structure $[PtHL(AsEt)_2]^{\oplus}ClO_4^-$ J(PtH) was found to *increase* as the σ-donor strength of a *trans* ligand (L) increased, but with the ligand in a *cis* position it actually decreased.[400] $J(PtCH_3)$ has been discussed[401] for a wide range of cationic methylplatinum(II) complexes, whose spectra



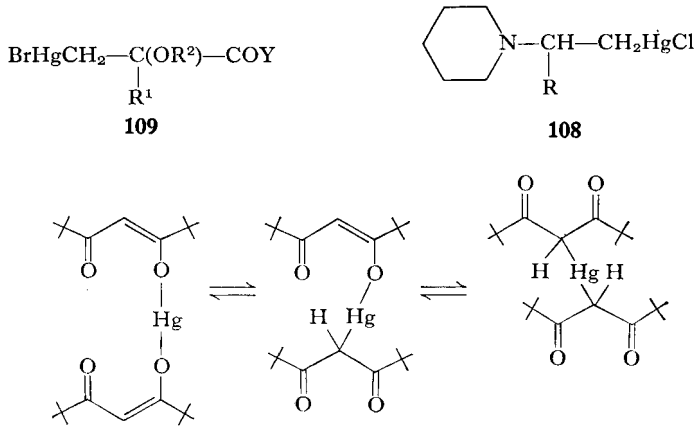
107

were obtained in liquid sulphur dioxide. The appearance of ^{195}Pt–H satellites has been used to provide evidence[402] that the exchange reaction responsible for averaging the two methyl proton signals of the trimethylaquobipyridine-platinum(IV) cation (**107**) in aqueous solution involves the exchange of a coordinated water ligand with bulk solvent.

A study of $J(PtCH_3)$ has been used to show that above room temperature, rapid dissociation of the bond between Pt and the γ-carbon atom of the adjacent β-dicarbonyl ligand occurs in a number of dimeric β-dicarbonyl complexes of $(CH_3)_3Pt^{IV}$.[403] Pt–H couplings show that in some Pt^{II} olefin complexes the olefin assumes a skewed position in the plane perpendicular to the Pt–ligand plane, for at low temperatures coupling non-equivalences are observed.[404]

6. *Mercury-199*

The observation of typical ^{199}Hg satellite bands with $^3J(HgH) > {}^2J(HgH)$ has provided evidence for the presence of a σ-bond between mercury and carbon in aminomercurials of the type (**108**).[405] Novel β-mercuration has been observed[406] in the oxymercuration of a series of α,β-unsaturated carbonyl compounds. In the case where the final product



(**109**) has $R^1 = CH_3$, evidence for this structure was derived from a $^4J(HgCCCH_3)$ of 20 to 25 Hz, which is too small by a factor of ten to permit the presence of a $HgCCH_3$ system. Variable temperature studies on bis(dipivaloylmethyl) mercury have shown the presence of the equilibrium (**110**).[407]

A PMR study of the fast reversible reaction of mercuric trifluoroacetate with cyclohexene, norbornene and apobornylene has shown that the life-

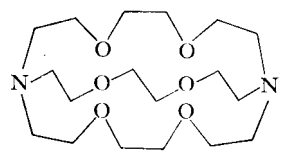
times of individual species must be longer than the NMR time scale, for ^{199}Hg–H satellites can be observed.[408] Some ^{199}Hg–H couplings and their relative signs have been discussed for indenyl-mercury derivatives, and the relevance of these parameters to the cyclopentadienyl-mercury systems was demonstrated.[409] In the isomers of difuryl- and dithienyl mercury the relative signs of both J(HH) and J(HgH) couplings were found to be alike, and a linear correlation was noted between J(HgH) and the corresponding J(HH) of furan or thiophene.[410] Coupling to aromatic ring protons has been measured for some phenylmercury alkoxides.[411]

7. Thallium -203 and -205

The synthetically valuable organothallium compounds have also been investigated widely from a spectroscopic viewpoint, and it is fortunate that the almost equally abundant ^{203}Tl and ^{205}Tl isotopes both possess a spin of $\frac{1}{2}$ and have virtually identical gyromagnetic ratios, thus giving the same spectral features as 100% monisotopic nuclei.

Spectral data have been given[412] for some mono-alkylthallium(III) halides and the observations of Tl–CH_3 couplings have been used to identify the SO_2 and CS_2 insertion products of some compounds containing Tl–O bonds.[413]

In a study[414] of cation exchange rates in some cryptates derived from **(111)** it was observed with TlCl that at 7°, the pure cryptate showed all NMR signals to be doubled, arising from coupling with ^{203,205}Tl with J[Tl–(CH_2–N)] = 14 Hz; J[Tl–(CH_2–O)] = 12 Hz. This indicates that the $Tl^{\oplus}$ ion is at the centre of the molecular cavity. H–Tl couplings have been given for a series of methyl(allyl)thallium(III) derivatives **(112)**.[415]



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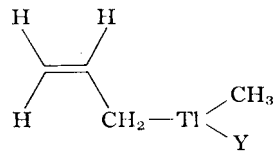


112

Comparison of these data with published H–H couplings for the parent propene shows that no linear relation exists, in this instance, between J(H–Tl) and the analogous J(HH). For some $ArTlX_2$ and Ar_2TlX compounds, where the aromatic ring is methyl substituted, J[Tl–(*m*-CH_3)] is smaller than J[Tl–(*p*-CH_3)].[416] This has been attributed to an enhanced π-electron contribution to *para*-coupling. The relative magnitudes of individual J(H–Tl) values were discussed for the Ar_3Tl–Ar_2TlX-$ArTlX_2$ series. It has been found [417] that the J(Tl–H) values in

$(CH_3)_2TlOEt$ and its dimer $[(CH_3)_2TlOEt]_2$ are opposite in sign; no simple explanation is possible on the basis of the Fermi contact term alone.

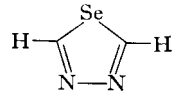
8. *Other nuclei*

Two papers have discussed spectra of the $B_3H_8^-$ anion.[418,419] Thermal "decoupling" resulting in the disappearance of $J(^{11}B–H)$ was observed at low temperature; partial decoupling could also be effected by the addition of paramagnetic ions. This quadrupole-induced spin relaxation induced by choice of a suitable temperature could produce substantially simplified spectra for boron compounds. This thermal effect has also been observed, together with rapid intramolecular exchange, in spectra from $(Ph_3P)_2CuBH_4$.[420] The 220-MHz PMR spectrum of decaborane has been analysed with the aid of spectra from bromo- and deutero- derivatives.[421] The magnitudes of $J(^{11}B–H)$ could be elucidated with greater accuracy than by ^{11}B-NMR.

^1J(HSi), ^2J(HH) and $^{2,3}J$(HF) couplings have been reported for a series of di-,[422,423] tri-[423] and tetrasilanes,[423] and a ^1J(HSi) coupling of 370 Hz has been found for $(HF_2Si)_2O$.[424]

The well-known cobalt (III) tris-diamine complexes have consistently given PMR spectra of such low resolution as to render accurate analysis impossible. Experimental proof has now been presented that this is due to *coupling* with long-lived nuclear spin states of ^{59}Co ($I=7/2$, 100%) as shown by spin decoupling of that nucleus.[425] The decoupled spectra were of sufficient quality to be analysed in terms of conformation.

Couplings giving rise to ^{77}Se satellites ($I=\frac{1}{2}$; 7·5%) have been described for some aliphatic and aromatic derivatives. ^2J(SeCH), ^3J(SeCCH) and ^3J(SeSeCH) values have been summarised for some alkyl selenides,[426] -diselenides[426] and selenols.[427] In 1,3,4-selenadiazole (**113**), ^2J(SeH)= 55·3 Hz,[428] while with seleno[2,3-*b*]- and seleno[3,2-*b*]- thiophene[429] the



113

^2J(SeH) and ^3J(SeH) couplings in the selenophene ring were *ca.* 48 Hz and *ca.* 8·5 Hz respectively and of the same relative sign. In a study of complex formation between R_2E (E = S, Se, Te) and boron halides,[430] J(Se–CH_3) (R = CH_3) was observed to decrease upon coordination by *ca.* 2·5 Hz; satellite lines could also be observed for $(CH_3)_2Te$ and its

complexes (^{125}Te has $I=\frac{1}{2}$; 7·03% abundance) which showed a decrease from ^2J(TeCH) = 21·2 to 19·5 Hz on complexation with BCl_3.

A definitive study of the exchange problem concerning methyl groups in methylcadmium compounds has been made *via* a study of the changes induced in ^{111}Cd and ^{113}Cd satellite signals.[431] A large increase in J(CdCH) was observed, analogous to those found in mercury derivatives, on going from $(CH_3)_2Cd$ to CH_3CdBr. In solutions of divinylcadmium no satellite signals could be observed, which was interpreted[432] as indicating rapid vinyl group exchange.

In an NMR study of some 3,3,3-trifluoropropyl-tin compounds it was found[433] that ^3J(SnH) *was* larger than ^2J(SnH) in most instances, despite reports that the opposite situation is a characteristic of this type of compound. It was indicated that it is not valid to derive tin atom hybridisations from ^2J(SnH) coupling constants.

Although osmium has a naturally occurring isotope ^{187}Os ($I=\frac{1}{2}$, 1·63% abundant) nuclear spin couplings to this species have not hitherto been reported. ^1J(OsH) couplings have now been observed for a series of osmium hydride complexes.[434] The *reduced* coupling constants ^1K(Os) lie, as would be expected, between the known values for $^1K(^{183}W)$ and $^1K(^{195}Pt)$.

In a study of some triphenyllead derivatives[435] $^2J(^{207}Pb–H)$ was found to be 60 Hz in Ph_3PbCCl_2H, while for two substituted derivatives Ph_3PbCCl_2R (R = CH_3 or CH_2Ph) ^3J(PbCCH) was also unexpectedly found to be *ca.* 60 Hz, in contrast with the normal value for unsubstituted Ph_3Pb derivatives of *ca.* 170 Hz. In the novel bicyclic compound 5-plumbaspiro[4.4]nonane, two couplings were observed[436] with $^3J(Pb–H_\beta)$ larger (134·0 Hz) than $^2J(Pb–H_\alpha)$ at 62·0 Hz; the relative signs were not determined.

Satellites corresponding to M–H coupling constants through two to four bonds were observed and analysed in the PMR spectra of some Pb, Sn and Hg allenic derivatives.[437] The relative signs were deduced; ^2J(MH) and ^4J(MH) were opposite in sign for M = ^{207}Pb, ^{117}Sn and ^{119}Sn, but were of similar sign for ^{199}Hg.

V. SPECTRA-STRUCTURE CORRELATIONS

A. Systems of biological importance

1. *Amino acids*

A variable temperature and solvent study has been reported of the aliphatic protons in tyrosine, tryptophan and histidine.[438] The variations in J(*vic*) could be interpreted in terms of variations in the relative

energies of the three classical staggered rotamers and reflected the presence of both solute-solute and solvent-solute interactions. The newly synthesised diastereomers of the artificial amino acids, β-methylnorleucine and β-methylleucine, were given configurational assignments on the basis of an NMR spectral analysis.[439] The protonation of a range of amino acids, together with some simple peptides and insulin, has been investigated using "superacid" media.[440] With amino acids, amino and carboxyl sites were protonated, as well as other available basic centres; no dehydration of α or β amino acids to oxocarbonium ions was found.

Mercury(II) has been shown to bond with the S atom of methionine and *S*-methylcysteine in Molar nitric acid,[441] contrary to the previously accepted idea that no such interaction occurs with these compounds. Shift studies indicate the presence of $Hg(LH_2)_2^{4\oplus}$ species. An NMR study has been made of D_2O solutions containing an α-amino acid, Al^{III} ions and pyridoxal.[442] Schiff bases were formed which yielded bis-Al^{III} complexes which exist as *three* readily distinguishable diastereomers; their structures were directly deduced from the 2-CH_3 signals of their pyridine aldehyde moieties.

The kinetics and mechanism of Co^{III} promoted hydrolyses of chelated glycine amides, glycylglycine and glycylglycine esters were investigated by NMR methods, and the relevance to metal ion activated enzymic hydrolysis was discussed.[443] The lysis of Co^{III} chelated glycine isopropyl ester by N and O bases has also been studied.[444]

2. *Peptides and enzymes*

Dipeptides from a range of amino acids have been studied[445] by NMR in aqueous solutions at various pH values and disagreements were found with a previous study,[446] which suggested that shifts were additive in nature; clearly a more sophisticated approach is needed, in which conformational effects can be separated from all others. The rates of exchange for the peptide protons of glycylglycine and triglycine have been measured as a function of pH in water and aqueous urea.[447] In contrast to the composite exchange rates reported for proteins, the rates for some of the peptide protons in these model peptides were slower in aqueous urea than in water and were markedly affected by their neighbouring groups. From the change in NMR parameters observed between amino acids and their di- and tri- peptides it has been concluded that the latter is a good model for polypeptides.[448] Spin couplings (and the populations of *trans*-rotamers) increased upon the formation of peptide bonds. From 220-MHz NMR studies it has been found that the α-protons of proline residues in an oligo- or poly- L-proline chain give rise to separate resonances for *cis* and *trans* peptide bonds.[449] Direct observation of the

populations and ratios of these bonds in various peptide chains has been achieved by this method. In a series of cyclic tetrapeptides containing sarcosine (sar, $=N$-methylglycine) the similarity of their low-temperature spectra with that of cyclo-$(sar)_4$ suggests that all have the same *cis-trans-cis-trans* ring conformation.[450] During studies on the secondary and tertiary structure of compounds related to actinomycin NMR studies suggested the skeletal arrangement shown, for the 16-membered lactone pentapeptide ring given in Fig. 6.[451] The ability of copolypeptides of

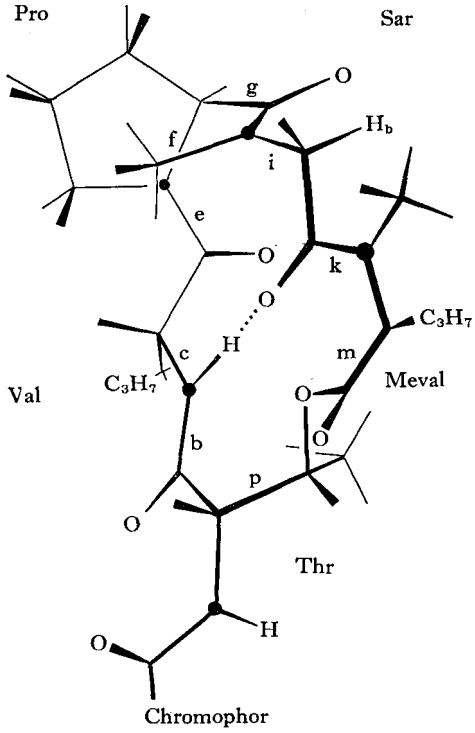


FIG. 6. R-[cyclo-(L-Thr-D-Val-L-Pro-Sar-L-*N*-Meval-O_{Thr})]. (From Lackner.[451])

L-proline and γ-benzyl-L-glutamate to adopt a helical structure has been studied as a function of molar ratio by an NMR method.[452] It was found that helix formation was favoured by high proline content.

Signals in the $\delta 10$ to 15 region of spectra obtained from myoglobins of various species (sperm whale, porpoise, horse) have been specifically assigned to tryptophan, arginine and histidine residues through chemical modification, considerations of X-ray structure, pH variation, etc.[106] A high resolution NMR study of the Michaelis complex, formed between

cinnamate ion and the proteolytic enzyme α-chymotrypsin, has been carried out.[453] The aromatic signals from the complexed anion were shifted 0·6 to 0·8 p.p.m. upfield, while the vinyl protons were little affected. Line-broadening effects suggested that the mode of binding with the enzyme was such that the cinnamate had no freedom of motion independent of the enzyme. Using enzymes chemically modified at the active site, *no* shifts were induced. Fig. 7 shows two possible arrangements of the cinnamate aromatic ring with respect to the aromatic group

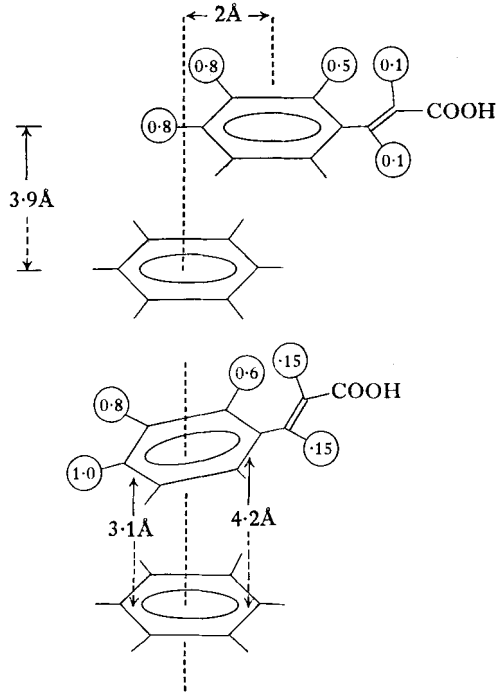


FIG. 7. Two possible arrangements of a cinnamic acid–aromatic ring complex that are consistent with the chemical shifts reported. (From Gerig and Reinheimer.[453])

at the active centre in the enzyme which are consistent with the observed shift changes. Mention has already been made of the potentiality of lanthanide cations as indicators of their environment when bound to enzymes (p. 10). Eu^{III} appears an excellent probe of tightly and loosely bound ligands; its binding site and dynamics of its conformational equilibria in biological molecules should be readily defined using NMR studies.[38]

The structure of heme A from Bovine heart has been established

through the study of NMR spectra and other properties.[454] A review of the present knowledge in structural studies of hemes and hemoproteins by NMR has been published; considerations of ring current shifts, low spin ferric hemes, etc., are described.[455]

3. *Polysaccharides, nucleosides, nucleotides and nucleic acids*

The application of high-field techniques in the study of polysaccharides has been mentioned earlier (p. 18),[104, 105] Proton and deuteron NMR measurements of the sol→gel transition, in agarose and carageenans,[456] have suggested that distinct changes in polysaccharide conformation occur with agarose, whereas most water molecules remain highly mobile; the results are compatible with a coil-to-double helix model suggested from other evidence.

A spectroscopic study has been reported[457] of the reaction of 6-chloropurine with xylals and arabinals. The geometry of the resulting pyranosylpurine isomers was discussed in detail. NMR investigations have been made of the chelation of uranyl ions by adenosine 5′-mono-[458] -di-[459] and -triphosphate[459] in basic media. With the monophosphate and $UO_2(NO_3)_2$ in equimolar proportions it was seen that above pD 10·9 a strong chelate with 1:1 stoichiometry was present, which disproportionated in less alkaline media to give uncomplexed AMP, two forms of sandwich chelates both with 2:1 (U:AMP) constitution, and non-sandwich complex(es). From pD 7·7 to 11·0 an equimolar U–ATP mixture consists of 2:2 sandwich-type chelates in which the ligands are the β- and γ- phosphoryl groups, but at pD 6·8 to 7·3 non-sandwich forms are observed, in which the U is bound only to the β- and γ- phosphoryl groups. The U–ADP system contains no 2:2 sandwich-type complexes at any pD. Unlike the behaviour of the non-sandwich U–AMP complexes, non-sandwich U–ADP and U–ATP complexes were found to ring-stack more readily than the free nucleotides. An NMR study of guanosine-cytidine pairing has been reported[460] using mixed solvents. In DMSO and mixtures of DMSO–CCl_4 or DMSO–CH_3CN, a hydrogen-bonded complex results. Extrapolation to zero DMSO concentration showed that a minimum equilibrium constant for the reaction $G + C \rightleftharpoons GC$, unperturbed by medium effects, was 38.

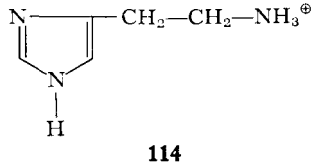
Nuclear Overhauser effect experiments[77] showed that purine molecules could become sandwiched in the single stranded nucleic acid poly-U. In a study of β-pseudouridine[461] the effect of added purine on NMR parameters showed that base stacked complexes were formed which were very similar to those formed between uridine and purine. The results of a computer analysis of the 100-MHz spectrum of β-pseudouridine, confirmed by double resonance experiments, were used to

determine a model for the conformation of the nucleoside. A complete analysis of the 220-MHz spectrum of uridine has also been reported, and the derived structure compared with β-pseudo-uridine.[462] It was concluded that in both compounds the ribose rings are in rapid equilibrium between classical puckered structures, and that both have a preference for the gauche-gauche rotamer about the exocyclic 4′-5′-bond (to CH_2OH), while the uracil bases exist in the *anti*-conformation. The report[290] of the assignment and conformational properties of the sugar-ring OH protons of the common nucleosides should again be noted at this point.

The interaction of Zn^{II} and Hg^{II} ions with cytidine and glycylglycine has been studied.[463] In solutions containing the two organic substrates and $ZnCl_2$ in equimolar proportions, a ternary complex is formed, in which cytidine is bound to the metal through N_3 and the metal in turn is chelated to glycylglycinate through the amino and amide groups. With Hg^{II} nitrate, no ternary complex is formed, only the two binary derivatives. Similar studies have shown that Co^{II} forms a ternary complex with two nucleosides, and Zn with both a pair of nucleosides, and a nucleoside plus imidazole.[464] By an NMR method the formation constants of the 1:1 Hg^{II} complexes with cytidine, adenosine and guanosine in DMSO at 36° were found to be 33·9, 7·2 and 5·9 l/mole.[465] The mercuration induced hindered rotation about the 4-C–N bond in cytidine. No ternary complexes were formed and Hg^{II} would not bind uridine.

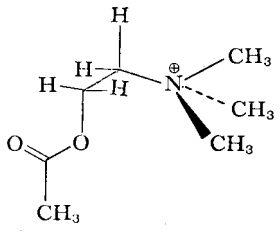
4. *Other studies*

An NMR study has been reported of the conformation of histamine in solution.[466] In contrast to the solid state, the side chain of the univalent cation (**114**) has approximately equal populations of the *trans* rotamer and



114

both *gauche* rotamers. The reaction rates and equilibria involved in the hydration and dehydration of pyruvic acid have been investigated by NMR over a range of pH values[467] and a tentative mechanism for dehydration was discussed. Iterative analyses have been performed on the NMR spectra from several acetylcholine analogues.[468] Whilst acetylcholine itself exists in the conformation (**115**), both the thia- and selena- analogues exist almost exclusively in the *anti*-periplanar shape (**116**). A model for



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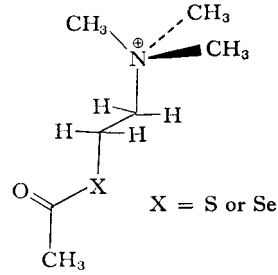

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the mode of self-association of caffeine has been suggested[469] following a study of the concentration dependence of chemical shifts, and by the application of nuclear Overhauser studies. The precise NMR parameters of some biologically important aromatic acids and their derivatives have been obtained by iterative computer analysis of their high-resolution spectra;[470] the importance of solvent effects on shift values was stressed.

The interactions of pyridoxal with a range of amino acids including serine, cysteine, histidine and cycloserine have been investigated by PMR techniques.[471] It was concluded that NMR spectroscopy provides a convenient method for examining equilibria and structure in the interaction of pyridoxal with inhibitors and for studying the reactivity of the azomethine bond toward various functional groups of polyfunctional amino acids. Although such studies involve relatively high coenzyme and substrate concentrations they appear to provide a realistic reflection of equilibria and observed reactivity at biological concentrations.

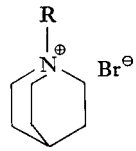
In a study of the cation-binding properties of the macrocyclic antibiotic nonactin,[472] 220-MHz spectra have been used. The binding constants in anhydrous acetone for $Na^{\oplus}$, $K^{\oplus}$, and $Cs^{\oplus}$ were drastically reduced when the solvent system was altered by the addition of appreciable amounts of water. Potassium was particularly favoured in an aqueous medium, and it was felt that the experimental results were pertinent to the $K^{\oplus}$ ion transport induced by nonactin in experimental lipid bilayers. The nonactin ring appears to undergo sizeable conformational changes upon ion incorporation.

A review has been published[473] of NMR studies on the biochemistry of biopolymers, covering the fields of amino acids and their polymers, nucleic acids and their components, and saccharide systems.

B. Magnetic non-equivalence

The causes of this phenomenon are now well documented and understood, and its observation is commonly put to structural use; a few examples from the 1970 literature are given here.

Intrinsic diastereotopism has been demonstrated for geminal protons in quaternary salts from quinuclidine and hexamine.[474] For example in (**117**), where R is the chiral group $PhCHCH_3$, $\Delta\delta$ for the α-methylene



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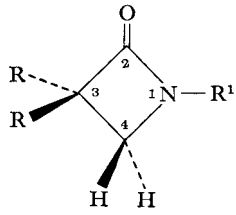
protons is 0·095 p.p.m., and when $R = CH_3CHCO_2Et$ the shift difference is 0·09 p.p.m. (both values in DMSO solution). These shift differences would presumably have their intrinsic magnitudes affected by conformational preferences. Intrinsic chemical shift non-equivalences have also been studied[475] for a series of carbinols with the general formula $R \cdot CH(OH) \cdot C(NO_2)Me_2$. A study has been reported[476] on the magnetic non-equivalence of the C-4 diastereotopic protons in a series of identically 3,3′-disubstituted β-lactams (**118**) bearing an asymmetric carbon



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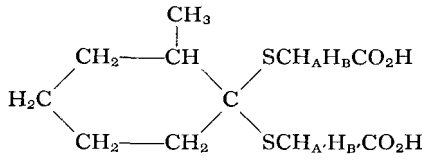
atom in positions ranging from β to ϵ along the chain of the *N*-substituent group. This asymmetric centre is able to induce non-equivalence in the ring protons over a maximum distance of five bonds. A coiled conformation for compounds having six bonds between C-4 and the asymmetric centre (which would bring it close to these protons) appears therefore to be unimportant.

The cyclohexane derivative (**119**) is yet another class of compound (along with some allene diacetals and dibenzylmercaptals) for which a *double* magnetic non-equivalence has been observed.[477] A further example has been described[478] of a compound (**120**) in which there is a magnetically non-equivalent *tert*-butyl group.

The observation that in the dioxanes (**121**) the C-4 methylene protons are non-equivalent excludes the possibility of twist forms, or a chair-boat



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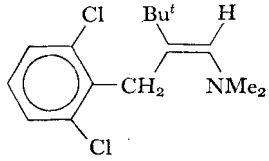

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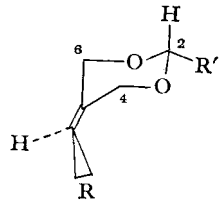
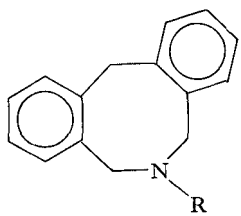


121

equilibrium; these derivatives are probably predominantly in the chair form.[479] The diastereotopic nature of H or CH_3 groups in *para*-substituted ethylphenyl- and isopropyl- phenylsulphoxides has been investigated by PMR.[480] Magnetic non-equivalence was affected by the substituent in such a way that the shift of one of the non-equivalent pair of protons or methyl groups was barely influenced while the other moved markedly; the non-equivalence was still present at a point five bonds from the centre of assymetry. The results were discussed in terms of the preferred conformations. The influence of substituents on the non-equivalent $-CH_2-$ protons in compounds of the type HO_2CCH_2SR' and RO_2CCH_2SR' has been discussed.[481]

PMR studies have shown that the dibenzazocine ring in (**122**) does not rotate freely at room temperature; a variable-temperature coalescence sequence is observed for all three methylene AB systems.[482] The monocyclic azocine (**123**), in either a tub or a chair form, has a chiral influence on the ethyl substituent which is only removed at 150°, when an A_2X_3 spectrum indicates the onset of fast ring inversion.[483]



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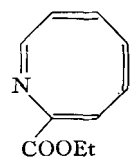
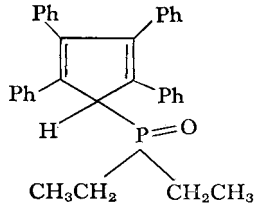


123

The asymmetric phosphorus atom in $^{i}PrPClNMe_2$ and some related compounds induces shift non-equivalence of the methyl groups[484] which may be removed at high temperature, or by addition of chloride ion, to induce inversion of configuration at P. In phosphinous esters of general formula R–PH(O)OR′ the asymmetric P has been shown to induce in-equivalence in geminal protons and methyl groups.[485] The methylene protons in (**124**) are diastereotopic and also show spin-coupling non-equivalence to phosphorus; $J(PA) = 7$ Hz, $J(PB) = 9$ Hz.[486]



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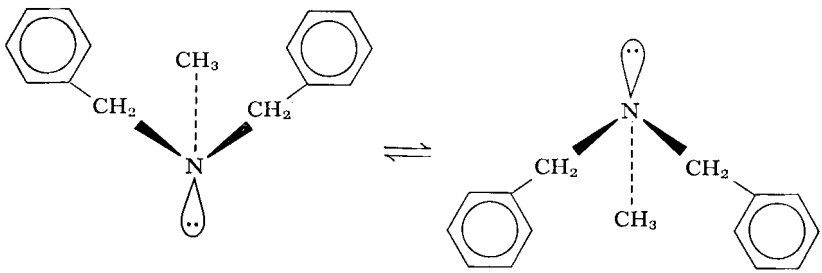
C. Inversion at Nitrogen

The dynamics of nitrogen inversion have been studied in a wide variety of molecules; some examples are described here. The observation of slow nitrogen inversion in free, unprotonated, dibenzylmethylamine has been reported.[487] At $-146°$, an AB spectrum was observed for the methylene protons, indicating a disymmetric environment arising from long-lived invertomers in (**125**). ($\Delta G^{\ddagger}_{-146°} = 6{\cdot}0 \pm 0{\cdot}5$ kcal/mole).



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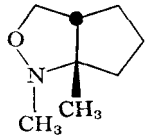
A line-shape analysis has been reported for some tertiary amines in a study of inversion rates which showed second-order dependence upon amine concentration.[488] This rate law closely followed the second-order proton exchange reaction for the amine in question. The barrier to inversion in some *m*- and *p*- substituted *N*-phenyl-2,2-dimethylaziridines shows a linear correlation with the Hammett substituent constant σ^{-}; the

results have been discussed in relation to conjugation of the lone-pair on the inverting centre with the attached arene π-system.[489] A series of studies have been made[490,491] of rate processes and conformations in a series of medium ring mono- and bi- cyclic amines. The barrier to inversion depends on ring size and decreases in the following order: $3 > 6 \sim 4 > 5 > 7$. Introduction of an electronegative *N*-substituent leads to a marked increase in the inversion barrier.

The nitrogen inversion rate of an amine may be brought to within the NMR time scale by the choice of an acidic medium of suitable pH, in which the inversion is almost completely prevented through protonation.[492] Equations have been presented for computing this rate from the mean lifetime of the ammonium cation.

As part of a series of studies on the stereochemistry at trivalent nitrogen,[493] chemical shift non-equivalence arising from slow nitrogen inversion was observed in (**126**). An assignment of the configurations at



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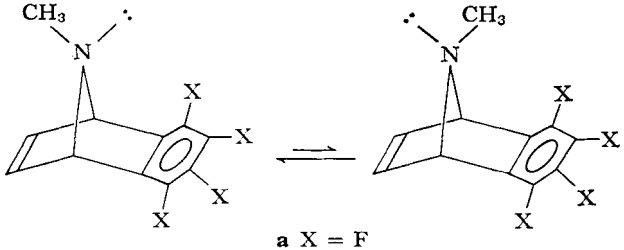
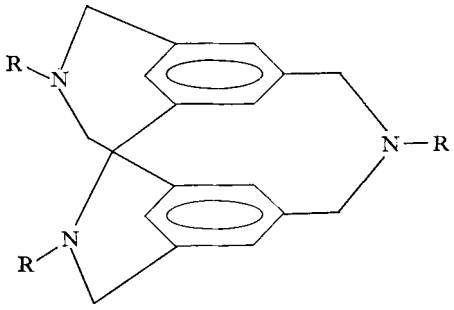
nitrogen in the two diastereomers observed at low temperatures could be made on the basis of steric and solvent effects on the equilibrium constant, and the effect of the lone-pair orientation on chemical shifts. A new example of relatively slow nitrogen inversion has been observed in the 7-azabenzonorbornadienes.[494] Two separate sets of signals are observed below about 0°, corresponding to the unequally populated isomers (**127**). The influence of substituents (Z) on the rates of *syn-anti* isomerism has been studied using guanidines as typical examples of



a X = F
b X = Cl

127



R = $SO_2C_6H_4CH_3$-*p*

128

imines $X_2C{=}NZ$.[495] In *p*-substituted phenyl guanidines ($Z = C_6H_4R$) a linear Hammett correlation was observed between σ^- and the inversion rate. Large *ortho*-substituents enhanced the inversion process.

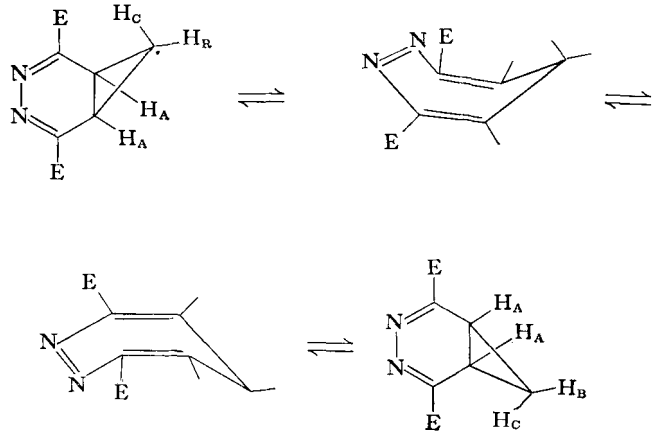
At $-57°$ the methylene bridge protons in (**128**) are seen as a clear AB group ($\Delta\delta = 1{\cdot}63$ p.p.m.). This probably arises from the freezing of nitrogen inversions, and possible ways in which the molecule may undergo ring and/or N inversions have been discussed.[496]

The detection of hindered rotation and inversion by NMR spectroscopy has been the subject of a review,[497] in which the application of this approach in the elucidation of activation barriers, and determination of stability limits is described.

D. Molecular dynamics

Mention has already been made (p. 20) of the general theory of exchange-broadened line shapes developed by Binsch,[119] which is of wide potential applicability. Experimental evidence has been put forward to support the claim that inherent shortcomings in NMR line-shape analysis can be alleviated by deliberately choosing more complicated spectra which are then analysed in the above manner.[498] Thus thermodynamic parameters were derived for the degenerate valence isomerisation of a 3,4-diazanorcaradiene ($E_a = 15{\cdot}30 \pm 0{\cdot}10$ kcal/mole; $\log A = 13{\cdot}12 \pm 0{\cdot}07$; $\Delta H^{\ddagger} = 14{\cdot}67 \pm 0{\cdot}11$ kcal/mole; $\Delta S^{\ddagger} = -0{\cdot}61 \pm 0{\cdot}34$ e.u.) which proceeds *via* the mechanism shown in Fig. 8.

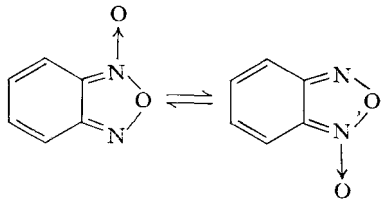
Equations for the line shape in strongly coupled NMR spectra of molecular systems undergoing intramolecular exchange have been evaluated according to the density matrix theory of Kaplan and Alexander, and a computer program developed by means of which the line-shape equations may be solved for up to four-spin systems.[499] The systems ABCD $\rightarrow$ $[AB]_2$, $[AB]_2 \rightarrow A_4$ and ABC $\rightarrow$ A_2B were dis-



$E = CO_2CH_3$

FIG. 8. Valence isomerism of 3,4-diazanorcaradiene. (From Kleier *et al.*[498])

cussed and the method has been applied to the benzo-furoxan (**129**) system,[500] where values of $E_a = 16{\cdot}1 \pm 0{\cdot}5$ kcal/mole, $\Delta H^{\ddagger} = 15{\cdot}5 \pm 0{\cdot}5$ kcal/mole, $\Delta F^{\ddagger}_{298^\circ} = 14{\cdot}0 \pm 0{\cdot}2$ kcal/mole and $\Delta S^{\ddagger} = 5{\cdot}1 \pm 2{\cdot}3$ e.u., were derived.

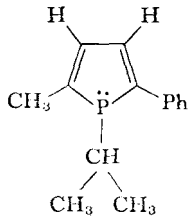


129

A novel approach to the analysis of two-site systems has been described[501] in which line shape was studied as a function of exchange rate $(1/\tau)$ and population $(P) - F(\tau,P)$. The dependence of F on τ and P was shown in a three-dimensional diagram. From this plot, "iso-F" parabolic curves could be obtained from which rate parameters and equilibrium data may be evaluated; the method was applied to the low-temperature spectra of the CHO group in furan-2-aldehyde, and gave parameters in good agreement with those already published.

The barriers to internal rotation in 2,4-dichloro- and 2,4-dibromo-1,3,5-tri*neo*pentylbenzene have been derived *via* a computer treatment of digitised NMR line shapes.[502]

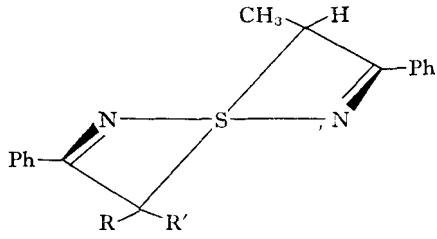
The barrier to pyramidal inversion at phosphorus in (**130**) has been derived *via* a total line shape analysis, and, at 16 kcal/mole, is extra-



130

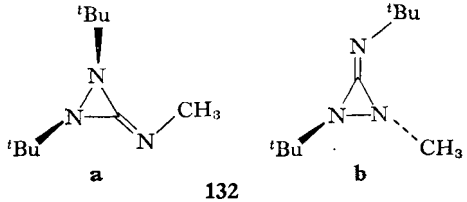
ordinarily low indicating $(3p\text{-}2p)\pi$ delocalisation and aromaticity in the phosphole system.[503] Figure 9 illustrates the remarkable correlations between observed and calculated spectra which may be obtained for this (and other) molecules by using the complete lineshape approach.

In an NMR investigation of stereoisomerism and ring inversion in some 2,7-dihydro-1,4,5-thiadiazepine derivatives large barriers were observed to interconversion between equivalent conformations.[504] For (**131b**) $\Delta G^{\ddagger} = 21{\cdot}2 \pm 0{\cdot}2$ kcal/mole which is believed to be the highest barrier yet reported for a monocyclic ring system. The favoured shape appears to be the skew-boat illustrated.



a R = H, R′ = CH_3
b R′ = H, R = CH_3

131



a **b**

132

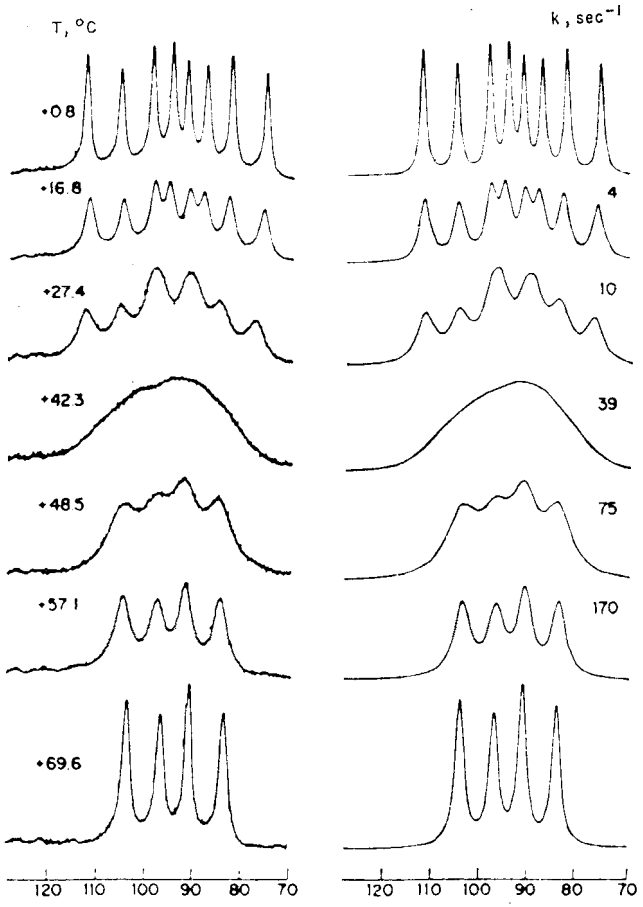
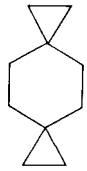


FIG. 9. Comparison of experimental spectra of **130** at different temperatures (left) and theoretical spectra at various rates (right). The scale is in hertz and is relative to the internal lock signal, TMS. The low-intensity broad signals at *ca.* 110–128 Hz are an unidentified impurity. (From Egan *et al.*[503])

The synthesis of some hitherto unknown diaziridine imines has allowed the first observation of the reversible valence isomerism of a heteromethylenecyclopropane.[505] The diaziridines (**132a** and **b**) rearrange at elevated temperatures, and the rate of this process has been determined by NMR studies. $\Delta H° = -2{\cdot}3 \pm 0{\cdot}3$ kcal/mole, and $\Delta S° = -1{\cdot}1 \pm 0{\cdot}4$ e.u. for this process; a triaza-analogue of the trimethylene methane is assumed to be an intermediate.

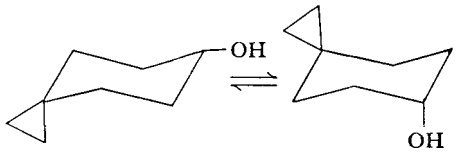
Variable temperature studies have allowed the calculation of activation

energies for ring inversion in dispiro[2.2.2.2]decane[506] (**133**) and in spiro[2.5]octan-6-ol[507] (**134**). The barrier to internal rotation in 2-acetyl



$E_a = 12{\cdot}1 \pm 0{\cdot}4$ kcal/mole

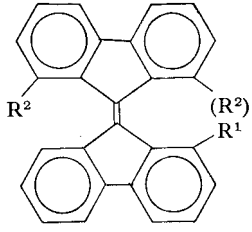
133



$E_a = 14{\cdot}4 \pm 1{\cdot}3$ kcal/mole

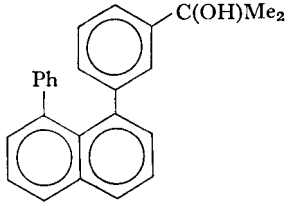
134

furan has been measured by an NMR line shape study between $+30°$ and $-115°$;[508] it was *ca.* 2 kcal/mole lower than in furan-2-aldehyde and the two rotamers were stated to be present in approximately equal amounts at low temperature, in contrast with the situation indicated by NOE studies for 2-acetyl thiophene.[63] For *N*-methylpyrrole-2-aldehyde, the two rotamers have been found to be present in very unequal proportions, with a rotational barrier between them *ca.* 1 kcal/mole higher than for furan-2-aldehyde.[509] The interconversions between various folded and twisted conformations of bisfluorenylidenes (**135**) have been examined by temperature dependent NMR spectroscopy.[510] The energy barriers associated with conformational isomerism and *cis-trans* isomerism in these compounds are both remarkably low (20 to 21 kcal/mole).



(*cis*/*trans* isomers)

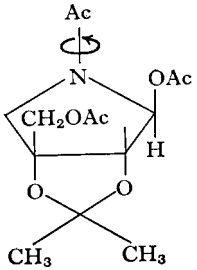
135



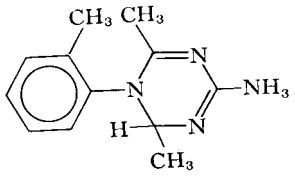
136

This possibly reflects the presence of strained ground states, and a diradical transition state for isomerism about a formal double bond. An examination has been reported of the ease of rotation of the aryl substituents in 1,8-diarylnaphthalenes.[511] The non-equivalence of the methyl signals at low temperature in (**136**) allows the calculation that the free energy of activation $\Delta G^{\ddagger}_{25°}$ for the substituted ring in this compound is 16 kcal/mole.

Direct observation has been reported[512] of an unusually high barrier to rotation about a C–N single bond in *tert*-butyldimethylaminoborane; a total line-shape analysis gave a value for $\Delta G^{\ddagger}$ of $9{\cdot}7 \pm 0{\cdot}3$ kcal/mole at $-80°$. Sources of error in the application of the NMR line-shape method for the evaluation of rate data have been discussed with reference to the barrier to internal rotation in *N*,*N*-dimethyltrichloroacetamide.[513] Small systematic errors in the effective relaxation time T_2 may lead to numerical discrepancies larger than the random errors for the system. An NMR study has provided activation parameters for conformational isomerism in the *N*-acetylpyrrolidine (**137**) *via* total line-shape analysis and direct thermal stereomutation.[514] The most important source of error here was in the determination of temperature at the sample site. The equilibrations of the diastereomeric rotational isomers of (**138**) and (**139**) have



137



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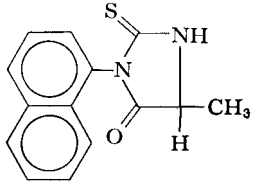
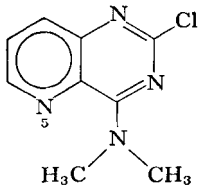


139

been followed by NMR, and the thermodynamic parameters for hindered rotation about the C–N single bonds were calculated.[515] It has been discovered[516] that while in (**140**) an activation energy for rotation of 14·0 kcal/mole was observed for the $N(CH_3)_2$ group, no such restricted motion could be induced in the analogous dimethylaminoquinazoline (**141**). There must be a strong influence from N(5), but it was not predicted by Hückel molecular orbital calculations; it was concluded that (**140**) was planar, while the proton in (**141**) at C(5) interfered with planarity.

Low-temperature NMR spectra of dialkyl-sulphamoyl chlorides



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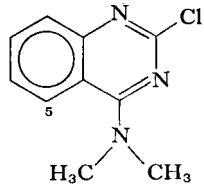
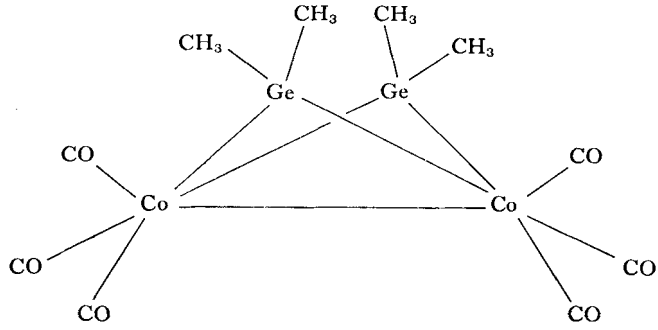


141

(R_2N–SO_2X) have indicated a considerable barrier (*ca.* 11·5 kcal/mole) to rotation about the N–S bond.[517] The ground-state conformation is similar to that predicted for an α-sulphonyl carbanion. PMR spectra of aminoarsines and aminostibines of the type $(Me_3C)_2E$–$N(MMe_3)_2$ (E = As, Sb; M = Si, Ge) have been measured as a function of temperature.[518] $\Delta G^{\ddagger}$ values ranged between 19·6 and 23·2 kcal/mole, and comparison with less hindered compounds supported the hypothesis that steric interactions and not ($p \rightarrow d$)π bonds between E and N caused this hindered rotation.

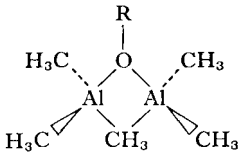
E. General considerations

A new type of fluxional molecule (bis-μ-dimethyl-germyl-dicobalt hexacarbonyl) has been described.[519] At room temperature this compound (**142**) shows a single sharp methyl signal, while at −89° two signals are observed, consistent with *syn-* and *anti-* methyl groups. The activation energy for the interchange process was 15 ± 1 kcal/mole, and plausible pathways were discussed.



142

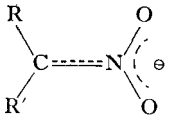
Exchange of methyl groups between bridge and terminal sites has been studied[520] by PMR for some newly described aluminium alkoxides of type (**143**). The exchange takes place by a dissociative process, with an activation energy of 20 ± 3 kcal/mole.



143

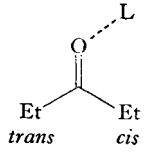
Spectroscopic data have been recorded[521] for a series of phosphorus ylids containing Si as the carbanion substituent. The "olefinic" signals appear at remarkably high field. For example in $Me_3P{=}CH{-}SiH_3$, $\delta(=CH) = -1{\cdot}28$ p.p.m. with a $^2J(HCP)$ of 6 Hz. (Reported shifts were measured from external TMS, for neat liquid samples.)

NMR evidence has been presented concerning the structure of sodium alkyl nitronates.[522] There has been dispute over the presence of a single or a double carbon-nitrogen bond. The singlets for H and CH_3 in (**144a** and **c**) are consistent with the freely rotating structure shown, as is the 6·6 Hz coupling observed for (**144b**).



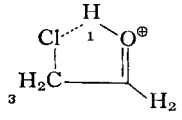
a R = R′ = H
b R = H, R′ = CH_3
c R = R′ = CH_3

144



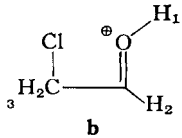
145

Spectra of the 1:1 $Et_2CO{-}BF_3$ complex obtained in $CHCl_2F$ solution below $-120°$ show discrete signals for the two ethyl groups.[523] This must be attributed to *cis-trans*-isomerism (**145**) and thus the coordination angle cannot be 180°. The spectra of protonated α-chloroacetaldehyde



a

$J(12) = 20$ Hz
$J(13) = 1{\cdot}4$ Hz



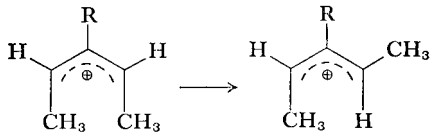
b

$J(12) = 9$ Hz
$J(13) = 0{\cdot}8$ Hz

146

and α-chlorobutyraldehyde in strong acid media show the presence of two isomeric species, e.g. (**146**), one of which can be explained in terms of intramolecular hydrogen bonding.[524] The observed vinylic and allylic

couplings are consistent with the proposed structures. Some 2-halopolymethylallyl cations have been prepared[525] for which it proved possible to measure free energies of activation for rotation. For example, with (**147a**) $\Delta G^{\ddagger} = 18{\cdot}7$ kcal/mole while in the methyl derivative (**147b**) $\Delta G^{\ddagger}$ rose to

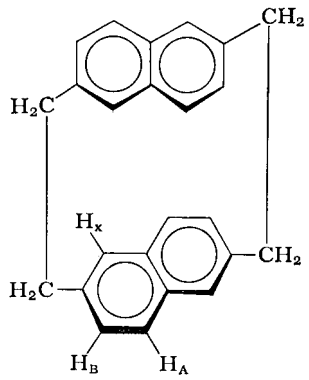


a R = H
b R = CH_3

147

23·6 kcal/mole. A review has appeared[526] which summarises the experimental methods and observations currently documented for a wide range of protonated heteroaliphatic compounds, including alcohols, thiols, ethers, ketones, acids, esters and nitrogen derivatives.

The considerable chemical shift difference (0·68 p.p.m.) between the two α-protons H_A and H_X in (**148**) suggest that this naphthalenophane exists in the less symmetrical structure shown, rather than one in which the aromatic rings are completely overlapped.[527]



148

NMR is now widely used in the measurement of association constants for charge transfer and other systems. Three examples are given here. The association constants for complexes of 1,3,5-trinitrobenzene with anilines and aza-aromatic compounds have been measured by an NMR method.[528] In many cases the magnitude of this association constant could be accounted for by *ortho* steric effects. It appeared that a major contribution to the interaction of the pyridines is *via* an *n*-electron. A

study has been described of the propensity of complex formation of silver ions with hydrocarbons and heterocyclic compounds containing N, O and S.[529] The results were compared with similar data using 1,3,5-trinitrobenzene as an acceptor and the differences discussed in terms of localised and delocalised interactions in the formation of weak complexes. PMR measurements have allowed the determination of association constants for the formation of some naphthalene picrates; the method has also been employed to determine the enthalpies and entropies of formation for some of these systems.[530] The results compared well with those obtained by optical spectroscopy.

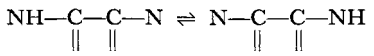
Two careful and complete analyses have been recorded, for the NMR spectra of furan[531] and pyrrole.[532] In the former, accuracy was gained by resolving some lines only 0·1 Hz apart and by assigning some weak outer transitions. With the latter partial decoupling showed that all signs were similar. The derived H–H couplings may be of use for future spectra-structure correlations, and are summarised in Table V using the usual ring numbering system.

TABLE V

Accurate coupling constants for furan and pyrrole (in Hz)

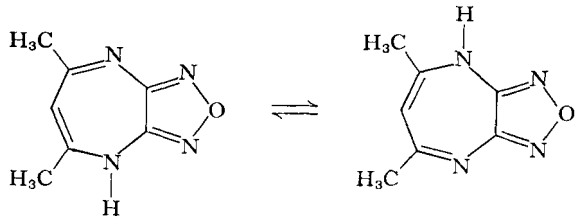
J	Furan	Pyrrole
12, 15	..	2·593 ± 0·02
13, 14	..	2·527 ± 0·02
23, 45	1·752 ± 0·030	2·734 ± 0·02
24, 35	1·814 ± 0·030	1·365 ± 0·02
25	1·486 ± 0·012	1·858 ± 0·05
34	3·271 ± 0·014	3·632 ± 0·05

On the basis of UV, IR and NMR spectra, a mono-imino structure has been suggested for a series of furazano-diazepines.[533] Low-temperature studies suggest a rapid

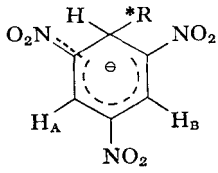


tautomerism for the dimethyl derivative (**149**); two methyl signals are only observed below −29°.

A continuing interest is being shown in PMR studies of Meisenheimer complexes. For example, spectra have been documented[534] for a series of asymmetrical Meisenheimer complexes of 1,3,5-trinitrobenzene, and in certain of the complexes (**150**) the ring protons H_A and H_B showed a

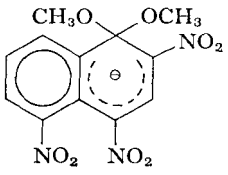


149

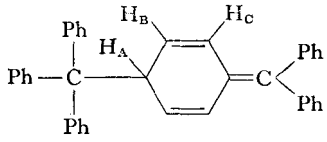


150

$\Delta\delta$ of *ca.* 0.1 p.p.m. Contrasting behaviour has been observed between 2- and 4- methoxy-3,5-dinitropyridine upon interaction with methoxide ion.[535] The latter gave both methine and acetal σ-complexes (the acetal being thermodynamically more stable) while the former gave only a C(6) methine σ-derivative. The observations were rationalised in terms of differential steric and solvation effects. The formation of an unstable methine complex has also been observed during the interaction of 2,4-dicyano-6-nitrobenzene with methoxide ion,[536] but only the normal acetal was obtained with 2,6-dicyano-4-nitro-benzene. The study of Meisenheimer complexes as models for intermediates in nucleophilic aromatic substitution has been extended to naphthalene derivatives; the product from interaction of methoxide ion with 1-methoxy-2,4,5-trinitronaphthalene has been characterised as the acetal (**151**) from NMR studies.[537]



151



J(AB) = 2·7 Hz
J(BC) = 10·6 Hz

152

From a chemical and spectroscopic study of the triphenylmethyl dimer[538] it has been concluded that the correct formulation is that of

Jacobsen (**152**). At $-22°$ in methylene chloride the ABC system can be clearly discerned.

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Fluorine-19 Nuclear Magnetic Resonance Spectroscopy

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I. GENERAL INTRODUCTION

THE year 1970 has again been an extremely active one in ^{19}F NMR spectroscopy, and the number of papers published containing ^{19}F parameters remains large, justifying the editorial decision to review the topic annually. During this period, an introductory text book on ^{19}F NMR spectroscopy has appeared,[1] and the trouble involved in locating ^{19}F chemical shifts in the literature, at least over the period 1951 to mid-1967 has been decreased by the appearance of an index[2] to published ^{19}F shifts.

As in previous years a major objective of this chapter has been the collection of the scattered information on ^{19}F NMR parameters and the presentation of this information in such a form that it can readily be retrieved and used. All chemical shifts have again been converted† to the δ scale, with $CFCl_3$ reference and positive shifts to low field of the reference.

The arrangement in the body of the chapter follows much the same pattern as in previous years, with the exception that, apart from the common organic functional groups containing oxygen, derivatives of the elements are classified under the element, and divided into fluoro-compounds (containing a M–F bond) and fluoro-organic compounds. Transition metal compounds containing fluorinated groups are, with few exceptions, considered under the heading of the transition metal involved, and transition metal fluorides and their complexes are considered in a further section.

II. FLUOROHYDROCARBONS

A. Fluorinated aliphatic hydrocarbons

The spectra of several polyfluoroiodoalkanes, formed by the addition of trifluoroiodomethane to olefins, have been reported.[3,4] The chemical shifts of the various fluorinated groups fall within the ranges previously

TABLE I

Ranges for ^{19}F shifts

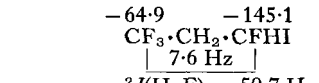
Group	δ_F	Group	δ_F
$CF_3 \cdot CF$[a]	*ca.* −128·5	CHFI[b]	−130·7 to −168·7
$CF_3 \cdot CH$[b]	−58·5 to − 63·7	CHF[b]	−185·8 to −217·6
CHFBr[b]	−128·5 to −158·5		

[a] M. G. Barlow, unpublished results cited in ref. 3.
[b] Unpublished results, Chemistry Department, UMIST, cited in ref. 3 and 4.

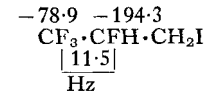
† The following ^{19}F shifts have been used where necessary to convert published values to the δ scale:

CF_3CO_2H	− 78·5(0)
C_6F_6	−162·9(0)
$PhCF_3$	− 63·9(0)
PhF	−113·15
$CFCl_2 \cdot CFCl_2$	− 67·3(0)
$CF_2 \cdot CF_2 \cdot CCl_2 \cdot CCl_2$	−114·1(0)
CF_2Cl_2	− 6·9(0)
F_2	+422·9(0)

published[5 to 7] or given in Table I, and are summarised, together with the coupling constants reported, in formulae **1** to **11**.



1



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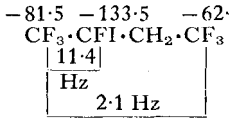

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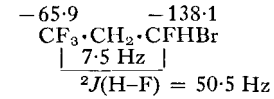

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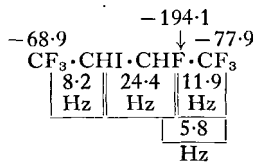
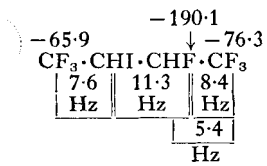
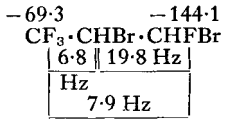


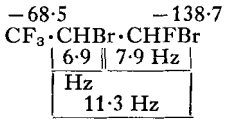
5 (*erythro*)



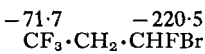
6 (*threo*)



7 (*erythro*)



8 (*threo*)



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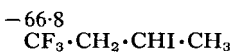
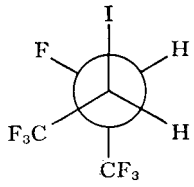


10

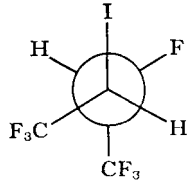
11

In several instances the complexity of the spectra and the overlapping of bands made it impossible to derive or assign all the coupling constants. The stereochemistry of the *erythro*- and *threo*- isomer pairs **5**–**6** and **7**–**8** was deduced in each case from the relative magnitudes of the vicinal coupling constants. For instance in **5**, the large value for J(H–F), together with the low values for J(H–H) and J(F–CF_3) imply *trans*, *gauche* and *gauche* dispositions of the groups respectively, which is possible only in the *erythro*-isomer, (see **5a**) whereas in **6** the relatively large values for J(H–H) and J(F–CF_3) and the small value for J(H–F) imply the *trans*,

trans and *gauche* dispositions of the *threo*-isomer (**6a**). Although the ^{19}F signal for the CHF group in 2-fluoro-3-halobutanes, $CH_3 \cdot CHF\text{-}CHX \cdot CH_3$, is at higher field for the *threo*-isomers,[8] it appears at lower field for the *threo*-isomers **6** and **8** than for the *erythro*-isomers **5** and **7**.†



5a



6a

1,1,2-Trichloro-1,2-difluoroethane was prepared[9] by the reaction of chloral with sulphur tetrafluoride; the parameters reported are shown with formula **12**.

Addition of bromine monofluoride (from $BrF_3 + Br_2$) to *trans*-(perfluoro-4-methylpent-2-ene) gave[10] a mixture of isomers **13** and **14**, the ^{19}F spectra of which, at 24°, are given with the formulae.

$$\underset{\underset{CFCl_2 \cdot CHFCl}{}}{\overset{-70{\cdot}6 \quad -140{\cdot}2}{}}$$
$^2J(H\text{–}F) = 49$ Hz
$^3J(H\text{–}F) = 4$ Hz
$^4J(F\text{–}F) = 22{\cdot}5$ Hz

12

$$\underset{\underset{(CF_3)_2CF \cdot CF_2 \cdot CFBr \cdot CF_3}{}}{\overset{-180{\cdot}8 \quad -142{\cdot}1}{-72{\cdot}2 \quad \downarrow \quad -105{\cdot}9 \quad \downarrow \quad -75{\cdot}5}}$$
$^2J(F\text{–}F) = 296$ Hz
$\nu_0\delta(F\text{–}F) = 8{\cdot}9$ p.p.m.

13

$$\underset{\underset{(CF_3)_2CF \cdot CFBr \cdot CF_2 \cdot CF_3}{}}{\overset{-171{\cdot}5 \quad -115{\cdot}8}{-69{\cdot}4 \quad \downarrow \quad -137{\cdot}7 \quad \downarrow \quad -77{\cdot}9}}$$
$^2J(F\text{–}F) = 283$ Hz
$\nu_0\delta(F\text{–}F) = 6{\cdot}1$ p.p.m.

14

At $-105°$, the geminal CF_3 groups in **13** appeared as two signals at $\delta_F = -71{\cdot}7$ and $-79{\cdot}8$, and $\nu_0\delta(F\text{–}F)$ increased to 568 Hz. The signals due to the CFBr and CF groups also moved to higher field ($-145{\cdot}0$ and $-181{\cdot}4$ p.p.m. respectively). Similar changes were observed in the spectrum of **14**, and it was suggested that they correspond to changes in rotamer populations, since interconversion at $-105°$ was still too rapid for observation of individual rotamers. The room temperature ^{19}F shifts for **15** and **16** were also reported.

$$\underset{\underset{CF_3 \cdot CFBr \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_3}{}}{\overset{-141{\cdot}2 \quad -119{\cdot}5 \quad -127{\cdot}1}{-76{\cdot}0 \quad \downarrow \quad -113{\cdot}9 \quad \downarrow \quad -123{\cdot}1 \quad \downarrow \quad -81{\cdot}8}}$$

15

$$\underset{\underset{CF_3 \cdot CF_2 \cdot CFBr \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_3}{}}{\overset{-117{\cdot}0 \quad -113{\cdot}4 \quad -127{\cdot}0}{-78{\cdot}8 \quad \downarrow \quad -139{\cdot}4 \quad \downarrow \quad -119{\cdot}9 \quad \downarrow \quad -81{\cdot}8}}$$

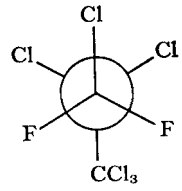
16

† Subsequent work on the magnitude of $J(CF_3\text{–}CF_3)$ suggests that the assignments should, in fact, be reversed, i.e. that **5** and **7** are the *threo*-isomers and **6** and **8** the *erythro*-isomers (A. E. Tipping, personal communication).

The ^{19}F shift for 1,1,4,4-tetrafluoro-1,2,2,3,3,4-hexachlorobutane was reported[11] to be $-55{\cdot}33$ and for 1,1,1-trifluoro-2-trifluoromethylpentane, $-68{\cdot}62$, with ^3J(H–F) in the usual range.[12]

Low-temperature studies[13] of a series of highly halogenated fluoroethanes have led to the estimation of the barrier to rotation between the conformers, which were mostly identified on the basis[14] that a *gauche* chlorine shifts the fluorine resonance further upfield than does a *gauche* bromine, and that a conformer with *trans* bromine atoms will be more stable than one with *gauche* bromines (although the authors note that this cannot be taken to have general validity, since the *gauche* conformer of 1,1,2,2-tetrabromoethane is known[15] to be somewhat more stable than the *trans*-conformer in the liquid state). In each case studied the least populated conformer gave the furthest upfield ^{19}F resonance and the most populated conformer gave the lowest field resonance; some of the theoretical spectra, and spectra obtained at a number of temperatures, are illustrated in the paper. It was also noted that replacement of chlorine by bromine did not affect either the ground-state energy or the barrier to interconversion very much. Chemical shifts, measured below the coalescence point, and free energies of activation for rotation are given in Table II. The shifts are somewhat temperature dependent.

The study was extended to halogenated propanes, and it was found that rotation about the C2–C3 bond in 1,2-dibromo-1,1,2-trichloro-3,3,3-trifluoropropane remained rapid at temperatures at which rotation about the C1–C2 bond was slow. The three sharp singlets obtained at *ca.* $-60°$ broadened again to give at $-140°$, the lowest temperature attainable, two broad, structureless peaks (intensity ratio 1:2) separated by *ca.* 850 Hz. The ^{19}F spectrum of 1,1,1-trifluoropentachloropropane at $-140°$ was similar, but that of 1,1-difluorohexachloropropane, a sharp singlet at $-120°$ which showed no temperature dependence, suggested the presence of the single preferred conformer **17** in which the two fluorines are magnetically equivalent.



17

Full analysis of the spectra of *sym*-tetrafluoroethane[16] as a pure liquid (see Fig. 1) and in a number of solvents of widely differing dielectric

TABLE II

Chemical shifts and free energies of activation for interconversion of rotamers[13]

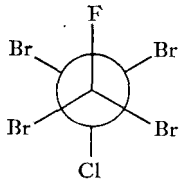
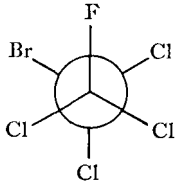
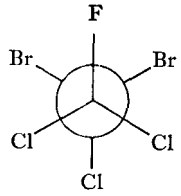
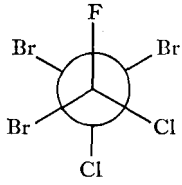
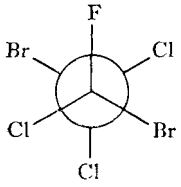
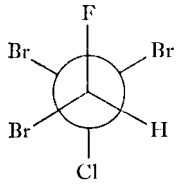
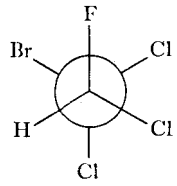
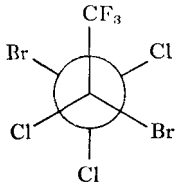
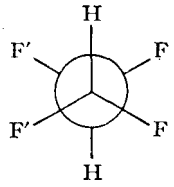
Most stable conformer	$\theta = 0°$ [a] δ_F	$\Delta G^{\ddagger}$ $0° \rightarrow 120°$ (kcal mole^{-1})	$\theta = 120°$ δ_F	$\Delta G^{\ddagger}$ $120° \rightarrow 240°$ (kcal mole^{-1})	$\theta = 240°$ δ_F	$\Delta G^{\ddagger}$ $240° \rightarrow 0°$ (kcal mole^{-1})
	−53·96	14·8	−57·66	..[b]	−57·66	14·8
	−60·66	..[b]	−60·66	13·1	−65·36	..[b]
	−57·76	13·2	−62·06	..[b]	−62·06	13·2
	−55·36	13·9	−59·06	14·7	−59·56	14·0
	−58·36	13·8	−58·96	14·5	−62·86	14·2

TABLE II (*continued*)

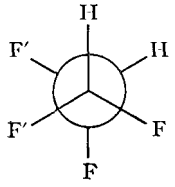
	−123·56 ^2J(H–F) = 46·0 Hz	9·6	−123·86 ^2J(H–F) = 47·8 Hz	10·2	−125·76 ^2J(H–F) = 48·7 Hz	10·0
	−125·96 ^2J(H–F) = 48·8 Hz	9·0	−126·86 ^2J(H–F) = 50·2 Hz	9·4	−128·86 ^2J(H–F) = 48·0 Hz	9·1
	−65·66	13·7	−66·46	14·1	−66·51	13·9

[a] Angle of clockwise rotation of *rear* carbon with respect to front carbon.
[b] Barrier between mirror-image conformers, not measurable by NMR method.

constants has resulted in the values for the coupling constants in the individual rotamers given below.



^3J(H–H) = 4·8 Hz
^3J(H–F) = 2·0 Hz
^3J(F–F) = −5·4 Hz
^3J(F–F′) = −0·9 Hz



^3J(H–H) = 1·4 Hz
^3J(H–F) = 5·5 Hz
^3J(F–F) = −4·7 Hz
^3J(F–F′) = −9·8 Hz

Low-temperature studies of 1,1,2-tribromo-1-chloro-2,2-difluoroethane in solution in carbon disulphide have been reported[17] and resulted in a value of $9{\cdot}5 \pm 0{\cdot}1$ kcal mole^{-1} for the rotational barrier for *trans-gauche* conformers. Double irradiation studies were also reported; strong

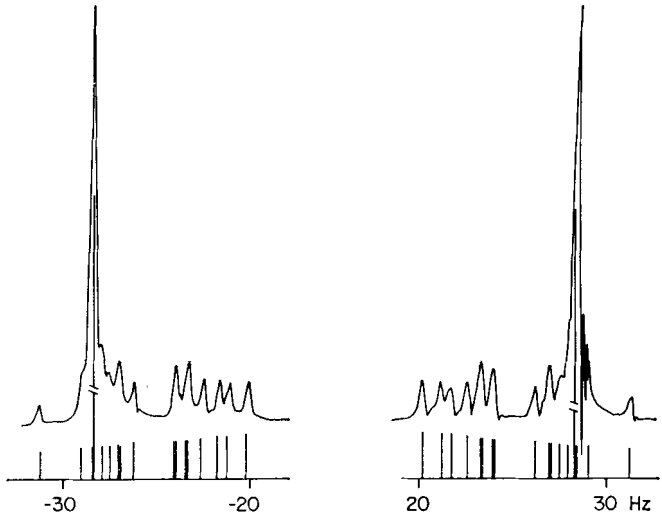


FIG. 1. The observed and calculated ^{19}F spectrum at 94·1 MHz of neat $CF_2H \cdot CF_2H$. (From Cavalli and Abraham.[16])

irradiation of one component of a strongly coupled multiplet with intramolecular exchange caused indirect saturation of the transitions connecting energy levels that have the same m_I values as that irradiated, but the intensities of other transitions were only slightly affected, and the authors suggested that this may be complementary to spin-tickling experiments in the determination of energy level diagrams and relative signs of coupling constants in suitable molecules.

B. Derivatives of fluorinated aliphatic hydrocarbons

1. *Ethers*

The reaction of dimethyl sulphoxide with sulphur tetrafluoride at 20°, or with tungsten hexafluoride at 0° gave a product formulated,[18] on the basis of its NMR spectra and on its identity with the product from the reaction of $(CH_2O)_3$ with sulphur tetrafluoride, as bis(fluoromethyl) ether. The spectra were analysed as an $AA'X_2X_2'$ system to give the parameters summarised in formula **18**.

$$\begin{array}{c} -157{\cdot}8 \\ CH_2F \cdot O \cdot CH_2F \\ \underline{\lfloor\ 0{\cdot}8\ \text{Hz}\ \rfloor} \\ \underline{\lfloor\ 11\ \text{Hz}\ \rfloor} \\ {}^2J(\text{H–F}) = 54\ \text{Hz} \end{array}$$

18

$$\begin{array}{c} -14{\cdot}3 \qquad -55{\cdot}9 \\ CFCl_2 \cdot O \cdot CF_3 \\ \underline{\lfloor\ 10{\cdot}7\ \text{Hz}\ \rfloor} \end{array}$$

19

The spectra were also identical with those reported for the product of the reaction of dimethyl sulphoxide with iodine pentafluoride, and assigned[19] the structure $CH_2F \cdot S(O)H$, showing that this structure is incorrect.

Dichlorofluoromethyl trifluoromethyl ether (**19**) was found[20] amongst the products of the reaction between trifluoromethyl hypofluorite and thiophosgene (see also p. 252), and parameters are given with the formula.

A number of fluoroalkyl ethers have been prepared by the reaction of fluoroalkyl hypochlorites with olefins at low temperature,[21] by ring-opening in the electrochemical fluorination of cyclic ethers,[22] and by the reaction of sulphur chloride pentafluoride with 2-chlorodifluorovinyl ether.[23] The reported NMR parameters and those of ethyl 2*H*-hexafluoropropyl ether[24] are summarised in formulae **20** to **30**. The absorptions for the $(CF_2)_4$ group in **29** were obscured by those of other components of the mixture.

$$\underset{(1)}{CF_3}\cdot\underset{(2)}{CHF}\cdot\underset{(3,4)}{CF_2}\cdot O\cdot C_2H_5 \qquad (-74{\cdot}7,\ -216{\cdot}0,\ -84{\cdot}1)$$

J(F1–F2) = 10·4 Hz; J(F1–F3) = 8·8 Hz; J(F1–F4) = 9·5 Hz; J(F1–H) = 5·9 Hz; J(F2–F3) = 11·7 Hz; J(F2–F4) = 12·3 Hz; J(F2–H) = 43·8 Hz; J(F3–F4) = 149·5 Hz; J(F3–H) = 4·6 Hz; J(F4–H) = 6·9 Hz

20

$$\underset{(9{\cdot}25\ \text{Hz})}{\underset{-55{\cdot}8}{CF_3}}\cdot O\cdot\underset{(1{\cdot}8\ \text{Hz})}{\underset{-89{\cdot}1}{CF_2}}\cdot\underset{-73{\cdot}9}{CF_2Cl}$$

21

$$\underset{-61{\cdot}6}{CF_3}\cdot O\cdot CH_2\cdot CH_2Cl$$

22

$$\underset{(9{\cdot}4\ \text{Hz})}{\underset{-56{\cdot}2}{CF_3}}\cdot O\cdot\underset{(9{\cdot}3\ \text{Hz})}{\underset{-77{\cdot}5}{CF_2}}\cdot CH_2Cl$$

23

$$(\underset{(6{\cdot}3\ \text{Hz})}{\underset{-80{\cdot}3}{\downarrow}\ \ \underset{-83{\cdot}8}{\downarrow}\ \ \underset{-143{\cdot}1}{CF_3}})_2CF\cdot O\cdot\underset{(2{\cdot}1\ \text{Hz})}{\underset{-73{\cdot}2}{CF_2}}\cdot CF_2Cl$$

(1·8 Hz; 21·8 Hz)

24

$$\underset{-73{\cdot}5}{(CF_3)_2}CH\cdot O\cdot\underset{-88{\cdot}1}{CF_2}\cdot\underset{-72{\cdot}8}{CF_2Cl}$$

25

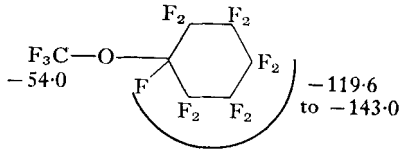
$$\underset{-74{\cdot}4}{(CF_3)_3}C\cdot O\cdot CH_2\cdot CH_2Cl$$

(0·7 Hz)

26

$$\underset{(9{\cdot}5\ \text{Hz})}{\underset{-70{\cdot}3}{(CF_3)_3}}C\cdot O\cdot\underset{(2{\cdot}0\ \text{Hz})}{\underset{-84{\cdot}0}{CF_2}}\cdot\underset{-73{\cdot}3}{CF_2Cl}$$

27



28

$-55{\cdot}6 \quad -85{\cdot}0 \qquad -81{\cdot}2$
$CF_3{\cdot}O{\cdot}CF_2{\cdot}(CF_2)_4{\cdot}CF_3$
29

$-68{\cdot}1 \quad -78{\cdot}1$
$CF_2Cl{\cdot}CFCl{\cdot}OEt$
$|6{\cdot}3\ Hz|$
30

2. *Alcohols and related compounds*

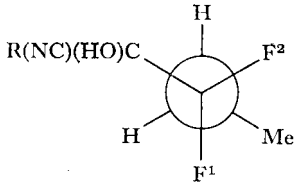
The ^{19}F shift for perfluoro-t-butyl alcohol was reported[25] to be $-74{\cdot}95$ p.p.m., that of its sodio derivative,[26] in $(CD_3)_2CO$, $-77{\cdot}5$ p.p.m., and of bis(perfluoro-t-butyl) peroxide,[27] -70 p.p.m.

Some of the parameters for secondary alcohols and cyanohydrins, prepared by the reaction of hydrogen fluoride on the corresponding epoxides, have been reported,[28] and are summarised below (**31**, **32**).

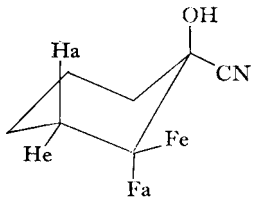
Each band of the AB quartet in **32** was split into a doublet of doublets, with a total width [termed $\sum J(F-H)$] (see Fig. 2) of 37 Hz, and it was suggested that, since this is the same as $\sum J(F-H)$ for the axial fluorine in **33**, the preferred conformation of **32** is as shown in **32a**, with each of the fluorines having one *trans* and one *gauche* hydrogen.

$PhCF_2{\cdot}CH(CH_3)(OH)$
$^2J(F-F) = 249$ Hz
$^3J(F-H) = 10$ Hz
31

-115
$EtCF_2{\cdot}CMe(CN)(OH)$
$^2J(F-F) = 243$ Hz
$\nu_0\delta = 3{\cdot}85$ p.p.m.
$\sum J(F-H) = 37$ Hz
32



32a



33

Fluoroalkyl hypochlorites have been prepared by the reaction of chlorine monofluoride on the corresponding fluoroalkyl alcohol,[29] and vicinal dihypohalites by the action of halogen on the sodium salt of perfluoropinacol.[30] The parameters reported are summarised in formulae **34** to **38**.

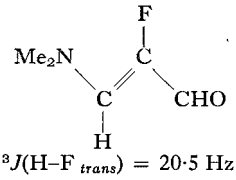
$-70{\cdot}1$
$(CF_3)_3COCl$
34

$-72{\cdot}5$
$(CF_3)_2CHOCl$
$|5{\cdot}6\ Hz|$
35

$-73{\cdot}4$
$CF_3{\cdot}CH_2OCl$
$|\ 8{\cdot}0\ |$
Hz
36

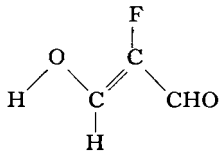
$$\underset{\underset{\underset{

coupling of 22 Hz (23 Hz in the sodium salt) was observed, similar to that found in the vinyl aldehyde **39**, implying that the molecule exists in the enol form **40**.



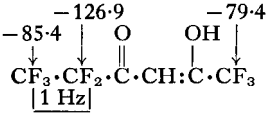
^3J(H–F $_{trans}$) = 20·5 Hz

39

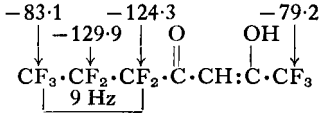


40

The ^{19}F spectrum of 3,3-difluoropentan-2-one[28] consisted of a triplet [^3J(H–F) = 17 Hz] at δ_F −108 p.p.m. The parameters for the enol forms of two fluoroalkyl β-diketones[32] are shown in formulae **41** and **42**.



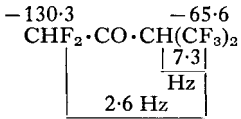
41



42

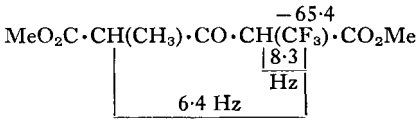
In the course of a series of papers on reactions of bis(trifluoromethyl)-keten,[33 to 36] England and Krespan reported NMR parameters for a number of ketones, diketones, keto-acids and keto-esters containing the group $(CF_3)_2CH \cdot CO$–. All had δ_F in the range −62·9 to −65·2, with ^3J(H–F) = 7·4 to 8·5 Hz. Difluoromethylhexafluoroisopropyl ketone, **43**, showed long-range fluorine-fluorine coupling, and **44** had ^5J(H–F) = 6·4 Hz.

Two fluorinated α-keto-esters prepared[37] in the course of work on α-fluoroglycidic esters (see p. 181) have the parameters shown with formulae **45** and **46**.

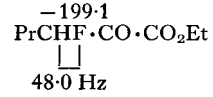


^2J(H–F) = 53·5 Hz

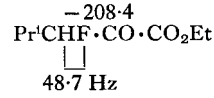
43



44



45



46

4. *Carboxylic acids and their derivatives*

Vicinal hydrogen-fluorine coupling in *N*-trifluoroacetyl-3,3,3-trifluoroalanine was reported[38] to be 7·0 Hz, but no other ^{19}F parameters were given. Methyl difluoronitroacetate[39] showed coupling to the nitrogen of the nitro-group at room temperature [$\delta_F - 93{\cdot}4$, $J(F\text{–}N) = 9{\cdot}8$ Hz]. The $\alpha\beta$-unsaturated acid **47** had $\delta_F - 62{\cdot}8$ and J(H–F) 9·3 Hz. The corresponding acid fluoride had the parameters shown in **48a** and **b** for the two geometrical isomers, but the stereochemistry was not assigned.[34]

Vapour-phase fluorination of propionyl fluoride gave mixtures of fluoroacyl fluorides, which were identified as their ethyl esters.[40] The parameters are given in formulae **49** to **58**, together with those for ethyl α-bromo-[24] and α-chloro-[41] tetrafluoropropionate (**59**, **60**).

$(CF_3)_2CH\cdot CPh{:}CH\cdot CO_2H$

47

a −56·1, **b** −62·9 **a** +43·5, **b** +46·0

$(CF_3)_2CH\cdot CPh{:}CH\cdot COF$

a 7·5 Hz **b** 8·0 Hz — **a** 1·0 Hz **b** 4·0 Hz

48

−235 −202

$CH_2F\cdot CHF\cdot CO_2Et$

11·4 Hz; 29·1 Hz

^2J(H–F) = 47·1 Hz; ^2J(H–F) = 48·5 Hz

49

−118

$CHF_2\cdot CH_2\cdot CO_2Et$

16·0 Hz

^2J(H–F) = 55·0 Hz

50

−221

$CH_2F\cdot CH_2\cdot CO_2Et$

26·0 Hz

^2J(H–F) = 47 Hz

51

−128 −215

$CHF_aF_b\cdot CHF\cdot CO_2Et$

12·0 Hz

^2J(H–F) = 46·3 Hz

$^2J(H\text{–}F_a) = {}^2J(H\text{–}F_b) = 53{\cdot}0$ Hz

$^3J(H\text{–}F_a) = 11{\cdot}0$ Hz $^3J(H\text{–}F_b) = 15$ Hz

$^3J(F_a\text{–}F) = 11{\cdot}9$ Hz $^3J(F_b\text{–}F) = 13$ Hz

52

−186

$CH_3\cdot CHF\cdot CO_2Et$

23·0 Hz

^2J(H–F) = 48 Hz

53

−78 −215

$CF_3\cdot CHF\cdot CO_2Et$

7·2 Hz; 11·2 Hz

^2J(H–F) = 40·5 Hz

54

-140 -127
$CHF_2 \cdot CF_2 \cdot CO_2Et$
6·9 Hz, 5·2 Hz
$^2J(H-F) = 51{\cdot}4$ Hz

55

-215 -119
$CH_2F \cdot CF_2 \cdot CO_2Et$
15·8 Hz, 12·2 Hz
$^2J(H-F) = 45{\cdot}5$ Hz

56

76
$CF_3 \cdot CH_2 \cdot CO_2Et$
10·8 Hz

57

-103
$CH_3 \cdot CF_2 \cdot CO_2Et$
19·3 Hz

58

$-79{\cdot}5$ $-136{\cdot}5$
$CF_3 \cdot CFBr \cdot CO_2Et$
8·8 Hz

59

$-81{\cdot}1$ $-133{\cdot}9$
$CF_3 \cdot CFCl \cdot CO_2Et$
6·9 Hz

60

The spectra of **52** were complicated by non-equivalence of the geminal fluorines, which coupled unequally to the vicinal hydrogen and fluorine, though no value for $^2J(F-F)$ was reported.

The solvent dependence of ^1H and ^{19}F NMR spectra of methyl fluoro-, difluoro-, and trifluoro- acetates has been reported.[42] The magnitude of the geminal fluorine-hydrogen coupling, 47·45 Hz in carbon tetrachloride, decreasing to 46·48 Hz in dimethyl sulphoxide, for the CH_2F group depends on the orientation of the CHF group relative to the carbonyl, being largest when the fluorine eclipses the oxygen. Long-range couplings (*ca.* 0·5 Hz) were largest when fluorine eclipsed the carbonyl group, and both hydrogen and fluorine absorbed at lower field when *gauche* to the carbonyl.

Enol esters of formula **61** have been prepared from bis(trifluoromethyl)keten.[33,35,36] The $(CF_3)_2CH$ groups had δ_F $-65{\cdot}0$ to $-66{\cdot}9$ with $^3J(H-F)$ 7·0 to 8·0 Hz, and the $(CF_3)_2C$: group gave rise to a pair of quartets (δ_F $-58{\cdot}8$ to $-67{\cdot}2$, $^4J(F-F)$ 8·2 to 11·1 Hz). For $R = CH_2$-$CH:CHMe$ and $CH_2 \cdot CPh:CH_2$, the $(CF_3)_2CH$ group was additionally split into quartets (2·0 and 2·5 Hz respectively) and one of the quartets of the $(CF_3)_2C$: group was described in each case as "broad".

$(CF_3)_2C(O \cdot CO \cdot CH(CF_3)_2):CR$

61

R = $CH_2 \cdot CH:CHMe$, $CH_2 \cdot CPh:CH_2$, $C:CMe_2$, $CH_2:CMe$, $C(H):C(H)(OEt)$

$$(CF_3)_2CH\cdot CO\cdot NH\cdot CH_2\cdot CF(CH_3)_2$$
$-143{\cdot}5$; 21 Hz, 21 Hz

62†

$$(CF_3)_2CF\cdot CO\cdot CO\cdot NMe_2$$
$-82{\cdot}5$, $-168{\cdot}5$; 7·4 Hz

63

Parameters have been reported for the amides **62**[43] and **63**.[44] *N*-cyclohexylchlorofluoroacetamide[24] showed the characteristic geminal H–F coupling of 51 Hz ($\delta_F = -144{\cdot}1$). *N*-cyclohexyl-$\alpha\beta\beta\beta$-tetrafluoropropionamide, similarly prepared by the action of the fluoroalkyl azide on cyclohexane, and also by the reaction of cyclohexylamine with hexafluoropropene, had the parameters shown in **64** (R = cyclohexyl). Other amides **64** [R = (e.g.) cyclohex-2-enyl, 1-methylcyclohexyl] prepared by the same routes,[45,46] and $\alpha\beta\beta\beta$-tetrafluoropropionitrile, prepared[47] by pyrolysis of the 1*H*-propenyl azide, have very similar ^{19}F parameters.

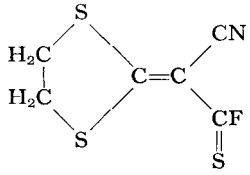
$$CF_3\cdot CHF\cdot CO\cdot NHR$$
$-76{\cdot}7$, $-203{\cdot}7$; 6·4 Hz, 11·3 Hz

$^2J(H\text{–}F) = 45{\cdot}5$ Hz

64

$$CF_3\cdot CFCl\cdot COF$$
$-70{\cdot}5$, $-68{\cdot}2$, $+34{\cdot}8$

65



66

Reaction of fluoro-olefins with chromyl chloride led to α-chloropolyfluoroacyl fluorides,[41] but ^{19}F shifts were reported only for **65**.

Dimethylmalonyl fluoride[36] showed a septet [$^4J(H\text{–}F) = 0{\cdot}8$ Hz] at $\delta_F = +30{\cdot}3$, and the thioacyl fluoride **66** had $\delta_F = +42{\cdot}9$ p.p.m.[48]

Both maleoyl and fumaroyl fluorides have been prepared by the reaction of sulphur tetrafluoride with maleic anhydride.[49] The AA′XX′ spectra were analysed (*via* LAOCN 3) to give the parameters overleaf.

† The value given is described in the paper as "δ CF_3", but that parameter has evidently been omitted.

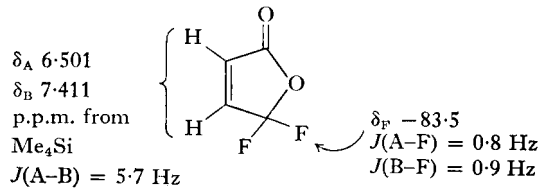
OFC·CH:CH·CFO
3 1 2 4

	Maleoyl	Fumaroyl
$\delta_1 = \delta_2$	6·73[a]	6·94[a]
$\delta_3 = \delta_4$	+41·18[b]	+30·40[b]
J_{12}	±12·13	±15·77
$J_{13} = J_{24}$	±4·17	±7·51
$J_{14} = J_{23}$	±1·83	∓0·21
J_{34}	4·78	±0·22
$J(^{13}C–F)$	346	345
$\delta^{13}CF - \delta^{12}CF$	−0·15[c]	−0·12[c]

a p.p.m. downfield from Me_4Si.
b δ_F.
c In p.p.m.

The small negative value for J_{14} in fumaroyl fluoride is consistent with the finding that J_{AX} and J_{BX} have opposite signs in fumaroyl chloride fluoride, for which the parameters $\delta_F + 31{\cdot}414$, $J_{AB} = \pm 15{\cdot}60$ Hz, $J_{AX} = 7{\cdot}11$ Hz and $J_{BX} = \mp 0{\cdot}28$ Hz were also obtained.

The lactone **67**, a minor product in the preparation of maleoyl and fumaroyl fluorides, was identified only on the basis of the NMR parameters shown.



67

−118·2
+24·1 ↓ −123·7
OFC·CF_2·CF_2·CF_2·CFO
68

−118·1
+24·2 ↓ −122·1
OFC·$CF_2(CF_2)_4CF_2$·CFO
69

−118·4 −121·7
+24·0 ↓ −122·4 ↓
OFC·CF_2·$CF_2(CF_2)_5CF_2$·CF_2·CFO
70

−121·6
+23·6 ↓ −85·7
OFC·CF_2·CF_2·O·CF_2·CF_2·CFO
71

−121·5 −83·3
+23·6 ↓ −86·0 ↓ −125·9
(OFC·CF_2·CF_2·O·CF_2·CF_2)$_2$
72

+13·3 −76·7
OFC·CF_2·O·CF_2·CFO
73

$$\underset{+13\cdot3}{\overset{-77\cdot0}{\overset{\downarrow}{\mathrm{OFC\cdot CF_2\cdot O\cdot CF_2\cdot CF_2\cdot O\cdot CF_2\cdot CFO}}}}\overset{-88\cdot2}{\overset{\downarrow}{}}$$

74

$$\underset{+13\cdot2}{\overset{-77\cdot2}{\overset{\downarrow}{\mathrm{(OFC\cdot CF_2\cdot O\cdot CF_2\cdot CF_2)_2O}}}}\overset{-88\cdot8}{\overset{\downarrow}{}}$$

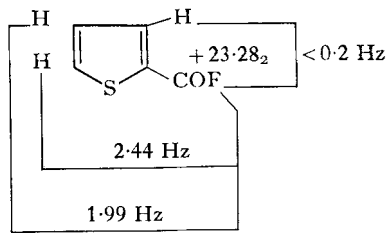
75

A series of dibasic acids and acid fluorides, some of which incorporate one or more ether linkages, has been reported.[50] ^{19}F shifts are shown in formulae **68** to **75** for some of the acid fluorides. The shifts for the corresponding acids and acid derivatives reported are similar, but δ_F for the α-CF_2 group in the nitrile **76a** is some 14 p.p.m. to low field of that shown for the acyl fluoride in formula **76**.

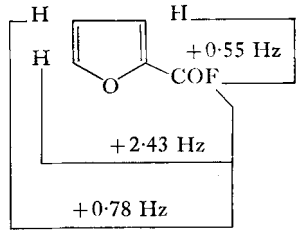
$$\underset{-121\cdot2}{\overset{-85\cdot4}{\overset{\downarrow}{\mathrm{XCF_2\cdot CF_2\cdot O[CF_2\cdot CF_2\cdot CF_2\cdot CF_2\cdot O]_3CF_2\cdot CF_2X}}}}\overset{-125\cdot5}{\overset{\downarrow}{}}\overset{-83\cdot0}{\overset{\downarrow}{}}$$

76 X = COF (δ_F = +23·6)

76a X = CN



77a



77b

Some parameters have been reported[51] for furan and thiophen carboxylic acid fluorides, and are shown with formulae **77a** and **b**. The couplings were reasonably reproduced by a CNDO/2 calculation.

A variable-temperature study of the vicinal H–F coupling constants in acyl fluorides of the type $CH_2X\cdot COF$ and $CHX_2\cdot COF$ has been reported.[52] The barrier to internal rotation was insufficient for the individual rotamers to be frozen out, but a least squares fit of the observed statistically weighted coupling constants $\langle J\rangle_T$ gave values for ^3J(H–F *trans*) and ^3J(H–F *gauche*). The observed values of $\langle J\rangle_T$ were small, and for bromoacetyl fluoride and phenylacetyl fluoride passed through zero when the temperature was reduced, demonstrating that ^3J(H–F *trans*) and ^3J(H–F *gauche*) have opposite signs. The values derived for these coupling constants [^3J(H–F *trans*) = 25·0 to 48·3 Hz, ^3J(H–F *gauche*) = −4·23 to −8·75 Hz] are in reasonable accord with values reported for frozen conformations of halogenated ethanes[53] and fluorinated carbohydrates.[54]

Mixed anhydrides of carboxylic and sulphinic acids have been prepared[55] by the reactions of silver perfluorocarboxylates with trifluoromethylsulphinyl chloride. The values of δ_F for the $CF_3S(O)$– group in **78a** below were relatively constant (−77·5 for R = *n*-C_3F_7 to −78·7 for R = Me; *cf.* −77·5 for $CF_3 \cdot S(O)Cl$).

$RC(O) \cdot O \cdot S(O) \cdot CF_3$ **78a** $\qquad$ $RC(O) \cdot O \cdot C(O)R$ **78b**

The ^{19}F parameters for the groups R in **78a** are very close to those for the corresponding carboxylic anhydrides[56] **78b**. [R = CF_3, δ_F **a** −74·6, δ_F **b** −75·99; R = C_2F_5, δ_F **a** −83·3, −121·2, ^3J(F–F) = 1·75 Hz, δ_F **b** −83·45, −122·00, ^3J(F–F) = 1·5 Hz; R = *n*-C_3F_7, δ_F **a** −81·3, −126·3, −118·8, ^4J(F–F) = 8·60 Hz, δ_F **b** −81·39, −127·03, −119·46, ^4J(F–F) 8·7 Hz]. The parameters for the perfluoroalkylcarboxy disulphides **79**,

$R_FC(O) \cdot O \cdot S \cdot S \cdot O \cdot C(O)R_F \qquad R_F = CF_3, \quad C_2F_5, \quad n\text{-}C_3F_7$

79

prepared[56] by the reaction of disulphur dichloride on the silver salt of the carboxylic acid, are also very similar.

5. *Nitroalkanes and their derivatives*

Fluorination of nitroalcohols $RCH(NO_2) \cdot CH_2 \cdot OH$ in aqueous alkali gave[57] fluoronitroalcohols $RCF(NO_2) \cdot CH_2 \cdot OH$ in which δ_F ranged from −137·7 to −139·8. The geminal hydrogens of the hydroxymethylene group had markedly different coupling constants to fluorine, $^3J(H_a\text{–}F)$ being 25·1 to 30·4 Hz, and $^3J(H_b\text{–}F)$ being 9·7 to 10·4 Hz. Similar disparity in the vicinal H–F couplings was observed in the trinitrocompound **80**, but in **81** and **82** the fluorine resonance was split into a triplet.

$CH_3 \cdot CF(NO_2) \cdot CH_aH_b \cdot C(NO_2)_2 \cdot CH_3$ (−122·5; 22·8 Hz; 7·5 Hz)

80

$EtO_2C \cdot CF(NO_2) \cdot CH_2 \cdot CH_2 \cdot CH_3$ (−125·2; 20·8 Hz)

81

$CH_3 \cdot CH_2 \cdot CBrF \cdot NO_2$ (−85·6; 18·5 Hz)

82

$O_2N \cdot CH_2 \cdot C(CH_3)CF_3$ (−78·96; 0·77 Hz)

83

$O_2N \cdot CH{:}CMe \cdot CF_3$ (−71·93; 1·45 Hz)

84

$O_2N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CF_3$ ($-67{\cdot}96$; 10·5 Hz)

85

$(O_2N)_3C \cdot CH_2 \cdot CH_2 \cdot CF_3$ ($-69{\cdot}1$; 9·4 Hz)

86

$(O_2N)_2CH \cdot CH_2 \cdot CH_2 \cdot CF_3$ ($-66{\cdot}7$; 10·0 Hz)

87

$(O_2N)_2CF \cdot CH_2 \cdot CH_2 \cdot CF_3$ ($-105{\cdot}32$; $-68{\cdot}97$; 9·5 Hz; 1·9 Hz)

88

The reaction of carboxylic acids containing nitro groups with sulphur tetrafluoride yielded a variety of trifluoromethylnitrocarbon compounds[58] such as **83** to **88**.

The vicinal H–F coupling constants in a number of secondary alcohols containing dinitrofluoromethyl groups (**89**) were reported[59] to be in the range 17 to 20·5 Hz. The magnitude of this coupling constant was markedly affected by the solvent system used (e.g. in **90**).

$RCH(OH) \cdot CF(NO_2)_2$

89

$CH_3 \cdot CH(OH) \cdot CF(NO_2)_2$ (1·0–1·2 Hz; 17 Hz in $CDCl_3$; 20·5 Hz in CD_3CN containing *ca.* 10% D_2O)

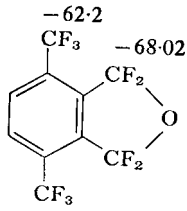
90

A number of derivatives of 2-fluoro-2,2-dinitroethanol have been prepared.[60] Sixteen derivatives of the form $(O_2N)_2CF \cdot CH_2OR$, with a wide variation in the nature of R, had δ_F in the range $-108{\cdot}7$ to $-111{\cdot}9$ and ^3J(H–F) 15·6 to 18·0 Hz. In some cases the ^{19}F resonance was broad, and ^3J(H–F) was derived from the ^1H spectrum. The corresponding alkyl chloride $(O_2N)_2CF \cdot CH_2Cl$ also showed a broad singlet, δ_F $-108{\cdot}2$, and ^3J(H–F)($=16{\cdot}1$ Hz) was obtained from the ^1H spectrum.

6. *Aromatic alkyl substituent groups*

Fluorination of 1,2,3,4-tetracarboxybenzene with sulphur tetrafluoride gave[61] compound **91**, with the chemical shifts shown.

The chemical shifts and long-range H–F couplings for a number of substituted benzotrifluorides **92** to **95** are shown in Table III.[62] The spectra were analysed as $ABCX_3$ systems *via* LAOCN3, the signs of the ring hydrogen couplings being assumed to be positive, and of the H–F couplings to be similar to those reported for 2-amino-5-bromobenzotrifluoride.[63]



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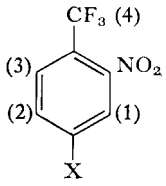

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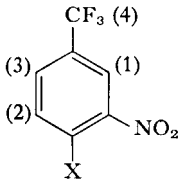

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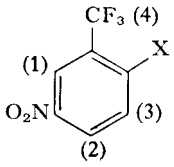

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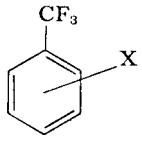


95

The chemical shift of the CF_3 group moved slightly to higher field with more electronegative substituents, and steric interaction of *ortho* groups was also important, as Gutowsky[64] has reported previously. The substitution pattern had more influence on the magnitude of the coupling constants than did the nature of the substituents, and it was concluded[62] that the results are best fitted by a σ–π-exchange polarisation mechanism for the transmission of coupling.

TABLE III

^{19}F parameters for substituted benzotrifluorides[62]

Compound	J_{14} (Hz)	J_{24} (Hz)	J_{34} (Hz)	δ_F p.p.m.
92 X = OH	0·49	0·47	−0·58	−60·04
92 X = OMe	0·58	0·51	−0·61	−59·93
92 X = Cl	0·61	0·50	−0·65	−60·14
93 X = OMe	−0·71	−0·72	0·77	−61·77
93 X = Cl	−0·68	−0·67	0·90	−62·79
93 X = Br	−0·58	−0·68	0·83	−62·88
94 X = OMe	−0·65	−0·54	0·76	−63·04
94 X = Cl	−0·55	−0·54	0·74	−63·05
95 X = 2-NO_2				−59·83
95 X = 2-CN				−61·79
95 X = 3-CN				−63·00
95 X = 4-CN				−63·32

The temperature dependence of ^{1}H and ^{19}F spin-lattice relaxation times in benzotrifluoride and in 1- and 2- naphthotrifluorides has been measured by the adiabatic fast passage method.[65] It was found that the ^{19}F relaxation rates in benzo- and 2-naphtho- trifluorides are determined by spin-internal rotation coupling, and are independent of intermolecular torques within the temperature range studied. The estimated barriers to rotation (0·2 and 0·4 kcal/mole respectively) were in agreement with calculated values. Steric hindrance between the CF_3 group and H(8) in 1-naphthotrifluoride was observed to quench the spin-internal rotation coupling.

Parameters for the trichlorofluoroethylbenzenes **96**, **97**[66] and the triarylfluoromethanes **98**, **99**[67] are shown with the formulae.

$-66{\cdot}3$
$PhCHF{\cdot}CCl_3$
$^{2}J(H\text{–}F) = 42{\cdot}0$ Hz

96

$-59{\cdot}3$
$PhCHCl{\cdot}CFCl_2$

97

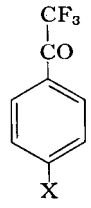
$-126{\cdot}5$
Ph_3CF

98

$-126{\cdot}4$
$FC(C_6H_4{\cdot}NO_2\text{-}p)_3$

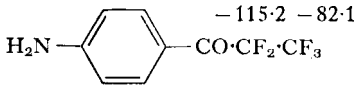
99

4-Amino- and 4-dimethylamino- α,α,α-trifluoroacetophenones **100a, b** have been prepared from the 4-fluoro-compound,[68] and provided routes to a number of other 4-substituted trifluoroacetophenones **100c** to **f**. Their ^{19}F shifts, and those of 3-amino-, 3-iodo- and 3-cyano- trifluoroacetophenones, all fall within the range $-70{\cdot}84$ to $-72{\cdot}07$ p.p.m. The parameters for the 4-amino ketones **101** and **102** were also reported.[68]



a X = NH_2
b X = NMe_2
c X = Cl
d X = Br
e X = I
f X = CN

100



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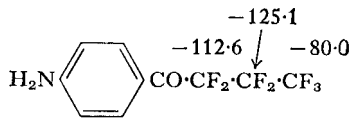


102

C. Fluorinated olefins and acetylenes

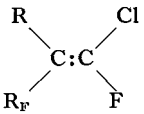
In this section are considered most of the acyclic olefins and acetylenes in which either fluorine or a fluoroalkyl group is attached to the multiply-bonded carbon. Exceptions are some fluoro-olefin derivatives of the elements which will be considered in later sections (e.g. pp. 259, 265, 266, 278, 279).

Chemical shifts for a number of monofluoroethylenes, prepared by defluorination of the ethanes,[13, 69] and of monofluorodichlorostyrenes[66] are shown below. The stereochemistry was not established for the olefins containing :CXY groups.

$CFBr{:}CCl_2$	−74·1
$CFCl{:}CClBr$	−72·2 and −72·3[69]; two singlets at −72·5, separated by 0·029 p.p.m.[13]
$CFCl{:}CClI$	−60·9 and −61·2
$CFBr{:}CClBr$	−66·5 and −67·0[69]; two singlets separated by 2·8 Hz[13]
$CFBr{:}CClI$	−54·9 and −55·1
$CFH{:}CBrCl$	−110·2 [^2J(H–F) = 82 Hz][13]
$PhCF{:}CCl_2$	−96·1
$PhCCl{:}CClF$	−73·7 and −81·0

The chemical shifts and coupling constants for a number of fluoro- and fluoroalkyl- olefins are collected in Tables IV and V. In many cases the assignment of stereochemistry rests on the magnitudes of the coupling constants observed.

A series of 1-chloro-1-fluoro-2-fluoroalkyl olefins (**103, 104**) has been prepared[76] by the reaction of the appropriate ketone with $Ph_3P{:}CFCl$. For $R_F = CF_3$, and R = aryl or alkyl, δ_F was in the range −60·5 to −68·0; the vinylic fluorine in both **103** and **104** absorbed in the range δ_F −59·0 to −59·4 when R was aryl, but varied more (δ_F −57·3 to −61·1) for $R = n\text{-}C_4H_9$ or *cyclo*-C_6H_{11}. The stereochemistry was assigned from the CF_3–F coupling constants (21 to 26 Hz for **103**, 12 to 13 Hz for **104**). In compounds with $R_F = CF_2Cl$, C_2F_5, C_3F_7, δ_F for the vinylic fluorine changed more markedly as shown below.



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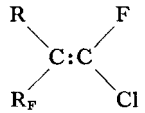
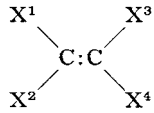


104

R	R_F	**103** δ_F	**103** J(*cis* CF–F)	**104** δ_F	**104** J(*trans* CF–F)
Ph	CF_2Cl	−46·1	31	−46·2	12
Ph	C_2F_5	−108·8	27	−109·5	7
Ph	$n\text{-}C_3F_7$	−105·2	28	−106·3	8

TABLE IV

Chemical shifts[a] for fluoro-olefins



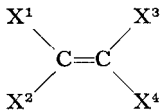
X^1	X^2	X^3	X^4	δ_1	δ_2	δ_3	δ_4	Ref.
CF_3	CF_3	H	F	−62·2	−65·6	(7·31)	−110·9	4
CF_3	F	H	N_3	−74·3	−149·9	(5·94)	..	47
CF_3	H	N_3	CF_3	−60·6	(5·59)	..	−71·1	47
CF_3	H	F	H	−60·9	(5·13)	−114·3	(6·63)	3
CF_3	H	H	F	−64·1	(5·59)	(7·16)	−124·5	3
CF_3	F	H	H	−76·7	−126·3	(5·17)	(5·10)	3
CF_3	H	CH_3	H	−58·7	n.r.[b]	n.r.	n.r.	3
CF_3	H	H	CH_3	−65·0	(5·60)	(6·42)	(1·79)	3
CF_3	CH_3	H	H	−74·3	(1·89)	(5·60)	(5·29)	3
CF_3	H	Me_2P	F	−56·5	(5·59)	(0·91)	−101·1	70
CF_3	H	F	Me_2P	−59·3	(5·14)	−97·9	(0·95)	70
F	F	F	*m*-B[c]	−97·6	−111·9	−158·5	..	71
F	Cl	F	*m*-B[c]	−91·1	..	n.r.[b]	..	71
Cl	F	F	*m*-B[c]	..	−126·5	−111·5	..	71
CF_3	F	F	*m*-B[c]	−67·9	−161·0	−124·9	..	71
F	*o*-B[d]	*o*-B[d]	F	−114·3	..	..	−114·3	72
o-B[d]	F	F	Cl	..	−107·6	−115·5	..	72
o-B[d]	F	F	CF_3	..	−125·5	−152·3	−68·8	72
F	F	F	CF_2-*o*-B[d]	−93·2	−106·3	−193·5	−98·3	72
o-B[d]	F	F	CF_2-*o*-B[d]	..	−140·5	−120·8	−97·8	72
o-B	F	CF_2-*o*-B[d]	CF_3	..	−78·5	−74·5	−55·3	72
F	Cl	H	F	−132·4	..	(6·05)	−176·4	9
F	Cl	F	H	−107·6	..	−159·1	(6·90)	9
CF_3	CF_3	CH_3CHOH	H	−58·5	−65·3	..	(6·70)	12
F	F	CF_3	$MeCH(OH)CH_2$	−76·22	−78·68	−60·66	..	12
CF_3	R[e]	CF_3	H	−60·4	..	−57·4	..	73
H	*n*-Pr	F	CO_2Et	..	..	−118·3	..	37
n-Pr	H	F	CO_2Et	..	..	−126·6	..	37
H	*i*-Pr	F	CO_2Et	..	..	−122·8	..	37
i-Pr	H	F	CO_2Et	..	..	−129·9	..	37
F	$PhS(O)_2$	Cl	H	−121·6	..	..	..	74

[a] Values in parentheses are δ_H values.
[b] n.r. = not reported.
[c] *m*-B = *meta*-carborane (*m*-$MeC \cdot B_{10}H_{10}$).
[d] *o*-B = *ortho*-carborane (*o*-$MeC \cdot B_{10}H_{10}$).
[e] R = 3-cyclopropenyl.

Chemical shifts for some perfluoro- and perfluorohalogeno- olefins are recorded[10,11] in formulae **105** to **110**, and parameters for one of the products isolated[77] from the free-radical reaction of tetrafluoroethylene with 1,2-dichloroethylene in **111**. The signal assigned to F_4 in this compound was stated to be a triplet, "which may be due to non-equivalence

TABLE V

Coupling constants in fluoro-olefins

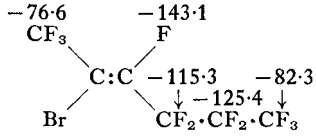


X^1	X^2	X^3	X^4	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	Ref.
CF_3	CF_3	H	F	6·7	1·8	6·7	0·9	19·5	72·0	4
CF_3	F	H	N_3	12·9	0·9	..	21·2	..	..	47
CF_3	H	N_3	CF_3	7·6	..	1·7	..	0·7	..	47
CF_3	H	F	H	7·5	17·3	0·4	36·7	5·7	77·5	3
CF_3	H	H	F	6·7	2·15	8·75	11·5	14·8	78·0	3
CF_3	F	H	H	9·6	0·5	1·7	43·5	13·6	4·5	3
CF_3	H	CH_3	H	8·5	2·8	n.r.[a]	n.r.[a]	n.r.[a]	n.r.[a]	3
CF_3	H	H	CH_3	6·0	2·1	2·6	15·9	1·5	6·3	3
CF_3	CH_3	H	H	0·4	1·1	1·5	n.r.[a]	n.r.	n.r.	3[a]
CF_3	H	Me_2P	F	7·8	43·1	12·0	15	20·8	33·4	70
CF_3	H	F	Me_2P	7·7	17·0	4·2	37·0	3·2	37·0	70
F	F	F	*m*-B [b]	69·5	43·5	..	117·0	..	..	71
F	Cl	F	*m*-B [b]	..	18·5	..	..	..	..	71
Cl	F	F	*m*-B [b]	..	..	..	130·0	..	..	71
CF_3	F	F	*m*-B [b]	9·7	23·5	..	137·0	..	..	71
o-B [c]	F	F	Cl	..	..	..	133·0	..	..	72
o-B [c]	F	F	CF_3	..	..	..	140·0	20·9	8·0	72
F	F	F	CF_2-*o*-B [c]	16·9	29·8	5·6	111·6	40·0	54·6	72
o-B [c]	F	F	CF_2-*o*-B [c]	..	..	..	150	32	10·5	72
F	Cl	H	F	..	1·2	132	..	..	74	9

F	Cl	F	H	..	11	12	..	..	73	9
CF_3	CF_3	$CH_3CH(OH)$	H	7	..	..	..	..	..	12
F	F	CF_3	$MeCH(OH)CH_2$	[d]	10	..	20	..	..	12
Ph	F	OEt	F	..	..	..	..	11	..	75
Ph	F	F	OEt	..	..	..	112	..	..	75
Ph	CF_3	OEt	F	..	..	..	..	25	..	75
Ph	CF_3	F	OEt	..	..	..	13	..	..	75
CF_3	R [e]	CF_3	H	..	11	..	..	..	9	73
H	*n*-Pr	F	CO_2Et	..	20·5	..	..	..	..	37
n-Pr	H	F	CO_2Et	..	..	..	31·8	..	..	37
H	*i*-Pr	F	CO_2Et	..	21·9	..	..	..	..	37
i-Pr	H	F	CO_2Et	..	..	..	31·8	..	..	37
F	$MeCH(OEt)$	H	Cl	26·5	11	..	..	..	..	74
F	PhS	H	Cl	..	6·25	..	..	..	..	74
F	PhS	Cl	H	..	..	18	..	..	..	74
F	$PhS(O)_2$	Cl	H	..	..	20	..	..	..	74
H	Cl	F	R [f]	..	7·5	..	..	..	..	74

[a] Not reported.
[b] *meta*-carborane.
[c] *ortho*-carborane.
[d] Not resolved.
[e] R = 3-cyclopropenyl.
[f] R = CCl:CF·CHMeOEt.

because of the asymmetry of carbon-5", but the only splitting parameter quoted was given as $J(F4–H5) = 9{\cdot}4$ Hz.



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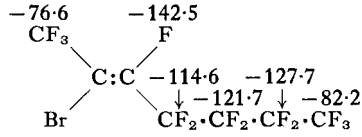

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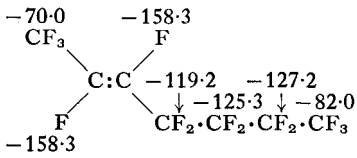

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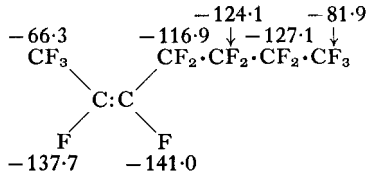

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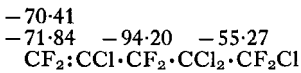

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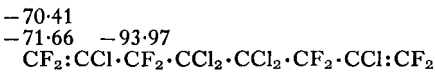

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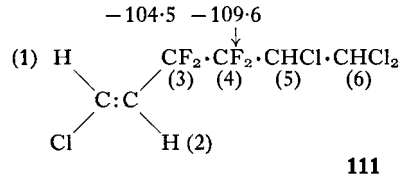
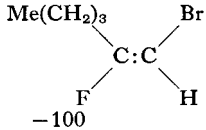


J(F3–H1) = 2 Hz
J(F3–H2) = 12·0 Hz
J(F3–F4) = 1·6 to 1·9 Hz

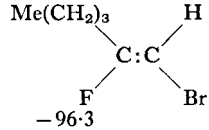
111

Addition of bromine monofluoride to alkynes[78] gave a series of monofluoro-olefins **112** to **115**. Addition to phenylacetylene gave α-fluoro-β-bromostyrene, in which the observed ^3J(H–F) (15·8 Hz) suggests *cis*-disposition of hydrogen and fluorine. The product resulting from fluoride-ion attack on diethyl acetylenedicarboxylate followed by proton abstraction had ^3J(H–F) 31 Hz, and was thus assigned[79] the *trans*-configuration, as were the products **116a**, **b** formed by fluoride ion addition to perfluorobut-2-yne followed by reaction of the anion so formed with pentafluoropyridine or tetrafluoropyridazine.



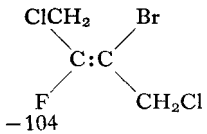
J(*cis* H–F) = 13 Hz
J(F–CH_2) = 21 Hz

112



J(*trans* H–F) = 27·5 Hz
J(F–CH_2) = 16·5 Hz

113



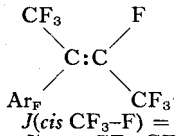
-104
^3J(H–F) = 21 Hz
^4J(H–F) = 3·5 Hz

114

$CH_3 \cdot CH_2 \cdot CF{:}CBr \cdot CH_2 \cdot CH_3$

115a *trans*-isomer δ_F -110;
^3J(H–F) = 23 Hz

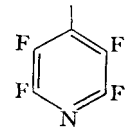
115b *cis*-isomer δ_F $-96{\cdot}3$
^3J(H–F) = 21 Hz



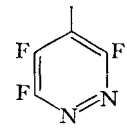
J(*cis* CF_3–F) = 21 Hz
J(*trans* CF_3–CF_3) = 1 Hz

116

a Ar_F =



b Ar_F =



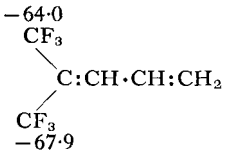
Fluoride-ion catalysed ring-opening of the cyclobutanone obtained from bis(trifluoromethyl)keten and methyl trifluorovinyl ether gave[35] the acid fluoride **117** in which only the CF_3 group at lower field was coupled to the CF_2 group, which is therefore presumably *cis* to it.

$-59{\cdot}1$, $-61{\cdot}2$ -105 $+16{\cdot}0$
$(CF_3)_2C{:}C(OMe)CF_2 \cdot COF$
$J(CF_3–CF_3)$ = 9·0 Hz
$J(CF_3–CF_2)$ = 13·6 Hz
$J(CF_2–F)$ = 10·9 Hz

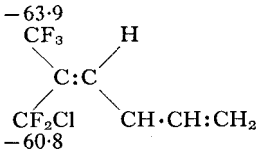
117

The CF_2Cl group of 2,3-dichlorotetrafluoropropene was reported[80] to be a doublet (32 Hz) of doublets (8 Hz) at δ_F $-52{\cdot}6$, but the geminal vinylic fluorines were reported only as six peaks at $-76{\cdot}9$ to $-78{\cdot}5$ and five at $-79{\cdot}2$ to $-79{\cdot}9$.

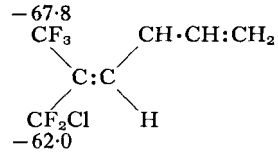
The spectra of a number of dienes have been reported,[12] and parameters are shown below. The coupling between geminal fluoro-alkyl groups in **118** to **120** is 7 Hz. The observation that the CF_2Cl group in **119** and the CF_3 group in **120** were each coupled to the vinylic hydrogen (J=1 Hz) was used to assign the stereochemistry shown.



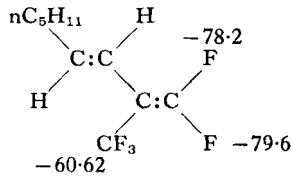
118



119



120



^2J(F–F) = 10 Hz
^4J(*cis* CF_3–F) = 10 Hz
^4J(*trans* CF_3–F) = 28 Hz

121

$CF_3 \cdot CX{:}CY \cdot CHR \cdot CH{:}CHR$
122a X = H, Y = Br
122b X = Br, Y = H

$CF_3CH{:}CH \cdot CHR \cdot CHR'{:}CR''R'''$

123

The dienes **122**[81,82] and **123**,[83] where the substituents R to R‴ are variously hydrogen and methyl groups, have chemical shifts in the range δ_F −57·68 to −60·3 and $^3J(CF_3–H)$ 7 to 8 Hz (except, of course, **122b**), but no other couplings were reported, and the stereochemistry was not assigned. Parameters for the diene **124** and enyne **125** have been reported;[34] in each case the vinylic fluorines appeared as a complex multiplet which was not analysed, and the couplings were taken from the CF_3-group signals.

−78·5 −60·5 +38·3
$CF_2{:}C(CF_3) \cdot C(Me){:}C(Me)COF$
$^4J(CF_3–F)$ = 11·5 Hz, 18·5 Hz

124

−69·4 −62·1
$CF_2{:}C(CF_3) \cdot C{:}CPh$
$^4J(CF_3–F)$ = 10·6 Hz, 21·6 Hz

125

The spectra of a number of dienes prepared[82] by addition of methanethiolate ion to allyl(trifluoromethyl)acetylenes showed that in most cases two geometric isomers were formed. For compounds containing the $CF_3 \cdot CH_2 \cdot C(SMe){:}CR \cdot CR'{:}$ grouping, δ_F was in the range −63·6 to −65·6, and $^3J(CF_3–H)$ *ca.* 11 Hz.

The spectrum of hexafluorobutadiene **126** has been studied[84] at temperatures from +34 to −90°. The coupling constants at the higher temperature agree well with those independently obtained by Manatt and Bowers,[85] with the exception of ^2J(F–F) (+52·4, *cf.* +50·74†) and the relative signs deduced are the same. J(A–M′), J(M–X′), and J(A–X′) were found to be practically invariant with temperature, but all the other couplings varied (see Fig. 3).

† The difference may be due at least in part to a medium effect. The coupling constants depend markedly on solvent (M. G. Barlow, personal communication) and Manatt and Bowers[85] used a mixed reference system which included C_6F_6.

It was suggested that the changes in coupling constant did not arise from changes in conformer populations, since the 4- and 5-bond couplings, which would be expected to be most sensitive to such changes, were relatively constant.

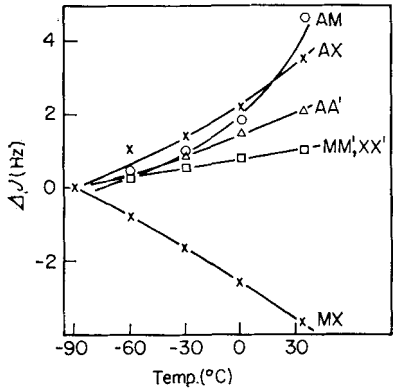
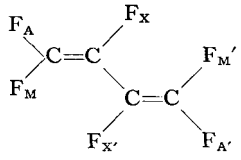
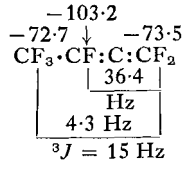


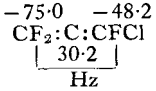
FIG. 3. The change, ΔJ, of coupling constants with temperature for **126**. (From Barlow and Cheung.[84])



126



127

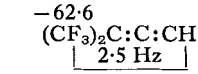


128

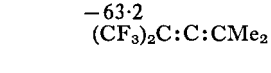
The preparation of three fluoro-allenes, by the reaction of fluoro-olefins with atomic carbon, has been reported[86] briefly and the parameters reported are given in formulae **127**, **128**.

Parameters for other allenes reported[35, 36, 82] are given in formulae **129** to **131**.

The highly explosive chlorofluoroacetylene (FC:CCl, δ_F −219) has been prepared[74] by dehydrochlorination of 1,1-dichloro-2-fluoroethylene, and its addition reactions with ethers and thiols gave olefins whose parameters are reported in Tables IV and V.



129



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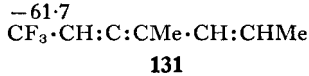

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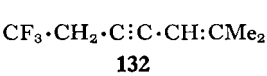


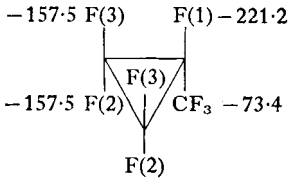
132

In a number of trifluoromethyl acetylenes $CF_3 \cdot C{:}CR$,[81,82,87] δ_F falls in the range −50·4 to −58·31, and where R is a group CHXY, $^5J(CF_3\text{–}H)$ is *ca.* 4 Hz.[81,82,88] In the germyl and stannyl acetylenes[87] $Me_nM(C{:}C\cdot\cdot CF_2 \cdot CF_3)_{4-n}$ (M = Ge, n = 3,2; M = Sn, n = 3) the CF_3 groups absorbed in the narrow range −86·4 to −86·8. The CF_2 groups for the two trimethyl compounds absorbed at −101, but the dimethyl compound showed a small shift to higher field (δ_F −104). The shifts in the perfluoroisopropyl group in $Me_3GeC{:}C \cdot CF(CF_3)_2$ (δ_{CF} −166, δ_{CF3} −73·0) are similar to those reported[89] for perfluoroisopropylchloroacetylene. The enyne[82] (**132**) has δ_F −68·4 with $^3J(H\text{–}F)$ = 8·2 Hz.

D. Fluorinated Cyclo Hydrocarbons

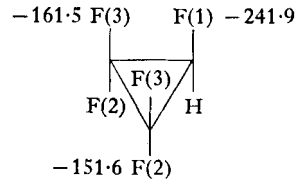
1. *Cyclopropanes and cyclopropenes*

The parameters for a number of polyfluorinated cyclopropanes, prepared by the reaction of hexafluoropropene oxide with appropriate olefins, have been reported,[9] and are shown with formulae **133** to **139**.



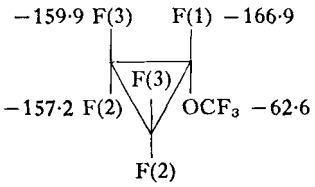
$J(CF_3\text{–}F1)$ = 9·2 Hz
$J(CF_3\text{–}F2)$ = 7·7 Hz
$J(CF_3\text{–}F3)$ = 6·0 Hz
$J(F1\text{–}F2)$ = 2·7 Hz
$J(F1\text{–}F3)$ = 4·3 Hz

133



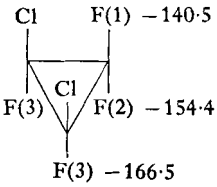
$J(H\text{–}F1)$ = 56 Hz
$J(H\text{–}F2)$ = 13·2 Hz
$J(H\text{–}F3)$ = 1·3 Hz
$J(F1\text{–}F2)$ = 4·9 Hz
$J(F1\text{–}F3)$ = 9·8 Hz
$J(F2\text{–}F3)$ = 208 Hz

134



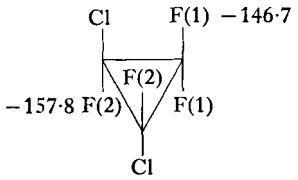
$J(CF_3–F1) = 4·9$ Hz
$J(CF_3–F2) = 4·6$ Hz
$J(CF_3–F3) = 1·2$ Hz
$J(F1–F2) = 3·2$ Hz
$J(F1–F3) = 9·2$ Hz
$J(F2–F3) = 201$ Hz

135



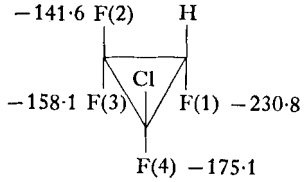
$J(F1–F2) = 174$ Hz
$J(F1–F3) = 5·3$ Hz
$J(F2–F3) = 5·6$ Hz

136



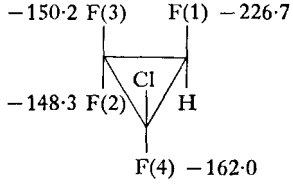
Triplet separation = 2·6 Hz

137



$J(H–F1) = 57$ Hz
$J(H–F2) = 10$ Hz
$J(H–F3) = J(H–F4) = 1·3$ Hz
$J(F1–F2) = 4·9$ Hz
$J(F1–F3) = J(F1–F4) = 7·5$ Hz
$J(F2–F3) = 184$ Hz
$J(F2–F4) = 2·1$ Hz
$J(F3–F4) = 4·8$ Hz

138



$J(H–F1) = 57$ Hz
$J(H–F2) = 9·1$ Hz
$J(H–F3) = 2·1$ Hz
$J(H–F4) = 16·8$ Hz
$J(F1–F2) = 2·8$ Hz
$J(F1–F4) = 11·1$ Hz
$J(F2–F3) = 190$ Hz
$J(F2–F4) = 5·7$ Hz

139

The spectra are complicated, and the coupling constants reported were obtained from first-order analysis (e.g. of the bands due to the CF_3 group and to F(1) in **133**) or from AB approximations for AA'BB' systems (e.g. in **135, 136**). Both bands in **137** appeared as triplets with separation 2·6 Hz, and no coupling constants could be derived.

The chemical shift assignments were based on the effects of substitution for fluorine in perfluorocyclopropane of hydrogen (which deshields *cis*-vicinal fluorines and shields *trans*-vicinal fluorines) and of chlorine

(which deshields both *cis*- and *trans*- vicinal fluorines, the effect being greater for the *cis*), and on the coupling constants ^3J(*cis* H–F) and ^3J(*cis* F–F) being larger than ^3J(*trans* H–F) and ^3J(trans F–F) respectively. The sole exception to the latter was that J(F1–F4) > J(F2–F4) in **139**; the assignment of these couplings, and J(F1–F2) [which, as expected, was smaller than J(F2–F4)] was confirmed by double resonance.

An additive relationship for the fluorine chemical shifts according to the disposition of the substituents was proposed based on δ_F for perfluorocyclopropane −158·9; the increments are *cis*-H, +7·3; *trans*-H, −2·7; *cis*-Cl, +9·2; *trans*-Cl, +2·3 p.p.m.

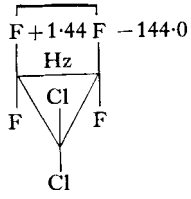
More detailed NMR studies[90] on **136**, **137**, and the geminal dichloro-compound **140** have also been reported. The parameters for **136** and **137** agree well with those shown with the formulae, and other parameters, and those for **140**, are given below. Frequency-swept double resonance experiments showed that J(F1–F3) and J(F2–F3) in **136** have opposite signs† [negative and positive respectively, compared with positive J(*gem* F–F)]. J(F2–F3) was more sensitive to changes in temperature (+5·62 Hz at +35°, +4·43 Hz at −75°) than J(F1–F3) (−5·23 Hz and −5·43 Hz at the same temperatures). A similar decrease was observed in the numerical value of J(*cis* F3–F3) in **136** and an almost constant value for J(*trans* F2–F2) in **137**, and on the basis of the trend to smaller absolute values of J(F–F) with decrease in temperature observed above, and reported previously[92] for 1,1,2-trichlorotrifluorocyclopropane, J(*cis* F3–F3) in **136** and J(*cis* F–F) in **140** were assigned positive signs and N in **137** [= J(*trans* F1–F2) + J(*cis* F1–F2)] was assigned a negative sign. The negative sign for J(F2–F2) in **137** was assigned from consideration of the trends of the couplings observed for a number of fluorocyclopropanes.[90, 92, 93] Thus replacement of a fluorine on a carbon adjacent to the carbons carrying the coupling nuclei by a less electronegative substituent caused a decrease in J(*cis* F–F) and an increase in J(*trans* F–F) the change in J(*cis*) being larger than that in J(*trans*), and being more sensitive to replacement of a *cis* group than one *trans* to the coupling nuclei.

Isotope shift (p.p.m.)		$^1J(^{13}C–F)$	Other values
136	−0·152(F3)	−315·2(F3)	J(F3–F3) = +5·5 Hz [a]
137	−0·059(F2)	−309·7(F2)	J(F2–F2) = −12·2 Hz [a]
140	−0·117	−323·2	J(*trans* F–F) = +4·10 Hz

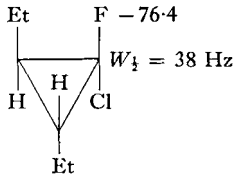
[a] From ^{13}C satellite spectra.

† Spin tickling experiments[91] also lead to these relative signs.

When the change was on the carbon carrying one of the coupling nuclei, both coupling constants decreased.



140



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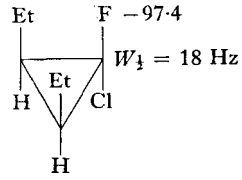
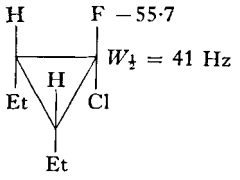


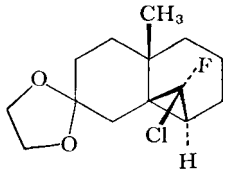
142



143

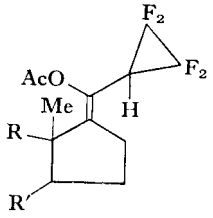
Addition of chlorofluorocarbene derived from dichlorofluoromethyl-(phenyl)mercury to *cis*- and *trans*- hex-3-enes gave the corresponding 1,2-diethyl-3-chloro-3-fluorocyclopropanes **141** to **143**,[94] the stereochemistry of which was assigned by comparison of the widths of the ^{19}F signals with those of the analogous 1,2-dimethyl-compounds.[95] Since J(*cis* H–F) > J(*trans* H–F), the multiplet for **143** is broader than that for **142**.

Deshielding by the ethyl groups (more effective for *cis*- than for *trans*-fluorine) is considerably greater than that reported for the methyl groups in the analogous dimethyl cyclopropanes. The stereochemistry of the addition of chlorofluorocarbene to a model steroidal olefin has also been deduced from the NMR parameters of the product.[96] The observation of a relatively narrow ^{19}F signal and of weak coupling to the angular methyl group led to the structure shown (**144**). A minor product was stated to have δ_F −129·8, with doublet splittings of 20·3 and 5·2 Hz, but no structure was assigned.



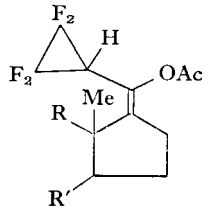
δ_F −149·2
$W_{\frac{1}{2}}$ = 8 Hz

144



AB1; δ_F −140, −154,
J_{AB} = 180 Hz.
AB2; δ_F −141·5,
−153,
J_{AB} = 180 Hz

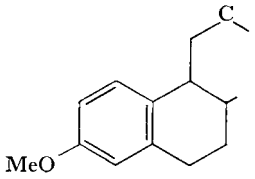
145



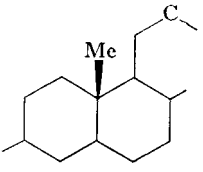
AB1; δ_F −139·5, −148;
J_{AB} = 178 Hz
AB2; δ_F −139·5, −150;
J_{AB} = 178 Hz

146

a R,R′ =



b R,R′ =

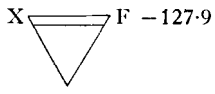


The addition of difluorocarbene to steroidal alkynes was originally thought to give bicyclobutane derivatives,[97] but X-ray examination has shown this to be incorrect, and the compounds are now formulated[98] as tetrafluorocyclopropanes. The parameters for **145b** and **146a** are shown; those for **145a** are very similar.[97] When a mixture of **145a** and **146a** was treated with dilute aqueous sodium hydroxide the corresponding cyclopropenes were produced. That corresponding to **145** showed an ABX pattern (δ_{F_A} −92·5, δ_{F_B} −94, δ_{F_X} −140, $2J$(F–F)=117 Hz, JAX=JBX=43 Hz) but that corresponding to **146** showed only a doublet (δ_F −91·5, CF_2) of triplets (δ_F −137·5, 43 Hz, :CF).

These parameters are similar to those of perfluorocyclopropene,[99,100] and 1-chlorotrifluorocyclopropene,[99] parameters for which are given with formula **147a**.† Parameters for **148** and **149** have also been reported.[99]

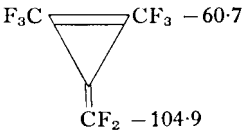
† Small differences in the values of δ_F reported for perfluorocyclopropene may be ascribed to the use of internal[99] compared with external[100] $CFCl_3$, but the difference for δ(CF:) (−134·1,[99] −145·1,[100] −145·18[101]) is too large to be accounted for in this way.

The reaction of bromotrifluoroethylene with atomic carbon gave a low yield of bromotrifluoroallene and a second compound for which the ^{19}F parameters are consistent[86] with its formulation as **147b** (δ_F −97·9, 2F, d, 40·7 Hz, δ_F −126·0, 1F, t, 40·7 Hz).

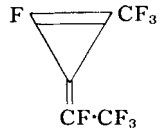


^3J(F–F) = 41·4 Hz

147 a X = Cl
b X = Br

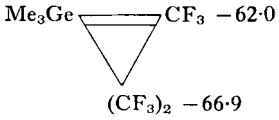


148



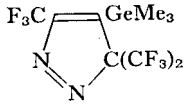
δ_{CF_3} −63·0, −65·5
$\delta_{:CF}$ −99·6, −100·0

149

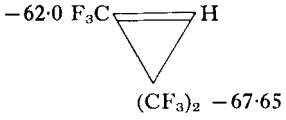


^5J(F–F) = 1·2 Hz

150

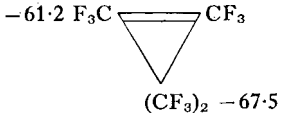


151

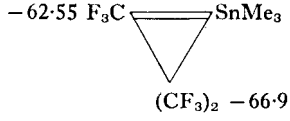


$^4J(CF_3C{:}\text{–}H)$ = 1·3 Hz
$^4J[(CF_3)_2\text{–}H]$ = 1·0 Hz

152



153



154

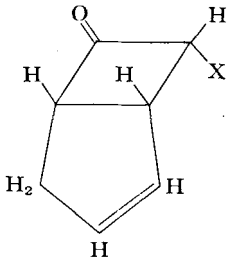
The product from the reaction of trimethylgermyl(trifluoromethyl)-acetylene and bis(trifluoromethyl)diazomethane is now reported[87] to be the cyclopropene **150**, and not the isopyrazole **151** as previously reported.[102] Other cyclopropenes **152** to **154** were prepared similarly or by pyrolysis of the iso-pyrazole.[103] All showed long-range coupling (1·15 to 1·25 Hz) between the $(CF_3)_2C$ and CF_3C: groups.

2. *Cyclobutanes and cyclobutenes*

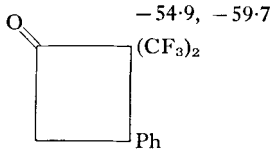
^{19}F NMR spectroscopy was used extensively in the study of the stereochemistry of the competing 1,2- and 1,4- addition reactions between

cyclopentadiene and *cis*- and *trans*- 1,2-dichlorodifluoroethylene. Although the form of the spectrum was described for many of the products, no parameters were quoted.[104]

Addition of cyclopentadiene to the C=C bond of halogenoketens[105] (halogen = F, Cl, Br) gave the cyclobutanones **155**. $2J$(H–F) in both **155a** and its dihydro-derivative was 55 Hz.

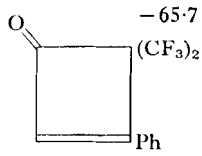


155a X = F
b X = Cl
c X = Br



^4J(F–F) = 8·6 Hz

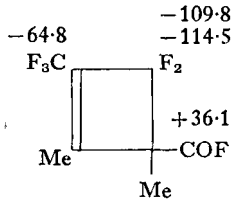
156



157

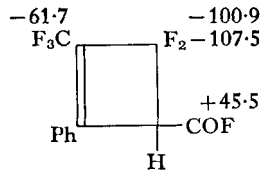
Krespan and England have reported parameters for a number of cyclobutanones[33, 35, 36] containing geminal trifluoromethyl groups (e.g. **156**). These are nonequivalent, and gave rise to a pair of quartets [$4J$(F–F) = 6·4 to 9·7 Hz] with δ_F −61·0 to −70·2. The ^{19}F spectra of two examples are illustrated in ref. 35. Similar cyclobutenones (**157**) gave[34] only singlets in the range δ_F −64·5 to −68·1.

The same authors reported parameters for some ring-fluorinated cyclobutenes[34] **158** to **161**, and the cyclobutanone **162**.[35] The parameters for the acid and the methyl ester corresponding to **159** are very similar.



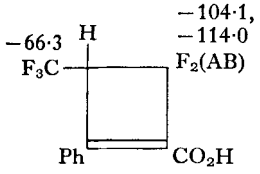
^2J(F–F) = 200 Hz
^4J(F–COF) = 6·2 Hz

158



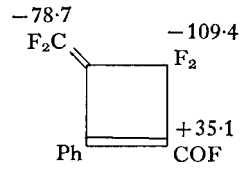
^2J(F–F) = 200 Hz
^4J(F–COF) = 5·6 Hz

159

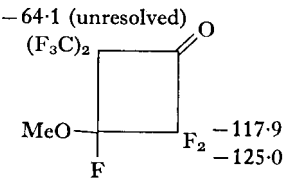


^2J(F–F) = 211 Hz
$J(CF_3–F_A)$ = 3·4 Hz
$J(CF_3–F_B)$ = 12·4 Hz
$J(CF_3–H)$ = 7·9 Hz

160



161



^2J(F–F) = 260 Hz

162

Chemical shifts were reported for two 1-aminoperfluorocyclobutenes[106] **163** and for 1-methoxycyclobutene[107] (**163**, R = MeO).

R	δ_F	δ_{F2}
	−135·5	−120·2, −117·7
Me_2N	−159·4	−116·5, −112·0
MeO	−143·6	−119·7, −117·1

163

The signal at low field in the spectrum of **163** (R = MeO) was assigned to F_B, in accord with the observation[108] that fluorines adjacent to the more electronegative substituent appear to high field, and the coupling constants are as shown below; double resonance experiments showed that J(AX) and J(BX) have the same sign.

J(AB) = ±26·56 Hz
J(AX) = ±20·03 Hz
$|J(AA')-J(BB')|$ = 1·44 Hz
$|J(B–CH_3)|$ = 0·47 Hz
J(AB′) = ∓16·85 Hz
J(BX) = ±7·89 Hz
$|J(X–CH_3)|$ = 1·40 Hz

However, on the basis of an investigation of a series of cyclobutenes, Newmark[109] suggested the opposite assignment of F(A) and F(B); Cavalli considers this to be a more reasonable assignment, and suggested that the trouble may have been caused by the use of *internal* trifluoroacetic acid reference, since this is known in some case to give anomalous shifts.[110] The assignments of couplings involving the A and B nuclei should therefore be interchanged, i.e.

$$J(AX) = \pm 7{\cdot}89 \text{ Hz} \qquad J(BX) = \pm 20{\cdot}03 \text{ Hz}$$

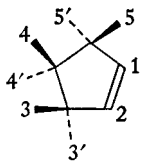
3. *Cyclopentenes and cyclopentadienes*

No reports on cyclopentanes have come to hand.

The parameters for a number of fluorinated cyclopentenes have been

TABLE VI

^{19}F parameters for fluorocyclopentenes[111]



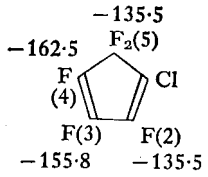
Chemical Shifts (δ)

Compound[a]	F1	F2	F3	F3′	F4	F4′	F5	F5′	$^2J_{FF}$[b]	$^2J_{FH}$[c]
Octafluoro[d]	−154	−154	−121	−121	−133	−133	−121	−121	..	..
3*H*,4*H*	−156	−141	..	−200	..	−217	−111	−111	..	3′,H 57
										4′,H 49
3*H*,5*H*	−144	−144	..	−188	−108	−127	..	−188	4,4′267	N[e]61
1*H*,5*H*[d]	..	−130	−128	−115	−122	−132	..	−189	3,3′265	..
										53
									4,4′255	
1*H*,4*H*[d]	..	−129	−113	−119	..	−213	−97	−107	3,3′269	
										49
									5,5′263	

[a] Undesignated atoms are all fluorine.
[b] ±5 Hz or better.
[c] ±1 Hz or better.
[d] Stated in the original paper to have been measured with external trifluoracetic acid reference, and converted to $CFCl_3$ reference by addition of 78. The values have not been reconverted here.
[e] $N = |J_{3,3'}+J_{3,5'}| = |J_{5,5'}+J_{3',5}|$.

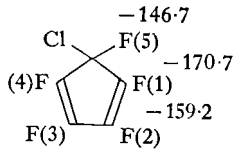
reported,[111] (Table VI); those for the manganese-substituted cyclopentenes which were also reported are considered later (pp. 260 to 261) with other transition-metal complexes.

1-Chloropentafluorocyclopentadiene **164** and the 5-chloro-isomer **165** have been isolated,[112] and their ^{19}F spectra analysed to give the parameters shown.



164

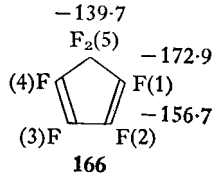
J(F2–F3) = 11·3 Hz
J(F2–F4) = 12·6 Hz
J(F2–F5) = 6·7 Hz
J(F3–F4) = 10·9 Hz
J(F3–F5) = 7·0 Hz
J(F4–F5) = 9·3 Hz
$\nu_2 - \nu_5$ = 0·93 Hz



165

J(F1–F5) = 11·6 J(F1–F4) = 17·1 Hz
J(F2–F5) = 1·7 J(F2–F3) = 11·2 Hz

J(F1–F2) = ±16·1 Hz
J(F1–F3) = ∓7·7 Hz



166

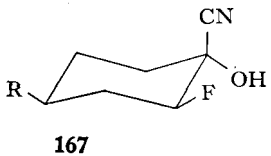
In view of the chemical shifts observed for **164** and **165**, and the effects of chlorine substitution in model compounds[113] it was suggested that the previous tentative assignments for perfluorocyclopentadiene[114] [F(1), F(4), δ_F −156·7; F(2), F(3) −172·9] should be reversed, and this is in accord with further analysis of the fine structure of the perfluorocyclopentadiene spectrum.[115] The revised assignments are shown in **166**.

Tetrakis(trifluoromethyl)cyclopentadienone formed an ylid with triphenylphosphine,[116] which showed complex bands at δ_F −52·5, and −51·7. Phosphorus-fluorine coupling was shown to be small, since each band collapsed to a singlet on irradiation at the other fluorine resonance frequency.

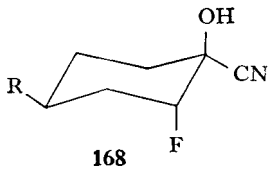
4. *Cyclohexanes and cyclohexenes*

Fluorinated derivatives of cyclohexane continue to find use in the study of conformational problems. Cantacuzène and his co-workers have

reported[117] parameters for a number of mono- and di- fluorocyclohexane derivatives. At 25°, the cyanohydrin of 2-fluorocyclohexanone showed a doublet ($W_{\frac{1}{2}} = 79$ Hz) at δ_F −184, due to the rapidly interconverting conformers with axial and equatorial fluorines. At −70°, the spectrum showed a doublet ($W_{\frac{1}{2}} = 66$ Hz) at δ_F −182·5 and a distorted triplet ($W_{\frac{1}{2}} = 107$ Hz) at δ_F −188·65, assigned to conformers **167a** and **168a** respectively, in view of the patterns obtained at 25° for the 4-t-butyl analogues **167b** (d, $W_{\frac{1}{2}} = 66$ Hz, δ_F −181·5) and **168b** (t, $W_{\frac{1}{2}} = 108$ Hz, δ_F −185·5), in which the conformations are locked.

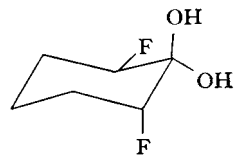


167



168

a R = H;
b R = Bu^t



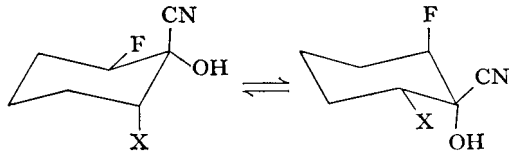
169

The observed room temperature line width L was related to the conformer population and the line widths observed under conditions of slow conformational change for axial and equatorial fluorines, L_a and L_e respectively by the equation:

$$L = L_a(x) + L_e(1-x)$$

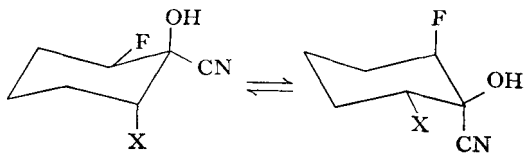
where x = mole fraction with axial fluorine.

The three known points for compound **169** (axial F, $W_{\frac{1}{2}} = 106$ Hz, equatorial F, $W_{\frac{1}{2}} = 66{\cdot}5$ Hz at −70°, equimolar mixture rapidly interconverted at room temperature, $W_{\frac{1}{2}} = 86$ Hz) were used to give the slope and intercept of the straight line, and the relationship was then used to read off the room-temperature conformer populations for cyanohydrins of the types **170**, **171**.



170

170a X = H
b X = F
c X = Cl
d X = Br



171

171a X = F
b X = Cl
c X = Br

The values obtained are compared in Table VII with those obtained by integration of the signals at −70°, and show clearly the difference in conformational preference for the two series **170** and **171**.

TABLE VII

Conformer populations[117] at +25° and −70°

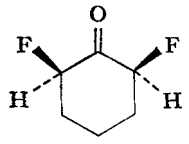
Compound	% F axial	
	+25°	−70°
170a	31%	15%
170b	72%	82%
170c	80%	93%
170d	78%	91%
171a	28%	18%
171b	55%	49%
171c	56%	77%

Cantacuzène also showed that the *t*-butyl group may significantly affect the chemical shift of fluorine in such compounds. Thus the equatorial fluorine in 4-*t*-butyl-1,1-difluorocyclohexane appeared some 4 p.p.m. to high field of the position (at low temperature) of the same fluorine in 1,1-difluorocyclohexane, the axial fluorines being within 1·5 p.p.m. of each other, but in **168b** the axial fluorine resonance was displaced by *ca.* 3 p.p.m. to low field of that in **168a**, the equatorial fluorines in **167a** and **167b** remaining within 1 p.p.m.

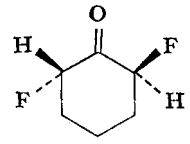
Similar parameters were reported, and spectra are illustrated in the paper, for the ketones corresponding to **167b** and **168b.**[118] The axial fluorine in that corresponding to **168b** showed a broad triplet [since $2J$(H–F) and $3J$ (axial H–F) are similar in magnitude] with an overall width at half height ($W_{\frac{1}{2}}$) of 114 Hz; the equatorial fluorine (*cf.* **167b**) appeared as a doublet [^2J(H–F) = 48 Hz] with $W_{\frac{1}{2}}$ 64 Hz. Conversely the

width of the components of the large doublet [$2J$(H–F)] in the absorption of the CHF group was small (6·5 Hz) for equatorial hydrogen (*cf.* **168b**) and large (18 Hz) for axial hydrogen (*cf.* **167b**). The relation between signal width in the ^1H and ^{19}F spectra of the CHF group was then used to determine the proportion of each conformer in the rapidly interconverting ketones corresponding to **167a** and **168a** under a variety of conditions. For example, the width of the fluorine signal increased steadily from 67·5 Hz in the pure liquid to 81 Hz for a 2·5% solution in cyclohexane, corresponding to 7% and 43 ± 2% respectively of the conformation with axial fluorine.

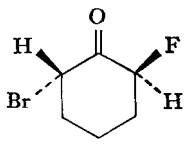
The parameters for a number of other cyclohexane derivatives containing one or more CHF groups[119] are summarised in formulae **172** to **177**.



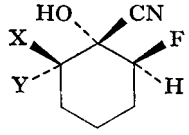
δ_F −187·5
$W_{\frac{1}{2}}$ 65 Hz
172



δ_F −190
$W_{\frac{1}{2}}$ 93 Hz
173

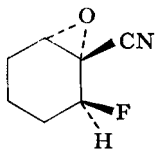


δ_F −191
$W_{\frac{1}{2}}$ 72 Hz
174



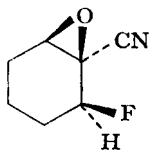
175

175a X = F, Y = H
δ_F −185
$W_{\frac{1}{2}}$ 67·5 Hz
b X = H, Y = F
δ_F −184·5, −186·5
$W_{\frac{1}{2}}$ 93 Hz, 83 Hz



176

δ_F −183
$W_{\frac{1}{2}}$ 96 Hz

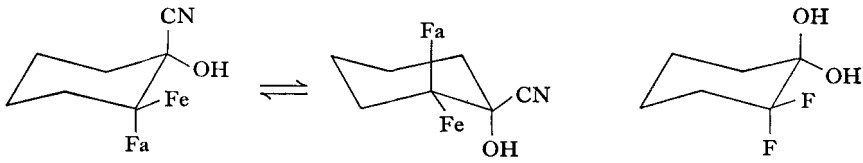


177

δ_F −200
$W_{\frac{1}{2}}$ 73 Hz

cis-2,5-Difluorocyclohexanone (**172**) was shown by the half-width of the ^{19}F and ^1H signals to be entirely the diequatorial conformer, and the *trans*-bromofluoroketone **174** was similarly shown to contain 88% of the conformer with axial bromine. The sharp singlet observed (δ_F −109, $W_{\frac{1}{2}}$ 15·5 Hz) for 2-bromo-2-fluorocyclohexanone showed that it, too, consists almost entirely of the conformer with axial bromine.

The spectra of the 2,2-difluoro-compound **178**[117] are also illustrated in the original papers, and those of **33a**[28] in Fig. 2 (p. 109). The room temperature spectrum of **33** was a distorted triplet (δ_F −110·5), but at

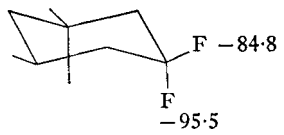


33a **178**

$-70°$, two AB patterns were resolved, the stronger (centred at δ_F $-105{\cdot}1$) with geminal F–F coupling 236 Hz being assigned to the conformer with axial OH, and the weaker (centred at δ_F $-114{\cdot}2$) with geminal coupling 229 Hz to that with axial CN. Similarly, the triplet ($W_{\frac{1}{2}}$ 26 Hz) observed for **178** at room temperature was resolved at $-70°$ into an AB pattern (δ_F -116, J(F–F) = 235 Hz), the low-field bands of which were distorted triplets ($W = 37$ Hz), ascribed to the axial fluorine, and the high field bands relatively sharp ($W = 15{\cdot}5$ Hz) singlets.

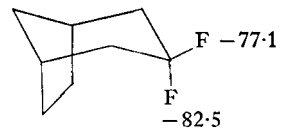
Another series of geminal difluorocyclohexanes has been studied by Jefford and his co-workers.[120] 1,1-Difluoro-3,3,5-trimethylcyclohexane **179** and the bridged compound **180** both showed AB quartets further split by vicinal H–F couplings at room temperature.

1,1-Difluoro-3,3-dimethylcyclohexane (**181**) and 1,1-difluoro-3,3,5,5-tetramethylcyclohexane (**182**) gave time-averaged spectra at room temperature (e.g. **181** showed a quintet with vicinal H–F coupling $\approx 13{\cdot}5$ Hz) but at low temperatures the AB quartets were observed, and line shapes were analysed to give the rates of conformational isomerisation and hence the Eyring parameters for the ring inversion.



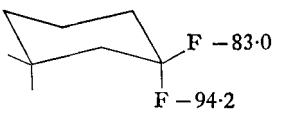
^2J(F–F) = 251 Hz
$^3J(F_{eq}–H_{ax}) \approx {}^3J(F_{eq}–H_{eq}) \approx$ 5 to 7 Hz
$^3J(F_{ax}–H_{ax})$ = 37·0 Hz
$^3J(F_{ax}–H_{eq})$ = 13·0 Hz

179



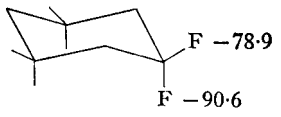
^2J(F–F) = 251 Hz
$^3J(F_{eq}–H_{ax}) \approx {}^3J(F_{eq}–H_{eq})$ = 10·0 Hz
$^3J(F_{ax}–H_{ax})$ = 50·0 Hz
$^3J(F_{ax}–H_{eq})$ = 20·0 Hz

180



^2J(F–F) = 240 Hz

181

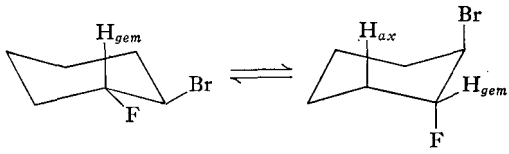


^2J(F–F) = 243 Hz

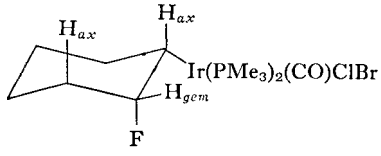
182

The effects of substitution by methyl groups on the chemical shift of the fluorine nuclei are discussed, and it was noted that introduction of an equatorial 3-methyl group shields both axial and equatorial fluorines by a similar small amount (1·8, 1·3 p.p.m.), but an axial methyl group causes a bigger shift to low field for equatorial fluorine (5·9 p.p.m.) than for axial (4·9 p.p.m.). Shifts predicted from these values for other methylcyclohexanes showed reasonable agreement for equatorial fluorines but rather poorer agreement for axial fluorine.

The configuration of *trans*-1-bromo-2-fluorocyclohexane was confirmed by its ^{19}F parameters.[121] A broad doublet (*J ca.* 50 Hz) at δ_F −166·8 at 25° broadened further on cooling, and at −80° the spectrum consisted of a doublet [^2J(F–H) = 48 Hz] at δ_F −166·0, ascribed to conformation **183a** and a broad, unresolved multiplet at δ_F −170·0 ascribed to conformation **183b** in the ratio 5·5:1. Reaction of this bromo-compound with *trans*-(Ir(PMe$_3$)$_2$(CO)Cl) gave a product† showing a quartet at δ_F −142·7 with separation *ca.* 50 Hz, consistent only with inversion of configuration to give the *cis*-compound **184** in which the coupling of the axial fluorine to the geminal hydrogen and to two vicinal axial hydrogens would all be expected to be *ca.* 50 Hz. The spectrum (illustrated in the original paper) was unchanged when the temperature was reduced, as expected for a compound with a bulky equatorial group.



183a **183b**

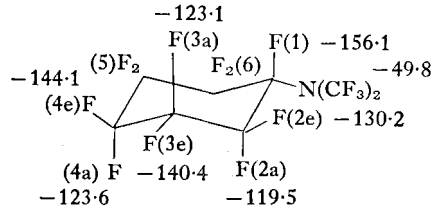


184

Electrochemical fluorination of *N*,*N*-dimethylcyclohexylamine (or of *N*,*N*-dimethylaniline or *N*,*N*-dimethylpentafluoroaniline) gave[122] a mixture which included perfluoro-*N*,*N*-dimethylcyclohexylamine **185**; the ^{19}F spectrum of the ring fluorines is similar to that of perfluoro-

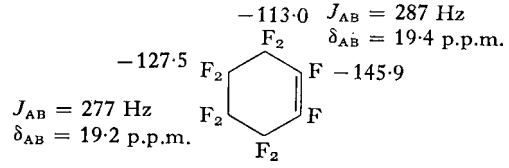
† Footnote added in proof. F. R. Jensen and B. Knickel (*J. Amer. Chem. Soc.*, 1971, **93**, 6339) report that they were unable to bring about this oxidative addition under the conditions reported,[121] nor under much more severe conditions.

methylcyclohexane, with the exception that the signal for F(1) is shifted to low field by *ca.* 30 p.p.m. The parameters reported are shown with the formula.

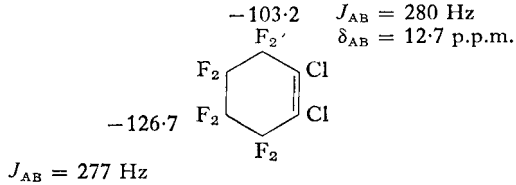


185

J(F2a–F2e) = J(F6a–F6e) = 291 Hz
J(F3a–F3e) = J(F5a–F5e) = 286 Hz
J(F4a–F4e) = 284 Hz
J(CF_3–F1a) = 21·1 Hz
J(CF_3–F2e, 6e) = 21·6 Hz
J(CF_3–F2a, 6a) = 6·6 Hz
J(F1–F3a, 5a) = 25 Hz
J(F1–F2e, 6e) = 14 Hz
J(F1–F2a, 5a) = 5 Hz



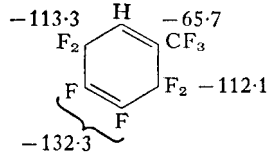
186



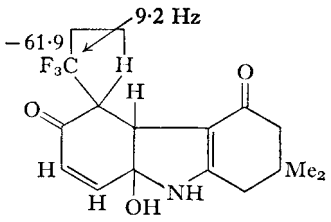
187

The ^{19}F spectra of perfluorocyclohexene (**186**) and 1,2-dichloroperfluorocyclohexene (**187**) have been studied at a series of temperatures.[123] Both compounds showed time-averaged spectra at room temperature, but at −152°, **186** showed two AB quartets with couplings and chemical shift differences as indicated, and below *ca.* −124° the dichloro compound **187** showed similar patterns. (Parameters at −150° are given with the formula.) The barrier to rotation is somewhat smaller in **187** ($\Delta G^{\ddagger}$ 6·28 ± 0·10 kcal mole^{-1} at −111·5°) than in **186** ($\Delta G^{\ddagger}$ 6·83 kcal mole^{-1} at −111·5°).

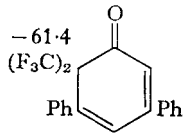
Fluorination of benzotrifluoride[124] over cerium(IV) fluoride gave a number of products, including 1*H*-2-trifluoromethylperfluorocyclohexa-1,4-diene **188**, ^{19}F shifts for which are shown with the formula.



188



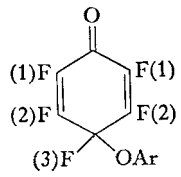
189



190

^{19}F Parameters for the fused-ring cyclohexenone **189**, formed by the reaction of trifluoromethylbenzoquinone with an enamine,[125] and for the hexadienone **190**, formed from bis(trifluoromethyl)keten and phenylacetylene[34] are given with the formulae.

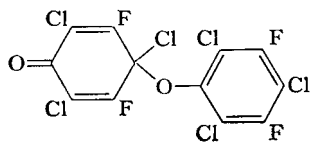
Parameters for other cyclohexadienones **191**, **192** obtained by oxidation of the phenols, have been reported[126] by Russian workers. The spectrum of **191a** is illustrated in the paper. The band at lowest field is a triplet of triplets (~23 and 9 Hz), and was thus assigned to F(3); the other bands listed are doublets of triplets. In addition, the bands of the C_6F_5 group appear at δ_F −150·9 (*ortho*), −155·9 (*para*) and 161·9 (*meta*).



191

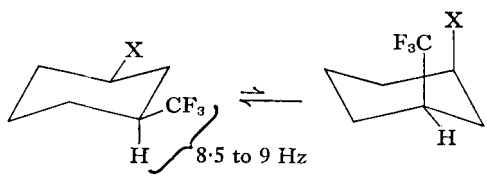
	Ar	δF(1)	δF(2)	δF(3)
a	C_6F_5	−151·9	−140·9	−122·9
b	C_6Cl_5	−152·9	−142·9	−114·9
c	2,4,6-$Cl_3C_6H_2$	−153·9	−140·9	−109·9
d	2,4,6-$Cl_3C_6F_2$§	−152·9	−140·9	−110·9

§ δ_F = −104·9



δ_F −100·9, −107·9†

192



193

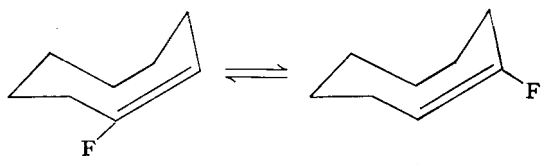
† The fluorine atoms in this compound have been mistakenly named "nitro groups" in the translation of the original paper.

Della has reported[127] the ^{19}F parameters for a number of *cis*-3-substituted-trifluoromethylcyclohexanes **193**, and concluded that the nature of the substituent X has little effect on the fluorine resonance.

The shifts for X = Me, NH_2, $\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$, OH, ONa, $CONH_2$, CO_2H, CO_2Me, CH_2OH, all fell in the range δ_F −73·66 to −74·26. The corresponding ketone absorbed at δ_F − 73·61 in dimethyl sulphoxide, but the NMR spectrum in methanol showed three doublets, attributed to the formation of two hemiacetals in addition to the original ketone.

5. *Cyclo-octene*

The room temperature ^{19}F spectrum of 1-fluorocyclo-octene[128] consisted of a triplet [J(FC–CH_2) = 22·5 Hz] of doublets [J(FC:CH) = 18·0 Hz] centred at δ_F −99·1. The signal broadened as the temperature was lowered, and then resharpened below −130° to two broad ($W_{½} \approx$ 70 Hz) peaks at δ −95·4 and −102·0, with intensity ratio 3:2. The observation of two distinct signals for the vinylic fluorine indicated that below −129° (the coalescence temperature) both ring inversion and pseudorotation were slow on the NMR time scale. The free energy barrier separating the two conformations (e.g. **194a** and **b**) agreed reasonably with that found[129] for pseudorotation in cyclo-octene-d_{13} (6·1 *vs.* 5·8 kcal mol^{-1} respectively).



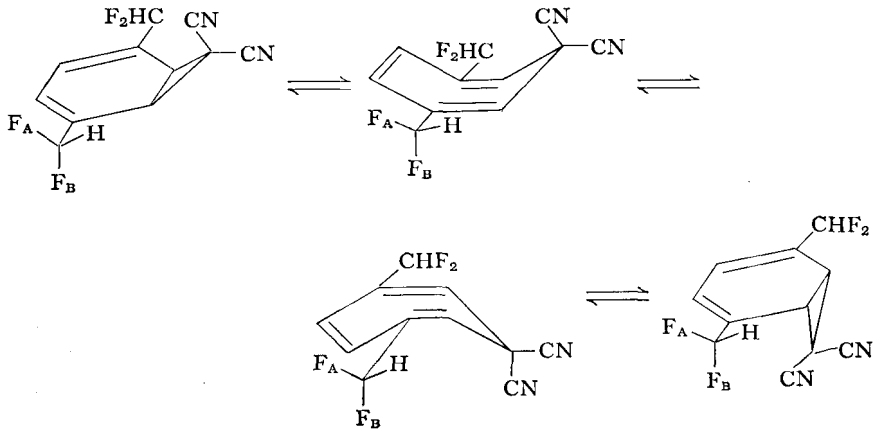
a **b**

194

6. *Bicyclic and polycyclic systems*

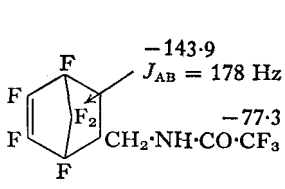
The temperature dependence of the magnetic nonequivalence of the CHF_2 groups in 7,7-dicyano-2,5-bis(difluoromethyl)norcaradiene has provided a means of studying[130] the inversion of this compound, which presumably involves the isomeric cycloheptatriene. At 60°, the CHF_2 group gave a doublet [$2J$(H–F) = 54·1 Hz, δ_F −118], but at −20°, the AB quartets of an ABX system were clearly defined [J_{AB} = 306 Hz, δ_{AB} = 113 Hz (at 56·4 MHz)]. From the parameters obtained for 17 temperatures between −10 and 60°, the Arrhenius parameters for the interconversion (E_a 14·6 ± 0·4 kcal mol^{-1}, log A, 13·4 ± 1·0, $\Delta G^{\ddagger}$, 13·8 kcal mol^{-1}) were obtained.

The ^{19}F spectrum of the isomeric 1,4-bis(difluoromethyl)-compound



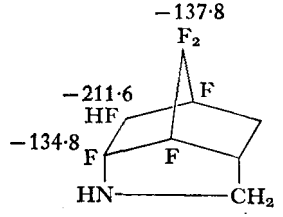
was also temperature dependent, but at $-60°$ one of the difluoromethyl groups still showed an A_2X pattern. The other, assigned to the 1-difluoromethyl group, showed the inner lines of an ABX pattern (δ_F -120) but the outer lines could not be observed.

Diels-Alder reactions of cyclic fluorinated dienes continue to attract attention, and parameters for a number of bicycloalkenes have been reported[131,132] and are shown with formulae **195** to **198**. The amine hydrochloride formed by hydrolysis of the amide **195** has parameters similar to those of the amide, but the formation of the free base led to cyclisation to the tricyclononane derivative **196**, in which the bridging methylene failed to show the AB pattern associated with the bicycloheptenyl system (e.g. **195**).



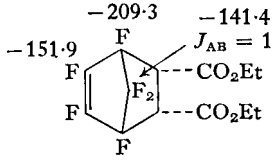
δ(:CF); −155·9, −158·3
δ (>CF); −209·7, −212·3

195

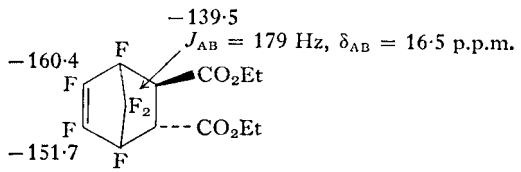


δ (>CF); −205·3, −209·5
^2J(H–F) = 56 Hz

196



197

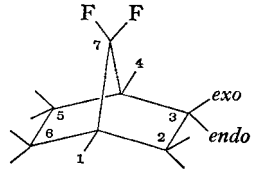


198

The chemical shifts for some bridgehead substituted perfluorobicyclo-[2,2,1]heptanes are given[133] in Table VIII. The assignments were made by consideration of the substituent additivity effects on the shifts, using initially the perfluoro-, the 1*H*- and the 1*H*,4*H*- compounds, and the assignments given in Table VIII were stated to be the only ones giving consistency throughout the series of compounds studied. These shifts were also found to be consistent with values calculated by use of an intramolecular electric field approach.[133]

TABLE VIII

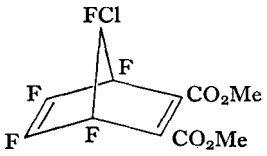
^{19}F parameters for some bicyclo[2,2,1]heptanes[a,133]



Substituents	δ_{F4}	δ_{F7}	F2,6			F3,5		
			δ_{Fendo}	δ_{Fexo}	^2J(Hz)	δ_{Fendo}	δ_{Fexo}	^2J(Hz)
1F,4F	−226·0	−130·9	−122·2	−123·8	258	−122·2	−123·8	258
1H,4F	−218·2	−122·5	−107·5	−115·8	259	−119·5	−124·5	253
1H,4H	..	−112·3	−106·2	−116·0	258	−106·2	−116·0	258
1Br,4Br	..	−119·5	−102·2	−119·7	244	−102·2	−119·7	244
1Br,4H	..	−116·5	−104·4	−120·7	248	−104·5	−115·5	252
1Br,4F	−218·8	−125·3	−105·6	−120·2	240	−118·4	−123·6	248
1I,4F	−216·1	−121·9	−95·8	−118·3	248	−117·2	−123·5	247

[a] The *endo-exo* ^{19}F shifts and geminal couplings were estimated from an approximate AB analysis. AA′BB′ analysis of the perfluoro-compound suggested that the parameters so derived may be within *ca.* 3% of the true values.

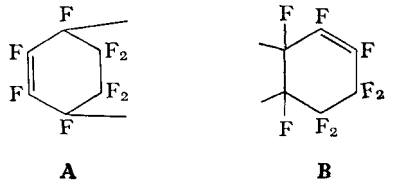
5-Chloropentafluorocyclopentadiene reacted[112] with dimethyl acetylenedicarboxylate to give two isomers of the norbornadiene derivative **199**.



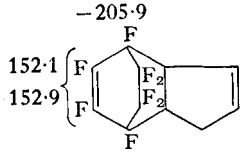
199

Major: δ_F −133·0 (CFCl), −152·7 (CF:CF), −207·5 (⩾CF)
Minor: δ_F −129·7 (CFCl), −152·7 (CF:CF), −210·9 (⩾CF)

Perfluorocyclohexa-1,3-diene also underwent Diels-Alder additions,[134] and the parameters for a number of compounds formed in this way, and for their derivatives, are shown with formulae **200** to **207**. The complexity of the fine structure of the bands of **207** suggested that it was a mixture of the compound shown and the isomer formed by addition of phenyl azide in the opposite sense. Distinction between 1,4-addition to the perfluorocyclohexadiene, which gives the fragment **A**, and 1,2-addition, which gives fragment **B**, is readily achieved by ^{19}F NMR since (a) the absorption of the CF_2 groups in **A** is centred at $\delta_F \approx -128$, but in **B**, in the range δ_F −118 to −123, (b) a greater chemical shift difference between vinylic fluorines is observed for **B** (> 10 p.p.m.) than **A** (< 5 p.p.m.), and (c) the bridgehead fluorines in **A** absorb in the region $\delta_F \approx -203$, but in **B** at $\delta_F \approx -168$, with a considerable (*ca.* 10 p.p.m.) shift difference between the two types of bridgehead fluorine in **B** (> *CF*·CF_2 *vs.* > *CF*·CF:).

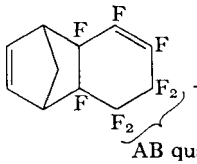


A **B**



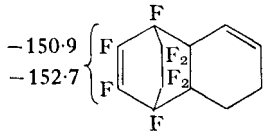
−205·9
152·1, 152·9
−205·9
CF_2), −127·5, −128·1

200



−123·9 singlet,
−118·5
AB quartet, J = 278 Hz,
δ_{AB} = 11·1 p.p.m.
δ(:CF), −141·3 and −156·5 or −156·9
δ (⩾CF), −162·9 and −156·9 or −156·5

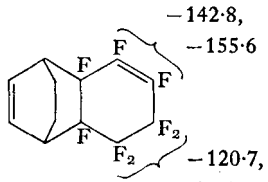
201



−150·9, −152·7
δ(CF_2), −128·3, −128·8
δ(⩾CF), −206·5, −207·4

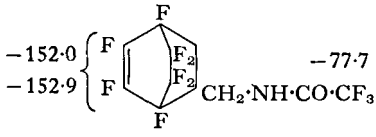
202

Diels-Alder adducts of perchlorocyclopentadiene with fluoro-olefins were prepared by Smith and Ihrig[135] in their study of the dependence of the vicinal hydrogen-fluorine couplings on substituent electronegativity and dihedral angle, and parameters are given in Table IX.



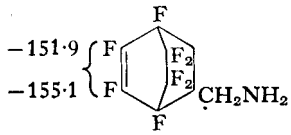
δ(>CF), −166·3, −177·6

203



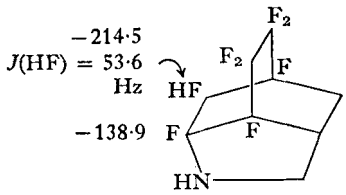
δ(CF_2), −129·5
δ(>CF), −201·8, −207·0

204



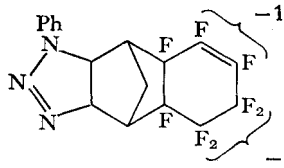
δ(CF_2), −128·9
δ(>CF), −201·3, −207·7

205



δ(CF_2), −125·3, −132·9
δ(>CF), −198·5, −199·9

206

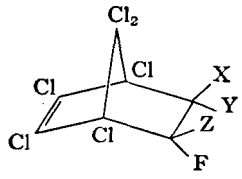


δ(>CF), −152·3, −161·2

207

TABLE IX

^{19}F parameters for bicyclo[2,2,1]hept-3-enes[135]



Substituents	δ_{Fendo}	δ_{Fexo}	J(*gem* H–F)[a]	J(*cis* H–F) *endo* H	J(*cis* H–F) *exo* H	J(*trans* H–F)[a]
X=Y=Z=H	−181	..	54·31	25·10	..	12·01
X=Z=H, Y=F[b]	−215	..	52·10	..	..	1·87
Y=Z=H, X=F[c]	−202	−95	51·73[c]	17·71	13·85	..
X=Y=H, Z=F[d]	−96	−95	..	15·86	13·07	7·36
X=Y=F, Z=H[e]	−100, −214	−114	51·72	..	9·13	0·31

[a] H is *exo*.
[b] $J(F\text{–}F_{cis})=16{\cdot}1$ Hz.
[c] $^2J(F\text{–}H_{endo})=52{\cdot}06$; $J(F\text{–}F_{trans})=0{\cdot}30$ Hz.
[d] $J(H_{endo}\text{–}F_{trans})=4{\cdot}46$ Hz; $J(F\text{–}F_{gem})=221{\cdot}6$ Hz.
[e] $J(F\text{–}F_{gem})=230$ Hz; $J(F\text{–}F_{cis})=4{\cdot}57$ Hz; $J(F\text{–}F_{trans})=0{\cdot}30$ Hz.

The considerable substituent effect is exemplified by the change from 12·01 to 0·31 Hz for the *trans* vicinal coupling between hydrogen and fluorine without change in dihedral angle ($\phi=120°$) and from 25·10 to 9·13 Hz for the corresponding coupling between *cis*-hydrogen and fluorine. The *cis*-coupling appeared to be more sensitive to changes in electronegativity ($\sum$ E) than the *trans*-coupling, suggesting that the magnitude of the substituent effect differs for each dihedral angle. The literature values of J(H–F *vic*) for almost constant electronegativities and different dihedral angles were used to derive modified Karplus equations of the form (see Fig. 4).

$$\begin{aligned} {}^3J(\text{H–F}) &= A\cos^2\phi \qquad 0 \le \phi \le 90° \\ &= B\cos^2\phi \qquad 90 \le \phi \le 180° \end{aligned}$$

with the constants

$$\begin{aligned} & A = 24, \quad B = 52 \quad \text{for} \quad \Sigma E \approx 9, \\ & A = 15, \quad B = 32 \quad \text{for} \quad \Sigma E \approx 11, \\ \text{and} \quad & A = 8, \quad B = 16 \quad \text{for} \quad \Sigma E \approx 13 \end{aligned}$$

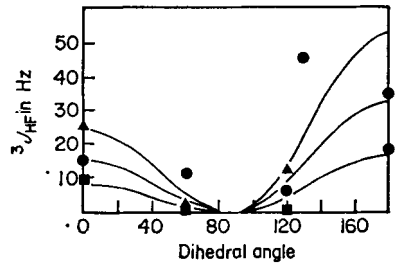
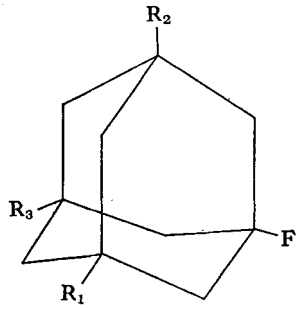


FIG. 4. Plot of $^3J_{HF}$ *vs.* $\cos^2 \phi$ for values of $\sum E = 9{\cdot}0$, $11{\cdot}0$ and $13{\cdot}0$. (From Ihrig and Smith.[135])

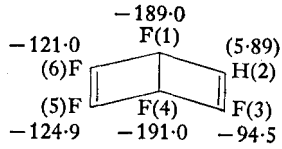
The ^{19}F shifts for some alkyl-substituted fluoroadamantanes[136] suggested an order of electron release by the substituents (Me > Et > *i*-Pr > *t*-Bu) opposite to that found in solvolysis studies,[137] and the authors quoted Stock's suggestion[138] of "substituent-induced structural changes" which might modify the shielding environment of the fluorine nucleus but offered no further explanation. Introduction of second and third methyl groups had an almost additive effect on the substituent chemical shift, as shown below.



R_1	R_2	R_3	δ_F	SCS
H	H	H	$-130{\cdot}0$	$0{\cdot}0$
Me	H	H	$-132{\cdot}7_9$	$-2{\cdot}7_9$ $(-2{\cdot}7_9/CH_3)$
Me	Me	H	$-135{\cdot}2_9$	$-5{\cdot}2_9$ $(-2{\cdot}6_5/CH_3)$
Me	Me	Me	$-137{\cdot}7_8$	$-7{\cdot}7_8$ $(-2{\cdot}5_9/CH_3)$
Et	H	H	$-132{\cdot}2_9$	$-2{\cdot}2_9$
i-Pr	H	H	$-131{\cdot}2_5$	$-1{\cdot}2_5$
t-Bu	H	H	$-130{\cdot}1_5$	$-0{\cdot}1_5$

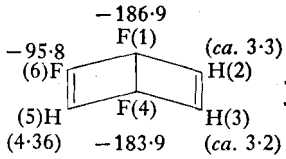
7. *Valence-bond isomers of fluorinated benzenes, and their derivatives*

The spectra of a number of new fluorinated[107] and fluoroalkyl[107, 139, 140] bicyclo[2,2,0]hexa-2,5-dienes (Dewar benzenes) have been reported. The spectrum of compound **208**, illustrated in the paper,[107] is complex, but could be analysed by a first order treatment, to give the coupling constants shown. The trihydro-compound **209**, and the trifluoromethyl compound **210** could also be analysed by first order treatments.[107]



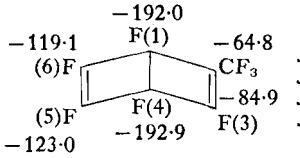
208

J(F1–H) = 3·1 J(F1–F3) = 6·6 J(F1–F4) = 7·9 J(F1–F5) = 9·4 J(F1–F6) = 7·9
J(H–F3) = 10·0 J(H–F4) = 1·9 J(H–F5) = 3·3 J(H–F6) = *ca.* 0
J(F3–F4) = 3·9 J(F3–F5) = 0·9 J(F3–F6) = 13·7
J(F4–F5) = 7·2 J(F4–F6) = 9·3
J(F5–F6) = 3·8 Hz.



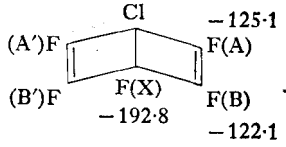
J(F1–H5) = 1·4 Hz; J(F1–F6) = 3·5 Hz;
J(H3–F6) = 3·5 Hz; J(F4–H5) = 4·4 Hz;
J(F4–F6) = 4·3 Hz; J(H5–F6) = 9·9 Hz.

209



J(F1–CF_3) = 2·8; J(F1–F3) = 6·5 to 7·5; J(F1–F4) = 6·5 to 7·5;
J(F1–F5) = 10·3; J(F1–F6) = 7·2; J(CF_3–F3) = 9·9;
J(F3–F4) = 6·5 to 7·5; J(F3–F5) ≤ 0·5; J(F3–F6) = 13·4;
J(F4–F5) = 7·4; J(F4–F6) = 10·2; J(F5–F6) = 3·1 Hz.

210

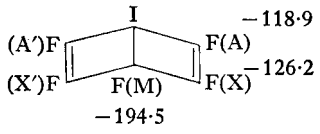


J(FA–FB) = ±2·25; J(FA–FB′) = ∓13·75;
J(FA–FX) = ±8·40; J(FB–FX) = ∓8·00;
J(FA–FA′) = ±0·23; J(FB–FB′) = ∓0·63 Hz.

211

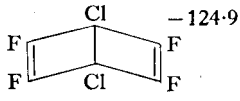
The 1-chloropentafluoro-compound **211** was analysed as an AA′BB′X spectrum, and trial-and-error calculations with LAOCOON III gave the best fit with the relative signs for the coupling constants shown. The spectrum of the analogous iodo-compound (**212**), which, like that of **211**, is illustrated in the paper, was insufficiently resolved for complete analysis.[107]

The parameters for other compounds of this type are summarised with formulae **213** to **218**.

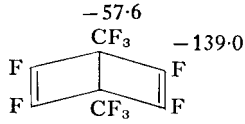


212

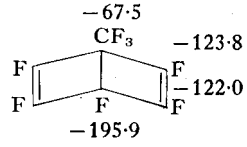
J(FA–FX) = ±1·4; J(FA–FX′) = ∓13·3; J(FA–FM) = 8·4; J(FX–FM) = 7·6 Hz.



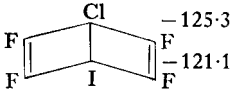
213



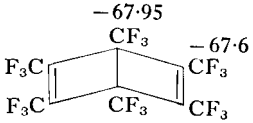
214



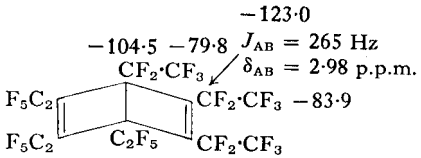
215



216



217



218

The geminal non-equivalence in the CF_2 groups of the vinylic pentafluoroethyl groups in **218** arises because all possible conformations lack a plane of symmetry dividing these geminal fluorines.[140]

Parameters have also been reported[139] for the 2-methoxy-compound but were not assigned to individual fluorines (⩾CF at δ_F −195·9, −201·9, =CF at δ_F −130·0, −123·7, −121·5); the parameters reported in this paper for the compound formulated as **215** differ considerably from those given above.

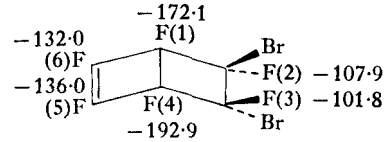
Examination[107] of the spectra of the 2,3-dibromo-adducts of hexafluorobicyclo[2,2,0]hexadiene allowed the assignment of the stereochemistry of the addition, since a bridgehead fluorine (F1 or F4) resonated at lower field when the adjacent bromine atom was *cis* to it. Use of this chemical shift difference to give a value for B in the equation

$$\delta = -B\Delta\langle E^2\rangle$$

allowed the calculation of the shifts for F4 for the possible orientations

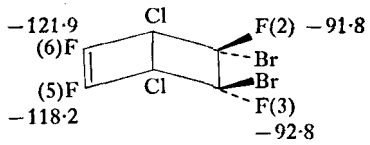
of the *cis*-dibromo compounds **224** and **226** and the *trans*-dibromo compound **221**, and the orientations shown were chosen because of the much better fit of calculated with observed shifts. Assignment of signals to F2 and F3 was also made in most cases from the chemical shifts, a fluorine *cis* to a bridgehead fluorine or chlorine being expected at lower field than one *cis* to carbon. In compounds **221** and **222**, the bridgehead chlorine and fluorine made assignment on this basis unreliable and the coupling constants were used.

The assignments for F5 and F6 were based on analysis of the spectrum of 1-methoxypentafluorocyclobutene (**163**, R = MeO), but since the assignments in that molecule may need to be reversed (see p. 135), the assignments to F5 and F6 may also need to be reversed. The parameters quoted here are those assigned in the original paper, on the basis that the larger coupling was ^3J [and thus J(F1–F6) or J(F4–F5) in the dibromo-adduct] and the smaller ^4J [and thus J(F1–F5) or J(F4–F6)]. As with the Dewar benzenes, some of the compounds (**219** to **223**) gave complicated patterns which could nevertheless be analysed by first order methods, but others (e.g. **224**, **226**) gave only values for K, L, M, and/or N. The parameters for the related octafluorobicyclo[2,2,0]hexene[141] are shown with formula **228**.



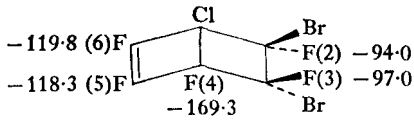
J(F1–F2) = 3·0; J(F1–F3) = 5·6; J(F1–F4) = 1·4; J(F1–F5) = 5·6; J(F1–F6) = 17·0; J(F2–F3) = 11·0; J(F2–F4) = 10·2; J(F2–F5) = 1·8; J(F2–F6) = 5·6; J(F3–F4) = 4·0; J(F3–F5) = 1·0; J(F3–F6) = 2·0; J(F4–F5) = 19·0; J(F4–F6) = 7·4; J(F5–F6) = 12·0 Hz.

219



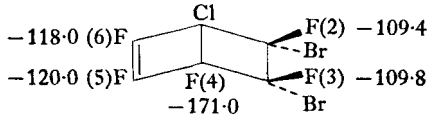
J(F2–F3) = 11·6; J(F2–F5) = 0·8; J(F2–F6) = 1·1; J(F3–F5) = 4·8; J(F3–F6) = 1·8; J(F5–F6) = 10·6 Hz.

220



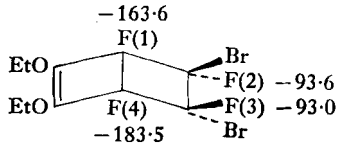
J(F2–F3) = 10·0; J(F2–F4) = 2·5; J(F2–F5) = 5·2; J(F2–F6) = 2·0; J(F3–F4) = 4·4; J(F3–F5) = 0·8; J(F3–F6) = 1·0; J(F4–F5) = 13·4; J(F4–F6) = 5·5; J(F5–F6) = 11·6 Hz.

221



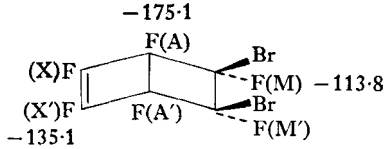
J(F2–F3) = 8·5; J(F2–F4) = 6·7;
J(F3–F4) = 4·4; J(F3–F5) = 0·8; J(F3–F6) = 1·7;
J(F4–F5) = 13·9; J(F4–F6) = 5·0; J(F5–F6) = 10·5;
J(F2–F5), J(F2–F6), J(F3–F5) ≤ 0·5 Hz.

222

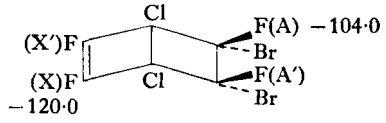


J(F1–F2) = J(F1–F3) = J(F3–F4) = 4 to 5 Hz.
J(F1–F4) = 8·5; J(F2–F3) = 13·0; J(F2–F4) = 18·6 Hz.

223

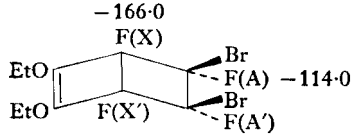


224

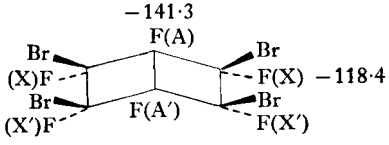


Both singlets

225

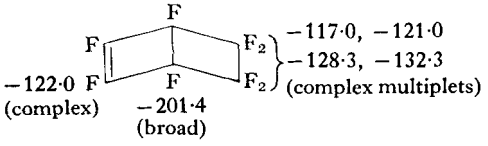


226



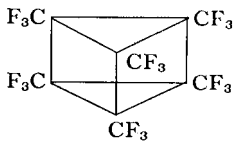
Deceptively simple quintet and triplet

227

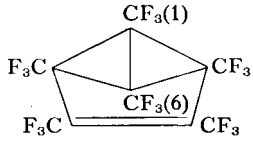


228

The ^{19}F spectra of the other valence bond isomers **229**, **230** of hexakis-(trifluoromethyl)benzene are illustrated in ref. 140. The prismane **229** showed a singlet (δ_F −65·8) and the benzvalene **230** a septet (J=6·2 Hz) at δ_F −58·2, assigned to the magnetically equivalent CF_3 groups at C1 and C6, and complex multiplets at δ_F −60·95 and −64·6, the latter of which was shown by spin decoupling to give rise to the septet splitting.



229



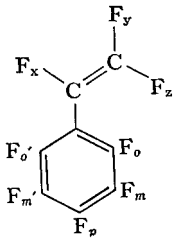
230

E. Fluoroaromatics

1. *General*

(a) *Isolated aromatic rings.* Parameters for a considerable number of fluoroaromatic compounds have been reported, and the ^{19}F shifts are given in Tables X to XIII. In general the assignments have been made by reference to the chemical shifts of model compounds, by comparison with values calculated according to the Gutowsky substituent constants, or by use of the coupling constants.

The 94·1 MHz spectrum of octafluorostyrene has been analysed completely;[142] (*cf.* ref. 143 for the shifts and the magnitudes of some of the coupling constants). The relative signs of the couplings $J(o\text{–}m)$ and $J(o\text{–}m')$ were obtained directly from the analysis, and the rest by tickling experiments. The values are given below.

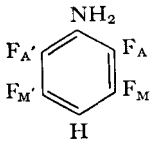


$J(o\text{–}o')$ = −6·1 Hz	$J(m\text{–}m')$ = −0·7 Hz
$J(o\text{–}m)$ = −20·0 Hz	$J(m\text{–}p)$ = −19·0 Hz
$J(o\text{–}p)$ = +4·0 Hz	$J(m\text{–x})$ = −0·8 Hz
$J(o\text{–}m')$ = +8·5 Hz	$J(m\text{–y})$ = +0·2 Hz
$J(o\text{–x})$ = +7·1 Hz	$J(m\text{–z})$ = −0·4 Hz
$J(o\text{–y})$ = +2·2 Hz	$J(p\text{–x})$ = +3·2 Hz
$J(o\text{–z})$ = +10·4 Hz	$J(p\text{–y})$ = +0·8 Hz
$J(x\text{–y})$ = +35·4 Hz	$J(p\text{–z})$ = +1·5 Hz
$J(x\text{–z})$ = −118·3 Hz	$J(y\text{–z})$ = +62·5 Hz

The relative signs deduced in this work allowed the establishment, *via* the known relation of intra-vinyl group coupling constants to the sign of

$^1J_{CH}$ (taken as positive), of absolute signs for the coupling constants shown above. On this basis, *ortho* F–F couplings were found to be negative, whence[144] *ortho* H–H couplings must be positive.

In a study of 2,3,5,6-tetrafluoroaniline, McFarlane[145] used heteronuclear double resonance to obtain the positions of the ^{19}F resonance lines, and, with the aid of some triple resonance tickling experiments, to determine the signs of the coupling constants relative to negative $^3J(F_A–F_M)$. The line positions so obtained agreed to $\pm 0{\cdot}1$ Hz with a spectrum obtained directly at 56·4 MHz.



$\Xi\ F_A = 94080574{\cdot}7 \pm 0{\cdot}3$ Hz
$\Xi\ F_M = 94078648{\cdot}0 \pm 0{\cdot}3$ Hz
where ΞX is the resonant frequency of X in a polarising field in which Me_4Si gives ^1H resonance at exactly 100 MHz. Thus $\delta_{FA} = -140{\cdot}8$ and $\delta_{FM} = -161{\cdot}2$.

$^3J(H–F_A) = +10{\cdot}5 \pm 0{\cdot}1$ Hz
$^4J(H–F_M) = +7{\cdot}3 \pm 0{\cdot}1$ Hz
$^3J(F_A–F_M) = -21{\cdot}3 \pm 0{\cdot}2$ Hz
$^5J(F_A–F_{M'}) = +9{\cdot}7 \pm 0{\cdot}2$ Hz
$^4J(F_A–F_{A'}) = +0{\cdot}4 \pm 0{\cdot}2$ Hz
$^4J(F_M–F_{M'}) = -6{\cdot}0 \pm 0{\cdot}2$ Hz

Parameters for perfluoro-*sec*-butylbenzene are noted on p. 174 together with those for the analogous perfluoro-4-*sec*-butylpyridine.

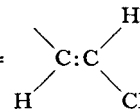
TABLE X

^{19}F shifts of pentafluorophenyl derivatives. C_6F_5X

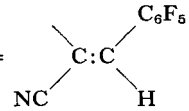
X	$F_{2,6}$	$F_{3,5}$	F_4	X	Ref.
CHF_2	−143·2	−161·1	−149·6	−113·4	146
$CF_2{\cdot}CH_3$	−138·8	−160·7	−150·7	−78·4	146
$CH_2{\cdot}CF_3$	−140·3	−162·0	−153·3	−63·6	146
$CHF{\cdot}CF_3$	−139·8	−160·4	−148·7	−202·2, −102·4(?)	146
$CF_2{\cdot}CF_3$	−135·9	−159·6	−145·9	−107·2, −82·6	146
R[a]	−141·9	−162·4	−156·4		146
	−141·4	−161·7	−155·9		146
$CH(CO_2Et)_2$	−140·8	−162·7	−154·8		147
$CNa(CO_2Et)_2$	−139·3	−168·1	−165·0		147
$CLi(CO_2Et)_2$	−138·8	−167·5	−163·6		147
$C(O){\cdot}C_6F_4{\cdot}NH_2(p)$	−144·9	−162·9	−152·9	See Table XI	148
CH_2CN	−143·5	−161·8	−154·0		149
$CH(CN){\cdot}CH_2OH$	−140·6	−162·1	−154·2		149
R[b]	−140·30	−161·22	−152·95		149
$CH(CN)CH(OH)C_6F_5$	−143·6	−162·06	−154·39		149

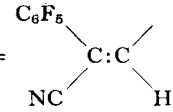
TABLE X (*continued*)

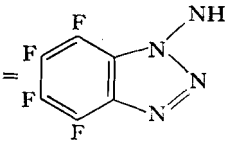
X	$F_{2,6}$	$F_{3,5}$	F_4	X	Ref.
$CH(OH)CH(CN)C_6F_5$	−141·65	−162·06	−154·39		149
R[c]	−135·40	−161·22	−148·87		149
R[d]	−139·10	−161·22	−151·10		149
$N{:}N{\cdot}C_6F_5$	−151·0	−164·9	−152·1		150
$N{:}N{\cdot}C_6F_4H(p)$	−152·4	−164·9	−152·5	See Table XI	150
$N{:}N{\cdot}C_6F_4{\cdot}OEt(p)$	−152·1 or −151·9	−166·4	−153·9	See Table XI	150
$N{:}N{\cdot}C_6F_4{\cdot}NH_2(p)$	−153·4	−166·4	−157·4	See Table XI	150
$N{:}N{\cdot}C_6F_4{\cdot}OH(p)$	−152·9	−165·7	−155·1	See Table XI	150
$N{:}N{\cdot}C_6F_4{\cdot}SPh(p)$	−150·8	−164·9	−152·0	See Table XI	150
R[e]	−158·4	−165·7	−165·7		151
$(C_6F_5)_2CF$	−141·4	−161·1	−151·7	−126·3	67
$(C_6F_5)PhCF$	−136·3	−161·8	−152·0	−121·6	67
p-πCpFe(CO)$_2{\cdot}C_6F_4$	−139·2	−162·9	−153·9	See formula **565**	152
R[f]	−140·2	−162·55	−152·55	See formula **294**	153
C_6H_5	−143·9	−163·5	−156·8		154
m-$F{\cdot}C_6H_4$	−143·5	−162·8	−155·6	See Table XIII	154
p-$F{\cdot}C_6H_4$	−144·0	−163·2	−156·3	See Table XIII	154
$C_6F_5{\cdot}CO{\cdot}CF_2{\cdot}C(O)$	−137·5	−159·4	−144·8	−111·7	155
$C_6F_5{\cdot}CO{\cdot}CF(CO_2Et)C(O)$	−139·4	−160·2	−146·5	−165·6	155
$C_6F_5{\cdot}CO{\cdot}CFBr{\cdot}C(O)$	−137·3	−159·7	−146·7	−130·3	155

[a] R = 

[b] R = $CH(CN){\cdot}CH_2{\cdot}CH(CN){\cdot}C_6F_5$.

[c] R = 

[d] R = 

[e] R = 

See formula **264** for ^{19}F shifts of this group.

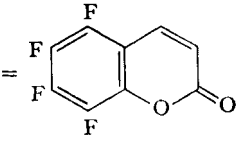
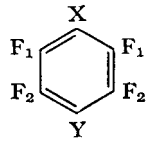
[f] R = 

TABLE XI

^{19}F shifts of para disubstituted tetrafluorophenyl derivatives

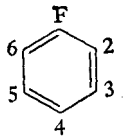


Substituents		Chemical shifts		Ref.
X	Y	F_1	F_2	
NO_2	NHMe	−148·7	−162·4	156
SO_2Me	NHMe	−141·6	−162·1	156
CO_2Et	NHMe	−140·2	−162·4	156
CO_2H	NHMe	−140·2	−162·4	156
COMe	NHMe	−141·9	−162·6	156
CN	NHMe	−136·6	−161·1	156
CF_3	NHMe	−143·1	−162·0	156
NO_2	NMe_2	−145·0	−151·6	156
SO_2Me	NMe_2	−140·0	−151·2	156
CO_2Et	NMe_2	−140·4	−150·8	156
CO_2H	NMe_2	−139·6	−150·1	156
COMe	NMe_2	−141·9	−152·3	156
CN	NMe_2	−135·5	−150·4	156
CF_3	NMe_2	−142·5	−151·2	156
R[a]	R[a]	−130·0	−130·0	157
$CH(CO_2Et)_2$	H	−139·0	−140·5	147
$CNa(CO_2Et)_2$	H	−138·9	−144·0	147
$CLi(CO_2Et)_2$	H	−139·2	−143·5	147
$C(O)\cdot C_6F_5$[b]	NH_2	−144·9	−164·7	148
H	$N{:}N\cdot C_6F_4H(p)$	−140·6	−149·9	150
EtO	$N{:}N\cdot C_6F_4\cdot OEt(p)$	−161·9	−154·2	150
$N{:}N\cdot C_6F_5$[b]	H	−151·2	−141·1	150
$N{:}N\cdot C_6F_5$[b]	OEt	−151·9 or −152·1	−160·6	150
$N{:}N\cdot C_6F_5$[b]	NH_2	−151·5	−167·1	150
$N{:}N\cdot C_6F_5$[b]	OH	−153·1	−165·6	150
$N{:}N\cdot C_6F_5$[b]	SPh	−151·3	−135·3	150
$N{:}N\cdot C_6F_3$–$2NH_2$–4H[c]	H	−153·0	−141·4	150
$CF(C_6F_4Cl(p))_2$[d]	Cl	−137·7	−139·1	67
Et	Et	−164	−164	158
Et	$C_6F_4\cdot SiMe_3(p)$	−146	−140	158
Me_3Si	$C_6F_4Et(p)$	−128	−140	158
H	$C_6F_4\cdot Fe(CO)_2\pi Cp(p)$[e]	−142·1	−139·4	152
Me_3Si	Me_3Si	−129·5	−129·5	159
Me_2HSi	Me_2HSi	−127·2	−127·2	160
$Me_2(OEt)Si$	$Me_2(OEt)Si$	−127·7	−127·7	160
$Me_2(OMe)Si$	$Me_2(OMe)Si$	−127·4	−127·4	160

[a] R = *o*-$MeCB_{10}H_{10}C$–, *o*-$PhCB_{10}H_{10}C$–.
[b] See Table X for shifts in C_6F_5– group.
[c] See Table XII for shifts in this group.
[d] $\delta_F(CF)$ −126·5.
[e] See formula **564** for shifts in this group.

TABLE XII

^{19}F shifts of polyfluorophenyl derivatives



Substituent on positions					Chemical shift, δ_F						Ref.
2	3	4	5	6	1	2	3	4	5	6	
F	F	F	NHMe	NO_2	−146·4	−173·9	−149·6	−157·6	..	..	156
F	F	F	NHMe	SO_2Me	−135·4	−174·8	−149·4	−156·5	..	..	156
F	F	F	NHMe	CO_2Et	−133·3	−175·5	−151·2	−160·8	..	..	156
F	F	F	NHMe	CO_2H	−133·5	−176·0	−151·7	−159·7	..	..	156
F	F	F	NHMe	COMe	−132·7	−177·2	−150·1	−159·4	..	..	156
F	F	F	NMe_2	NO_2	−149·6	−161·9	−144·8	−152·1	..	..	156
F	F	F	NMe_2	SO_2Me	−136·9	−157·6	−142·7	−148·6	..	..	156
F	F	F	NMe_2	CO_2Et	−140·8	−160·0	−144·3	−155·5	..	..	156
F	F	F	NMe_2	CO_2H	−134·5	−156·6	−144·6	−149·8	..	..	156
F	F	F	NMe_2	COMe	−144·5	−161·9	−146·3	−155·9	..	..	156
F	CN	OEt	F	H	−137·5	−132·9	..	..	−126·9	..	161
Cl	F	Cl	F	$SiMe_3$	−99·5	..	−108·3	..	−99·5	..	162
H	F	Cl	F	$SiMe_3$	−96·7	(6·58)	−108·6	..	−97·2	..	162
$SiMe_3$	F	Cl	F	$SiMe_3$	−83·4	..	−96·5	..	−96·5	..	162
$SiMe_3$	F	H	F	$SiMe_3$	−81·0	..	−93·8	(6·35)	−93·8	..	162
$SiMe_3$	F	$SiMe_3$	F	$SiMe_3$	−80·1	..	−80·1	..	−80·1	..	162

Cl	F	F	F	$SiMe_3$	−104·5	..	−130·8	−161·8	−122·3	..	162
H	F	F	F	$SiMe_3$	−101·4	(6·53)	−130·7	−166·5	−120·3	..	162
Cl	F	CO_2H	F	$SiMe_3$	−90·1	..	−105·3	..	−93·8	..	162
$SiMe_3$	F	CO_2H	F	$SiMe_3$	−74·1	..	−91·6	..	−91·6	..	162
CO_2H	F	F	F	$SiMe_3$	−113·1	..	−97·9	−164·2	−128·3	..	162
F	F	$SiMe_3$	F	$SiMe_3$	−121·2	−168·0	−121·2	..	−87·7	..	159[a]
F	$SiMe_2H$	$SiMe_2H$	F	F	−153·8	−123·3	..	..	−123·3	−153·8	160
F	$SiMe_2$—O—$SiMe_2$		F	F	−153·2	−129·7	..	..	−129·7	−153·2	160
F	$SiMe_2H$	F	$SiMe_2H$	F	−167·1	−117·9	..	−85·2	..	−117·9	160
F	$SiMe_2OEt$	F	$SiMe_2OEt$	F	−167·4	−118·2	..	−84·1	..	−118·2	160
F	$SiMe_2OMe$	F	$SiMe_2OMe$	F	−167·2	−118·0	..	−84·9	..	−118·0	160
F	$SiMe_2OH$	F	$SiMe_2OH$	F	−168·3	−119·0	..	−84·9	..	−119·0	160
Cl	F	Cl	OH	Cl	−112·9	..	−112·9	..	..	..	126
CO_2H	F	Br	H	H	−113·1	..	−105·1	..	..	..	163
CO_2H	F	Br	H	Br	−104·7	..	−104·7	..	..	..	163
CO_2H	F	H	H	CO_2H	−107·3	..	−105·5	..	..	..	163
Br	H	Br	F	H	−105·0	..	..	..	−105·0	..	163
CO_2H	H	Br	F	H	−106·1	..	..	..	−97·8	..	163
CO_2H	H	CO_2H	F	H	−98·6	..	..	..	−98·6	..	163
CO_2H	F	Cl	F	CO_2H	−111·2	..	−107·9	..	−107·9	..	163
CO_2H	F	H	F	H	−108·5	..	−108·5	..	−104·5	..	163
CO_2H	F	H	F	CO_2H	−101·2	..	−97·5	..	−97·5	..	163
CO_2H	F	H	CO_2H	H	−110·2	..	−110·2	..	..	..	163
H	CO_2H	F	H	Br	−114·5	..	..	−114·5	..	..	163
CO_2H	H	F	CO_2H	H	−111·7	..	..	−111·7	..	..	163
CO_2H	H	F	H	H	−116·7	..	..	−120·1	..	..	163
Cl	F	F	CN	CN	−109·4	..	−124·0	−131·6	..	..	164
Me_2N	F	F	CN	CN	−118·3	..	−139·4	−134·9	..	..	164
PhNH	F	F	CN	CN	−119·0	..	−137·1	−134·3	..	..	164
R[b]	F	F	CN	CN	−112·2	..	−129·9	−132·7	..	..	164
R[c]	F	F	CN	CN	−121·9	..	−138·0	−130·7	..	..	164

TABLE XII (*continued*)

H_2N	F	F	CN	CN	−129·4	..	−149·1	−135·9	..	..	164
Cl	Cl	F	CN	CN	−107·3	..	..	−107·3	..	..	164
F	F	F	H	R[d]	−149·8	−157·5	−151·9	−140·2	..	..	150
F	F	F	Br	R[e]	−151·6	−157·4	−152·6	−132·0	..	..	150
H	F	F	R[f]	NH_2	−140·0	(7·25)	−156·5	−151·4	..	(7·82)	150

[a] Similar values are given independently in ref. 162.
[b] PhMeN
[c] 1-$C_{10}H_7O$
[d] R=N:N·C_6F_4H(*o*).
[e] R=N:N·C_6F_4Br(*o*).
[f] R=N:N·C_6F_4H(*p*).

TABLE XIII

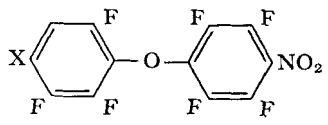
^{19}F shifts in monofluorophenyl compounds

Substituent(s)	δ_F	Ref.
$4(CH_2)_4CH_3$	−118·25	165
$4(CH_2)_2C_6H_4F(p)$	−117·69	165
$2Me,3,5(NO_2)_2$[a]	−117·5	166
$2CO_2Me$	−109·2	166
$3CO_2Me$	−112·3	166
$4CO_2Me$	−106·3	166
2COMe	−110	166
$2CCl_3$	−104	166
$3CCl_3$	−112	166
$3C_6F_5$[b]	−112·00	154
$4C_6F_5$[b]	−111·37	154
$3C_6Cl_5$	−111·96	154
$4C_6Cl_5$	−112·32	154
3Me, 4Me	−118·62	167
3Me, 4Ac	−109·86	167
3Me, 6Ac	−110·58	167
4Me, 5Ac	−116·98	167
4Me, 6Ac	−115·24	167

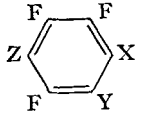
[a] J(F–H*ortho*) = 8 Hz, J(F–CH_3) = 2 Hz.
[b] See Table X for C_6F_5 group shifts.

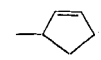
Chemical shifts were given, but not assigned, for the following compounds.

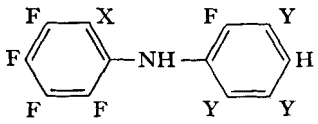
X	Y	δ_F	Ref.
PhNH	$CH{:}CH_2$	−148·7, −153·9	168
EtO	CO_2Et	−140·7, −157·2	161
EtO	Br	−135·3, −156·0	161
EtO	COMe	−141·8, −156·2	161
H	C(:NH)OEt	−137·0, −140·8	161
MeO	COPh	−143, −157	169
$CH(OEt)_2$	$NH{\cdot}NH_2$	−148·0, −162·7	170
$CH(OEt)_2$	H	−141·6, −144·5	170
CHO	NMe_2	−147·0, −154·0	170
CHO	$N(CH_2)_2O(CH_2)_2$	−143·0, −150·0	170
HS	$C_6F_4{\cdot}SH(p)$	−137·6, −139·4	171
Me	$C_6F_4Me(p)$	−143·4, −140·6	158
Ph	$C_6F_4Ph(p)$	−143, −139	158
C_6F_5	Me	−162·4, −151·6, −142·8, −140·7, −138·4	158



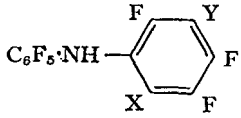
X	δ_F				Ref.
Me	−160·2	−157·1	−148·2	−144·6	172
H	−153·9	−155·6	−145·1	−137·1	172
Br	−153·3	−153·3	−144·6	−130·6	172
CF_3	−152·6	−152·6	−144·4	−138·6	172
NO_2	−153·9	−153·9	−145·2	−145·2	172
p-C_6F_4·O·C_6F_4·NO_2	−153·9	−152·9	−144·9	−135·9	172



X	Y	Z	
CO_2Me	OMe	OMe[169]	−144, −152, −159
CO_2H	OH	H[173]	−147·75, −138·15 (2) †
H		F[174]	−139·30, −145·30, −157·05, −159·53
H		F[174]	−139·70, −144·90, −156·87, −159·97
H	OBu	F[174]	−141·6, −156·88, 160·86, −168·56

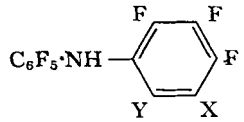


X = NO_2, Y = F[175] −139·2(2), −144·9, −147·4, −149·9, −153·1(2), −162·3†
X = NH_2, Y = F[175] −140·0(2), −150·0, −159·3(3), −162·6, −173·3
X = NO_2, Y = H[175] −129·7, −147·1, −151·5, −166·0, −148·8



Y = OMe, X = NO_2[176] −145·8(1), −146·7(1), −152·7(2), −159·2(1), −161·4(1), −162·9(2)†
Y = OMe, X = NH_2[176] −151·7(1), −155·7(1), −159·0(2), −164·8(2), −170·4(1), −176·0(1)
Y = Br, X = NO_2[176] −119·3(1), −134·1(1), −148·1(1), −152·9(2), −164·3(3)
Y = Br, X = NH_2[176] −121·8(1), −133·3(1), −159·1(2), −160·8(1), −165·0(1), −168·2(2)

† Numbers in parentheses are relative intensities.
Superscripts are reference numbers.

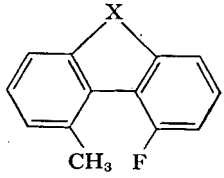


X = OMe, Y = NO_2[176] −150·7(1), −151·8(1), −153·4(2), −155·6(1), −162·1(3)†
X = Br, Y = NO_2[176] −127·2(1), −142·8(1), −149·5(1), −153·8(2), −161·9(3)
X = Br, Y = NH_2[176] −126·9(1), −144·7(1), −158·1(2), −162·9(2), −166·4(1), −170·9(1)

$C_6H_5 \cdot C(OAc):CH \cdot CO \cdot C_6F_5$[155]
−160·9 (*meta*), −149·6 (*para*), −140·8 and −139·3 (*ortho*)

$C_6F_5 \cdot C(CH_2Br)CH \cdot CO \cdot C_6F_4 \cdot OMe(p)$[177]
−140·8(2), −142·9(2), −154·8, −159·3(2), −164·3(2)†

Hydrogen-fluorine coupling constants derived from ^1H spectra of dimethyl- and trimethyl- fluorobenzenes[178] and of 2,4,6-trineopentylfluorobenzene[179] have been reported. As expected, J(H–F *meta*) was in the range 6·8 to 8·1 Hz, and coupling to *ortho* methyl[178] or methylene[179] groups was 2 to 2·7 Hz. Long-range F–H coupling between methyl groups and aromatic fluorine was observed[180] in compounds of the type **231**, where the groups are held in close proximity.



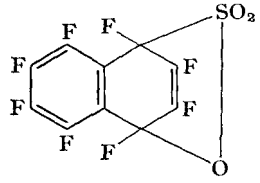
231

	X	^6J(H–F)
a	CH_2	8·3 Hz
b	C=O	7·3 Hz
c	CH(OH)	7·8 Hz
d	CHCl	8·1 Hz
e	CH(OAc)	7·8 Hz

The magnitudes of J(F–H) observed accord roughly with the internuclear separations. Thus the shorter bridging bonds in **231b**, due to the sp^2 carbon, and in **231c** to **e**, due to increasing s character because of the higher electronegativity of the substituent, led to increased separation of the groups and reduction in coupling. In the corresponding biphenylene derivative [X = $(CH_2)_0$], where the groups are well separated, the methyl resonance was a sharp singlet.

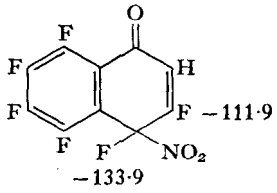
† Numbers in parentheses are relative intensities.

(b) *Fused-ring aromatic compounds.* Reaction of octafluoronaphthalene with sulphur trioxide,[181] and of heptafluoronaphthalene with nitric acid[182] gave compounds of the type **232** to **234**. The fluorine atom attached to the saturated C4 atom in **233** showed coupling to the vinylic [J(F4–F3) = 27 Hz] and to the adjacent aromatic [J(F4–F5) = 13 Hz] fluorine, but the signals for the aromatic fluorines were not specifically assigned. Irradiation of the Diels-Alder adduct of tetrafluorobenzyne and benzene gave a low yield of tetrafluorobenzocyclo-octatetraene, but the polycyclic compound **235** was produced in moderate yield.[183] Anodic oxidation in the presence of fluoride ion was used[184] to give compounds **236** and **237**, and the reaction of tetrafluoroanthraquinone with amines gave **238** and **239**.[185]



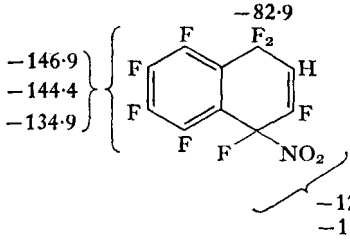
−102·9, −112·9, −157·9, −145·9, −142·9, −136·9 (2), −130·9

232

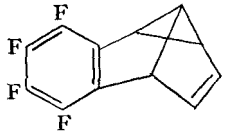


Other signals at −145·9, −143·9, −137·9, −136·9.

233

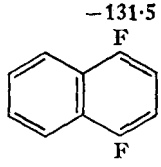


234

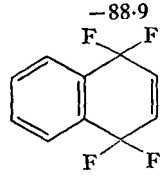


−146·2, −149·8, −159·8(2)

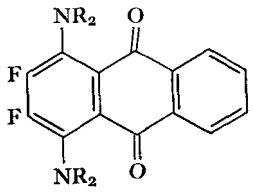
235



236

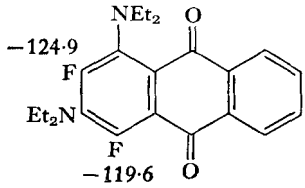


237



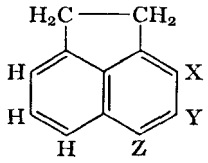
238

R = Et −134·4
R = Bu^n −135·5
R = Bu^t −133·9
R = $PhCH_2$ −134·3



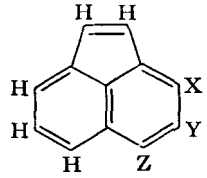
239

Dewar and Michl[186] have reported the preparation and, briefly, the ^{19}F shifts and splitting patterns for a number of monofluoro fused-ring aromatic compounds **240** to **243**, and indicated that the spectra will be reported in more detail at a later date. Chemical shifts for the octafluorochrysene **244** have also been reported,[187] but not assigned.



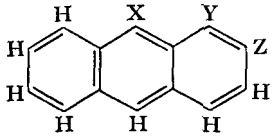
240

a X = F, Y = Z = H; δ_F −123·58
b X = Z = H, Y = F; δ_F −114·06
c X = Y = H, Z = F; δ_F −131·44



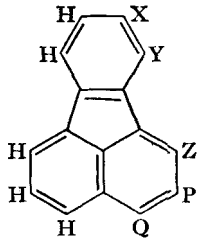
241

a X = F, Y = Z = H; δ_F −111·79
b X = Z = H, Y = F; δ_F −114·49
c X = Y = H, Z = F; δ_F −123·95



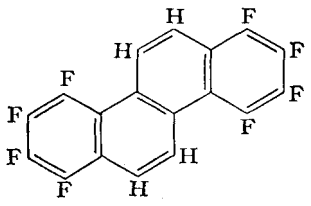
242

a X = F, Y = Z = H; δ_F −132·02
b X = Z = H, Y = F; δ_F −123·82
c X = Y = H, Z = F; δ_F −115·27



243

a X = F, Y = Z = P = Q = H; δ_F −115·43
b Y = F, X = Z = P = Q = H; δ_F −123·05
c Z = F, X = Y = P = Q = H; δ_F −115·04
d P = F, X = Y = Z = Q = H; δ_F −113·23
e Q = F, X = Y = Z = P = H; δ_F −124·09



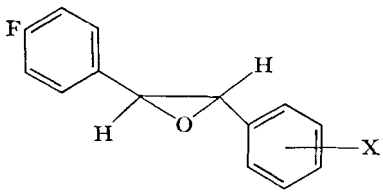
244

δ_F −154·5 (2), −146·7, −136·7

2. *^{19}F shifts of fluorinated aromatics and the study of electronic interactions*

As in previous years, several papers on this aspect have appeared; again those dealing with metal compounds will be considered later (see pp. 206, 256, 259, 263). In a long and detailed paper, Brownlee and Taft[188] presented CNDO/2 calculations of charge densities for a series of *meta-* and *para-* substituted benzenes and showed that these provide some theoretical justification for the empirical σ_I and σ_R parameters.

The ^{19}F shifts for a series of *meta-* and *para-* substituted stilbene epoxides of the type **245** have been used[189] to show that the transmission of conjugation by the epoxide ring is some 26% of that by a double bond (conjugative transmission by CH_2–CH_2 being taken as zero), and equal to that of a cyclopropane ring.

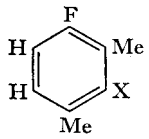


245

The electronic effects of the C_6F_5- and C_6Cl_5- rings as *meta-* and *para-* substituents on a fluorobenzene ring have been studied[154] and the shifts are given in Table XIII. Sheppard concluded that both the C_6F_5 and the C_6Cl_5 groups withdraw electrons inductively ($CF_3 > C_6Cl_5 \approx C_6F_5 > Ph$), and that mesomeric withdrawal is insignificant for both.

Russian workers have reported[190] that for electron-acceptor substituents the relationship $\delta_{F\ para} - \delta_{F\ meta} = -29{\cdot}5\ \sigma_c$ shows deviations from linearity because of direct polar conjugation of the *para* substituent with the fluorine; they proposed a two-term dependence $\sigma_c = \sigma_c^\circ + \Delta\sigma_c^\circ$, where the second term arose from the direct polar conjugative contribution, and proposed methods of separating the two by means of the ^1H and ^{13}C shifts.

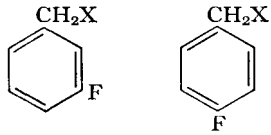
The steric effects of methyl groups flanking the substituent X in *meta*-substituted fluorobenzenes have been studied[191] and the ^{19}F shifts for a number of such compounds (in CCl_4 solvent) are given below. The substituent chemical shifts were smaller than those of the unhindered compounds, but the precise nature of the substituent effect on δ_F remained undefined.



X	δ_F	X	δ_F
NH_2	−121·08	I	−113·83
NMe_2	−118·53	H	−123·14
OH	−119·68	CO_2Me	−120·84
OMe	−118·67	CN	−118·87
Cl	−116·72	NO_2	−117·38
Br	−115·48		

In a related study of substituent electronic effects, the position of the CF_3 resonance of 4-substituted trifluoroacetanilides was reported[192] to correlate well with Brown's σ^+ constants for the substituents, although the range of shifts observed (from 100·7 Hz upfield of external trifluoroacetic acid for $-NO_2$ to 110·5 Hz upfield for MeO) was very small.

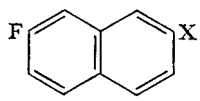
The ^{19}F shifts of *meta*- and *para*- fluoro benzyl derivatives have been reported,[167] and are given below. The shifts were in accord with an inductive effect of the substituent (X), insulated from the ring by the methylene group, taking place through space, and a similar mechanism was suggested for the fluorotetralones (7-fluorotetral-1-one, δ_F −115·85; 6-fluorotetral-2-one, −116·91; 7-fluorotetral-2-one, −117·00) which were also reported.



X	δ_F*meta*[a]	δ_F*para*[a]
CO_2Me	−114·02	−116·82
Br	−113·01	−113·53
CN	−112·63	−115·05
CO_2H	−114·03	−116·73

[a] In dimethyl formamide

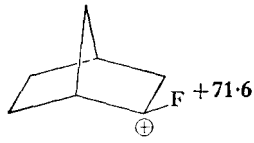
The studies on 6-fluoro- and 7-fluoro- α-substituted naphthalenes previously reported[193] were also extended to the 7-fluoro-β-substituted naphthalenes and the ^{19}F shifts are given below. The substituent chemical shifts observed[167] were in accord with expectation based on Dewar's suggestion that π-interaction in the *meta*-position is a combination of a mesomeric field effect (with the same sign as the mesomeric effect) and a true *meta*-mesomeric interaction of opposite sign.



X	δ_F	X	δ_F
NO_2	−112·60	OH	−116·31
CN	−112·80	OMe	−115·87
CO_2H	−114·61	NH_2	−116·88
CO_2Me	−114·36	NHAc	−115·76
Br	−114·00	$NH_3^{\oplus}$	−114·27

F. Fluorocarbonium ions

In a mixture of antimony trifluoride and sulphur dioxide as solvent, 2,2-difluorobicyclo[2,2,1]heptane formed[194] the carbonium ion **246**, with the ^{19}F shift as usual showing considerable positive character at the fluorine.



246

The CHF_2 group has been used[195] as a probe into the interconversion of enantiomers and diastereoisomers in triarylmethyl cations. Suitably substituted triphenylmethyl cations with a high barrier to rotation of the phenyl rings can form both enantiomers and diastereoisomers, and the change in line shape as the spectrum of the CHF_2 group changed from an AX_2 doublet at room temperature [^2J(F–H) = 56 Hz] to non-equivalent fluorines below −30° [^2J(F–F) = 301·5 Hz, $\nu_0\delta = 140$ Hz] is illustrated in Fig. 5. Line-shape analysis of these spectra and of the less symmetrical

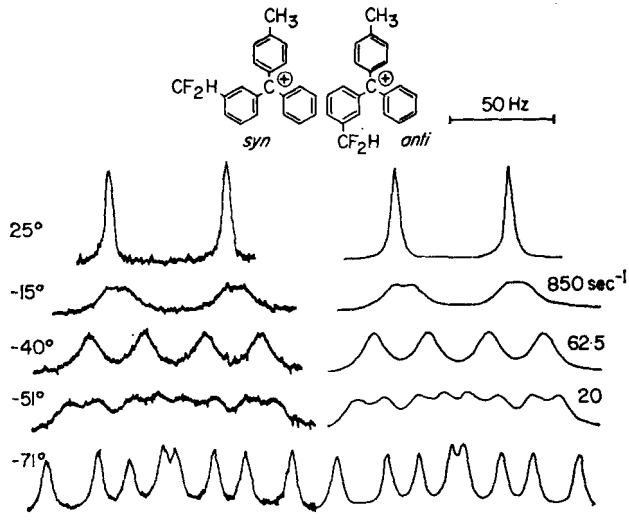


FIG. 5. Temperature dependence of fluorine NMR spectra of *m*-CF_2H, *p'*-CH_3-trityl$^{\oplus}$ $BF_4^{\ominus}$ in propionitrile along with calculated spectra and corresponding rate constants. The low intensity outer eight lines of both calculated and experimental spectra are not reproduced, but are included in the line-shape calculations. (From Rakshys *et al.*[195])

cases with one *para* substituent, which give rise to two ABX patterns at low temperature, was used to derive activation energies and to show that the interconversion process involves a transition state in which two rings simultaneously become perpendicular to the trigonal plane.

G. Fluoropolymers

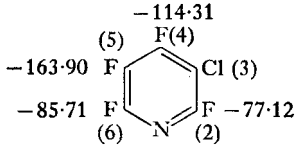
The ^{19}F NMR spectrum of the unstretched solid poly(difluorophosphazene) was reported[196] to remain a sharp doublet at the lowest temperature investigated ($-70°$) and this, together with the fact that the polymer remained elastomeric below this temperature, was taken as indicative of considerable torsional mobility in the backbone.

A mathematical analysis of NMR relaxation times in polymers with fibre symmetry has been reported.[197] Relaxation times T_1, T_2 and $T_{1\rho}$ (the rotating frame relaxation time) were measured[198] by pulse techniques for a copolymer of tetrafluoroethylene and hexafluoropropene (FEP) in the bulk phase and in the drawn fibre for the temperature range -200 to $+250°C$. T_2 and $T_{1\rho}$ were found to be markedly anisotropic with fibre orientation, but T_1 was less so. Relaxation effects were assigned to molecular reorientations. The spectra provide evidence that the CF_3 groups do not rotate freely in the polymer. The dependence of the ^{19}F relaxation times in poly-chlorotrifluoroethylene on temperature was measured,[199] along with the ^1H parameters for a number of hydrocarbon polymers, but the authors stated that they were unable to interpret the variations of T_1, T_2, and $T_{1\rho}$ for the fluoropolymer (which are illustrated in the paper) with confidence.

III. HETEROCYCLIC SYSTEMS

A. Nitrogen heterocycles

Nitrogen-fluorine couplings in some fluorochloropyridines have been obtained[200] by a combination of detailed band-shape analysis of the broad bands in the ^{19}F spectrum, ^{14}N resonance, and observation of ^{15}N satellites in the ^{19}F spectra. Although coupling of nitrogen to the α-fluorines was relatively large [$^2J(^{15}N\text{–}F) = 52{\cdot}60$ Hz in 3,5-dichloro-2,4,6-trifluoropyridine] there was no broadening of the γ-fluorine resonance.



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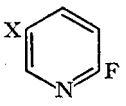


248

Chemical shifts and coupling constants were also reported for 3-chlorotetrafluoropyridine (**247**), and double resonance experiments were used to show that J_{26}, J_{45}, and J_{56} have the same sign, and J_{24}, J_{25} and J_{46} all have the same sign which is opposite to that of the other group. The ^{19}F shifts for a series of 5-substituted 2-fluoropyridines (**248**; X = Me,

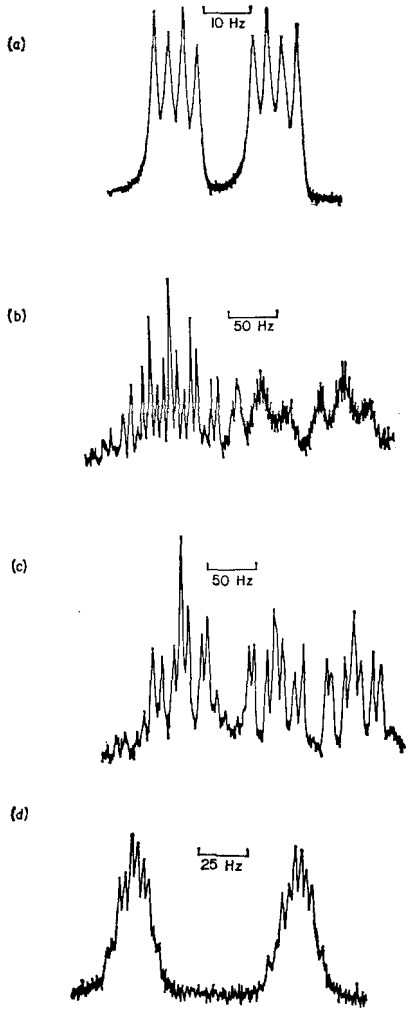
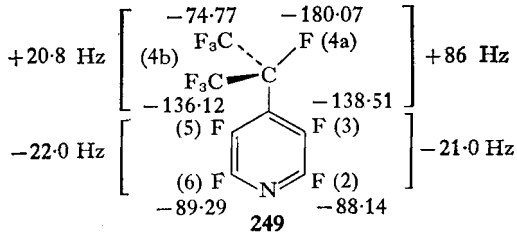


FIG. 6. The ^{19}F spectrum of a saturated solution of perfluoro-(4-isopropyl pyridine) (**249**) in acetone at −40° (a) the F-4b resonance at δ_F −74·77, (b) the F-3 and F-5 resonances at −138·51 and −136·12, (c) as (b) but with double irradiation of CF_3 group resonances, (d) the F-4a resonance at −180·07. (From Chambers *et al.*[202])

Br, Cl, NO_2, NH_2, CN) have been shown[201] to follow the Taft relationship for *para*-substituted fluorobenzenes.

The ^{19}F spectra of a number of perfluoroalkylpyridines, prepared by the fluoride-ion initiated reaction of perfluoropropene with pentafluoropyridine, have been reported.[202] The spectra were mostly temperature dependent, consisting of broad bands at room temperature, but quite sharp lines at *ca.* −40° (see Fig. 6). Decoupling experiments showed that in compounds containing a perfluoroisopropyl group in the 4-position the CF_3 groups were strongly coupled (20 to 30 Hz) to one of the *ortho* fluorines, and the tertiary fluorine was even more strongly coupled (83 to 92 Hz) to the other *ortho* fluorine. These couplings were considered to arise from through-space coupling between almost eclipsed fluorine atoms, e.g. in **249a**. The tertiary fluorine of a perfluoro-



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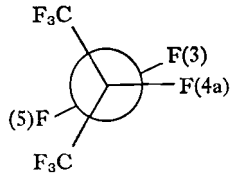
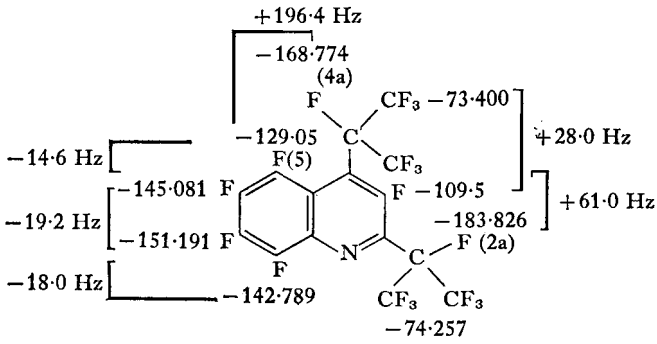


249a

isopropyl group at C2 or C6 was strongly coupled (*ca.* 60 Hz) to the adjacent ring fluorine, but the CF_3 groups were only weakly coupled, since they are far from any ring fluorine in the preferred conformation.

The assignment of the structure of tris(perfluoroisopropyl)difluoropyridine isomers is discussed in the paper, and a number of spectra are illustrated.

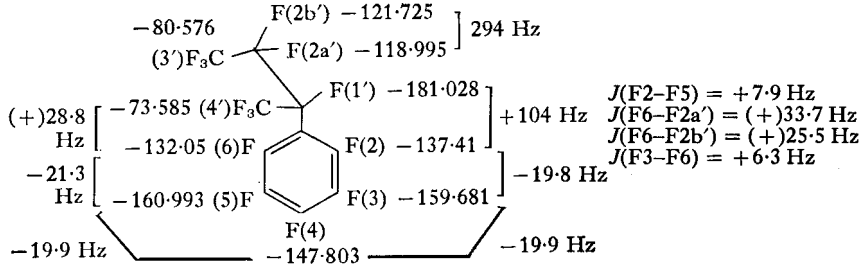
Spectra of some similar pyridines and quinolines were discussed in a



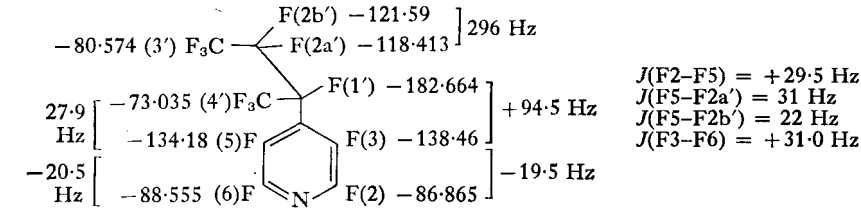
250

further paper[203] and a coupling of 196·4 Hz, between the tertiary fluorine F4a and the ring fluorine F5 in compound **250**, was noted.

The relative signs of some of the coupling constants were obtained by double resonance experiments, and the "through-space" coupling between the tertiary fluorine and the *ortho*-fluorines was found to be positive (negative *ortho*-F–F coupling being assumed). Parameters were also given for perfluoro(*sec*-butylbenzene) and perfluoro(4-*sec*-butylpyridine); in both compounds, strong coupling was observed between F1′, F4′, F2′, and the adjacent ring-fluorine atoms, but because of the broadness of some of the signals, all the signs and couplings were not determined. Some of the parameters are given with formulae **251** and **252**. Signs enclosed in parentheses were assigned by analogy with other compounds.



251



252

Parameters for several mono- and di- fluoropyridines and the corresponding pyridinium ions have been reported,[204] and are summarised in Table XIV.

The authors pointed out the considerable effect of the hetero atom on the *ortho* hydrogen-fluorine coupling constant for the 2-fluoropyridines, a decrease of 11·5 Hz compared with that for fluorobenzene, and the similar, but smaller, effect on the 3-fluoro-compounds. The coupling was more negative in the free bases than in the pyridinium ions, demonstrating that the hydrogen-fluorine and hydrogen-hydrogen[205] couplings

are subject to similar electronic perturbations by neighbouring nuclei. As expected, the ^{19}F resonance moved to low field on protonation of the nitrogen for the 3-fluoro- and, to a smaller extent, for the 2-fluoro-5-chloro-compound, but for most of the 2-fluoropyridines the resonance moved, as yet inexplicably, to high field (see Table XIV).

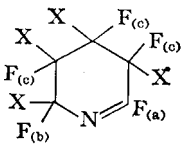
TABLE XIV

^{19}F parameters for some mono- and di- fluoropyridines[204]

Sub-stituents	Solvent	δ_F	J(2-3)	J(2-4)	J(2-5)	J(2-6)
2F	Neat	−60·7[a]	−2·63	+8·19	+2·49	≈0
2F	TFA	−79·4	(+)2·61	+6·38	+0·52	+2·06
2F,5Cl	$CDCl_3$	−71·3	−3·26	+6·77	..	(−)1·38
2F,5Cl	TFA	−67·4				
2F,5NO_2	$CDCl_3$		−2·96	+6·41	..	0
2F,6Cl	$CDCl_3$	−66·9	−2·69	+7·97	+1·54	..
2F,6Cl	TFA	−71·1	±0·63	+7·77	+1·00	..
2F,6F[b]	$CDCl_3$	−62·1	−2·47	+7·97	+1·19	(−)12.23
2F,6F	TFA	−72·0	≈0	(+)7·6	≈0	..
		δ_F	J(2-3)	J(3-4)	J(3-5)	J(3-6)
3F	$CDCl_3$	−131·5	+0·66	+8·79	+4·83	+1·97
3F	TFA[c]	−115·6	(+)2·7	7·1	4·5	0·8
3F,2Cl	$CDCl_3$	−135·2	..	8·27	3·67	0·76
3F,6Cl	$CDCl_3$	−123·1	1·16	7·92	4·82	..

[a] This value for 10–15% solution in $CDCl_3$.
[b] It is stated that the full analysis of the spectra of this compound will be published.
[c] Many lines were broadened, precluding accurate measurement.

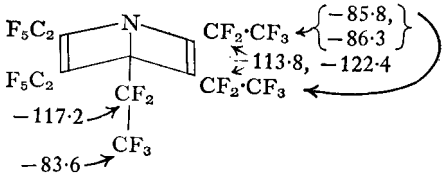
Pentafluoropyridine reacted[206] photochemically with chlorine to give 2,3,4,5-tetrachloro-2,3,4,5,6-pentafluorotetrahydropyridine (**253**, X = Cl). Although the ^{19}F spectrum was complex, presumably because several stereoisomers were present, three distinct regions of absorption were assigned as shown. The reaction with bistrifluoromethyl nitroxide gave the analogous compound **253**, X = $(CF_3)_2NO$. UV irradiation of pentakis-(pentafluoroethyl)pyridine gave the *para*-bonded and prismane valence-bond isomers, chemical shifts for which have been briefly reported (**254**, **255**).[207]



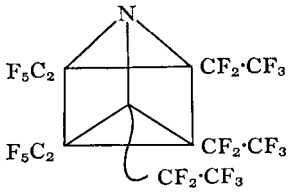
253

	δ_{F_a}	δ_{F_b}
X = Cl	−43·5 to −50·5	−74·5 to −90·5
X = $(CF_3)_2NO$	−38·5 to −44·5	−94·5 to −103·5
$\delta(CF_3)$ −68·9		

	δ_{F_c}
X = Cl	−106·5 to −134·5
X = $(CF_3)_2NO$	−118·5 to −130·5



254

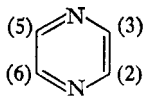


−84·0 (6F), −84·6 (9F),
−114·1 (AB, 4F), −118·6 (4F)

255

TABLE XV

^{19}F parameters of pyridazines[a, 208]



Substituent	δ_{F3}	δ_{F5}	δ_{F6}	J_{FF} (Hz) *ortho*	*meta*	*para*
None	−94·5	−94·5	−94·5			
2-NH_2	−95·5	−100·6	−113·6	16·2	10·8	49·8
2-Br	−77·5	−92·2	−91·8	17·5	6·9	39·9
2-Cl	−80·9	−92·9	−91·1	17·2	5·6	44·6
2-$NH·NH_2$	−94·0	−101·9	−116·1	15·0	13·2	50·1
2-OH	−94·3	−99·2	−107·2	16·5	12·0	51·0
2-OBu^t	−91·9	−98·9	−107·1	16·1	12·0	50·1
2-OEt	−93·1	−99·6	−107·5	13·8	12·0	50·7
2-$O[CH_2]_2OH$	−92·7	−99·6	−106·5	14·8	11·7	50·6
2-OMe	−92·8	−99·4	−106·9	15·1	12·3	51·2
2-Bu^t	−84·3	−93·2	−92·0	20·7	6·9	43·9
2-Me	−83·7	−94·3	−93·1	19·7	7·9	43·9
2-Cl, 6-Cl	−77·8	−77·8	..	..	<8[b]	..
2-Cl, 5-Cl[c]	−81·0	..	−81·0	..	..	..
2-Cl, 5-OMe	−85·5	−91·2	..	..	..	47·0
2-OMe, 3-OMe	..	−111·7	−111·7	..	..	..
2-$O[CH_2]_2OH$, 3-$O[CH_2]_2OH$	..	−111·1	−111·1	..	..	..
2-Me, 5-OMe	−87·3	..	−90·1	..	..	49·3
2-Me, 3-OMe	..	−65·7	−104·7	22·5	..	..
2-Bu^n, 5-Bu^n	−84·8	..	−84·8	..	..	..
2-Me, 5-OMe, 6-OMe	−97·0	..	..	..	..	..
2-Bu^n, 3-Bu^n, 5-Bu^n	..	..	−91·4	..	..	..
2-Cl, 3-Cl, 5-Cl	..	..	−77·6	..	..	..

[a] The numbering of the substituents differs in some cases from that used in the original paper. All undesignated substituents are fluorine.
[b] From ^{13}C satellites.
[c] From ref. 210.

TABLE XVI

^{19}F shifts for fluoropyrimidines[209]

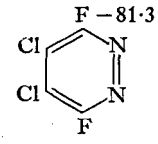
Substituent X[a]	δ_{F2}	δ_{F4}	δ_{F5}	δ_{F6}	δ_{FX}
5-CF_3	−36·5	−51·1	..	−51·1	−60·4
4-CF_3	−46·7	..	−156·9	−70·6	−68·9
2-CF_3	..	−75·9	−167·3	−75·9	−73·0
5-NO_2	−34·5	−55·9	..	−55·9	..
5-CN	−31·7	−45·5	..	−45·5	..
4-Cl, 5-CN	−32·5	..	..	−46·9	..
5-CF_3, 6-OMe	−39·9	*ca.* −59·5	..	..	−60·1
2-OMe, 5-CF_3	..	−55·5	..	−55·5	−59·1
4-OMe, 6-CF_3	−49·1	..	−156·5	..	−68·8
5-CF_3, 2-CH:CHMe	..	−57·3	..	−57·3	−59·3
5-CF_3, 6-CH:CHMe	−40·9	..[b]	..	..	−58·9
4-CH:CHMe, 6-CF_3	−49·5	..	−142·7	..	−69·1
6-CH:CHMe, 2-CF_3	..	..[b]	−151·7	..	−72·3
5-Cl, 6-OMe	−46·6	−65·7	..	..	..
2-OMe, 5-Cl	..	−61·1	..	−61·1	..
2-NH_2, 5-Cl	..	−65·1	..	−65·1	..
4-NH_2, 5-Cl	−49·3	..	..	−70·3	..
5-H, 6-OMe	−44·1	−62·9	..	..	..
2-OMe, 5-H	..	−56·9	..	−56·9	..
2-NH_2, 5-H	..	−59·9	..	−59·9	..
4-NH_2, 5-H	−47·3	..	..	−68·7	..
4-Cl, 5-CN, 6-Cl	−35·5	..	..	..	..
2-Cl, 4-Cl, 5-CN	..	..	..	−50·9	..
4-NH_2, 5-NO_2, 6-NH_2	−41·5	..	..	..	..
2-OMe, 5-CN, 6-OMe	..	−57·1	..	..	..
4-OMe, 5-CN, 6-OMe	−37·9	..	..	..	..
2-NH_2, 4-NH_2, 5-CN	..	..	..	−58·5	..

[a] All other substituents are fluorine.
[b] Not assigned.

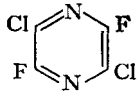
A number of mono- and di- substituted polyfluoropyridazines[208] and pyrimidines[209] have been prepared and ^{19}F parameters are given in Tables XV and XVI. It was assumed that substituent shifts obtained from the mono-substituted pyridazines could be added to predict ^{19}F shifts in the disubstituted pyridazines, and some structures initially obtained on this basis were confirmed by the coupling constants, which fall in the ranges J(F–F *ortho*) 13·8 to 20·7 Hz, J(F–F *meta*) 5·6 to 13·2 Hz and J(F–F *para*) 39·9 to 51·2 Hz; the substitution pattern in 2,6-dichloro-3,5-difluoropyridazine was deduced from the ^{13}C satellites, which appeared as unresolved singlets, indicating that J(F–F) < 8 Hz. The preparation[210] of 2,5-dichloro-3,6-difluoropyridazine **256** by UV irradiation of the pyridazine **257** has been reported independently.

It is noteworthy that J(F–F *para*) in the fluoropyrimidines is much smaller (25 to 30 Hz in the compounds reported) and that CF_3 substituents couple strongly (16·8 to 17·5 Hz) to fluorine on an adjacent ring-carbon.

The reaction of potassium fluoride with hexachlorophthalazine[211] and hexachloroquinazoline[212] gave the corresponding hexafluoro-compounds **258** and **259**.



256



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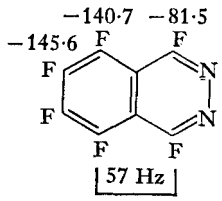

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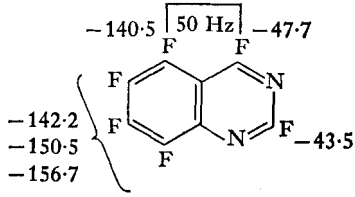
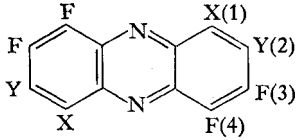


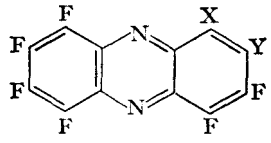
259

The tetramethoxydifluoroquinazoline obtained by treatment of **259** with sodium methoxide in methanol at reflux temperature was assigned the 2,4,5,7-tetramethoxy-structure,[212] since its ^{19}F spectrum showed two bands [δ_F −150·0, −151·5] with J(F–F) < 3 Hz.



260[150]

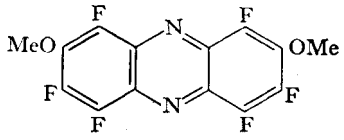
		$\delta_{F(1)}$	$\delta_{F(2)}$	$\delta_{F(3)}$	$\delta_{F(4)}$
a	X = Y = F	−154·1	−152·0	−152·0	−154·1
b	X = F, Y = H	−131·3	(7·99)	−124·3	−155·7
c	X = H, Y = F	(8·05)	−126·5	−153·2	−148·0
	Dihydro derivative of **260b**	−140·6	(6·34)	−147·9	−166·9



261[176]

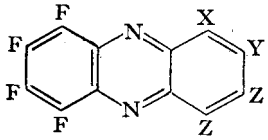
a	X = Br, Y = F	−113·0, −146·4, −148·3, −149·6(2), −151·6(2).
b	X = F, Y = Br	−117·1, −124·7, −149·6(2), −151·8(3).
c	X = OMe, Y = F	−145·8, −149·7, −151·3(2), −152·2(2), −154·4.
d	X = F, Y = OMe	−144·3, −151·1, −152·8(2), −154·0(2), −156·0.
e	X = F, Y = OH	−133·9, −139·6(2), −143·6, −146·2(2), −151·2.

Parameters for some polyfluorophenazines obtained by oxidation of the polyfluoroanilines are shown with formulae **260** to **263**, and for some benztriazoles and a quinoxaline with **264** and **265**.



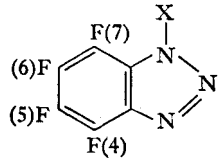
$-137{\cdot}4$, $-149{\cdot}6$, $-152{\cdot}1$.

262[176]



X = Y = Z = H	$-141{\cdot}95$, $-149{\cdot}0$
X = H, Y = Z = F	$-123{\cdot}0$, $-124{\cdot}9$, $-145{\cdot}2$, $-147{\cdot}0$, $-151{\cdot}2(2)$, $-154{\cdot}1$.

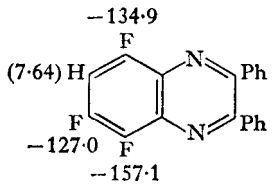
263[175]



	δ_{F4}	δ_{F5}	δ_{F6}	δ_{F7}
X = NH·C_6F_5[a]	$-156{\cdot}5$	$-163{\cdot}8$	$-154{\cdot}2$	$-162{\cdot}5$
X = OH	$-158{\cdot}6$	$-164{\cdot}1$	$-155{\cdot}4$	$-162{\cdot}5$
X = (⊖)	$-155{\cdot}9$	$-167{\cdot}0$	$-167{\cdot}0$	$-155{\cdot}9$

[a] See Table X for C_6F_5 group.

264[151]

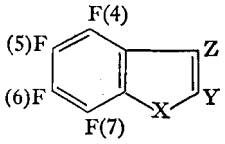


265[150]

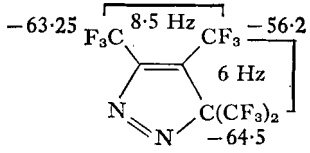
Chemical shifts reported[213] for *N*-alkyl-4,5,6,7-tetrafluoroindoles **266** (X = *N*-alkyl, Y, Z = H or methyl) fall in the ranges F(4) $-6{\cdot}7$ to $-13{\cdot}0$, F(5) $+7{\cdot}3$ to $+10{\cdot}3$, F(6) $+3{\cdot}5$ to $+6{\cdot}9$ and F(7) $+1{\cdot}5$ to $+4{\cdot}8$ p.p.m. from hexafluorobenzene, but there is no indication in the paper which direction has been taken as positive.

The same authors reported[214] shifts for the tetrafluoroindoles **266** (X = NH; Y = Me, Z = H 8·95, 6·33, 0·60, $-11{\cdot}7$; Y = H, Z = Me, 8·50, 3·90, 1·21, 8·33; Y = Z = Me, 8·68, 5·37, 1·77, $-7{\cdot}04$) and for the corres-

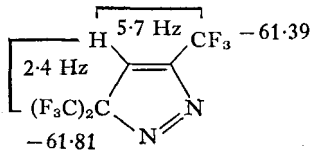
ponding 2,3-dihydro-3-hydroxy compound (10·9, 0·71, −5·06, −18·6 p.p.m. from hexafluorobenzene), but did not assign them.



266



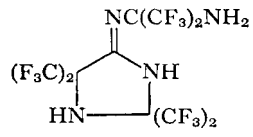
267



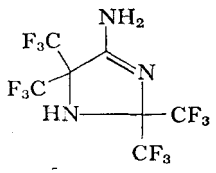
268

Reaction of bis(trifluoromethyl)diazomethane with hexafluorobut-2-yne or with 3,3,3-trifluoropropyne gave[103] the isopyrazoles **267** and **268**. The spectra and splitting diagrams are illustrated in the original paper.

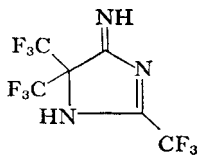
The reaction of sodium cyanide with a series of fluoroketone imines has been used to give aminoimidazolines[215] such as **269**, whence compounds **270**[215] and **271**[216] were readily obtained.



269



270

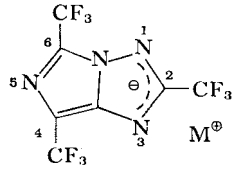


271

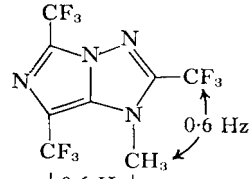
Coupling between the two sets of CF_3 groups in **269** and **270** of *ca.* 5 Hz was observed, and is believed to be an average value between those of *cis*- and *trans*- groups, but the bands were singlets in **271**. Shifts for a large range of such compounds and their derivatives were reported.[215, 216]

The dihydrotetrazapentalene compounds **272** have been prepared[217] by the reaction of trifluoroacetonitrile with sodium cyanide in a polar solvent. The band at highest field in the spectra of compounds **272a** and **b** was a singlet, and was assigned to the CF_3 group in the 2-position but the other two bands were weakly coupled (**a**, 2·1 Hz, **b**, 0·9 Hz). The low-field band was assigned to the CF_3 group at position 4 since earlier work[215] had shown that a CF_3 group attached to carbon flanked by two

nitrogens appears at higher field (*cf.* the assignment[215] in compounds **269**, **270**). The major product from the reaction of **272b** with diazomethane was assigned structure **273** on this basis, together with the observation of weak coupling between the methyl group and the CF_3 absorbing at highest field.



272a M = Me_4N, δ_F −57·2, −60·9, −64·2
b M = H, δ_F −59·8, −62·9, −64·9

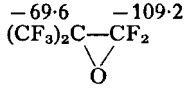


δ_F −57·5, −62·2, −64·1

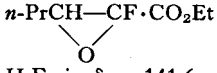
273

B. Oxygen and sulphur heterocycles

Oxidation of perfluoroisobutene with cold alkaline hydrogen peroxide gave the oxiran **274**, with the parameters shown.[25] The ^{19}F shifts for the oxirans[37] (glycidic esters) **275**, **276** and the fully substituted compounds **277**[218] and **278**[218] have also been reported. The hydrogen-fluorine coupling in the *cis*-isomers of **275** and **276** was undetectable.

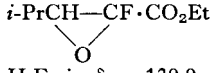


274



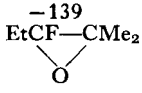
H,F *cis*; δ_F −141·6
H,F *trans*; δ_F −158·7
J(*trans* H–F) = 3 Hz

275

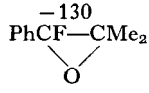


H,F *cis*; δ_F −139·9
H,F *trans*; δ_F −159·1
J(*trans* H–F) = 3 Hz

276



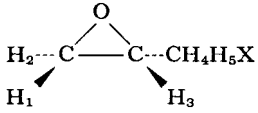
277



278

The fluorine in **277** and **278** coupled only to the *trans* methyl group (J=2·5 Hz).

The NMR spectra of the halomethyl epoxides **279a** to **d** have been investigated in detail;[219] the couplings involving the fluorine in **279a** (±0·03 Hz) are given below.



J(F–H_4) = 47·34 Hz
J(F–H_5) = 47·87 Hz
J(F–H_1) = −1·44 Hz
J(F–H_2) = 3·74 Hz
J(F–H_3) = 11·87 Hz

279a X = F
b X = Cl
c X = Br
d X = I

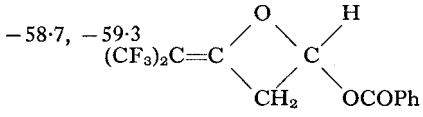
The signs of the coupling constants involving fluorine agree with those assigned by Thomas[219a] (but not with those given by Granger and Canet[219b]), but others do not. Macdonald and Reynolds argue persuasively for their sign allocation, and note in particular that good computer fits with the observed spectra were obtained for both sign sets

$$^4J_{14},\ ^4J_{15} > 0 > {}^4J_{24},\ ^4J_{25}$$

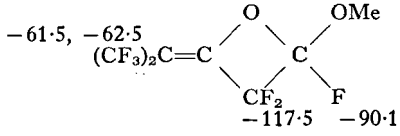
and

$$^4J_{24},\ ^4J_{25} > 0 > {}^4J_{14},\ ^4J_{15}.$$

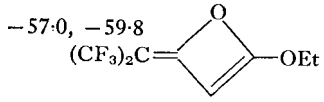
Several oxetanes, e.g. **280, 281** containing the $(CF_3)_2C$: group have been prepared[35] from bis(trifluoromethyl)keten. Evidence for the formation of the oxete **282** from the keten and ethoxyacetylene was provided by the observation at $-80°$ of two quartets, which disappeared as the singlet due to the allene (**129**, p. 128) increased.[35]



280



281



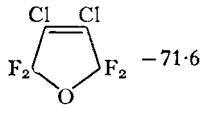
J(F–F) = 7·0 Hz

282

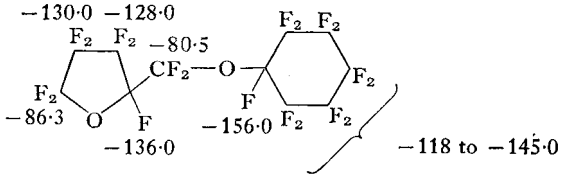
A number of furans[220] (Table XVII), and di- and tetra- hydrofurans (Table XVIII,[220] and formulae **283** to **286**[12, 22, 221]) have been prepared, mostly by fluorination methods and subsequent reactions of the products. In the furans, α-fluorines and hydrogens are expected to absorb to low field of the corresponding β-atoms, and assignment on this basis, together with an unambiguous synthesis of 2,5-difluorofuran, led to a consistent pattern of chemical shifts and coupling constants.

Parameters for the 2,5-addition products (3-oxolens) derived from some of these furans are given in Table XVIII. The isomers were assigned the *cis-* and *trans-* configurations on the assumption that J(F2–F5) or J(F2–H5) will be larger when the nuclei are mutually *cis* rather than *trans*.[220] All the other coupling constants fell into the relatively narrow ranges shown below, with J(F2–F4) of opposite sign to J(F2–F3) in the tetrafluoro-compounds.

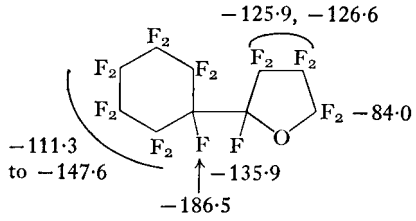
J(F2–F3) 17·5 to 19·2 Hz J(F2–F4) 3·9 to 6·0 Hz
J(F3–F4) 12·7 to 14·7 Hz for tetrafluoro-compounds
10·1 to 12·9 Hz for trifluoro-compounds
J(F3–F5) 3·9 to 4·8 Hz J(F3–H5) 4·1 to 5·1 Hz
J(F4–F5) 18·8 to 19·0 Hz J(F4–H5) 2·4 to 3·6 Hz



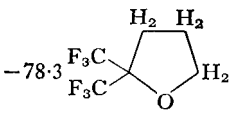
283[221]



284[22]



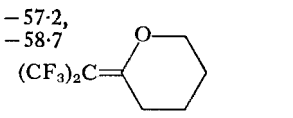
285[22]



286[12]

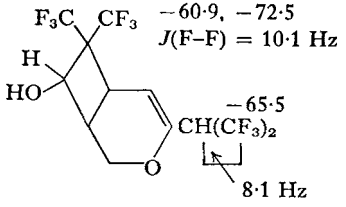
Parameters for the 4′-trifluoromethyl derivative of **284** were also reported.[22]

Several derivatives of pyran, mostly containing $(CF_3)_2CH$ or $(CF_3)_2C$:

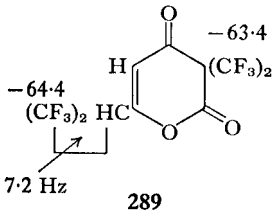


J(F–F) = 9·8 Hz,
J(F–CH_2) = 2·2 and 1·8 Hz

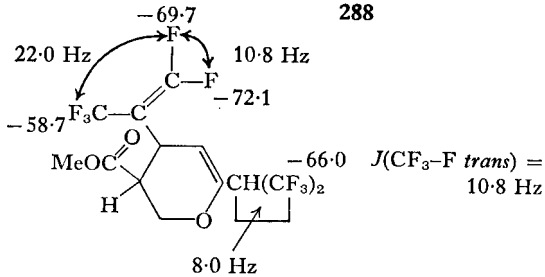
287



288



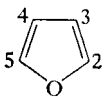
289



290

TABLE XVII

Parameters for polyfluorofurans[220]



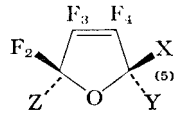
Substituent at position				Chemical shifts[a]				Coupling constants (Hz)					
2	3	4	5	2	3	4	5	2,3	2,4	2,5	3,4	3,5	4,5
F	F	F	F	−137·0	−196·0	−196·0	−137·0	15·5	13·5[b]	20·5	5·5	13·5	15·5
F	F	F	H	−121·5	−195·4	−170·9	(+6·76)	15·1	9·9	1·0	7·4	3·2	4·1
F	F	H	F	..[c]	..[c]	(+5·37)	..[c]	..[c]	1·0	..[c]	2·5	..[c]	5·8
F	F	H	H	−130·1	−187·8	(+6·22)	(+6·57)	13·5	0·5	2·4	4·0	1·2	2·6
F	H	H	F	−122·8	(+5·28)	(+5·28)	−122·8	8	1[b]	25	0	1	8
H	F	F	H	(+7·13)	−182·0	−182·0	(+7·13)	4·6	2·8[b]	2·1	8·8	2·8	4·6
CO_2H	F	F	F	..	−145·6	−189·1	−111·4	..	..	..	9·0	5·0	12·0

[a] δ_H values in parentheses.
[b] Opposite sign to J(2–3).
[c] Not measured.

side chains, have been prepared[33] and the parameters for a few representative structures are shown with formulae **287** to **290**.

TABLE XVIII

Nmr parameters for 2,3,4-trifluoro-3-oxolens[220]



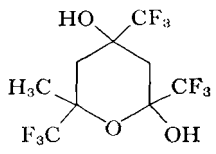
Substituent			Chemical shifts[a]				
X	Y	Z	2	3	4	5	J(2-5) (Hz)
F	Cl	Cl	−54·5	−154·0	−154·0	−54·5	11·2
Cl	F	Cl	−61·0	−153·8	−153·8	−61·0	8·5
F	Br	Br	−47·7	−152·6	−152·6	−47·7	13·0
Br	F	Br	−56·6	−152·5	−152·5	−56·6	9·4
H	Cl	Cl	−45·9	−155·7	−149·5	(+6·7)	16·5
Cl	H	Cl	−52·4	−156·5	−149·5	(+7·0)	2·8
H	Br	Br	−40·8	−153·4	−148·6	(+6·65)	17·1
Br	H	Br	−46·0	−154·7	−148·9	(+6·8)	2·8
H	OAc	NO_2[b]	−70·4	−156·0	−149·4	(+6·2)	16·2
OAc	H	NO_2[c]	−77·1	−154·3	−149·0	(+6·3)	3·5

[a] δ_H values in parentheses.
[b] Tentative structure assignment. X = H, Y = NO_2, Z = OAc cannot be ruled out.
[c] Tentative structure assignment. X = NO_2, Y = H, Z = OAc cannot be ruled out.

With the π-cyclopentadienyldicarbonyliron anion 1,1,1-trifluoroacetone gave[222] a volatile crystalline material identical with that produced by Henne's[223] method. The ^{19}F NMR showed the presence of at least two isomers, presumed to be configurational isomers of **291**, each with three separate CF_3 absorptions (A, δ_F −82·0, −85·7, −88·5; B, −86·4, −86·7, −89·0).

Parameters for the benzpyrones **292** and **293** are given with the formulae.[224] The shifts for the C_6F_5 group in the coumarone **294**[153] are given in Table X. Shifts have been reported,[173] but not assigned, for 2-methyl-3-ethoxycarbonyl-4,5,7-trifluorobenzofuran (δ_F −144·6, −142·9, −142·2).

Ring inversion in perfluoro-1,4-dithian **295** has been studied[225] by means of variable temperature ^{19}F NMR. The sharp singlet (δ_F −91·1) observed at +70° broadened as the temperature was lowered, and gave an AB pattern with small additional splitting centred (at −90°) at



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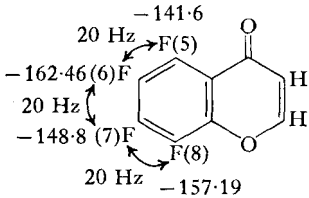
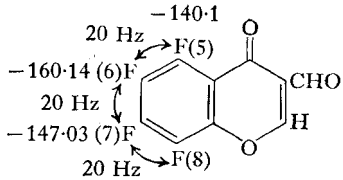
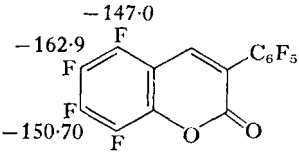


292



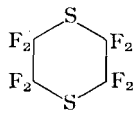
293



294

δ_F −92·9 ($\nu_0\delta$ 15·02 p.p.m., J_{AB}=230 Hz). Comparison of $\nu_0\delta$ with values for non-inverting or slowly inverting cyclohexanes suggests a chair form, possibly puckered, for the compound.

A large number of dithietanes **296** and thietanes, e.g., **297** containing the $(CF_3)_2C$: substituent have been prepared[80] by the reaction of bis-(trifluoromethyl)thioketen with appropriate substrates.



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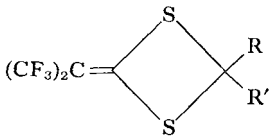
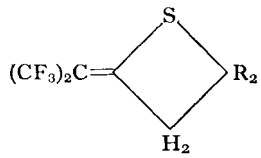


296



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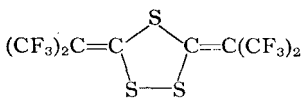
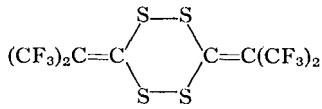


298



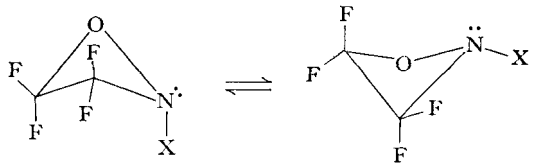
299

The dithietanes showed singlets in the range δ_F −57·45 to −58·89, but the thietanes showed two quartets, one in the range δ_F −57·7 to −59·7,

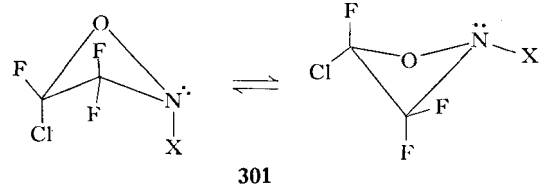
and the second some 1·2 to 1·6 p.p.m. to higher field. Compounds of the type **297** had the low-field quartet further split into apparent triplets (*ca.* 2·6 Hz), and those with a CHR′ group adjacent to the $(CF_3)_2C{:}C$ showed doublet splitting. The trithiolane **298** and *s*-tetrathiane **299** were prepared from 2-diazohexafluoropropane and carbon disulphide;[80] **298** showed two quartets (δ_F −59·8, −58·75), but **299**, a symmetrical structure, showed only a singlet (δ_F −56·3).

TABLE XIX

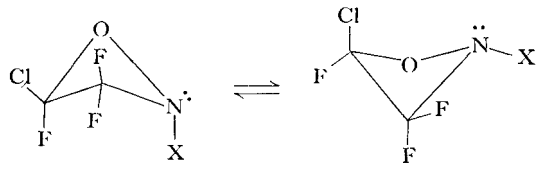
Parameters for oxazetidines at 24°[226,227]



300



301



302

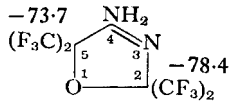
Compound		δ_{CFO}[a]	J_{AB}	δ_{CFN}	J_{AB}	δ_{NF}
300	X = F	−78·4, −80·1	89	−105·0, −106·9	140	+25·3
300	X = Cl	−78·0, −81·6	89	−95·5, −100·2	122	
301	X = F	−62·4	..	−97·4, −103·8	128	+26·9
301	X = Cl	−60·3	..	−87·4, −97·9	116	
302	X = F	−61·7	..	−99·8, −103·1	128	+30·0
302	X = Cl	−63·0	..	−91·3	..	

[a] CF_2O for **300**, CFClO for **301**, **302**.

C. Mixed systems

Variable temperature studies of perfluoro-[226] and perfluoro-4-chloro-[227] 2-halo-1,2-oxazetidines have shown that the ring is puckered, with restricted nitrogen inversion, so that even at room temperature, signals arising from molecules with the two distinct configurations at nitrogen were observed for the 2,4-dichloro-compound. The spectra were analysed in terms of chemical shift differences in the CF_2–O and CF_2–N groups *vs.* changes in conformer populations with temperature. Room temperature parameters are given in Table XIX.

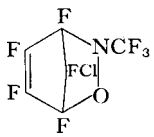
Amino-oxazolines containing fluoroalkyl substituents (e.g. **303**) have been prepared[228] by the reaction of mixtures of fluoro-ketones and fluoroketone imines with sodium cyanide. The high-field absorptions (δ_F −78 to −82) were assigned to the CF_3 groups at position 2, flanked



303

TABLE XX

^{19}F shifts for some polyfluoro 3-trifluoromethyl-2-oxa-3-azabicyclo[2,2,1]hept-5-enes[111,112]



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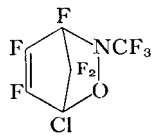

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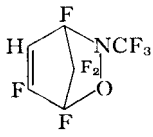

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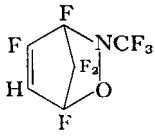
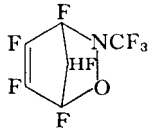


307



308

Compound	CF_3	F_1	F_4	F_5	F_6	F_7	H
304 (major)	−71·5	−172·1	−184·5	−150·2[a]	−156·7[a]	−131·3	..
304 (minor)	−71·5	..[b]	−189·2	−148·7[a]	−152·0[a]	−134·5	..
305	−71·5	..	−186·3	−148·7	−150·5	−138·7[c]	..
306	−71·3	−176·5	−176·5	..	−125·8	−143·8[d]	(+5·95)
307	−68·1	−163·7	−187·4	−119·1	..	−143·3[e]	(+5·95)
308	−68·1	−168·0	−182·2	−150·7	−156·8	−191·3[f]	(+4·50)

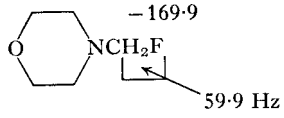
[a] Not specifically assigned to F_5 and F_6.
[b] Obscured by band of major isomer.
[c] $\nu_0\delta_{AB}$ 13·4 p.p.m., J_{AB}=158 Hz.
[d] J_{AB}=174 Hz.
[e] J_{AB}=174 Hz.
[f] J_{HF}=59·5 Hz.

by oxygen and nitrogen (*cf.* the corresponding imidazolines, p. 180) and the absorptions at δ_F *ca.* −74 to those at position 5. As in the spectra of the imidazolines, each set showed septet splitting (*ca.* 5 Hz).

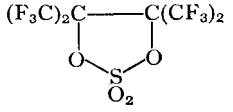
The reaction of trifluoronitrosomethane with 5-chloropentafluorocyclopentadiene gave a mixture of stereoisomers of compound **304**.[112] Similarly, reaction with 1-chloropentafluorocyclopentadiene gave **305**, and with a mixture of 2-*H*- and 5-*H*- pentafluorocyclopentadiene,[111] **306** to **308**. The ^{19}F shifts are given in Table XX.

Parameters for *N*-(fluoromethyl)morpholine (**309**) prepared by the reaction of oxalyl fluoride on dimorpholinomethane, have been reported.[229]

A series of 1,3-dioxolanes containing another hetero-atom has been prepared[230] from the dilithio-derivative of perfluoropinacol.† The CF_3 groups absorbed in the range δ_F −62·7 to −68·8, and appeared as two sets of multiplets where the hetero-atom was unsymmetrically substituted with respect to the plane of the ring, e.g. **310** to **313**

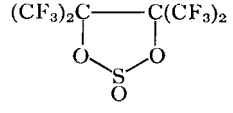


309



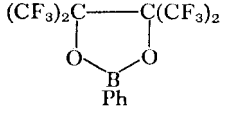
δ_F −66·5

310



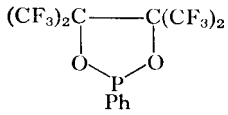
δ_F −67·8, −66·3

311



δ_F −68·8

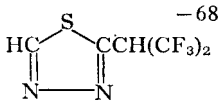
312



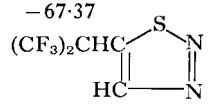
δ_F −65·4, −66·8

313

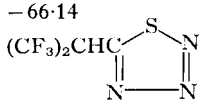
Parameters for a number of mixed systems formed by addition of bis(trifluoromethyl)thioketen to various multiple bonds have been



314



315



316

† The preparation of several such 1,3-dioxolanes from the disodio derivative has previously been reported (M. Allan, A. F. Janzen and C. J. Willis, *Canad. J. Chem.*, 1968, **46**, 3671) and essentially the same parameters were given for **311**.

reported.[80] Those containing the $(CF_3)_2C$: group absorbed at $\delta_F \approx -57$. Addition to diazomethane gave a mixture of **314** and **315**, and to hydrogen azide gave the first aliphatic derivative of the 1,2,3,4-thiatriazole system to be stable at 25° (**316**).

IV. BIOCHEMICAL APPLICATIONS AND FLUORINATED DERIVATIVES OF NATURAL PRODUCTS

Grant and Hall[231] have shown that although the ^{19}F signal of 2-α-fluorocholestan-3-one is barely visible under normal operating conditions, noise decoupling of the hydrogens leads to a sharp signal (δ_F −194·5). Coupling constants [(J(F–H*gem*) = 48·0 Hz, J(F–H1α) = 11·5 Hz, J(F–H1β) = 4·5 Hz, J(F–H4α) = 7·3 Hz, J(F–H4β) = −2·0 ± 1·0 Hz] were also reported.

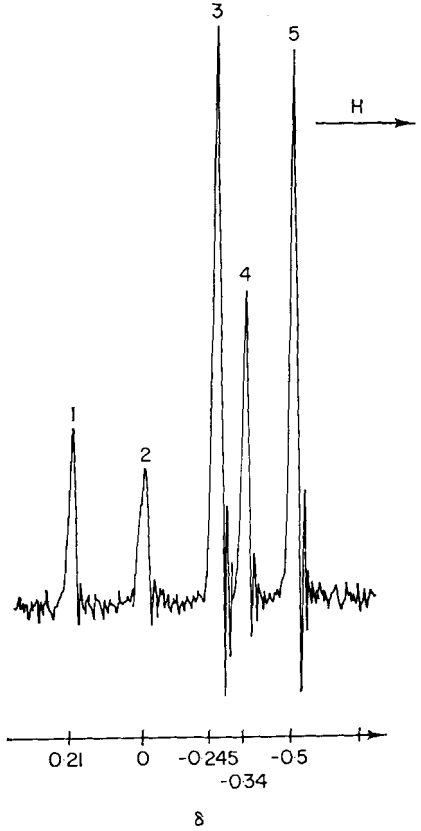


FIG. 7. ^{19}F-NMR-spectrum of a mixture of *O*-trifluoroacetyl Reichstein's substance S, (peaks 1 and 2) allopregnane-3α,20α-diol (peaks 3 and 5) and 16α-methylpregnenolone (peak 4). (From Voelter *et al.*[234])

Precise ^{19}F shifts for the trifluoroacetates of a number of mono- and bi- cyclic alcohols have been measured in carbon tetrachloride and in dimethyl sulphoxide,[232] and the results correlated with the stereochemistry. The extension of these studies to the location of hydroxyl groups in steroids and bile acids has also been reported.[233, 234] Thus the trifluoroacetates of steroids with a hydroxyl at C3 absorbed in the range 0·33 to 0·38 p.p.m. to high field of internal methyl trifluoroacetate, and at C11 at 0·38 to 0·6 p.p.m. to high field. Those at a secondary C17 absorbed between 0·15 and 0·2 p.p.m. to high field, and at a tertiary C17 between 0.1 p.p.m. below and 0.1 p.p.m. above the reference, and those at a primary C21 from 0·2 to 0·3 p.p.m. below the reference. The spectrum of a mixture of *O*-trifluoroacetyl steroids is shown in Fig. 7.

Further examples of the introduction of trifluoromethyl groups into biochemical systems to act as labels have been reported, for instance in the study of the trifluoroacetylphenylalanine-α-chymotrypsin interaction,[235] and of the interaction of serum albumin with 8,8,8-trifluorooctylbenzene-*p*-sulphonate.[236] The chemical shifts of fluoromethylcobalamins (see below) were markedly different from those of trifluoromethylcobaloxime, and the authors suggest[237] that this may indicate that the alkylcobaloximes are not particularly good models for alkylcobalamines.

	δ_F
Trifluoromethylcobaloxime	−30·6
Trifluoromethylcobalamin	−94·2
Difluorochloromethylcobalamin	−94·2
Difluoromethylcobalamin	−212·0
Fluorodichlorocobalamin	−213·5

The ^{19}F shift for *para*-fluorophenyl ortho-esters and acetals has also been used[238] as a probe into the localisation of substrates in micellar systems.

Parameters for a number of fluorinated furanose and pyranose monosaccharides have been reported,[239 to 242] and the ^{19}F shifts and couplings are summarised in Tables XXI and XXII. Analysis of the ^{1}H spectrum by first-order methods was frequently possible, and was often greatly simplified by heteronuclear noise decoupling of the fluorine. Hall and his co-workers point out, however, that this often caused changes in chemical shifts because of the heating effect of the decoupling irradiation. In the 1-fluorofuranoses, the configuration at C1 was originally assigned from the size of the H1–H2 coupling,[243] as in unfluorinated compounds. The ^{19}F shift, however, and the couplings of fluorine to H2 and H4 also provided a means of assigning stereochemistry; the 1α-fluorine absorbed to high field of that at 1β, the *cis* coupling to H2 was much smaller (*ca.*

TABLE XXI

Parameters for some fluorinated furanoses

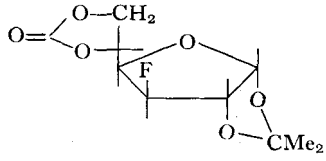
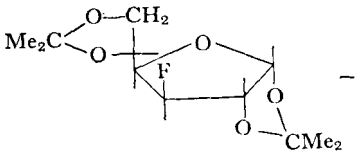
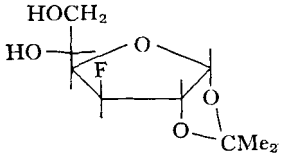
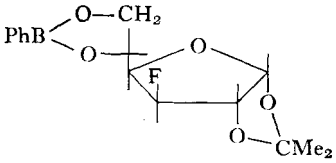
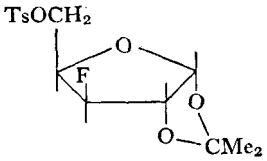
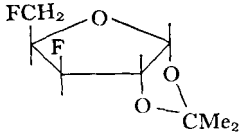
	δ_F	J(F–H1)	J(F–H2)	J(F–H3)	J(F–H4)	Ref.
	−207·1	..	10·8	49·9	29·2	241
	−208·0	..	10·5	*ca.* 49	*ca.* 28	241
	−209·4	..	10·5	50·0	28·8	241
	−207·8	..	10·5	50·0	28·9	241
	−210·6	..	10·5	50·5	*ca.* 25	241
	−209·5 −231·2	..	unresolved			241

TABLE XXI (*continued*)

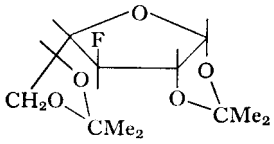
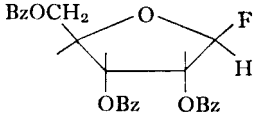
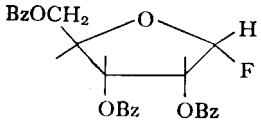
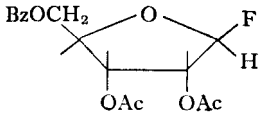
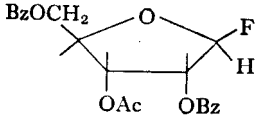
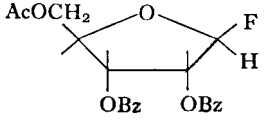
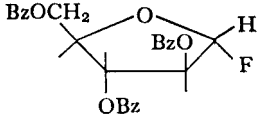
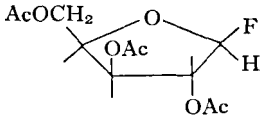
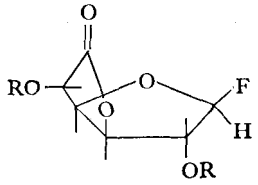
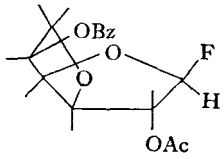
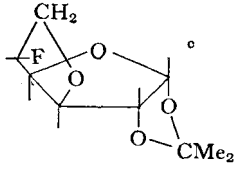
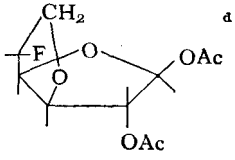
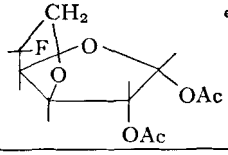
	δ_F	J(F–H1)	J(F–H2)	J(F–H3)	J(F–H4)	Ref.
 **317**	−187·9	..	15	51·6	23·7	242
	−115·9	61·5	4·8	2·2	6·6	239
	−133·3	64·4	20·6	≈0	1·0	239
	−115·8	60·9	4·7	2·4	6·7	239
	−115·5	61·6	4·5	1·7	7·9	239
	−115·7	61·3	4·9	2·1	7·2	239
	−123·8	58·4	6·4	<0·7	1·5	239

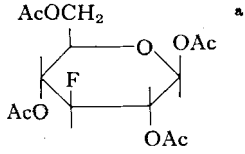
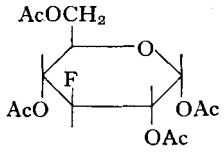
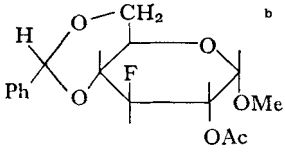
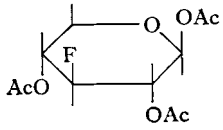
TABLE XXI (*continued*)

	δ_F	J(F–H1)	J(F–H2)	J(F–H3)	J(F–H4)	Ref.
	−113·2	60·5	5·2	<0·5	5·2	239
	R=Bz[a] −118·5 R=Ac[b] −118·3 α-Fluoro-isomer −138	60·1 60·1	4·0 4·5	<0·5 <0·5	4·6 4·4	240a
	−119·8	62·3	5·8	<0·5	4·8	240a
	−189·7	1·5	<0·5	1·5	7·5	240b
	−186·7	2·7	<0·5	≈1·0	10·8	240b
	−190·8	2·0	<0·5	<1·0	8·1	240b

[a] J(F–H5) = 0·3 Hz.
[b] J(F–H5) < 0·5 Hz.
[c] J(F–H5) = 50·4 Hz; J(F–H6^1) = 26·1 Hz; J(F–H6^2) = 38·3 Hz.
[d] J(F–H5) = 50·6 Hz; J(F–H6^1) = 39·8 Hz; J(F–H6^2) = 25·5 Hz.
[e] J(F–H5) = 50·6 Hz; J(F–H6^1) = 38·1 Hz; J(F–H6^2) = 22·3 Hz.

TABLE XXII

Parameters for some fluorinated pyranoses[242]

	δ_F	J(F–H1)	J(F–H2)	J(F–H3)	J(F–H4)	J(F–H5)
 [a]	−196·2		12·8	51·2	12·8	1·1
	−200·4	4·0	12·5	52·0	12·5	
 [b]	−198·6		14·1	53·0	15·1	1·5
	−195·3		12·4	49·4	12·4	4·2[c]

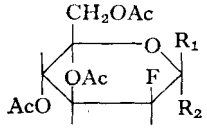
[a] J(F–H6^2) = 1·5 Hz.
[b] J(F–H6^1) = 2·0 Hz.
[c] H5 *eq.*

4·0 to 6·4 Hz) than the corresponding *trans* coupling (*ca.* 20 Hz), and the *trans* coupling to H4 (4·4 to 7·9 Hz) was much larger than the *cis* coupling (1 to 1·5 Hz).

The ^{19}F shifts of the 3-fluorosaccharides were markedly different from those of the 1-fluoro compounds. The vicinal hydrogen-fluorine couplings were generally *ca.* 10 Hz for the *cis* F–H2 coupling and 25 to 30 Hz for the *trans* F–H4 coupling in the furanoses, although the change in configuration at C4 in compound **317** (Table XXI) led to different values.

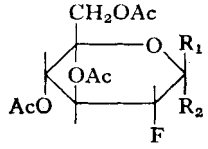
The magnitudes of the couplings in the furanose and pyranose compounds were discussed in terms of the angular relationship between the C–H and C–F bonds and the implications of the results for the molecular geometries of the molecules. A number of spectra are illustrated in the papers, and typical analyses are worked through instructively.

Fluorine-fluorine coupling constants in four difluoropyranoses **318, 319** have been briefly reported,[244] and the magnitudes related to the dihedral angle (see also p. 199).



318

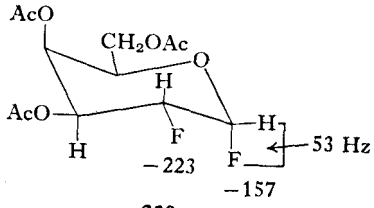
318a $R_1 = H$, $R_2 = F$
$J(F-F) = -20$ Hz
b $R_1 = F$, $R_2 = H$
$J(F-F) = -13{\cdot}5$ Hz



319

319a $R_1 = H$, $R_2 = F$
$J(F-F) = -18{\cdot}8$ Hz
b $R_1 = F$, $R_2 = H$
$J(F-F) = -15{\cdot}8$ Hz

Chemical shifts for some other fluorinated pyranoses,[245] mostly obtained by the action of trifluoromethyl hypofluorite on an acetylated pyranose, have been reported. Equatorial fluorine at C2 absorbed at δ_F -211 to -223, and axial fluorine at C1 at -152 to -158; coupling constants were also reported for compound **320.**



320

$J(F1-H2) = 23$ Hz
$J(F2-H2) = 47$ Hz
$J(F2-H3) = 12$ Hz
$J(F1-F2) = 20$ Hz

Trifluoroacetylation of methylglycopyranosides gave a series of chemically shifted ^{19}F singlets,[246] and attempts have been made to relate the precise shift values to the configuration for each trifluoroacetoxy group. As expected, the range of shifts is extremely small, and it was difficult to assign many of the groups even in compounds of known geometry, but the method may well be useful in certain instances.

V. THEORETICAL STUDIES

Anisotropies of ^{19}F chemical shifts have been measured for a number of polyfluorobenzenes (1,2-, 1,3-, and 1,4- difluorobenzene, 1,2,4,5-

tetrafluorobenzene), using the nematic phase method.[247] The authors pointed out that the values obtained, together with those for hexafluoro-, 1,3,5-trifluoro- and monofluoro- benzene already in the literature, do not appear to be consistent with the Karplus-Das equations. The spectra of 1,2-difluoro- and monofluoro- ethylene in nematic solvent have also been reported[248] and the geometrical parameters calculated from the results compared with those obtained by other techniques.

The multiple-pulse coherent averaging technique[249] has been applied to solid fluoranil to give direct measurement of the chemical shielding anisotropies ($\sigma_{11} = -101 \pm 6$; $\sigma_{22} = -62 \pm 6$; $\sigma_{33} = 86 \pm 6$ p.p.m.). The application of the multiple pulse technique to give high resolution spectra of solid samples has also been reported.[250] Solid perfluorocyclohexane at 200°K thus gave an AB quartet as was previously observed for the liquid.[251]

Measurements of the second moment of the wide-line ^{19}F spectrum of xenon tetrafluoride as a function both of temperature and of field strength indicated[252] that the assumption of axial symmetry about the Xe–F bonds was an over-simplification.

Spectra obtained[253] for $^{13}CH_3F$ (55% enriched) in the nematic phase gave the coupling constants $J(C\text{–}H) = +148{\cdot}8 \pm 0{\cdot}4$ Hz, $J(C\text{–}F) = -161{\cdot}9 \pm 0{\cdot}7$ Hz, and $J(H\text{–}F) = +46{\cdot}3 \pm 0{\cdot}3$ Hz, and led to the large anisotropies ($J_{\parallel} - J_{\perp}$) of the carbon-hydrogen and carbon-fluorine couplings of +1890 and +700 Hz respectively, with that for $J(H-F)$ negligible.

Measurement of line width as a function of temperature and pressure of gaseous samples has been used[254] to obtain relaxation times for silicon tetrafluoride, tetrafluoromethane, and sulphur hexafluoride comparable with those obtained by pulse techniques. The relaxation time $T_{1\rho}$ in perfluorocyclohexane showed[255] a transition at 180 K, and then dropped to a minimum at 294 K. In this region the effective relaxation mechanism was taken[255] to be diffusion within the solid.

Measurement of the concentration dependence of ^{19}F spin-lattice relaxation and of ^{1}H chemical shifts for hexafluorobenzene-hydrocarbon mixtures indicated weak interaction between C_6F_6 and dimethyl formamide, but no specific interactions in the systems C_6F_6-benzene or C_6F_6-cyclohexane.[256] ^{19}F spin-lattice relaxation times for benzotrifluoride and for hexafluorobut-2-yne, measured by standard pulse techniques, were reported[257] and discussed in terms of a nuclear spin-internal rotation coupling which modifies the spin-rotational interaction. The same authors have reported[258] the effect of solvent and concentration on ^{19}F spin-lattice relaxation for CF_3CH_2Cl, CF_3CH_2Br, CF_3CH_2I and CF_3CCl_3.

Intermolecular isotopic shifts (i.e. the difference between ^{19}F shifts

in a solvent and in the corresponding deuterated solvent) have been studied by Russian workers.[259] In general they appear, from the rather small number of organic compounds studied, to be an order of magnitude smaller than intra-molecular isotopic shifts. The corresponding shifts for fluoroanions in D_2O *vs.* H_2O were considerably larger,[260] and were thought to reflect different degrees of hydration.

Chemically induced dynamic nuclear polarisation spectra have been observed[165] for ^{19}F in the reaction between *p*-fluorobenzyl chloride and butyl lithium. The polarised spectrum (Fig. 8) appears as a more complex multiplet than those reported for ^{1}H spectra, and reasons for this were discussed briefly.

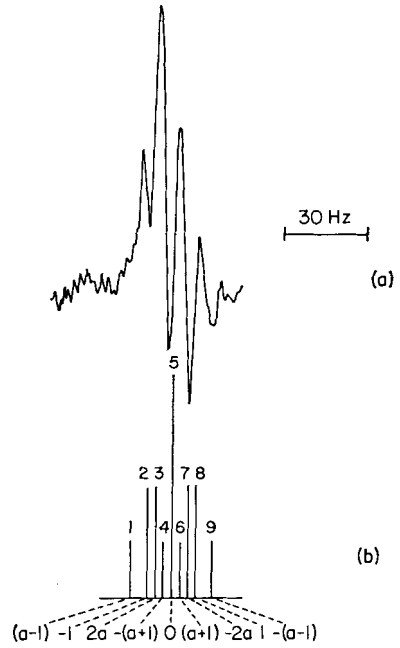


FIG. 8. (a) Polarised ^{19}F spectrum of bis(*p*-fluoro)bibenzyl; (b) Stick diagram simulation of equilibrium spectrum and predicted relative intensities for polarised transitions. (From Rakshys.[165])

Saturation at the hydrogen frequency in some monofluoroaryl compounds is reported[261] to lead to considerable enhancement of the ^{19}F signals (heteronuclear Overhauser enhancement), and in a reversal of this process, the signals due to the *ortho*-hydrogens were enhanced. It was suggested that the technique may be of particular value in conformational analysis.

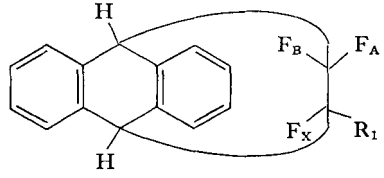
The possibilities of magnetic resonance with stochastic excitation have been discussed by Ernst,[262] with the ^{19}F spectrum of 2,4-difluorotoluene as an example. Advantages over conventional scanning methods are the increased sensitivity and the possibility of independently optimising sensitivity and resolution.

Calculation[263] of the ^{19}F shift for first-row binary fluorides using Hartree-Fock perturbation methods and avoiding the "average energy approximation" was reported to give reasonable agreement with the observed shifts. The reasons for the over-estimate of the shielding in OF_2 and NF_3 were discussed.

Approximate SCMO calculations have been used to evaluate Fermi contact contributions to C–X couplings,[264] including C–F couplings. The calculations were not as successful as for C–C couplings. Blizzard and Santry[265] have also calculated carbon-fluorine couplings, and showed that orbital and spin dipolar terms must be included to reproduce the observed trend of C–F couplings in fluorinated methanes and simple derivatives. Sum-over-states calculations of the spin-spin coupling constant for hydrogen fluoride have been repeated[266] without the approximations (in particular the assumption that the excited states were one-electron transitions without configurational interaction, which appeared to be responsible for the poor convergence of the sum-over-states formula) used by Kato and Saika.[267] The strongly positive coupling thus obtained (836 Hz) is in accord with molecular beam experiments.

Studies of the angular dependence of vicinal hydrogen-fluorine couplings have already been mentioned (ref. 135, p. 148).

The angular dependence of vicinal fluorine-fluorine couplings has also



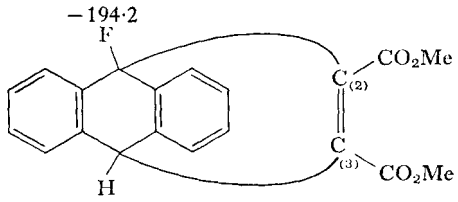
321

	R_1	R_2	ϕ	J(F–F)
318†	H	F	180	−20·0
318	F	H	60	−13·5
319†	H	F	60	−18·8
319	F	H	60	−15·8
321	Cl		120	−2·2 (AX)
			0	+11·4 (BX)
321	H		120	−1·2 (AX)
			0	+9·4 (BX)

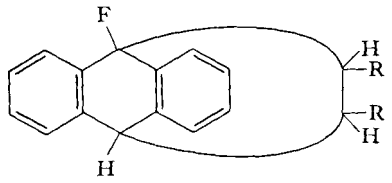
† For structure **318** and **319** see p. 196.

been discussed,[244] with molecules of known geometry selected from fluorinated pyranoses **318**, **319** and Diels-Alder adducts of anthracene **321**. The couplings obtained (see formulae) showed minima at dihedral angles of 60°, 180°, and maxima at 0°, 120° suggesting dependence on cos $3\phi/2$ or $\cos^2 3\phi/2$.

Other workers[268] have prepared Diels-Alder adducts from 9-fluoroanthracene, and found only very weak five-bond coupling between the 9-fluorine and the 10-hydrogen, although the stereochemistry is that expected to be favourable for indirect coupling (i.e. a *trans* coplanar relation between F and C2 and H and C3). Thus in the acetylene adduct **322** the coupling was 0·88 Hz, and in the adducts **323a** and **b** was less than 0·5 Hz, though probably more than 0·3 Hz.



322



323a R = H; δ_F −186·9
b R_2 = C(O)OC(O) δ_F −192·7

VI. DERIVATIVES OF MAIN GROUP ELEMENTS

Group II

Beryllium

Equilibrium constants for the reactions in aqueous solution of fluoride and beryllium ions have been obtained from the ^{19}F spectra of such solutions.[269] Although ambient temperature spectra showed broad bands without fine structure, signals due to the species $BeF_4^{2\ominus}$, $BeF_3^{\ominus}$, BeF_2 and $BeF^{\oplus}$ were resolved when spectra were taken as the solid solution warmed from its melting point (*ca.* −10°) to room temperature. Each species gave rise to a 1:1:1:1 quartet ($I=3/2$ for Be), with line widths at half-height of *ca.* 20 to 30 Hz. A series of spectra is illustrated

in the paper, and the coupling constants and chemical shift ranges (the shifts vary slightly with concentration) are given below.

	$BeF_4^{2\ominus}$	$BeF_3^{\ominus}$	BeF_2	$BeF^{\oplus}$
δ_F	−162·9 to −163·5	−165·2 to −166·6	−167·8 to −168·8	−170·3 to −171·5
J(Be–F)	33·84	36·47	38·50	40·53

The signals in the spectra of BeF_2 in water previously assigned[270] to "BeF_2 polymer" (δ_F −168·5) and "BeF_2 monomer" (δ_F −170·7, J(Be–F) = 39·9) were reassigned[269] to BeF_2 and BeF^+ respectively.

Group III

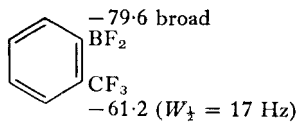
Boron

Chemical shifts and coupling constants for some carborane-substituted olefins (Tables IV and V) and aromatic compounds (Table XI) have already been mentioned.

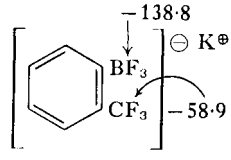
The ^{19}F spectra of isotopically pure liquid $^{10}BF_3$ have been studied over the range −32 to −105°, and are illustrated in a paper by Gillespie and his co-workers.[271] The central trough of the broad doublet observed at low temperature became shallower, the maxima moved further apart, and the slope of the sides became steeper as the temperature was raised. Curve fitting gave $J(^{10}B–F) = 7·36$ Hz at −49°, and 8·07 Hz at −105°, with a reduced coupling constant K(B–F) some 6% higher than that derived from the ^{11}B spectrum at the same temperature, which it was suggested may be due to a curve-fitting error. Anomalous values were obtained above −50°.

The spectrum of diethyltin boron trifluoride, the first example of a tin-group III complex has been reported.[272] The broad singlet (δ_F −131·1, $W_{\frac{1}{2}} = 54$ Hz) showed no tin satellites, implying rapid exchange of BF_3 between the ether-tetrahydrofuran solvent and the complex.

The reaction between (*o*-trifluoromethylphenyl)trimethyltin and boron trifluoride[273] gave the boron difluoride **324** which, with aqueous potassium fluoride, gave the salt **325** in which coupling between the CF_3 and BF_3 groups could be observed in the CF_3 group signal.



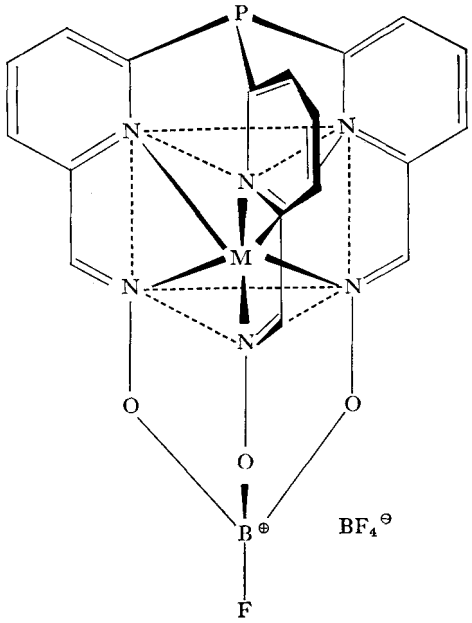
324



325

Two 6-co-ordinate metal complexes with non-octahedral symmetry (**326**) have been prepared,[274] and their ^{19}F parameters are shown with the

formula. The nickel complex is paramagnetic, and no fine structure was reported.



326

326a M = Zn δ_{BF} −166·9; J(B–F) = 11 Hz
$\delta_{BF_4}^{\ominus}$ −150·7; J(B–F) = 0·9 Hz
b M = Ni δ_{BF} −244·9
$\delta_{BF_4}^{\ominus}$ −148·6

Secondary amines reacted[275] with boron trifluoride etherate in the presence of a Grignard reagent to give bis(dialkylamino)boron fluorides $(R_2N)_2BF$ with δ_F −133·6 (R = Et), −131·4 (R = *n*-Pr) and −131·2 (R = *n*-Bu).

Boron tri(bistrifluoromethylnitroxide) formed complexes with tertiary amines,[276] and the ^{19}F shifts reported are in the range δ_F −67·5 to −68·1 for the compounds $R_3NB[ON(CF_3)_2]_3$ (R = H, R = Me), $C_5H_5NB[ON(CF_3)_2]_3$, and $Me_2NB[ON(CF_3)_2]_2$. ^{19}F shifts for a number of *meta*- and *para*- fluorophenyl derivatives of carboranes, carborane anions, and metallocarboranes, prepared by known routes, were measured[277] in order to determine the electronic properties of the carborane species. The shifts are given in Table XXIII. The carborane numbering systems are shown and the values for the σ_I and σ_R constants thus obtained are discussed fully in the paper.

TABLE XXIII

^{19}F shifts of *meta*- and *para*- fluorophenylcarborane derivatives[277]

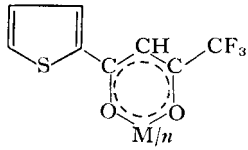
Compound[a]	Ar = *m*-FC_6H_4	Ar = *p*-FC_6H_4	Solvent[b]
1-Ar-1,2-$B_{10}C_2H_{11}$	−111·66	−111·55	DME
1-Ar-1,2-$B_{10}C_2H_{11}$	−111·19	−110·94	CCl_4
1-Ar-1,7-$B_{10}C_2H_{11}$	−112·24	−113·30	DME
3-Ar-1,2-$B_{10}C_2H_{11}$	−113·67	−111·88	DME
1-Ar-1,8-$B_9C_2H_{10}$	−113·04	−112·81	CCl_4
[1-Ar-(3)-1,2-$B_9C_2H_{11}$]NMe_4	−115·28	−120·10	DME
[1-Ar-(3)-1,7-$B_9C_2H_{11}$]NMe_4	−116·35	−121·88	DME
[1-Ar-(3)-1,2-$B_9C_2H_{10}$]Na_2	−117·13	−124·84	DME
[1-Ar-(3)-1,7-$B_9C_2H_{10}$]Na_2	−118·34	−126·17	DME
[1-Ar-(3)-1,2-$B_9C_2H_{10}$]CoC_5H_5	−112·29	−115·13	DME
[1-Ar-(3)-1,7-$B_9C_2H_{10}$]CoC_5H_5	−113·32	−116·50	DME
[(1-Ar-(3)-1,2-$B_9C_2H_{10}$)$_2$Fe]NMe_4Na	−115·68	−121·17	HDA
	−116·79	−122·08	
[(1-Ar-(3)-1,2-$B_9C_2H_{10}$)$_2$Co]Me_4N	−113·35	−115·89	DME
	−113·84	−117·02	
[1-Ar-(3)-1,2-$B_9C_2H_{10}$]$_2$Ni	−110·21	−110·34	CH_2Cl_2
	−109·17	−109·15	

[a] Ar = FC_6H_4
[b] DME = 1,2-dimethoxyethane; HDA = hexadeuteroacetone

Aluminium

^{19}F spectra of aqueous solutions of $AlF_3 \cdot 9H_2O$ plus $Al(NO_3)_3 \cdot 9H_2O$ showed[278] the presence of the species $AlF(H_2O)_5^{2\oplus}$, in addition to the species $AlF_4(aq)^{\ominus}$, $AlF_3(H_2O)_3$, $AlF_2(H_2O)_4^{\oplus}$. Spectra are illustrated in the paper for several compositions and temperatures. The ^{19}F shifts of the individual complex ions depend markedly on temperature and on the composition of the solution. No signal assignable to free fluoride ion was detected.

^{19}F and ^1H NMR spectra have been used[279] for quantitative analysis of mixtures of metal thenoyltrifluoroacetonates, **327** including mixtures of aluminium with calcium, indium, and zinc.



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Group IV

Silicon

^{19}F spectra for fluorosilanes have been reported by a number of workers, and ^{19}F shifts and coupling constants are given in Table XXIV.

TABLE XXIV

^{19}F parameters for fluorosilane derivatives

Compound	δ_F	J(Si–F)	Ref.
Me_3SiF[a]	−158·5		280
Me_2EtSiF	−164·4		280, 281
$MeEt_2SiF$	−170·6		280
Et_3SiF	−176·5		280
Me_2PhSiF	−161·3		280
$MePh_2SiF$	−165·1		280
Ph_3SiF	−169·0		280
$(n\text{-}C_3H_7)_3SiF$	−171·6		280
$(n\text{-}C_4H_9)_3SiF$	−171·6		280
$(n\text{-}C_5H_{11})_3SiF$	−171·4		280
$MeSiF_3$	−136·5	268	282
$CH_2Cl\cdot SiF_3$	−145·5	267	283
$CHCl_2\cdot SiF_3$	−152·5	266	283
$CCl_3\cdot SiF_3$	−158·5	264	283
$CF_3\cdot CO_2SiF_3$[b]	−155·8	194	284
$C_2F_5\cdot CO_2SiF_3$[c]	−156·7	195	284
$n\text{-}C_3F_7\cdot CO_2SiF_3$[d]	−156·5	197	284
$(SiHF_2)_2O$[e]	−134	270	285
$(Me_3Si)_3SiF$[f]	−261	335 ± 2	286
$(Cl_3Si)_2N\cdot SiF_3$	−135·7		287
$(Cl_3Si)N(SiFCl_2)$[g]	−99·5	245	287
$\quad\quad\vert$			
$\quad SiF_2Cl$	−113·9		
$(Cl_2FSi)_3N$	−100·1		287
$(n\text{-}C_4H_9O)_3SiF$	−155·7		288

[a] $^3J(H_3C\text{–}F) = 7{\cdot}2$ Hz.
[b] $\delta(CF_3)$ −77·6.
[c] $\delta(CF_3)$ −85·0, $\delta(CF_2)$ −121·9, $^3J(F\text{–}F) \approx 1{\cdot}3$ Hz.
[d] $\delta(CF_3)$ −81·1, $\delta(\beta\text{–}CF_2)$ −127·6, $\delta(\alpha\text{–}CF_2)$ −119·5, $^4J(F\text{–}F) = 8{\cdot}5$ Hz.
[e] δ_H +4·0, $J(H\text{–}F) = 97$ Hz.
[f] $^3J(Si\text{–}F) = 16{\cdot}8 \pm 0{\cdot}2$ Hz, $^4J(H\text{–}F) = 0{\cdot}4$ Hz.
[g] $^4J(F\text{–}F) = 8$ Hz.

The isotope shift in the series $CH_{3-n}Cl_n\cdot SiF_3$ showed an almost regular increase from 0·009 to 0·023 p.p.m. with increase in n (from 0 to 3).

Parameters for a number of fluoroalkyl-chloro- and -fluoro- silanes

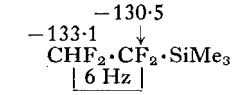
have been reported[283] and are shown in Table XXV; those for some trialkylfluoroalkylsilanes **328** to **331** are summarised below.

TABLE XXV

^{19}F parameters for compounds $RSiX_3$[283]

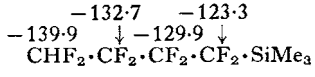
R	X	$\delta_{F\alpha}$	$\delta_{F\beta}$	^2J(H–F)	^3J(H–F)	^3J(F–F)
CFH_2CH_2	Cl	..	−210·5	48	20·5	..
CF_2HCH_2	Cl	..	−105·8	57	16·9[a]	..
CH_3CFH	Cl	−169·5	..	46	26·4	..
CH_3CF_2	Cl	−106·4	..	..	22·7	..
CF_2HCFH	Cl	−232·5	−124·4	46,56, 54[b]	16·4, 12·0, 8·2[c]	17·0,21·2[d]
CH_2ClCF_2	Cl	−113·5	..	..	14·3	..
$CHCl_2CF_2$	Cl	−116·8	..	..	10·1	..
CFH_2CF_2	Cl	−122·8	−236·5	46	14·8[a]	18·8
CF_2HCF_2	Cl	−127·5	−132·5	54	5·0	3·5[a]
CF_2HCFCl	Cl	−150·5	−125·8	54,55[e]	5·1	14·5,15·3[e]
CFH_2CF_2	F[f]	−126·5	−249·5	46	15·2[a]	18·5
CF_2HCF_2	F[g]	−127·5	−132·5	54	5·0	3·5[a]

[a] Mean value; geminal inequivalence not observed.
[b] HαFα, HβFβ (low field) HβFβ (high field) respectively.
[c] HαFβ (low field), HαFβ (high field), HβFα respectively.
[d] FαFβ (low field) and FαFβ (high field) respectively, based on estimated ^2J(F–F) = 305 Hz.
[e] Coupling to low-field fluorine quoted first.
[f] δ_F −150·5, J(F–Fα) = 5·8 Hz, J(F–Fβ) = 5·5 Hz, J(F–Hβ) = 1·4 Hz.
[g] δ_F −149·5, J(Si–F) = 278 Hz, J(F–Fα) = 4·9 Hz, J(F–Fβ) = 2·5 Hz, J(F–Hβ) = 2·5 Hz.



^2J(H–F) = 54 Hz

328[289]

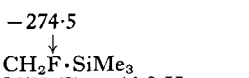


^2J(H–F) = 52 Hz
^3J(H–F) = 6 Hz
J(Fγ–Fβ) = 12 Hz
J(Fγ–Fα) = 6 Hz

329[289]

$Et_3Si{\cdot}CFClH$
^2J(H–F) = 45·5 Hz

330[94]



^2J(H–F) = 46·8 Hz
^4J(H–F) = 0·7 Hz

331[281]

$CF_3{\cdot}CHCl{\cdot}CHCl{\cdot}SiCl_3$
332a *erythro* δ_F −70·66; J(H–F) = 5·90 Hz.
b *threo* δ_F −72·73; J(H–F) = 5·50 Hz.

$CF_3{\cdot}CHBr{\cdot}CHBr{\cdot}SiCl_2Me$
δ_F −67·60; J(H–F) = 6·50 Hz.
δ_F −70·80; J(H–F) = 6·01 Hz.

333

Additions to 3,3,3-trifluoropropenylsilicon compounds gave[290] mixtures of *erythro-* and *threo-* isomers; the configuration was assigned for the 1,2-dichlorotrichlorosilanes **332a** and **b**. The fluorines all coupled approximately equally to the adjacent hydrogen, and the chemical shift difference for each pair of isomers was *ca.* 2 p.p.m.

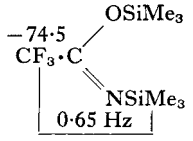
Free-radical addition of silanes $HSiX_3$ to *N*,*N*-bis(trifluoromethyl)-vinylamine gave[281] the corresponding silanes of formula **334**. The $(CF_3)_2N$ group absorbed in the range δ_F −59·3 to −57·9, and was coupled weakly to the adjacent CH_2 group (*ca.* 1·3 Hz).

The ^{19}F spectra of a number of perfluorocarboxysilanes

$$Me_nSi(O_2CR_F)_{4-n} \quad (n = 1\text{–}3,\ R_F = CF_3,\ C_2F_5,\ n\text{-}C_3F_7)$$

have been reported.[56] As might be expected, the shifts and couplings were similar to those in (e.g.) the acid anhydrides. It was pointed out that the α-fluorine resonance was shifted to higher field by 0·2 p.p.m. for each methyl group attached to the silicon. The $OSiMe_3$ group in **335** was a singlet,[291] but the $:NSiMe_3$ group coupled weakly with the CF_3 group.

$(CF_3)_2N\cdot CH_2\cdot CH_2\cdot SiX_3$
334a X = F δ_F −139·5
b X = Cl
c X_3 = $MeCl_2$
d X = Me



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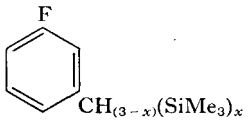

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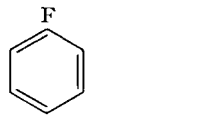

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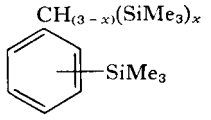


338

Substituent effects on fluoroaromatic chemical shifts have been reported for a number of compounds. ^{19}F shifts for compounds[292] **336** and **337** ($x = 1\text{–}3$), shown below, led to values of σ_I which imply decreasing electron donation compared with a methyl group as x increases, and in fact imply that $C(SiMe_3)_3$ withdraws electrons, in marked contrast to the results from Ar–Si cleavage in compounds of the structure **338**. It was suggested that the anomaly here arises from through-space interaction

between the very bulky $CH_{(3-x)}(SiMe_3)_x$ groups and the *meta*-fluorine, leading to breakdown of the usual equation

$$\delta_{Fm} = -7{\cdot}10\sigma_I + 0{\cdot}60,$$

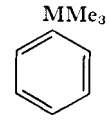
and a similar trend in the series Me, $MeCH_2$, Me_3C was noted. The authors pointed out that, in view of the uncertain reliability of the values of σ_I, the values for σ_R for these substituents are also suspect.

Compound	δ_{Fm} (**336**)	δ_{Fp} (**337**)
$x=0$	−114·38	−118·49
1	−114·29	−120·21
2	−113·99	−120·62
3	−112·85	−120·08

Another series of group IV substituents has been studied and parameters for compounds **339a** to **e** and **340a** to **e** in a number of solvents are given in the original paper.[293] Values obtained for solutions in cyclohexane are summarised in Table XXVI; dioxan and dimethyl formamide gave similar values, but the stronger oxygen donor dimethyl sulphoxide perturbed the shift values. The *meta*-shifts in **339a** to **e** were very similar, indicating electron donation by the group IV atom; deshielding of the *para*-fluorine was observed only for **340b**, and the shielding by the other groups implied that conjugative withdrawal contributed to the observed shift for the other compounds. Conjugative interaction between the Me_3Si group and fluorine in **341a** was also indicated by the observed shift, and also resulted in **341b** in deshielding, the mesomeric effect being more important compared with the opposing inductive effect in this system than in **340c**.

The authors pointed out the poor correspondence between σ_I and σ_R values obtained by these methods and those obtained from pentafluorophenyl compounds. Not only is there the possibility of interaction between adjacent fluorine atoms in the pentafluorophenyl group, but the effective electronegativity of the metalloids is probably different. Substituent chemical shifts of compounds **342a** to **c** suggested an electronegativity sequence C > Si ≈ Ge > Sn. On the other hand, use of the *meta*-fluoro compounds **343a** to **c** with the relationship proposed by Stewart and Treichel[294] led to the order Sn > Ge > Si > C, as did the shifts in the series **339a** to **d**. The authors attribute this[293] to the fact that the substituent chemical shifts for *meta*-fluorine are a result of combination of the inductive effect and a mesomeric effect which is composed

339



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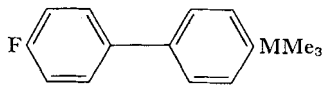
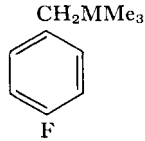
a M = C; **b** M = Si; **c** M = Ge
d M = Sn; **e** M = Pb



341a M = Si
b M = Ge
c M = Sn



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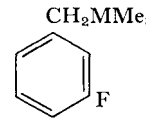
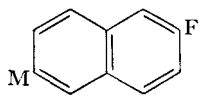


343

a M = Si; **b** M = Ge; **c** M = Sn



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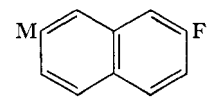


345

a M = Me; **b** M = Me_3Si; **c** M = Me_3Ge; **d** M = Me_3Sn;
e M = Me_3Pb (**344** only)

TABLE XXVI

^{19}F shifts for substituted fluorobenzenes[a, 293]

Substituent	$\delta_{F(meta)}$	$\delta_{F(para)}$
Me_3C	−113·70	−118·75
Me_3Si	−114·00	−112·65
Me_3Ge	−113·85	−113·70
Me_3Sn	−113·75	−113·35
Me_3Pb	−113·55	−113·35
Me_3SiCH_2	−114·20	−120·20
Me_3GeCH_2	−114·05	−120·20
Me_3SnCH_2	−114·00	−120·90
p-$C_6H_4SiMe_3$		−112·97[b]
p-$C_6H_4GeMe_3$		−113·04[b]
p-$C_6H_4SnMe_3$		−113·25[b]

[a] In cyclohexane. [b] In dimethyl formamide.

of both a field effect and a true mesomeric interaction with no *a priori* prediction whether they will reinforce or oppose being possible.

Small substituent chemical shifts to low field for **344b** to **d** indicated[295] that conjugative withdrawal of electrons was greater than the +I donation, and the small shift to high field for **344e** compared with **344a** suggested that mesomeric withdrawal was still significant for $M = Me_3Pb$. The substituent chemical shift was still to low field in **345b** to **d**, suggesting that in these compounds indirect mesomeric withdrawal outweighed the inductive donation of electrons.[295]

The concentration dependence of the ^{19}F resonance of metal hexafluorosilicates in aqueous solution has been reported by Haque and Cyr.[296] The exchange between ion-paired and free hexafluorosilicate ions was rapid, so that the ^{19}F signal was averaged, and at infinite dilution corresponded in each case to isolated hexafluorosilicate. The paramagnetic shifts for the ions were then calculated to be: $Cu^{2\oplus}$, 41 p.p.m.; $Ni^{2\oplus}$, 69 p.p.m.; $Co^{2\oplus}$, 83 p.p.m.; $Fe^{2\oplus}$, 104 p.p.m.

Parameters for other fluorosilicon(IV) complexes have also been reported[297] and are given below.

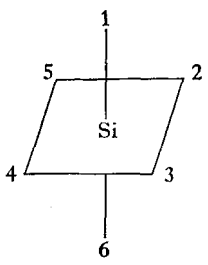
Compound[a]	δ_F[b]	$J(^{29}Si–F)$	$J(F–F)$
$[Si(ox)^{1,2}F_4]^{2\ominus}$	$F^{4,6}$ −140·0	118·5 ± 0·9	2·4
	$F^{3,5}$ −128·4	137·7 ± 0·7	
$[Si(ox)_2{}^{1,2,3,4}F_2]^{2\ominus}$	$F^{5,6}$ −135·5	142·9 ± 1·0	
$[Si(mal)^{1,2}F_4]^{2\ominus}$	$F^{4,6}$ −135·6		
	$F^{3,5}$ −128·2		
$[Si(Memal)F_4]^{2\ominus}$	F_a −124·6		
	F_b −123·4		
	F_c −135·0		

[a] ox = oxalato, mal = malonato, Memal = methylmalonato. Assignments as in **346**, **347**. Solvent methanol.

[b] Based on $SiF_6^{2\ominus}$ in methanol δ_F −133·0.

As with the tin complexes reported previously[298] an approximate additivity of the effects of *cis*- and *trans*- ligands on the ^{19}F shift was observed, and the coupling between silicon and fluorine followed the same trend as that between tin and fluorine. No fine structure was observable for the malonato and methylmalonato complexes, suggesting that an exchange process occurred. In view of the fluorine-fluorine couplings reported for tin compounds and the increased values for the

corresponding germanium compounds (see Table XXVII), the low value for J(F–F) for the oxalato silicon complex was surprising.



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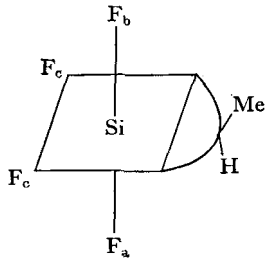


347

Germanium

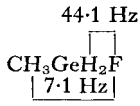
The ^{19}F shifts for fluorotriphenylgermane and for some trialkylfluorogermanes are summarised below.[280]

Me_3GeF	−188·6	Et_3GeF	−213·5
$(n\text{-}C_3H_7)_3GeF$	−207·7	$(n\text{-}C_4H_9)_3GeF$	−207·5
Ph_3GeF	−202·6		

These shifts are some 23 to 30 p.p.m. to high field of the corresponding silicon compounds (see Table XXIV, p. 204).

Hydrogen-fluorine couplings have been observed[299] in the ^1H spectra of methylfluoro- (**348**) and methyldifluoro- germane (**349**). The spectra were obtained at low temperature and high dilution to avoid exchange processes which collapsed the coupling under other conditions.

The cyclopropene **350** was obtained[103] by the reaction of 3,3,3-trifluoropropynyltrimethylgermane with either bis(trifluoromethyl)-diazomethane or the corresponding diazirine.



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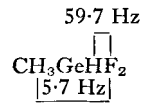

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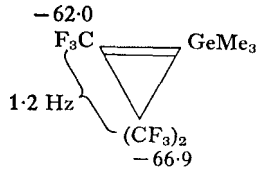


350

−216·5	−111·6	−135·3
$Et_3Ge\cdot CHF\cdot CO_2Et$	$Et_3Ge\cdot CF_2\cdot CO_2Et$	$Et_3Ge\cdot CFCl\cdot CO_2Et$
49·9 Hz		
351	**352**	**353**

A series of α-triethylgermyl-α-fluoroacetic acids and their derivatives was prepared[300] by the reaction of bis(triethylgermyl)mercury with α-mercurated fluoroacetic acids, but only the parameters given with formulae **351** to **353** were reported.

The cause of the line broadening in $(C_6F_5)_4Ge$, $(C_6H_5)_2Ge(C_6F_5)_2$ and $(C_6H_5)_3GeC_6F_5$, which decreased in that order, has been reinvestigated.[301] Invariance over the temperature range 20° to 70° was used to show that restriction of rotation about the C–Ge bond was not the cause, and measurement of the relaxation time showed that reduction in the spin-spin relaxation time by the presence of more than one C_6F_5 group was not the cause either. The authors thus concluded that the observed broadening was due to unresolved inter-ring coupling of about 0·5 Hz.

The ^{19}F shift for the hexafluorogermanium(IV) ion varied[297] markedly with solvent (δ_F −125·5 in MeOH, −124·0 in EtOH, and −122·4 in $CHCl_3$). Parameters were also reported for a number of substituted fluorogermanium(IV) ions, and some are shown in Table XXVII. The

TABLE XXVII

^{19}F spectra of substituted fluorogermanium(IV)[297] complexes

Compound[a]	Solvent	Assignment	δ_F	J(F–F)
$[Ge(OMe)^1F_5]^{2\ominus}$	MeOH	F^2–F^5	−126·6	35·2 ± 0·5
		F^6	−117·6	
$[Ge(OEt)^1F_5]^{2\ominus}$	EtOH	F^2–F^5	−123·2	36·3 ± 0·5
		F^6	−114·7	
$[Ge(ox)^{1,2}F_4]^{2\ominus}$	MeOH	$F^{4,6}$	−134·5	49·2 ± 0·5
		$F^{3,5}$	−119·3	
$[Ge(ox)_2{}^{1,2,3,4}F_2]^{2\ominus}$	MeOH	$F^{5,6}$	−130·2	
$[Ge(mal)^{1,2}F_4]^{2\ominus}$	MeOH	$F^{4,6}$	−128·6	46·7 ± 0·9
		$F^{3,5}$	−120·4	
$[Ge(mal)_2{}^{1,2,3,4}F_2]^{2\ominus}$	MeOH	$F^{3,5}$	−138·2	
$[Ge(Memal)F_4]^{2\ominus}$	MeOH	Fa	−119·8	(a–b) < 3
		Fb	−118·8	(a–c)44·0 ± 0·6
		Fc	−128·5	(b–c)48·9 ± 0·6
$[Ge(Me_2mal)^{1,2}F_4]^{2\ominus}$	MeOH	$F^{4,6}$	−128·5	44·5 ± 0·5
		$F^{3,5}$	−119·6	

[a] Assignments refer to formulae **346** and **347**. ox = oxalato, mal = malonato, Memal = methylmalonato, Me_2mal = dimethylmalonato.

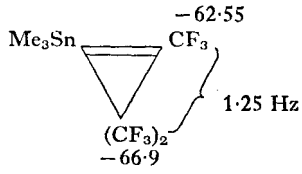
monocarboxylatopentafluorogermanium(IV) complexes also reported have δ_{F6} −122·4 to −119·1 and, with the exception of the chloroacetato and *o*-nitrobenzoato complexes, for which no coupling was observable, the coupling between F^{2-5} and F^6 was 45 to 48 Hz.

Tin

A number of trimethylfluoroalkyltin compounds have been prepared[302] by reaction between hexamethylditin and the corresponding fluoroalkyl iodide, and parameters are shown below. The methyl groups on tin were weakly coupled (0·1 to 0·5 Hz) to β-fluorines, but not observably to the α-fluorines.

	$\delta_{F\alpha}$	$\delta_{F\beta}$	J	$J(^{117}Sn-F_\alpha)$	$J(^{119}Sn-F_\alpha)$
Me_3SnCF_2H	−127·0		45(F–H)	254·5	265·5
$Me_3SnCF_2CF_3$	−113·2	−84·90	1·4(F–F)	208·0	217·8
$Me_3SnCH(CF_3)_2$		−56·1	11·5(F–H)		
$Me_3SnCF(CF_3)_2$	−211·4	−71·1	12·4(F–F)	160·5	167·5

Reaction of bis(trifluoromethyl)diazomethane with 3,3,3-trifluoropropynyltrimethyltin gave the corresponding cyclopropene **354**, with the ^{19}F parameters indicated,[103] which are very similar to those of the germanium analogue **350**.



354

^{19}F shifts in a series of 3,3,3-trifluoropropyltin compounds[303] all fall in the range δ_F −67·5 to −70·0, with vicinal H–F coupling 9·7 to 10·6 Hz. Coupling to tin was small (0 to 5 Hz).

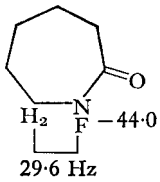
Tin tetrafluoride formed addition compounds[304] with two equivalents of a pyridine-*N*-oxide or quinoline-*N*-oxide which may exist as *cis*- or *trans*- isomers; these showed an unresolved multiplet and a sharp singlet respectively at −40°. Only the *trans*-isomer was observed for the quinoline-*N*-oxides and for 2- or 6- substituted pyridine-*N*-oxides. The ^{19}F shift for these compounds was in the range δ_F −152·2 to −161·4, the lower-field shifts arising from the more bulky substituents. Both isomers

were obtained from pyridine-*N*-oxides with substituents in the 3, 4, or 5-positions; δ_F for the *trans*-isomers was in the narrow range $-161{\cdot}0$ to $-162{\cdot}6$, and for the *cis*-isomers, δ_F $-163{\cdot}7$ to $-166{\cdot}0$. The coupling between ^{119}Sn and fluorine in these complexes ($J = 1956$ to 2056 Hz) was considerably higher than in $[SnF_6]^{2\ominus}$ ($J = 1570$ to 1600 Hz), and appeared to increase with the bulkiness of the ligand.

Group V

Nitrogen

(a) *N–F compounds.* Direct fluorination of amides frequently leads to replacement of N–H by N–F. ^{19}F shifts for such *N*-fluoroamides vary rather unpredictably over a wide range, and a number of examples[305] are given in formulae **355** to **363**. Many of the coupling constants shown were derived from ^1H spectra, since the ^{19}F resonances were often broad and unresolved.



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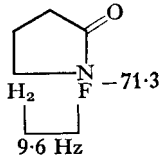

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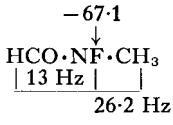

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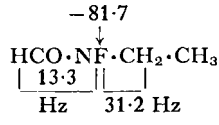

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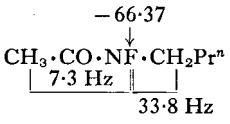

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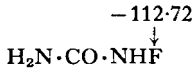

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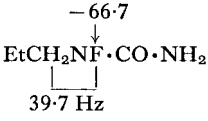

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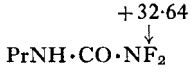

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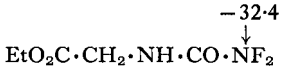
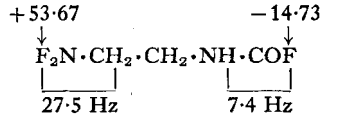


363

Further fluorination of the fluoroamides sometimes led to cleavage and formation of alkyl-NF_2 compounds.[305] As shown in formulae **364** to **367**, and noted previously,[306] δ_F was more constant for these compounds, and coupling to adjacent methylene hydrogens was quite strong. Further examples of derivatives of the type $F_2N{\cdot}CH_2CH_2X$, with parameters similar to those in formulae **364** to **367**, are reported in ref. 305a.

Parameters for other NF_2 compounds, formed by reaction of the NF_2 radical with alkanes and alkenes,[307] are shown in formulae **368** to **371**.



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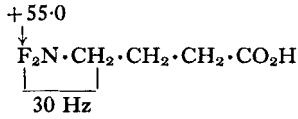

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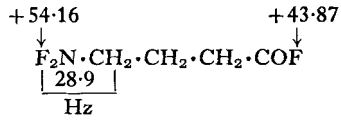

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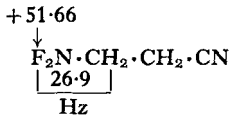

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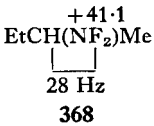

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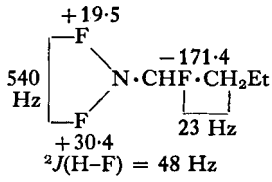

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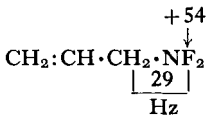

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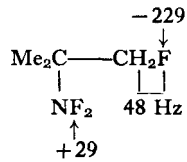
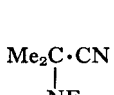


371

Secondary alkyl-NF_2 groups reported[307, 308] had δ_F in the range +37 to +43, with coupling to the adjacent hydrogen again *ca.* 28 Hz. Two examples with the $-NF_2$ group adjacent to an asymmetric centre were reported,[307] and in both the geminal fluorine-fluorine coupling was 540 Hz. For tertiary alkyl-NF_2 compounds δ_F is again to higher field (compounds **371** and **372**). The reaction of olefins with N_2F_4 to give vicinal difluoroamino compounds has been used by Russian workers[308, 309] to give compounds **373** to **375**, and the same workers have also reported parameters for other NF compounds. The shifts of the vicinal NF_2

groups were somewhat to higher field than those of the corresponding mono-difluoroamino compounds.



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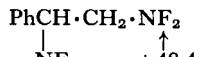

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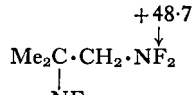

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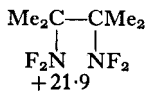

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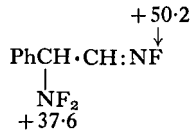

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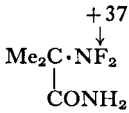

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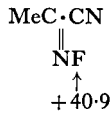

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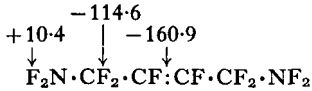

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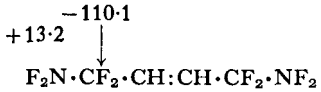

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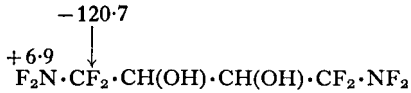

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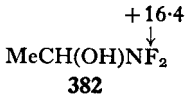

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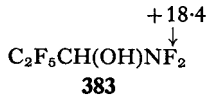

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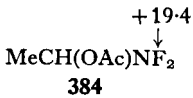

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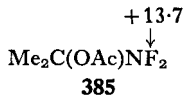

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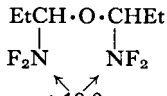
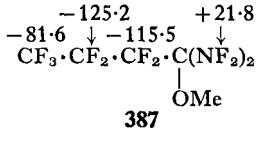


386

Geminal hydroxy difluoroamino compounds have also been prepared[310] by the reaction of carbonyl compounds with difluoroamine, and ^{19}F shifts for some such compounds and some of their derivatives are given with formulae **382** to **386**. Geminal difluoroamino compounds and fluoroamino-difluoroamino compounds, such as those shown in formulae **387** to **390**, have also been reported.[39]

The tris(difluoroamino)methane derivatives $(F_2N)_3C \cdot OR$ (R = Me, Et) were reported[311] to have δ_F +22·2 and +22·8 respectively. Tris[(difluoroamino)-methyl]amine[312] $[(F_2N \cdot CH_2)_3N]$ had δ_F +42·7, with $^3J(F–H) = 24$ Hz. The heterocyclic compounds **391** and **392** had similar values for the $CH_2 \cdot NF_2$ groups, with the $CH \cdot NF_2$ group at higher field.[313]



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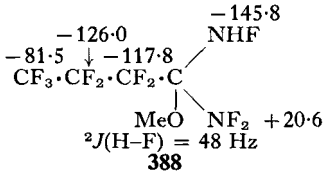

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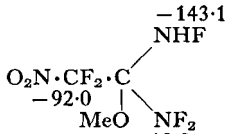

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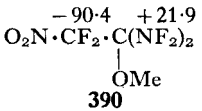

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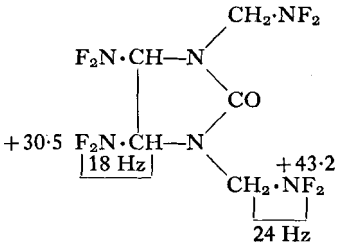

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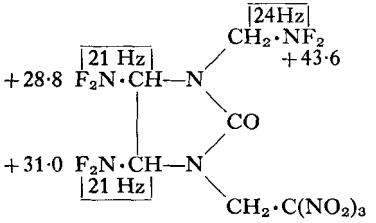

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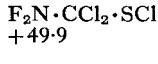

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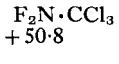

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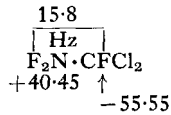
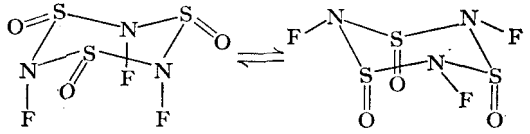


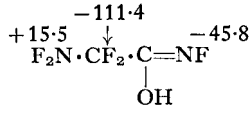
395

The reaction of tetrafluorohydrazine with thiocarbonyl chloride gave several products,[314] with structures and ^{19}F parameters shown in formulae **393** to **395**.

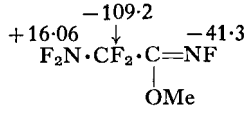
Displacement of fluorine in trimeric sulphanuric fluoride by amines gave mono- and di- substituted products which all showed single signals; those at δ_F +73 appeared to be associated with axial fluorine, and the authors suggest that those at δ_F +77 can be assigned to equatorial fluorine as below and suggest structures on this basis.[315]



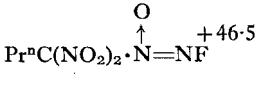
Several groups have prepared a variety of =NF compounds, and parameters are summarised with formulae **396** to **404**.



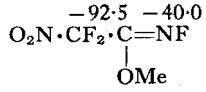
396[316]



397[316]



398[317]



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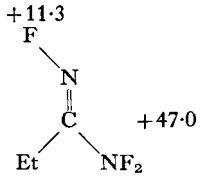
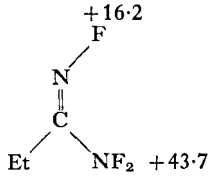
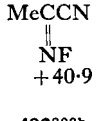


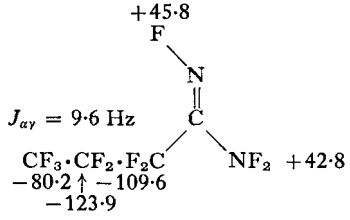
400[39]



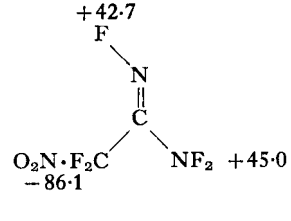
401[39]



402[308b]



403[39]

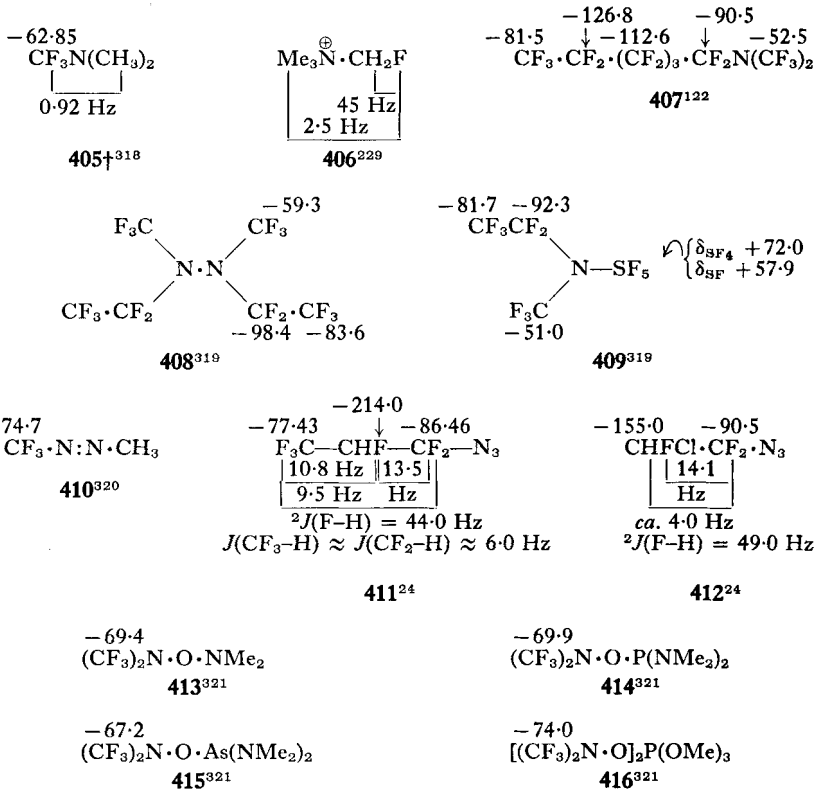


404[39]

Similar parameters were obtained for the *syn* and *anti* isomers corresponding to **401** and **400** with amyl and 2-chloroethyl substituents in place of the ethyl group. The geometry of the *anti*-isomer **400** was deduced from its higher volatility and lower g.l.c. retention time compared with

401. The single isomers **403** and **404** were assigned the structures shown, but the geometry could not be confirmed in the absence of the other isomers. The shift of the =NF group changed markedly on replacement of alkyl by fluoroalkyl substituents on carbon. Coupling to the nitrogen of the nitro-group was observed for compounds **390, 399** and **404.**

(b) *Fluoroalkyl derivatives of nitrogen.* Parameters for a number of fluoroalkylamine and hydrazine derivatives have been reported, and are summarised in formulae **405** to **416**. Parameters for some *N,N*-bis-(trifluoromethylamino)alkyl silicon compounds,[281] and the perfluorocyclohexylamine[122] **185** have already been referred to (pp. 206, 142).



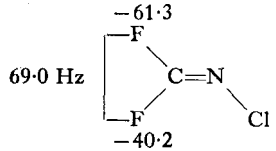
Chang, Porter and Bauer reported[320] δ_F −74·0 for hexafluoroazomethane, rather lower than the value reported by Chambers *et al.*[322]

† R. J. Harder and W. C. Smith (*J. Amer. Chem. Soc.*, 1961, **83**, 3422) reported a singlet, δ_F −71·0.

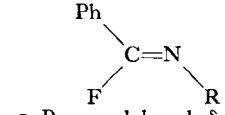
(δ_F −79·7). Electron diffraction showed that this was a *cis*-azo compound, although its IR spectrum was identical to that previously prepared and assumed to be the *trans*-isomer. Trifluoroazomethane, however, was shown to have the *trans*-configuration.[320]

The ^{19}F shift of the $(CF_3)_2N$– group in **413** to **416** was not greatly affected by the groups attached to oxygen. The single signal observed[321] for **416** may be due either to symmetrical disposition of the two $ON(CF_3)_2$ groups or to an exchange process, but this was not investigated.

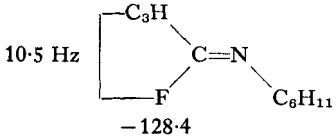
Parameters for compounds containing the C=N bond are summarised in formulae **417** to **422**, and C·N= in formulae **423** to **427**.



417[323]



418[324]



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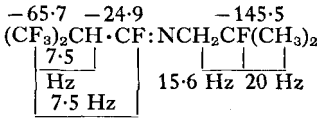
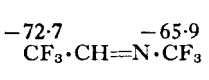
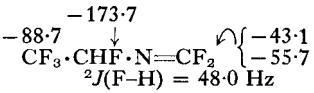


420[43]

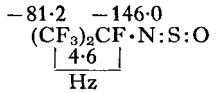


421[24]

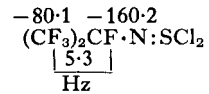


422[24]

423[325]



424[291]



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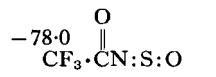
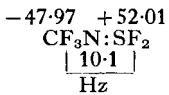


426[291]



427[314]

The high-field band in the spectrum of **417** was broader than the other band, and was assigned[323] to the fluorine shown on the basis of the expected greater interaction with the *trans*-chlorine. Compound **418b** was reported to show two ^{19}F signals of equal intensity separated by 43 Hz, assigned to *syn*- and *anti*- isomers, but only one signal was observed for the other compounds reported.[324]

Phosphorus

(a) *P–F compounds*

(i) *Trico-ordinate phosphorus.* ^{19}F parameters for a number of trico-ordinate P–F compounds are summarised in Table XXVIII. The parameters for di(*t*-butyl)fluorophosphine[326] are similar to those previously reported for dimethylfluorophosphine;[327] δ_F for diphenylfluorophosphine[328] is similar to the value reported for bis(pentafluorophenyl)-fluorophosphine,[329] but the phosphorus-fluorine coupling constant is some 100 Hz smaller. The ^{19}F shifts of the alkoxy- and alkylamino monofluorophosphines are at considerably lower field, and the phosphorus-fluorine couplings are considerably stronger than in the alkyl and aryl compounds. Phosphorus-fluorine coupling in *t*-butyldifluorophosphine[326] is stronger than in other alkyldifluorophosphines, and is similar to that found in the alkoxy- or alkylamino- difluorophosphines.

Aminodifluorophosphine was prepared by a vapour-phase reaction between ammonia and chlorodifluorophosphine.[330] Dideuteroaminodifluorophosphine was also prepared, and a doublet [J(P–F) = 1184 Hz] was reported. Difluoroaminodifluorophosphine is reported[331] to be explosive in all phases and at temperatures down to $-196°$. The parameters in Table XXVIII were recorded at $-60°$.

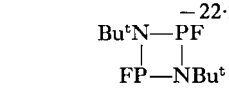
The spectrum of μ-thiobis(difluorophosphine), illustrated in the paper[332] for two temperatures, was analysed as an XX′AA′X″X‴ system for a number of temperatures, and spin-tickling experiments were used to determine the signs of all the coupling constants relative to ^1J(P–F) negative. The phosphorus-phosphorus coupling constant was markedly temperature dependent (+274 Hz at 39°, +392 Hz at 120°), but not very dependent on concentration. Other coupling constants apart from ^2J(F–F)[125 Hz at $-42°$, 100 Hz at $-1°$ neat, 125 Hz at $-1°$ for 20 mol %, 141 Hz at $+31°$†] showed only smaller variations; at $-1°$ they were: ^2J(P–P) = 302·2 Hz, ^3J(P–F) +30·1 Hz, ^4J(F–F) = +8·86 Hz, ^4J(F–P′) = +2·12 Hz. The spectrum of methylaminobis(difluorophosphine)[333] was reinvestigated[332] at a number of temperatures. The values obtained

† The spectrum is not, however, very sensitive to changes in ^2J(F–F) and the probable errors are quoted as "about 30 Hz".

at +30° agree well with those previously reported, except that the present authors[332] found $^2J(F-F) = 39 \pm 4$ Hz, compared with 0 Hz for best fit of computed with observed spectrum in the previous analysis. The variation in $^2J(P-P)$ (+442·7 Hz at −70°, +433·0 Hz at +30°) was much less marked than in the sulphur compound, and it was suggested that the P–S–P bonding is much less rigid than that for P–N–P.

The spectrum of diphosphorus tetrafluoride[334] has also been re-investigated over a range of temperatures (spectra for two temperatures are illustrated in the paper) with spin-tickling.[332] The experimental value for $^1J(P-P)$ (−230 Hz) was opposite in sign to the prediction from theory. Other coupling constants obtained were: $^2J(P-F) = +65{\cdot}8$ Hz, $^2J(F-F) = +277$ Hz, $^3J(F-F) = +34{\cdot}99$ Hz, $^3J(F-F') = -1{\cdot}70$ Hz.

The difluorodiazadiphosphetidine (**428**) has also been prepared,[335] and the parameters derived by analysis of the AA'XX' spectrum are given with the formula.



$^1J(P-F) = -1190$ Hz $^4J(F-F') = 29{\cdot}0$ Hz
$^3J(P-F') = +25{\cdot}5$ Hz $^2J(P-P') = 92{\cdot}5$ Hz

428

TABLE XXVIII

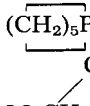
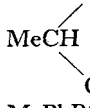
^{19}F parameters for trico-ordinate P–F compounds

Compound	δ_F	J(P–F)	J(F–H)	Ref.
Ph_2PF	−202	905	..	328
$(Me_3C)_2PF$	−223·5	848	2·1	326
$(MeO)_2PF$	−63·4	1210	0·6	336
$(EtO)_2PF$	−58·9	1209	..	336
$(Bu^tNH)_2PF$	−54	1013	4·6(F–NH)	337
$(MeO)(Et_2N)PF$	−72·2	1120	3·1(F–CH_2)	336
$(C_4H_9S)(Me)PF$	..	960	..	338
$Me_3C \cdot PF_2$	−111·5	1219	*ca.* 1·8	326
$EtO \cdot PF_2$	−49·0	1284	..	336
$EtNH \cdot PF_2$	−67	1195	10·8(F–NH) 2·0(F–CH_2)	337
$Bu^nNH \cdot PF_2$	−67	1193	10·9(F–NH) 1·9(F–CH_2)	337
$Bu^tNH \cdot PF_2$	−61	1195	12·4(F–NH)	337
$(CH_2{:}CH \cdot CH_2)_2N \cdot PF_2$	−63·7	1202	2·5	336
$H_2N \cdot PF_2$[a]	−58·3	1188	12·6	330
$MeN(PF_2)_2$[b]	−74·69	−1263·1	..	331
$F_2N \cdot PF_2$	−71·8[c]	1336	..	332
$F_2P \cdot PF_2$[d]	−114·0	−1194·1	..	332
$S(PF_2)_2$[e]	−65·3	−1307·0	..	332

[a] Neat liquid at −1°C.
[b] 37 mol% in light petroleum (36 mol%) and $CFCl_3$ (27 mol%) at +1°C.
[c] For PF_2; δ_{NF_2} +2·0, ^2J(F–NP) = 120 Hz, ^3J(F–F) = 13·2 Hz.
[d] Neat liquid at −1°C.
[e] 90 mol% in $CFCl_3$ at −1°C.

TABLE XXIX

Monohalogeno tetraco-ordinate P(O) compounds

Compound	δ_F	^1J(P–F)	J(F–H)	Ref.
$Me_2P(O)F$	−65·0	980	8·5	336
$n Bu_2P(O)F$	−77·3	1009	7	336
$t Bu_2P(O)F$	−104·2	1090	<1	326
	−84·9	1016		336
	−91·8	1200		336
$MePhP(O)F$	−66·5	997	8	336
$(H_2N)PhP(O)F$	−58·6	985·3		339
$(H_2N)(C_6H_{11})P(O)F$	−66·0	1022·0		339
$(H_2N)EtP(O)F$	−58·7	1003·9	4	339
$(H_2N)MeP(O)F$	−49·4	986·5	6·5	339
$(Me_2N)MeP(O)F$	−60·0	1017	6·0 (F–CH_3) 2·4 (F–NCH_3)	336
$(Me_2N)PhP(O)F$	−72·4	1019	2·3	336
$(MeO)HP(O)F$	−67·8	1056	115 (F–PH)	340
$(MeO)MeP(O)F$	−62·0	1039	6·1 (F–CH_3) 0·8 (F–OCH_3)	336
$(MeO)PhP(O)F$	−66·3	1035	0·5	336
$(EtO)EtP(O)F$	−73·1	1055		341
$(EtO)PhP(O)F$	−63·8	1035		336
$(n BuO)PhP(O)F$	−64·0	1037		336
$(EtSCH{:}CH)(EtO)P(O)F$	−64·0	1013		336
$(EtO)_2P(O)F$	−81·5	970		336
$(i PrO)_2P(O)F$	−77·5	968		336
$(PhO)_2P(O)F$	−78·5	1001		336
$(H_2N)(MeO)P(O)F$	−72	942·6		339
$(H_2N)(PhO)P(O)F$	−67·5	952·5		339
$(H_2N)(EtO)P(O)F$	−69·3	942·1		339
$(H_2N)_2P(O)F$	−59·4	913		339
$(Me_2N)_2P(O)F$	−82·9	941		336
$(H_2N)(MeNH)P(O)F$	−67·5	919·0		339
$(H_2N)(PhS)P(O)F$	−66·6	1023		339
$MeP(O)(O^{\ominus})F$	−56·0	962	6·0	336
$ClCH_2P(O)(O^{\ominus})F$	−62·1	980	4·2	336
$PhP(O)(O^{\ominus})F$	−53·9	963		336
$MeOP(O)(O^{\ominus})F$	−70·5	896		336
$i PrOP(O)(O^{\ominus})F$	−76·0	920		336
Na_2PO_3F	−73·0	863		336
$(NH_4)_2PO_3F$	−73·3	895		336

(ii) *Tetraco-ordinate phosphorus.* ^{19}F parameters for a number of monofluorophosphonic acids and their derivatives, and monofluorophosphoric acid derivatives are collected in Table XXIX, and of some thio-analogues in Table XXX. With few exceptions δ_F for the former was in the range -55 to -80 and ^1J(P–F) 950 to 1035 Hz. For the thio compounds the coupling constant was generally a little higher and δ_F spanned a rather wider range. The correlation between Pauling electronegativity of the group R and δ_F for the series $(H_2N)RP(O)F$ has been pointed out.[339] The parameters for difluorophosphinic and difluorophosphoric acid derivatives are given in Table XXXI, and of some thio-analogues in Table XXXII. Where direct comparisons are possible, it appears that the thio-compounds have δ_F some 20 p.p.m. to low field of the oxygen-compounds, with J(P–F) greater by some 40 to 80 Hz. As with the monofluoro compounds, the *t*-butyl compounds had larger coupling constants than normal, and absorbed at higher field.

TABLE XXX

Monohalogeno P(S)F compounds

Compound	δ_F	^1J(P–F)	J(F–H)	Ref.
$Me_2P(S)F$	−75·7	985	7·8	336
$nBu_2P(S)F$	−88·1	1009	7·0	336
$tBu_2P(S)F$	−119·6	1093	<1	326
$(CH_2)_5P(S)F$	−75·7	985	13·3	336
MePhP(S)F	−76·4	1003	7·2	336
(EtS)MeP(S)F	−41·8	1093	6·4 (F–CH_3) 1·8 (F–CH_2)	336
(EtO)EtP(S)F	−49·9	1100	3·9 (F–PCH_2)	336
(MeO)PhP(S)F	−47·5	1084		336
$(Me_2N)MeP(S)F$	−51·5	1046	6·2 (F–CH_3) 3·1 (F–NCH_3)	336
(MeNH)MeP(S)F	−45·4	1043	6·4 (F–CH_3) 3·0 (F–NCH_3)	336
$(Et_2N)PhP(S)F$	−59·6	1059		336
$(Me_2N)(CH_2{:}CH)P(S)F$	−57·7	1045		336
$(MeO)_2P(S)F$	−48·5	1080		336
$(PhO)_2P(S)F$	−41·7	1105		336
$(Me_2N)_2P(S)F$	−59·5	1014	1·6	336

The preparation of difluorophosphine oxide from alcohol and F_2POPF_2 has been reported.[340] With boron trifluoride it first formed a weak complex **429** which dissociated in the vapour phase at room temperature, but this subsequently formed compound **430**, together with

TABLE XXXI

Dihalogeno P(O) compounds

Compound	δ_F	^1J(P–F)	J(F–H)	Ref.
MeP(O)FBr	−21·1	1153		342
$MeP(O)F_2$	−60·4	1104	6·0	336
$EtP(O)F_2$	−74·1	1135		341
$c\text{-}C_6H_{11}P(O)F_2$	−74·2	1153	2·5	336
$m\text{-}FC_6H_4P(O)F_2$	−65·8	1100		336
$2,5\text{-}Me_2C_6H_3P(O)F_2$	−64·0	1118		336
$PhCH{:}CHP(O)F_2$	−64·5	1084		336
$[c\text{-}(CH_2)_4C(Me)]P(O)F_2$	−79·3	1167		336
PhP(O)ClF	−36·6	1135		336
$t\text{-}BuP(O)F_2$	−84·3	1195	*ca.* 1·0	326
$F_2(S)P{\cdot}O{\cdot}P(O)F_2$	−79·4[a]	1057·2		343
$Me_2NP(O)F_2$	−81·4	1004		336
$Et_2NP(O)F_2$	−78·6	1001		336
$MeNHP(O)F_2$	−80·8	985·5	2·5 (F–NH) 1·3 (F–PNMe)	339
KPO_2F_2	−82·2	960		336
$MeOP(O)F_2$	−87·5[b]	1008	0·5	336
$PhOP(O)F_2$	−84·1	1027		336
$F_2P(O)OP(O)F_2$	−85·7	980		336

[a] For $P(O)F_2$ group $^3J(P'\text{–}F) \leq 0{\cdot}5$ Hz, $^4J(F\text{–}F) = 2{\cdot}7$ Hz; δ_F for $P(S)F_2$ −41·0, $^1J(P\text{–}F) = 1177{\cdot}1$ Hz, $^3J(P'\text{–}F) = 3{\cdot}5$ Hz.
[b] Roesky and Kloker (ref. 339) give −89·4.

TABLE XXXII

Dihalogeno P(S) compounds

Compound	δ_F	^1J(P–F)	J(F–H)	Ref.
$MeP(S)F_2$	−41·5	1147	6·2	336
$t\text{-}BuP(S)F_2$	−65·5	1209	0·8	326
$PhP(S)F_2$	−46·1	1140		326
$ClCH_2P(S)F_2$	−52·8	1180	5·5	326
$PhCH{:}CHP(S)F_2$	−45·3	1118		326
$Me_2NP(S)F_2$	−51·5	1081	2·1	326
$Et_2NP(S)F_2$	−49·0	1082		326
$MeOP(S)F_2$	−48·4	1121	0·7	326
$PhOP(S)F_2$	−45·6	1140		326
$CCl_3S{\cdot}S{\cdot}P(S)F_2$	−25·2	1261		344
$CCl_3{\cdot}CO{\cdot}S{\cdot}P(S)F_2$	−23·5	1261		344
$NC{\cdot}P(S)F_2$	−33·15	1148		345
$N_3{\cdot}P(S)F_2$	−42·9	1140		345
$OCN{\cdot}P(S)F_2$	−41·7	1176		345
$SCN{\cdot}P(S)F_2$	−37·80	1120		345

PF_3 and BF_3. The parameters for these compounds, and for the products of reaction of the phosphine oxide with amines, are given with the formulae.

$$\underset{\underset{\underset{

TABLE XXXIII

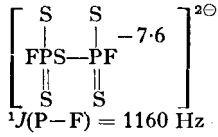
^{19}F parameters of phosphazene derivatives

Compound	$\delta_{FP:N}$	^1J(P–F)	Other δ_F	Assignment	J	Assignment	Ref.
$(S)PF_2 \cdot N:PF_2Ph$	−67·6	1092	−35·02	$P(S)F_2$	1050	^1J(P(S)–F)	347
$(S)PFCl \cdot N:PF_2Ph$	−67·5	1105	−4·01	P(S)F	1096	^1J(P(S)–F)	347
$P_3N_3F_5 \cdot N:PF_2Ph$	−66·5	..	..	..	..	..	347
$(S)PCl_2 \cdot N:PF_2Ph$	−66·9	1106	..	..	..	..	347
$FSO_2N:PF_2Ph$	−71·2	1127	+59·4	SO_2F	7·2	J(F–P)	347
					4·2	J(F–F)	
$FSO_2N:PF_2 \cdot NMe_2$	−79·43	1025	+58·0	SO_2F	4·2	J(F–P)	348
					8·1	J(F–F)	
$FSO_2N:PF_2 \cdot NCS$	−72·24	983	+57·62	SO_2F	8·7	J(F–P)	348
					6	J(F–F)	
$FSO_2N:PF(NMe_2)_2$	−82·50	955	+58·90	SO_2F	5·5	J(F–P)	348
					2·0	J(F–F)	
$ClSO_2N:PF_2 \cdot NMe_2$	−79·20	1036	..	..	2·1	J(F–H)	348
$ClSO_2N:PF_2 \cdot NCS$	−72·51	993	..	..	..	..	348
$(S)PF_2 \cdot N:PF_2 \cdot N:PCl_3$	−67·3	..	−35·1	$(S)PF_2$	..	..	349
$(S)PFCl \cdot N:PF_2 \cdot N:PCl_3$	−66·9	..	−3·7	(S)PFCl	..	..	349
$(S)PF_2 \cdot N:PF_2 \cdot NHSiMe_3$	−66·5	..	−36·4	$(S)PF_2$	..	..	349
$(CF_3)_2(H_2N)C \cdot N:PF_2Me$	−69·1	1115	..	..	..	..	350
$(S)PF_2 \cdot N:PF_2(NH_2)$	−67·4	..	−35·8	$(S)PF_2$	..	..	346
$(S)PFCl \cdot N:PF_2(NH_2)$	−68·9	..	−5·3	(S)PFCl	..	..	346
$(S)PF_2 \cdot N:PCl_2Me$	..	..	−33·4	$(S)PF_2$	..	..	351
$(S)PFCl \cdot N:PCl_2Me$	..	..	−3·05	(S)PFCl	1102	^1J(P–F)	351
					20·5	^3J(P–F)	
$(S)PF_2 \cdot N:PCl_2CCl_3$	..	..	−32·7	$(S)PF_2$	1070	^1J(P–F)	351
$(S)PFCl \cdot N:PCl_2CCl_3$	..	..	−2·66	(S)PFCl	1102	^1J(P–F)	351
					16	^3J(P–F)	
$(O)PFCl \cdot N:PCl_2Me$	..	..	−30·25	(O)PFCl	1033	^1J(P–F)	351
					21·5	^3J(P–F)	
$(O)PF_2 \cdot N:PCl_2CCl_3$	..	..	−69·0	$(O)PF_2$	955	^1J(P–F)	351
$(O)PFCl \cdot N:PCl_2CCl_3$	..	..	−29·2	(O)PFCl	1041	^1J(P–F)	351
					19·5	^3J(P–F)	

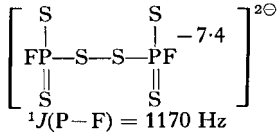
15·8
HF_2PS_2
1214 Hz
436†[355]

28·6
$(F_2PS_2)_2$
1268 Hz
437†[355]

24·2
$EtPS_2F_2$
1206 Hz
438†[355]



$^1J(P-F) = 1160$ Hz
439†[355]



$^1J(P-F) = 1170$ Hz
440†[355]

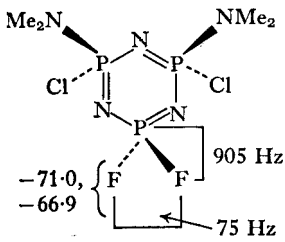
−39·24
$(MePS_2F)_3As$
$^1J(P-F) = 1111$ Hz
$^3J(H-F) = 39$Hz
441[356]

−48·3
$(EtPS_2F)_3Sb$
1123 Hz
442[356]

−46·8
$(EtPS_2F)_2SnCl_2$
1133 Hz
443[356]

Phosphonitrilic Compounds

The reaction of *cis-* and *trans-* 1,3-bis(dimethylamino)tetrachlorotriphosphonitrile[357] with potassium fluorosulphite led to replacement of the geminal chlorines and formation of **444** and **445**, readily distinguished by their ^{19}F spectra. The reaction with antimony trifluoride gave different products which were clearly the 1,3-difluoro-compounds **446** and **447**, but assignment of stereochemistry was less certain. Treatment of **446** and **447** with potassium fluorosulphite gave the tetrafluoro compounds **448** and **449**. The spectra are illustrated in the paper, and the parameters given with the formulae are those obtained by the authors by measurement without second-order analysis.



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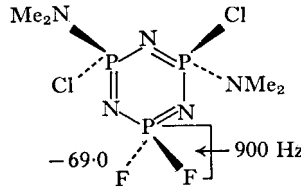

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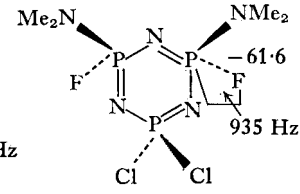


446

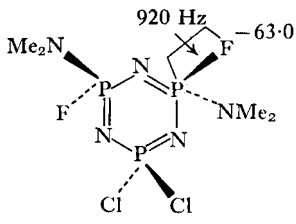
† ^{19}F shift values are given in this paper and in ref. 353 as δ values from $CFCl_3$, and it is assumed here that the low field +ve convention has been used.

TABLE XXXIV

Substituted phosphonitrilic compounds

Compound	PFX group δ_F	PFX group "J(P–F)"[a]	PF_2 group δ_F	PF_2 group "J(P–F)"[a]	Ref.
$N_3P_3F_6$			−71·9	868	358
$N_4P_4F_8$			−71·9	836	358
$N_5P_5F_{10}$			−69·0	874	358
$N_6P_6F_{12}$			−68·6	885	358
$N_3P_3F_5NMe_2$	−62·1	870	−70·9	809	358
$N_4P_4F_7NMe_2$	−59·2	905	−69·9	854	358
$N_5P_5F_9NMe_2$	−57·3	924	−67·2	889	358
$N_6P_6F_{11}NMe_2$	−58·3	930	−66·9	902	358
gem $N_3P_3F_4(NMe_2)_2$			−70·1	863	358
1,3-$N_3P_3F_4(NMe_2)_2$	−61·6	900[b]			358
	−63·0	890[b]			
$N_4P_4F_6(NMe_2)_2$	−60·0	916	−69·4	913	358
$N_5P_5F_8(NMe_2)_2$	−58·9	918	−66·9	889	358
$N_6P_6F_{10}(NMe_2)_2$	−59·0	923	−66·4	907	358
$N_6P_6F_9(NMe_2)_3$	−59·5	924	−66·3	907	358
$N_3P_3F_5NCS$	−49·6	865	−67·9	908	358
$N_4P_4F_7NCS$	−53·9	843	−69·9	849	358
$N_5P_5F_9NCS$	−52·3	864	−67·1	932	358
$N_6P_6F_{11}NCS$	−51·7	866	−67·1	903	358
$N_3P_3F_5Cl$[c]	−30·7	994	−70·2	886	358
$N_4P_4F_7Cl$[c]	−38·2	924	−70·3	851	358
$N_5P_5F_9Cl$	−33·9	952	−67·4	895	358
$N_6P_6F_{11}Cl$	−32·8	974	−67·1	907	358
$N_3P_3F_5Br$	−19·6	1056	−70·0	925	358
$N_4P_4F_7Br$	−30·6	974	−70·6	884	358
$N_5P_5F_9Br$	−25·0	1016	−67·5	905	358
$N_6P_6F_{11}Br$	−23·4	1032	−67·0	918	358
$N_3P_3F_5N{:}SF_2$[d]	−51·5	900	−70	880	359
$N_3P_3F_5N{:}S{:}O$	−57	920	−70	890	359
$N_3P_3F_5N{:}SCl_2$	−51·5	920	−69	900	359
$(N_3P_3F_5N)_2S$	−55·5	920	−70	890	359
$N_3P_3F_3(NMe_2)_3$	−63	890			360
$N_3P_3F_3Cl(NMe_2)_2$	−63	890 ($PFNMe_2$)			360
	−29	960 (PFCl)			
$N_3P_3F_3Br(NMe_2)_2$	−62	910 ($PFNMe_2$)			360
	−18·5	1020 (PFBr)			
$N_3P_3F_4Cl_2$	−31·5	960	[e]		360
$N_3P_3F_4Br_2$	−20	1000	[e]		360
$N_3P_3F_4BrCl$	−30·5	980 (PFCl)	[e]		360
	−20	1040 (PFBr)			

[a] Measured values, no account taken of long-range coupling.
[b] Probably *cis*- and *trans*- isomers. Ref. 360 also gives δ_F −63, J(P–F) = 890 Hz for $N_3P_3F_4(NMe_2)_2$.
[c] Supersede values given in J. Emsley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 2590.
[d] NSF_2 group δ_F +59·5, ^3J(F–P) = 26 Hz, ^4J(F–F) = 5 Hz, ^5J(F–P) = 1·8 Hz.
[e] Not reported.



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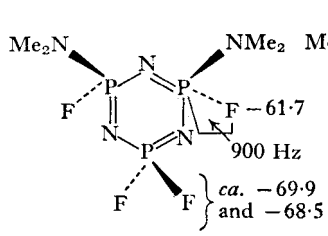

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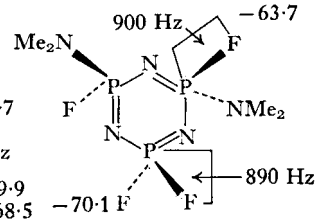

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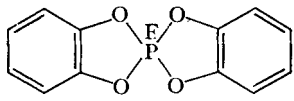
Dimethylamination of phosphonitrilic fluorides $(NPF_2)_n$ ($n=3$ to 6) has been reported;[358] the dimethylamino group allowed the formation of a range of substituted phosphonitrilic fluorides, and parameters are given in Table XXXIV.

(iii) *Pentaco-ordinate phosphorus*. The fluorine in mono- and di- fluorophosphoranes is usually found, unless there is some compelling reason to the contrary, in the axial position of the trigonal bipyramid. ^{19}F shifts are usually low, and the phosphorus-fluorine coupling constant is also usually considerably lower than the values found for equatorial fluorines. One instance (**450**) where a single fluorine occupied an equatorial position has been reported,[361] the other ligands requiring *cis* positions; rather similar compounds containing chelating nitrogen have previously been reported.[362]



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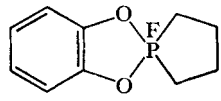

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^{19}F parameters for mono- and di- fluorophosphoranes, prepared by a variety of routes, are listed in Table XXXV.

Further parameters for trimethyldifluorophosphorane have been obtained,[363] and relative signs deduced from double resonance experiments are given below, relative to positive ^1J(C–H).

$$^1J(\text{P–F}) = -552{\cdot}2 \pm 1{\cdot}0 \text{ Hz}$$
$$^2J(^{13}\text{C–F}) = +30{\cdot}9 \pm 0{\cdot}5 \text{ Hz}$$
$$^3J(\text{H–F}) = +12{\cdot}17 \pm 0{\cdot}05 \text{ Hz}$$

The dichlorodifluorophosphoranes, $ROPF_2Cl_2$, were detectable only at low temperatures, and were assigned[364] structures with axial fluorine because of the low value of the phosphorus-fluorine coupling. The dialkoxy compounds $(RO)_2PFCl_2$ were even less stable, and only the cyclic compounds could be examined spectroscopically. The regular

movement of the ^{19}F signal to high field as methyl groups of Me_3PF_2 were replaced by phenyl groups has been noted.[336] The rather surprising difference (35 p.p.m.) between δ_F for Me_3PF_2 and the ethyl compound

TABLE XXXV

^{19}F parameters for mono- and di- fluorophosphoranes

Compound	δ_F	^1J(P–F)	Ref.
Me_3PF_2	−4·8	−552·2	336, 363
Et_3PF_2	−39·8	580	336
Ph_3PF_2	−40·4	660	336
$PhMe_2PF_2$	−16·9	586	336
Ph_2MePF_2	−28·5	636	336
$(CH_2)_2CHMeCH_2—PF_2Ph$	−28·6	613	336
$(MeNH)_2PHF_2$[a]	−62	655	337
$(EtNH)_2PHF_2$[b]	−60	660	337
$(n\text{-}BuNH)_2PHF_2$[a]	−59	658	337
Ph_2PHF_2[c]	−52·5	637	328
$t\text{-}Bu_3PF_2$	−59·1	808	326
$o\text{-}C_6H_4O_2PPh_2F$	−31	797	361
451	−21·65	829·2	361
450	−70·4	1018	361
$MeOPF_2Cl_2$	+44·9	960	364
$BuOPF_2Cl_2$	+46·9	910	364
$PhOPF_2Cl_2$	+48·9	1020	364
$PhOPF_2Br_2$	+77·9	1025	364
$O(CH_2)_2OPFCl_2$	+47·9	915	364
$O(CH_2)_3OPFCl_2$	+49·9	930	364
$o\text{-}C_6H_4O_2PFCl_2$	+41·9	940	364
$o\text{-}C_6H_4O_2PFBr_2$	+77·9	975	364
$(MeS)Ph_2PF_2$	−25·0	760	365
$(EtS)Ph_2PF_2$	−25·2	752	365
$(PhS)Ph_2PF_2$	−23·5	796	365
$(PhCH_2NMe)Ph_2PF_2$	−39·1	717	366
$(Me_2N)Me_2PF_2$[d]	−14·4	654	367
$(Et_2N)Me_2PF_2$[e]	−18·0	663	367
$(Et_2N)MePhPF_2$	−28·2	693	367
$(Me_2N)Ph_2PF_2$	−35·8	709	367
$(Et_2N)Ph_2PF_2$	−40·1	730	367

[a] ^2J(F–H) = 118 Hz.
[b] ^2J(F–H) = 117 Hz.
[c] ^2J(F–H) = 115 Hz; identified only by NMR spectra.
[d] J(MeN–F) = 2·6 Hz, J(CH_3–F) = 13·1 Hz.
[e] J(CH_3–F) = 12·7 Hz.

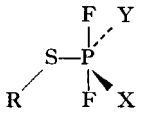
has been discussed,[336] and rationalisation in terms of closer proximity of the methyl hydrogens of the ethyl groups suggested. There is a further move to high field (*ca.* 20 p.p.m.) for the *t*-butyl compound.[326] When the alkyl groups are one atom removed from phosphorus there is little difference between ethyl and methyl compounds.

The two axial fluorine atoms in alkylthiodifluorophosphoranes[365] $(RS)Ph_2PF_2$ (R = Me, Et), and in (benzylmethylamino)diphenyldifluorophosphorane,[366] equivalent at room temperature, became non-equivalent as the temperature was reduced, and the parameters obtained at $-80°$ are shown below.

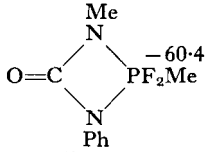
	$J(P-F_1)$	$J(P-F_2)$	$J(F_1-F_2)$	δ_{F1}	δ_{F2}
$(MeS)Ph_2PF_2$	694	823	28	−22·2	−31·1
$(EtS)Ph_2PF_2$	700	800	[a]	−23·0	−32·2
$(PhCH_2NMe)Ph_2PF_2$	712	710		−37·3	−40·0

[a] Solution too viscous for resolution.

The temperature variation of the spectra was ascribed to slowing down of rotation about the P–S or P–N bond, which resulted in the alkyl group being held closer to one of the axial fluorines than the other.

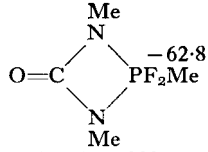


The difluorophosphoranes **452** to **455** were expected to have one axial and one equatorial fluorine because the four-membered ring uses one axial and one equatorial position for bonding.[368] In **452** and **454** the two positions were distinguished at low temperature (-40 to $-50°$), and parameters for axial and equatorial fluorines are given below. The activation energy for the interconversion was found to be 18 ± 3 kcal mole^{-1}. The symmetrically substituted compounds **453** and **455**, however, showed no change in their spectra down to $-90°$, apparently because the pseudo-rotation process made the fluorine atoms equivalent.



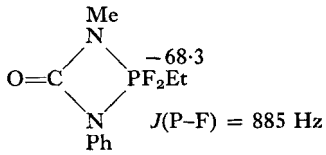
$J(P-F) = 945$ Hz

452

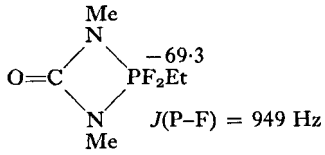


$J(P-F) = 930$ Hz

453



454



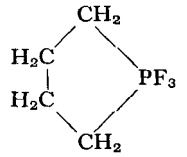
455

Compound	Temp.	δ_{Fa}	δ_{Fe}	J(P–Fa)	J(P–Fe)	J(Fa–Fe)
452	−40°C	−43·8	−78·2	868	966	49
454	−50°C	−56·2	−81·3	840	980	48·4

Intermolecular exchange in trimethyldifluorophosphorane has also been studied.[369] The compound had a ^{1}H spectrum which consisted, either at low temperature (−110°) or at low concentration and higher temperature (−40°), of a doublet of triplets [J(P–H) = 17·3 Hz, J(F–H) = 12·8 Hz]. This broadened as the temperature was raised, or as the concentration was increased, to give a sharp doublet (17·3 Hz). The process was shown to be bimolecular, and the loss of fluorine-hydrogen coupling suggested that phosphorus-fluorine bonds were being broken in the exchange process. In accord with this, the phosphorus-fluorine coupling in the ^{19}F spectrum was collapsed at ~100° compared with a calculated temperature of 99·2°.

The diethylamide of difluorophosphorous acid formed[370] a 1:2 complex with hexafluoroacetone [δ_{PF} −66·1, J(P–F) = 810 Hz; δ_{CF_3} −67·1]. Similar complexes for $(MeO)_2PF$ and $(i\text{-}PrO)_2PF$ with two equivalents of hexafluoroacetone had phosphorus-fluorine couplings of 915 and 930 Hz respectively.

Trifluorophosphoranes frequently show distinct signals for the axial and equatorial fluorine atoms (Table XXXVI), but exchange at room temperature sometimes allows the observation of only a time-averaged spectrum, as with compound **456**.[336]



J(P–F) = 916 Hz

456

Signs of coupling constants have been determined[363] for dimethyltrifluorophosphorane at −40°, relative to ^1J(C–H) positive, and are as follows: $^1J(P\text{–}F_{ax}) = -781{\cdot}6 \pm 1{\cdot}0$ Hz; $^1J(P\text{–}F_{eq}) = -976{\cdot}2 \pm 1{\cdot}0$ Hz; $^2J(F_{ax}\text{–}F_{eq}) = -28{\cdot}1 \pm 0{\cdot}5$ Hz; $^3J(H\text{–}F_{ax}) = +12{\cdot}6 \pm 0{\cdot}2$ Hz; $^3J(H\text{–}F_{eq}) = +3{\cdot}05 \pm 0{\cdot}1$ Hz.

TABLE XXXVI

^{19}F parameters for trifluorophosphoranes

Compound	$\delta_{F_{ax}}$	$^1J(P-F_{ax})$	$\delta_{F_{eq}}$	$^1J(P-F_{eq})$	$^2J(F-F)$	Ref.
$(t\text{-Bu})_2PF_3$[a]	−48·6	907·6	−92·3	975·8	30·0	326
$(MeS)MePF_3$	+1·2	925	−75·2	1062	62·0	365
$(MeS)PhPF_3$[b]	−15·0	942	−71·9	1042	60·5	365
$(EtS)MePF_3$	+1·2	897	−72·7	1022	[c]	365
$(PhS)PhPF_3$	−13·6	970	−71·3	1066	60·0	365
$(MeNH)_2PF_3$[d]	−62	703	−78	868	41·2	371
$(EtNH)_2PF_3$	−62	694	−76	875	41·7	371
$(t\text{-BuNH})_2PF_3$[e]	−47	726	−69	897	47·7	371
$(EtO)MePF_3$	−33·1	850	−77·1	990	62	341
$(EtO)EtPF_3$	−33·1	875	−75·1	1005	60	341
$CH_2(CH_2)_3CH_2PF_3$	−19·4	801	−83·0	998	..	336
$(H_2N)_2PF_3$	−51·3	672	−77·3	860	40	372
$(i\text{-PrMeN})MePF_3$[f]	−36·1	803	−74·3	965	55	373
$(PhCH_2NMe)PhPF_3$	−42·5	824	−68·3	975	..	366

[a] Parameters at −40°. At room temperature the F–F coupling is not resolved.
[b] Similar parameters are reported for $(EtS)PhPF_3$ in ref. 365 and also in ref. 373.
[c] Not resolved at room temperature.
[d] $J(F_{eq}\text{–NCH}) = 1·9$ Hz.
[e] $J(F_{ax}\text{–NH}) = 16·1$ Hz.
[f] Axial fluorines non-equivalent below 0°, but parameters not given.

TABLE XXXVII

^{19}F parameters of tetrafluorophosphoranes

Compound	δ_F	$^1J(P-F)$	Ref.
$t\text{-BuPF}_4$[a]	−59·4	1060	326
$m\text{-CF}_3\cdot C_6H_4\cdot PF_4$[b]	−53·9	964	336
$p\text{-MeO}\cdot C_6H_4\cdot PF_4$	−55·8	951	336
$S\cdot CH{:}CH\cdot CH\cdot C\cdot PF_4$	−52·5	928	336
$2,5\text{-Me}_2C_6H_3\cdot PF_4$	−45·6	980	336
$EtNHPF_4$	−75	800	371
$t\text{-BuNHPF}_4$	−65	830	371
$MeSPF_4$[c]	−45·5	1032	365
$EtSPF_4$	−42·1	1045	365
$PhSPF_4$	−45·1	1060	365
$[PhCH_2NMe]PF_4$	−67·6	876	366

[a] At −40°, $J(F_{ax} - F_{eq}) = -30·0$ Hz.
[b] δ_{CF_3} −63·9.
[c] Ref. 375 gives δ_F −41·5, $J(P\text{-}F) = 1019$ Hz, $J(H\text{-}F) = 1·5$ Hz.

The low-temperature spectra of the alkyl- and aryl- thiotrifluorophosphoranes,[365] (RS)R'PF_3, and of the benzylmethylamino-compound[366] showed similar non-equivalence of the axial fluorine atoms to that shown by the corresponding difluorophosphoranes and attributed to hindered rotation about the phosphorus-sulphur or -nitrogen bond. Similar non-equivalence was reported for a series of bis(alkylamino)trifluorophosphoranes at room temperature.[373, 374] Parameters are given below.

Compound	$\delta_{F_{eq}}$	$\delta_{F_{ax}}$	$^1J(P-F_{eq})$	$^1J(P-F_{ax})$	$^2J(F_{ax}-F_{eq})$	Temp.	Ref.
(*i*-PrNH)(Me_2N)PF_3	−80·1	−56·1 −67·1	870	720, 710	48	r.t.	373
(MeNH)(Me_2N)PF_3[a]	−80·1	−57·1 −66·6	875	720, 705	52	r.t.	373
(BuNH)(Me_2N)PF_3	−82·3	−76·6 −69·5	897	815, 775	55	[b]	374
(BuNH)(Et_2N)PF_3	−80·1	−67·1 −57·1	875	730, 715	50	[b]	374
(MeS)$MePF_3$	−73·1	+5·4 −2·2	1058	854, 999	50, 65	−90	365
(EtS)$MePF_3$	−71·4	+4·8 −3·2	1038	841, 953	62, 62	−80	365
(EtS)$PhPF_3$[c]	−70·5	−13·1 −21·4	1049	871, 1015	62, 62	−60	365
($PhCH_2NMe$)$PhPF_3$[d]	−76·0	−42·2 −44·8	977	836, 830	30, 28	−50	366

[a] Slightly different parameters are given in ref. 374.
[b] Temperature not specified.
[c] $J(F_{ax}-F_{ax'})=32$ Hz. Ref. 373 reports $J(P-F_{ax})=1030$ and 940 Hz at −55°.
[d] $J(F_{ax}-F_{ax'})=15$ Hz.

Tetrafluorophosphoranes usually undergo more or less rapid exchange of fluorines between axial and equatorial positions, and the ^{19}F spectra thus show doublets due to a time-averaged phosphorus-fluorine coupling (Table XXXVII). At lower temperatures the axial and equatorial environments may be distinguished, and the alkylthiotetrafluorophosphoranes again showed non-equivalence of the axial fluorines. The equatorial fluorines remained equivalent, and only one of the axial fluorines coupled to the alkyl hydrogens, suggesting that the alkyl group was held close to one of the axial fluorines with the sulphur-carbon and phosphorus-axial fluorine bonds in the same plane. The parameters[365] are given below. A similar effect was shown by (benzylmethylamino)tetrafluorophosphorane.[366]

Compound	$\delta_{F_{eq}}$	$\delta_{F_{ax}}$[a]	$^1J(P-F_{eq})$	$^1J(P-F_{ax})$[a]	$J(F_{eq}-F_{ax})$[a]	$J(F_{ax}-F_{ax'})$
$MeSPF_4$	−66·1	−14·1 −19·8	1075	930, 1088	104, 91	19
$EtSPF_4$[b]	−65·8	−15·1 −21·7	1074	950, 1082	88, 103	20
$PhSPF_4$	−65·0	−13·9 −16·9	1064	1071, 943	113, 96	18
$[(PhCH_2)MeN]PF_4$	−72·5	−56·2 −58·5	925	788, 778	76, 74	

[a] The coupling constants are given in the same order as the shifts.
[b] These values correct those given in the preliminary communication, *Chem. Comm.*, 1968 1662.

It is interesting that in each of the thiophosphoranes one of the axial fluorines was coupled more strongly than the equatorial fluorines to the phosphorus, reversing the usual order.

Even at −70°, methyltetrafluorophosphorane failed to show distinct axial and equatorial fluorines, but the following signs were determined:[363] $^1J(P-F) = -967{\cdot}7 \pm 1{\cdot}0$ Hz; $^3J(H-F) = +7{\cdot}0 \pm 0{\cdot}1$ Hz.

Hexaco-ordinate phosphorus

The hexaco-ordinate $[PF_6]^{\ominus}$ ion shows only a single ^{19}F resonance, with parameters relatively insensitive to the cation [δ_F −70·3 to −71·7, $^1J(P-F) \approx 710$ Hz], but substitution of one of the fluorines allows distinction between the four equatorial and the single axial fluorine *trans* to the substituent. Parameters for some ions $[RPF_5]^{\ominus}$ and $[R_2PF_4]^{\ominus}$ are given in Table XXXVIII.

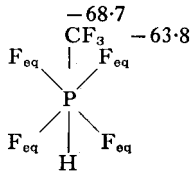
TABLE XXXVIII

^{19}F parameters for hexaco-ordinate phosphorus anions

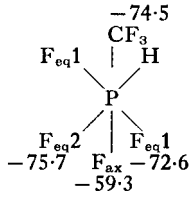
Compound	$\delta_{F_{eq}}$	$^1J(P-F_{eq})$	$\delta_{F_{ax}}$	$^1J(P-F_{ax})$	$^2J(F_{ax}-F_{eq})$	Ref.
$Cs^{\oplus}[PhPF_5]^{\ominus}$	−57·3	820	−60·9	687	38	367
$Cs^{\oplus}[Me_2NPF_5]^{\ominus}$[a]	−66·9	767	−54·2	664	35·5	367
$M^{\oplus}[EtPF_5]^{\ominus}$[b]	−56·0	853	−57·5	693	≈32	336
$K^{\oplus}[HPF_5]^{\ominus}$[c]	−56·4	−817	−66·2	−729	−41	376, 379
$Cs^{\oplus}[Ph_2PF_4]^{\ominus}$	+44·5[d]	947				367

[a] $J(F_{eq}-H) = 1{\cdot}8$ Hz, $J(F_{ax}-H) \approx 0$ Hz.
[b] M = $(Me_2N)_2EtPF$, δ_F −91·0, $J(P-F) = 1051$ Hz.
[c] $J(F_{eq}-H) = +128$ Hz; $J(F_{ax}-H) < 2{\cdot}5$ Hz.
[d] See text.

The observation of only a single type of fluorine in the spectrum of the diphenyl tetrafluorophosphate ion is consistent with the two phenyl groups occupying axial positions, but the authors pointed out[367] that in the absence of a variable-temperature study an exchange process cannot be ruled out. Distinct *cis-* and *trans-* isomers have, however, been observed[376] for the ion $[CF_3PF_4H]^{\ominus}$, and parameters are given below.



$^1J(P-F_{eq}) = 858$ Hz
$^2J(P-CF_3) = 156$ Hz
$^2J(H-F_{eq}) = 123$ Hz
$^3J(F_{eq}-CF_3) = 15{\cdot}3$ Hz
$^3J(H-CF_3) \approx 0$ Hz



$^1J(P-F_{ax}) = 784$ Hz
$^1J(P-F_{eq}1) = 767$ Hz
$^1J(P-F_{eq}2) \approx 758$ Hz
$J(P-CF_3) = 124{\cdot}5$ Hz
$J(H-F_{eq}1) = 96$ Hz
$J(H-F_{eq}2) \approx 0$ Hz
$J(H-F_{ax}) = 125$ Hz

$J(CF_3-F_{eq}1) = 14$ Hz
$J(CF_3-F_{eq}2) = 14$ Hz
$J(CF_3-F_{ax}) = 4{\cdot}5$ Hz
$J(CF_3-H) = 8{\cdot}2$ Hz
$J(F_{ax}-F_{eq}1) \approx 43$ Hz
$J(F_{ax}-F_{eq}2) \approx 40$ Hz

The spectrum of $Cs^{\oplus}[(CF_3)_2PF_4]^{\ominus}$, previously reported by Chan and Willis,[377] has been re-examined[378] at 56·4 and 94·1 MHz (see Fig. 9), and the bands have been re-assigned to give the parameters $^1J(P-F) = \mp 898{\cdot}0 \pm 2{\cdot}0$ Hz; $^2J(P-F) = \pm 148{\cdot}5 \pm 1{\cdot}0$ Hz; $^3J(F-F) = 14{\cdot}3 \pm 0{\cdot}2$ Hz.† The relative signs of the two couplings to phosphorus were deduced from the partial second-order effects observed in the spectrum. The original conclusion that the CF_3 groups are mutually *trans* is undisturbed by the new assignment of the bands.

Signs have also been determined[363] by decoupling experiments for $[HPF_5]^{\ominus}$ (see Table XXXVIII), and for $[MePF_5]^{\ominus}$ are as follows: $^1J(P-F_{eq}) = -832{\cdot}4 \pm 1{\cdot}0$ Hz; $^3J(H-F_{eq}) = +8{\cdot}9 \pm 0{\cdot}5$ Hz; $^3J(H-F_{ax}) \approx 0$ Hz. $^1J(P-F_{ax})$ (832·4 ± 1·0 Hz) and $^2J(F_{ax}-F_{eq})$ (35·9 ± 1·0 Hz) were also assigned negative signs by analogy with the signs obtained for the corresponding coupling in Me_2PF_3.

Parameters for the $[(CF_3)_2PF_3H]^{\ominus}$ anion have been reported,[376] and are shown with formula **457**. The spectra were complicated, because of the number of coupling nuclei, but were analysed successfully by first-order methods. It appeared that, in addition to depending on the nature

† Slightly different magnitudes are reported in ref. 379 together with positive sign for $^3J(F-F)$ from decoupling experiments.

of the other groups attached to phosphorus, the magnitude of ^2J(H–P–F) increased as the HPF bond angle decreased, being small or zero for *trans* hydrogen and fluorine and large (*ca.* 70 to 125 Hz) for a 90° bond angle.

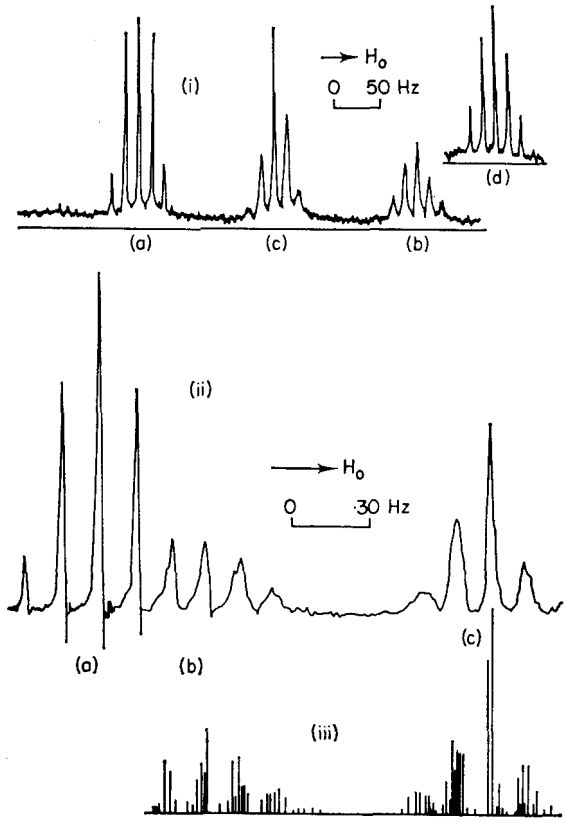
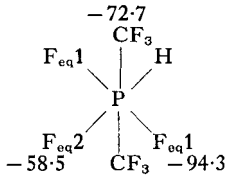


FIG. 9. Fluorine-19 spectra of $Cs[(CF_3)_2PF_4]$ in acetonitrile. (i) Single-scan spectrum at 94·1 MHz. The high-field multiplet (d) is displaced and shown inset. (ii) Multi-scan spectrum at 56·4 MHz; multiplet (d) not shown. (iii) Calculated part-spectrum at 56·4 MHz. The narrow, intense lines of (a) are not shown; that at highest field would be superimposed on the lowest-field component of (b). (From Bishop *et al.*[378])

^2J(P–CF) was reported[379] to increase (i.e. become more positive) with increased *s*-character of the phosphorus in contrast to ^2J(P–CH), which becomes more negative.



457

^1J(P–$F_{eq}1$) = 725 Hz
^1J(P–$F_{eq}2$) = 834 Hz
^2J(P–F) = 132 Hz
^3J(CF_3–$F_{eq}1$) = 12·5 Hz
^3J(CF_3–$F_{eq}2$) = 15·5 Hz
^2J($F_{eq}1$–$F_{eq}2$) = 25·0 Hz

^2J(H–$F_{eq}1$) = 69·5 Hz
^2J(H–$F_{eq}2$) = 18·0 Hz
^3J(H–CF_3) = 9·5 Hz

The addition compounds formed[371] by phosphorus pentafluoride with primary amines are also octahedral in structure, with the parameters shown below.

	$\delta_{F_{ax}}$	$\delta_{F_{eq}}$	^1J(P–F_{ax})	^1J(P–F_{eq})	J(F_{ax}–F_{eq})
$2MeNH_2 \cdot PF_5$	−80	−64	759	780	55
$EtNH_2 \cdot PF_5$	−79	−62	758	785	56
t-$BuNH_2 \cdot PF_5$	−78	−54	758	802	55

Although the stoichiometry of the solid adduct from methylamine was as shown, the ^{19}F spectrum suggested that it dissociates in solution. No 1:1 adduct could, however, be isolated.

(b) *Fluoroalkyl derivatives of phosphorus*

Parameters for a number of trifluoromethyl derivatives of phosphorus have been reported, and are summarised in Table XXXIX.

The coupling between phosphorus and fluorine in a number of these and previously reported compounds has been related[380] to the Huggins electronegativity of the atomic substituents X, and the curves are shown in Fig. 10.

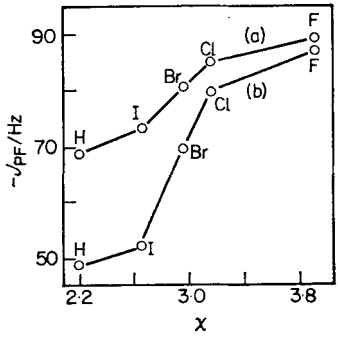


FIG. 10. Dependence of J_{PF} upon Huggins eletronegativity of X for compounds (a) $(CF_3)_2PX$ and (b) CF_3PX_2. (From Dyer and Lee.[380])

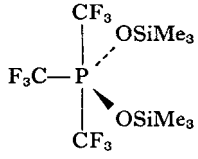
TABLE XXXIX

^{19}F parameters for trifluoromethyl phosphorus compounds

Compound	δCF_3	J(P–F)	Ref.
CF_3PH_2	−42·4	48·5	380
$(CF_3)_2PMe$	−58·2	76·7	380
$(CF_3)_2PEt$	−55·2	71·2	380, 381
$(CF_3)_2PPr^n$	−53·9	71·2	380, 381
$(CF_3)_2PBu^n$	−56·6	71·4	381
$(CF_3)_2PCHMeEt$	−53·4	[a]	381
$(CF_3)_2PCF_2 \cdot CF_2H$ [b]	−49·9	77	381
$(CF_3)_2P \cdot CH_2 \cdot CHF_2$ [b]	−55·5	78	70
$(CF_3)_2 \cdot P \cdot CH_2 \cdot CH_2F$ [b]	−57·3	75·8	70
$(CF_3)EtP \cdot CH_2 \cdot CH_2 \cdot CF_3$ [c]	−60·5	62	70
$(CF_3)_2PCHF \cdot CF_2H$ [b]	−49·3	[a]	382
$(B_5H_8)(CF_3)_2PNi(CO)_3$	−57·8	75	383
$(CF_3)_3P(OSiMe_3)_2$	−69·7	108·5	384
$(CF_3)_2P(O)(OSiMe_3)$	−73·1	122	384
$(CF_3)P(NMe_2)_2$	−62·1	86·6	385
$(CF_3)(MeO)PMe$	−68·5	68·9	386
$(CF_3)MePHO$	−97	91	386
$(CF_3)Me_2P(O)$	−76·3	84·3	386
$(CF_3)MeP(OBu^t)$	−92·8	74·0	386
$(CF_3)MeP(SMe)$	−62	64	386
$(CF_3)MeP(SBu^t)$	−21·1	65	386
$(CF_3)MePHS$ [d]	−72·3	93·9	386

[a] Complex resonance.
[b] See Table XL for fluoroalkyl group parameters.
[c] γ-CF_3: $\delta_F = -69·8$, $J(CF_3\text{–P}) = 4·0$ Hz, $J(CF_3\text{–H}) = 9·7$ Hz.
[d] ^3J(F–H) = 4·7 Hz.

The couplings were also related to δ_F for the CF_3 group, and mostly followed a similar sigmoid curve, but a number of substituents gave anomalous results for no obvious reason. The doublet observed[384] at room temperature in the ^{19}F spectrum of $(CF_3)_3P(OSiMe_3)_2$ collapsed at 0°, and at −70° gave a doublet (115·5 Hz) of septets (13·5 Hz), implying coupling between non-equivalent CF_3 groups, at δ_F −63·7. The other band (δ_F −72) was resolved partially at −100° to give a doublet (*ca.* 108 Hz) of quartets, together with additional peaks spread over several hundred Hz. Since the ^{1}H spectrum was unchanged from room temperature to −140°, **458** was suggested as the most probable structure.



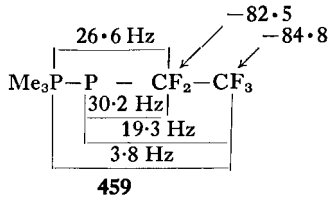
458

Parameters for a number of other fluoroalkyl groups attached to phosphorus have also been reported and are summarised in Table XL. The phosphorus-fluorine coupling to an adjacent CF_2 group may range between 56 and 99 Hz, depending on the other substituents on phosphorus, and coupling to a β-fluorine may also vary considerably, although over a narrower range. The other parameters within the fluoroalkyl groups fall within the expected ranges.

The reaction of pentafluoroethylphosphinous iodide with mercury was reported[387] to give a cyclic tetramer $(C_2F_5P)_4$ and a species assigned the structure $(C_2F_5P)_3$, since the peak at highest *m/e* corresponded to this formula. The ^{19}F spectrum was reported as two complex resonances at δ_F values given below. Other workers[388] have reported the formation under the same conditions of the tetramer and pentamer $(C_2F_5P)_5$, the latter having the boiling point ascribed to the trimer, a mass spectroscopic parent ion, and a ^{19}F spectrum which comprised two bands very similar in shift to those ascribed to the trimer and a third band in the CF_2 region.

	Ref. 387	Ref. 388
δCF_3	−100·8	−84·2
δCF_2	−83·1	−99·8
		−104·3
Relative intensities	Not given	15:6:4

The "trimer" reacted with an excess of trimethylphosphine to give the phosphine-phosphinidene **459** similar to that described for $(CF_3P)_4$ and $(CF_3P)_5$.



459

$3J(F\text{–}F) = 6{\cdot}9$ Hz

The cyclic phosphine sulphide **460** has been prepared from the cyclic thiotetraphosphine **461**, and ^{19}F parameters were briefly reported.[389]

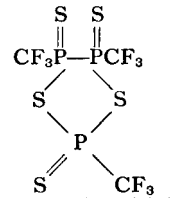
TABLE XL

^{19}F parameters of fluoroalkyl phosphorus compounds

Compound	δ_F[a]	^2J(P–F)	^3J(P–F)	$J(H_\beta–F_\beta)$	$J(H_\alpha–F_\beta)$	$J(F_\alpha–F_\beta)$	Ref.
$CHF_2·CH_2·PH_2$	−111·5		7·6	57·6	17·5		380
$CHF_2·CH_2·PCl_2$	−109·8		13·4	56·0	16·8		380
$CHF_2·CF_2·PH_2$†	−102·0, −133·1	97		54·6	3·5		380
$CH_2F·CF_2·PCl_2$	−117·0, −238·5	99	49·1	49·1	13·1	18·4	380
$CHF_2·CF_2·PCl_2$	−125·2, −135·1	81	26·9	53·3	5·0	5·4	380
$CHF_2·CHF·PCl_2$	−210·5, −126·4	83	7·5, 12·0	[b]	[b]	[b]	380
$CHF_2·CF_2·PMe_2$	−123·7, −133·7						381
$CHF_2·CF_2·P(CF_3)_2$[c]	−112·6, −134·6	56	31	55			381
$CHF_2·CH_2·P(CF_3)_2$[c]	−113·5		27	56	18		70
$CH_2F·CH_2·P(CF_3)_2$[c]	−217·5		31·4	47	23·4		70
$CHF_2·CH_2·PMe_2$	−107·9		11·0	57·5	19·0		70
$CH_3·CF_2·PMe_2$	−99·7	72·5			20·5		70
$CH_2F·CH_2·PMe_2$	−212·1		14·0	48	22		70
$CHF_2·CHF·P(CF_3)_2$	−215·1, −127·5						382
$CHF_2·CHF·PMe_2$	−225·7, −127·3	57·0		47·5			382
$CH_2F·CF_2·PMe_2$	−118·0, −233·9	63·5	23·4	46·8	17·2		382

[a] In the order α-CF, βCF, relative to phosphorus.
[b] All the coupling constants within the group $CHF_2·CHF$ except $J(F_\beta–F_\beta)$ are also given in ref. 380.
[c] See Table XXXIX for CF_3 group parameters.
† This compound is formulated incorrectly in the Table in ref. 380 as '$CH_2F·CF_2·PH_2$'.

$(CF_3P)_4S$
δ_F −44·2, −52·3
460



δ_F −70·3, −74·5
J(P–F) = 131 Hz
461

The ^1H spectrum of the aminophosphine $CH_3NH{\cdot}P(CF_3)_2$, which consisted of two doublets of unequal intensities but identical coupling constants, which collapsed at 88°C to one doublet with the same coupling constant, was previously[390] ascribed to the presence of unequal amounts of two rotamers. The ^{19}F spectrum, however, showed[391] only one doublet [J(P–F) = 82 Hz], and provided no support for the idea of two distinct rotamers. Further investigation[391] of the ^1H spectrum at 60 and 100 MHz showed that the observed pattern arose from coupling to phosphorus and to the amino-hydrogen, and from the proximity of the N–H resonance, and that the collapse at 88° was due to intermolecular exchange of N–H. Signs and magnitudes of couplings in the analogous compound $(CF_3)_2PNH_2$ have been obtained,[392] and those involving ^{19}F are: $J(^{15}N–F) = -1{\cdot}53$ Hz, J(P–F) = −81·33 Hz, J(F–H) = −0·055 Hz.

Parameters for other fluoroalkyl derivatives of phosphorus are summarised with formulae **462** to **468**. Parameters for the ethyl and *n*-butyl analogues of **463** and **464** are almost identical to those shown.

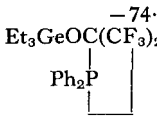
−68·125
$Ph_2P(O)CH(CF_3)OPPh_2(O)$
7·8 Hz, 3·5 Hz
462[393]

−75·1
$(MeO)_2P(O)OCH(CF_3)_2$
6 Hz
463[394]

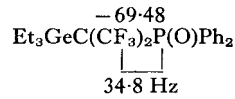
−72·3
$(MeO)_2P(O)C(OH)(CF_3)_2$
3 Hz
464[394]

−74·7
$Et_3GeOC(CF_3)_2$
Et_2P
12·4 Hz
465[395]

−69·94
$Et_3GeC(CF_3)_2P(O)Et_2$
25·3 Hz
466[395]



467[395]



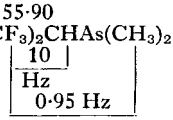
468[395]

Arsenic

Variation in the resonance position of arsenic pentafluoride and of the fluorine in weak bases such as sulphuryl chloride fluoride, thionyl fluoride, and methanesulphonyl fluoride has been used[396] to show the formation of complexes between AsF_5 and the bases. Sulphuryl fluoride failed to form a complex even at low temperature and was used as solvent. The order of base strength: $CH_3SO_2F > SO_2 > SOF_2 > SO_2ClF > SO_2F_2$ is the same as that previously found with antimony pentafluoride. The authors pointed out that the resonance of fluorine attached to arsenic was much narrower in the complexes than in free AsF_5, indicating a more rapid quadrupolar relaxation of the coupling between arsenic and fluorine. Although the complexes have a more symmetrical octahedral arrangement about arsenic, the electric field gradient is greater (five strong As–F bonds and one As–O bond) than in the free pentafluoride in which the rapid intramolecular exchange of fluorines averages the electric field gradient to a low value.

A 3:2 mixture of arsenic pentafluoride and antimony in liquid sulphur dioxide gave[397] volatile material and a precipitate with composition $SbAsF_6$. Its ^{19}F spectrum in acetone (with which some reaction also occurred) showed the 1:1:1:1 quartet [$J(As\text{–}F) \approx 930$ Hz] at δ_F −64·5, associated with the $[AsF_6]^{\ominus}$ ion, e.g. $Bu_4N^{\oplus}AsF_6^{\ominus}$ in fluorosulphonic acid has δ_F −63, and $Se_8(AsF_6)_2$[398] in the same solvent, δ_F −61·6, and $(Sb_n^{h\oplus})(AsF_6^{\ominus})_n$ was suggested as the best formulation for the solid. A solution of antimony pentafluoride in arsenic trifluoride gave[399] peaks attributable to $[Sb_2F_{11}]^{\ominus}$ (see below) and another antimony fluoride species, suggested to be $[SbF_6]^{\ominus}$, and it was suggested that the solvent and $AsF_2^{\oplus}$ or possibly $As_2F_5^{\oplus}$, with rapid fluorine exchange, gave rise to the remaining strong singlet.

The reaction of bis(trifluoromethyl)diazomethane with dimethylarsine gave 1,1,1,3,3,3-hexafluoroisopropyldimethylarsine (**469**) for which the parameters are as shown.

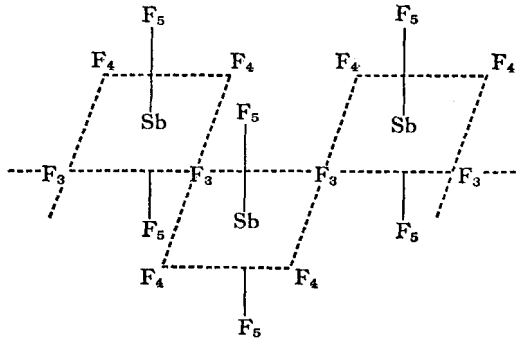


469

Parameters for a few arsenic complexes of transition metals are noted later (e.g. pp. 269, 276).

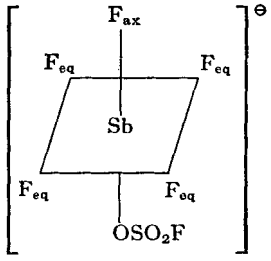
Antimony

^{19}F NMR studies of antimony pentafluoride under various conditions continue. Davies and Moss[399] have illustrated spectra of SbF_5 in perfluorocyclobutane at $-55°$ which consisted of three signals—a broad low field peak, assigned to bridging fluorines in a polymeric chain (F_3 in Dean and Gillespie's[400] notation), a multiplet assigned to those fluorine atoms *cis* to one bridging fluorine and *trans* to the other (F_4) (*cis* disposition of the bridges in the chain being assumed (**470**)) and a high-field multiplet assigned to fluorine atoms *cis* to both bridging fluorines (F_5), in the ratio 1·0:2·1:2·0, close to the theoretical. No "terminal" fluorine signals were observed, indicating that the chains were either very long or cyclic. Approximate (first order analysis) coupling constants obtained are shown with the formula.



$J(F_3–F_4) \approx 150$ Hz
$J(F_3–F_5) \approx 45$ Hz
$J(F_4–F_5) \approx 100$ Hz

470



471

The ^{19}F spectrum of $Se_8(Sb_2F_{11})_2$[398] had shifts and couplings in agreement with previous reports[401] of $(Sb_2F_{11})^{\ominus}$ spectra. In fluorosulphonic acid (HSO_3F), however, the spectrum consisted of a broad peak (δ_F −166) attributed to $[SbF_6]^{\ominus}$, together with a doublet (δ_F −156) and quintet (δ_F −184) with coupling constant 100 Hz, assigned to F_{eq} and F_{ax} in **471**.

Bacon, Dean, and Gillespie[402] have also studied the spectrum of SbF_5 in perfluorocyclobutane, in $CF_2Cl \cdot CF_2Cl$, or in arsenic pentafluoride, and have also found considerably improved resolution of the bands (Fig. 11.). They assigned the midfield resonance to F_5 and the high-field

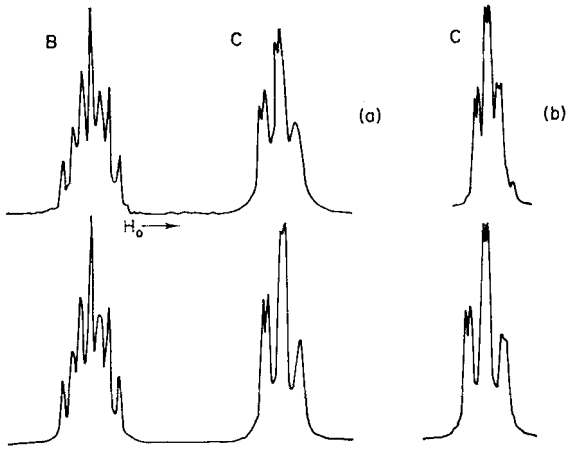
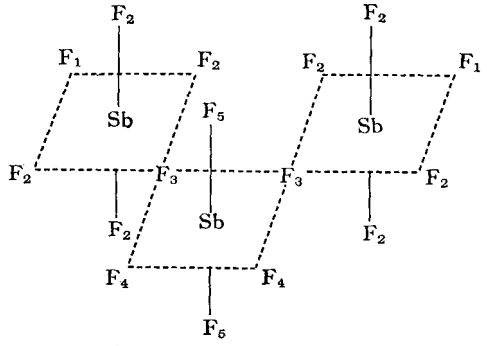


FIG. 11. (a) The 56·4 MHz ^{19}F spectrum of a solution of SbF_5 in Freon-114; mole ratio of SbF_5/Freon-114 = 2·5 (lowfield resonance A omitted). (b) The 94·1 MHz spectrum (highfield triplet only) of SbF_5 diluted with AsF_5. The calculated spectra are shown below; in (b) the horizontal scales are slightly different. (From Bacon *et al.*[402])

resonance to F_4 by analogy with the known values of the couplings in other antimony compounds, including $[Sb_2F_{11}]^{\ominus}$. Since J(3–4) was expected to be considerably larger than J(3–4′), theoretical spectra were computed via LAOCN3 and a line-shape programme, and gave the best fit with the experimental spectra for the values: J(F3–F5) = 85·6 Hz, J(F4–F5) = 144·3 Hz, J(F3–F4) = 61·5 Hz, J(F3–F4′) = −8·5 Hz, J(F3–F3′) = 25 Hz, J(F4–F4′) = 85 Hz, consistent with those found in similar systems.

The spectrum of *t*-butyl fluoride in antimony pentafluoride and sulphuryl chloride fluoride showed the presence of the $[Sb_2F_{11}]^{\ominus}$ anion and a further species identified from the form of its spectrum and the coupling constants, given with the formula, as [*cis* $Sb_3F_{16}]^{\ominus}$ (**472**).



472

δ_{F1} −141·1 δ_{F2} −112·4 δ_{F3} −89·7
δ_{F4} −127·8 δ_{F5} −108·3

J(F1–F2) = 99 Hz J(F2–F3) = 54 Hz
J(F3–F4) = 79·3 Hz J(F3–F5) = 85·6 Hz
J(F3–F4′) = −11·1 Hz J(F4–F5) = 135·7 Hz
J(F3–F3′) = 27·5 Hz J(F4–F4′) = 112·5 Hz

Evidence for the presence of higher polyanions e.g. $Sb_4F_{21}^{\ominus}$ in solutions containing more SbF_5 was also presented.[402]

The complexes $5SbF_3 \cdot SbF_5$, $2SbF_3 \cdot SbF_5$, $4SbF_3 \cdot SbF_5$, and $3SbF_3 \cdot SbF_5$ were originally reported by Ruff and Plato,[403] but Woolf[404] found that SbF_3 appeared insoluble in SbF_5 and could not detect the complexes by electrical conductivity measurements. Davies and Moss[399] have also found no trace of the complexes by ^{19}F NMR under a variety of conditions. With niobium pentafluoride there was indication, in the shift of the NbF_5 signal, that interaction with SbF_5 occurred, though no definite reaction could be established. However, the formation of a solid 1:1 adduct from a small excess of NbF_5 with SbF_5 has been reported,[405] together with X-ray studies which indicated an endless chain with the major contributing form $[NbF_4]^{\oplus}[SbF_6]^{\ominus}$.

The wide-line spectrum of a molten mixture of bromine pentafluoride and antimony pentafluoride (molar ratio 1:2) appeared[406] as two signals (δ_F −116·5, +165·5). The former corresponded to $[Sb_2F_{11}]^{\ominus}$ and the latter was thus assigned to $[BrF_4]^{\oplus}$. The relative intensities were 1:3·2 compared with 1:2·75 required for this structure.

Group VI

Oxygen

Most of the oxygen compounds have already been mentioned in the sections on ethers and peroxides, alcohols and hypohalites, and acid derivatives. A few remaining compounds are given here.

The reaction of bis(fluoroxy)difluoromethane with caesium trifluoromethoxide gave[407] a mixture of CF_3OOCF_3 and CF_3OOOCF_3, both of which are known compounds, together with the new compound **473**, with the parameters shown.

$$\underset{\underset{\underset{

Aminosulphur monofluoride imides and related compounds have been prepared[410] by Glemser and von Halasz by the reaction of sulphur tetrafluoride with diethylaminotrimethylsilane. The diethylamino-compounds analogous to **478** and **479** had ^{19}F resonances markedly to low field of the methyl compounds (δ_F +49·2 and +61·3 respectively). The trifluorosulphur compound **480** showed a singlet (δ_F +46·4) at room temperature, but at −80° showed two signals at δ_F +54·1 and +37·2 in the ratio 2:1 assigned to axial and equatorial fluorines in the trigonal bipyramid. Compound **481** also showed axial (δ_F +76·82) and equatorial (δ_F +66·47) fluorines, and the A_2B pattern was analysed *via* LAOCONII to give the fluorine-fluorine coupling as 163·07 Hz.[410]

Sulphur tetrafluoride reacted[411] with sulphamide at room temperature to give **482**, and the oxyfluoride[412] with tris(trimethylsilyl)amine gave **483**, which in turn was converted into the mercurial **484** with HgF_2. Other sulphur difluorides have been prepared by the reaction of sulphur nitride trifluoride with lithium bis(trimethylsilyl)amide[413] to give **485**, by the reaction[414] of $MeSO_2N{:}S{:}O$ with fluorine to give **486**, by the reaction of fluoroalkylsulphur trifluorides with dialkylaminotrimethylsilanes[415] to give **487**, and by the photochemical addition of aminosulphur difluorides to olefins[416] to give **488** to **490**. The fluorines in **488** to **490** were reported to be magnetically inequivalent, with coupling in the range 3 to 20 Hz.

Et_2NSF_3 **480**

$Me_2NS(O)F_3$ **481**

+41·5
$(F_2S{:}N)_2SO_2$ **482**

+55·9
$Me_3SiN{:}SOF_2$ **483**

+58·7
$Hg(N{:}SOF_2)_2$ **484**

+77·4
$Me_3SiN{:}SF_2{:}NSiMe_3$ **485**

+47·6
$MeSO_2N{:}SOF_2$
0·3 Hz **486**

−156·7
−72·7 ↓ +9·8
$(CF_3)_2CF{\cdot}SF_2{\cdot}NMe_2$
3·6 Hz
20·3 Hz
12·3 Hz **487**

64·8 to 65·7
XCH_2NSF_2 **488**
X = $CH_2Cl, CHCl_2, CCl_2Br$

56·9,58
$XCHClNSF_2$ **489**
X = $CHClBr, CCl_2Br$

48·9
$CCl_2Br{\cdot}CCl_2NSF_2$ **490**

A wide range of sulphonyl fluorides has been reported;[348, 414, 417 to 423] a few representative compounds are shown in formulae **491** to **503**.

+24·75
CCl_3SO_2F

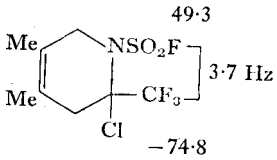
491[414]

+61·2
$(CHCl_2)_2NSO_2F$
| 1·6 Hz |

492[414]

−117·2
−83·5 ↓ 41·5
$CF_3CF_2SO_2F$

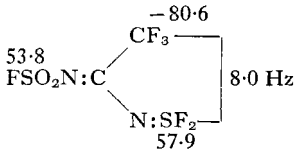
493[419]



494[417]

50·3 to 59·6
$R_FCX:NSO_2F$
R_F = CF_3 or C_2F_5 X = H,NH_2,NEt_2, Cl,NCO,NCS

495[417]



496[417]

60·3
$FSO_2N:C(OMe)(NMe_2)$

497[418]

42·4
$FSO_2NMe\cdot CONMe_2$
| 1·4 Hz |

498[418]

39·7 to 43·03
$FSO_2N:CHR$
R = Me, Et, *i*-Pr, Ph

499[418]

59·7
$FSO_2N:C:NSiMe_3$

500[420]

48·5
$FSO_2NMeSiMe_3$

501[420]

57·6 68·7
$FSO_2NS(O)F\cdot N:PCl_3$
| 7 Hz || 7 | Hz

502[421]

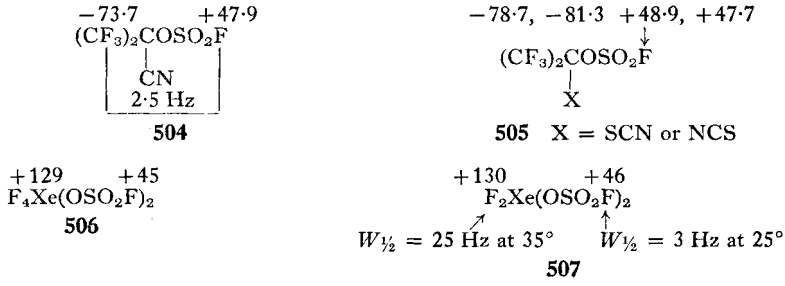
+57·0 −62·6
$FSO_2N:C(CF_3)NEt_2$
| 8·5 Hz |

503[423]

The low temperature reaction between trisulphuryl fluoride ($S_3O_8F_2$) and the sodium salt of hexafluoroacetone cyanohydrin gave[424] the fluorosulphate **504**, for which the parameters are shown. The corresponding reaction using hexafluoroacetone and sodium thiocyanate gave a mixture of the thiocyanate and isothiocyanate fluorosulphates **505** for which the shifts shown were reported without assignment.

Fluorosulphatoxenon fluorides **506** and **507** have been prepared by the reaction of xenon hexa- and tetra- fluoride with fluorosulphonic acid.[425] The authors commented that the spectra show large changes compared

with those of xenon tetra- and hexa- fluorides. The signals for XeF in **507** were broad at 35°, and no coupling to the other fluorines was observed at temperatures down to −70°, although there was further differential broadening of the signals.



Fluorodisulphuryl isocyanate[426] ($OCNSO_2OSO_2F$) absorbed in the same region (δ_F +47·7) as **504** to **507**.

The polysulphuryl fluorides $H(SO_3)_nF$ ($n=1$ to 7) have been observed[427] by ^{19}F NMR at low temperatures in solutions of sulphur trioxide in fluorosulphonic acid or in mixtures of fluorosulphonic acid with the inert diluent sulphuryl chloride fluoride (see Fig. 12).

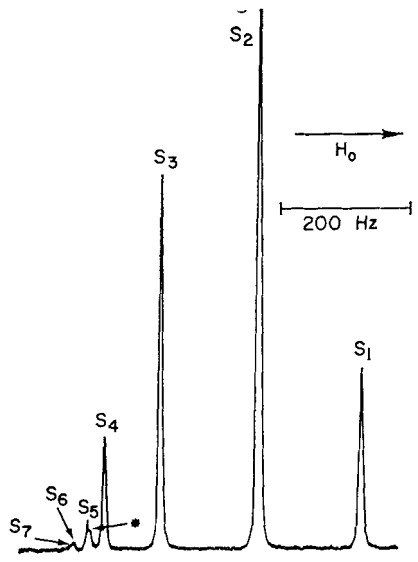


FIG. 12. ^{19}F NMR spectrum (−110°, 56·4 MHz) of HSO_3F (1·94) and SO_3(1) in SO_2ClF (excess). (* = impurity peak) (From Dean and Gillespie.[427])

The shifts indicated that the bands found by Commeyras and Olah[428] in the spectra of concentrated solutions of antimony pentafluoride in fluorosulphonic acid (32 and 69 Hz to low field of the HSO_3F resonance) were not due to HS_2O_6F and HS_3O_9F as these authors suggested, and Dean and Gillespie[427] suggested that the lines observed in the SbF_5–HSO_3F system may be due to fluorosulphates. The shifts observed in the SO_3–HSO_3F–SO_2ClF mixtures depended on the composition of the mixture, and all merged at $-60°$. Some values are given below, in Hz to low field of HSO_3F in SO_3/SO_2ClF for a 1:1·94 mixture of SO_3 and HSO_3F in an excess of SO_2ClF.

HS_2O_6F	+158	HS_3O_9F	+312	$HS_4O_{12}F$	+400
$HS_5O_{15}F$	+427	$HS_6O_{18}F\sim$	+448	$HS_7O_{21}F\sim$	+453

Pentafluorothio-compounds with functional alkyl substituents have been prepared by the reaction of sulphur chloride pentafluoride with alkyl trifluorovinyl ethers, to give compound **508**, or the ethyl analogue, and by further reactions of these ethers.[23] Alkoxypentafluorosulphur compounds **511** and **512** were prepared by the reaction of the "hypochlorite" SF_5OCl with olefins.[21] The parameters for **511** and **512** were checked *via* a generalised 7-spin programme.

+64·8, +43·5 −78·2
↓ −93·6 ↓
$SF_5\cdot CF_2\cdot CFClOMe$
508

+62·0 to +62·2 −92·5
+40·0 to +41·5 to −93·7
↓ ↓
$SF_5\cdot CF_2\cdot CO_2R$
509 R = Me, Et, H

+64·5, +34·0
↓ −90·8
$SF_5\cdot CF_2I$
510

+74·9 +59·8
$FSF_4\cdot O\cdot CH_2\cdot CH_2Cl$
146 Hz
511

+60·2 +71·0 −72·5
↓ −87·1 ↓
$FSF_4\cdot O\cdot CF_2\cdot CF_2Cl$
12·6 Hz | 1·95
153·6 Hz | Hz
2·6 Hz
512

(b) *Fluoroalkyl derivatives of sulphur.* The ^{19}F shift for the CF_3 group in a wide range of CF_3SO_2 compounds[420, 421, 429, 430] was relatively insensitive to the nature of the rest of the molecule; δ_F was in the range −75·12 to −80·5 for all but one of the compounds noted (see formula **515**), and was commonly within the narrower range −79·1 to −80·5.

The parameters reported for some other compounds with sulphur attached to a fluoroalkyl group are shown with formulae **513** to **530**.

$-79{\cdot}3 \quad -112{\cdot}7$ $(CF_3{\cdot}CF_2)_2SO_2$ **513**[419]	$-70{\cdot}0$ $(CF_3)_2SO$ **514**[431]	$-70{\cdot}3 \quad -49{\cdot}5$ $CF_3SO_2N(SCF_3)_2$ 3·4 Hz **515**[430]
$-52{\cdot}8$ $(CF_3SNH)_2SO_2$ **516**[430]	-71 $CF_3SF{=}N{\cdot}COF$ 19 Hz δ_F +8, −50 **517**[432]	$-75{\cdot}3 \quad -52{\cdot}0$ $CF_3SO_2NHSCF_3$ 2 Hz **518**[430]
$-42{\cdot}0 \quad +53{\cdot}0$ CF_3SCOF 19·5 Hz **519**[433]	$-43{\cdot}1$ CF_3SCOCl **520**[433]	$-34{\cdot}4$ CF_2ClSCl **521**[434]
$-46{\cdot}5 \quad +41{\cdot}5$ CF_3SSCOF **522**[433]	$-46{\cdot}2$ $CF_3SSCOCl$ **523**[433]	$-51{\cdot}0$ $CFCl_2SCl$ **524**[434]
$-38{\cdot}9 \quad -56{\cdot}0 \quad +44{\cdot}3$ $CF_3SCClFSSCOF$ 9·6 Hz, 2·0 Hz **525**[433]	$-61{\cdot}4 \quad -28{\cdot}0$ $CF_3OSCFCl_2$ 9·2 Hz **526**[20]	$-148{\cdot}8$ $CHCl_2{\cdot}CHF{\cdot}SPh$ 57·2 Hz, 9·3 Hz **527**[74]
$-26{\cdot}4 \quad +45{\cdot}0$ $CFCl_2SSCOF$ 2·4 Hz **528**[433]	$-33{\cdot}3 \quad +42{\cdot}3$ $CF_2ClSSCOF$ 2·2 Hz **529**[433]	$-34{\cdot}7$ $CF_2ClSSCOCl$ **530**[433]

As noted in an earlier section (see p. 116) the ^{19}F parameters for the fluorocarboxy disulphides $[R_FCO_2S]_2$[56] are very similar to those of the carboxylic anhydrides, which are also quoted in the paper. The reaction between trifluoromethyl hypofluorite and carbonyl sulphide[20] gave $(CF_3O)_2CO$ and $CF_3OC(O)F$, both of which are known, and a compound which the authors state "is almost surely" **531**, showing two equally intense bands at δ_F −58·5 and −62·2, with coupling constant less than 1 Hz.

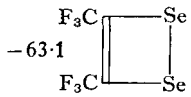
$CF_3OSC(O)OCF_3$
531

Line-shape studies[435] of the ^{19}F spectra of solid sulphur, selenium and tellurium hexafluorides have shown that these are all rigid molecules at low temperatures, with reorientation at higher temperatures and translational movements below the melting points.

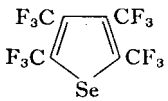
Selenium

Diorganoselenium difluorides R_2SeF_2 have been prepared[436] by the reaction of silver difluoride with dialkyl selenides. The ^{19}F shifts moved to progressively higher field as the alkyl group became more branched at the α-carbon [δ_F: Me, −66·6; Et, −87·8; *i*-Pr, −107·5, but *n*-Pr, −84·0; $(CH_2)_4$, −84·5; and Ph, −65·4]. For the methyl and tetramethylene compounds, coupling to hydrogen (9·0, 12·1 Hz) was observed, but the signals were singlets for the other compounds. Coupling to ^{77}Se ($I=\frac{1}{2}$, relative abundance 7·5%) was also reported for the methyl and tetramethylene compounds (650·2, 688 Hz respectively), but was much weaker (312·6 Hz) for the phenyl compound. Exchange in these compounds was slow, compared with SeF_4, in which exchange takes place even at −200°, but was apparently dependent on the presence of impurities.

Selenium itself reacted with hexafluorobut-2-yne under reflux[437] to give bis(trifluoromethyl)selenetene (**532**), together with an impurity which showed two complex signals (δ_F −57·0, −53·7) of equal intensity assigned to the selenophene (**533**).

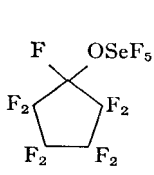


532



533

Fluorination of seleninyl fluoride ($SeOF_2$) in the presence of potassium fluoride[438] gave fluoroxypentafluoroselenium SeF_5OF (**534**) as major product, together with *trans*-bis(fluoroxy)tetrafluoroselenium which showed a quintet [J(F–F) = 26·8 Hz] at δ_F 179·0 for the fluoroxy groups, and a triplet at δ_F 47·0, defining the stereochemistry; the latter band showed coupling to selenium of 1420 Hz. Parameters for **534** were reported[439] as an AB_4 pattern centred at δ_F +55·7, with coupling to selenium of 1410 Hz, and a complex pattern for the OF group, similar to that of SF_5OF, centred at δ_F +177·5.

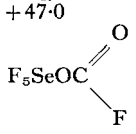


AB_4, centred
δ_F +73·0
J(Se–F)
= 1436 Hz

δ_{CF} −131

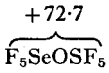
535

AB_4,
+47·0



536

+72·7



538

+32·2
$(F_5Se)_2O$

537

With perfluorocyclopentene, SeF_5OF added[439] to the double bond to give **535**. The fluoroxy-compound also reacted with carbon monoxide, to give the fluoroformate **536** and a compound formed in low yield and thought to be the oxide **537**, and with sulphur tetrafluoride, to give the pentafluorosulphur compound **538**. The ^{19}F spectra are all illustrated in the paper, and chemical shifts of the band centres are summarised with the formulae.

Tellurium

Analysis as AB_4 systems of the ^{19}F spectra of a number of compounds of the formula $YTeF_5$ has been reported and the parameters are given in Table XLI.† No hydrogen-fluorine coupling could be detected in

TABLE XLI

^{19}F parameters for $YTeF_5$ compounds

Compound	δ_{FA}	δ_{FB}	δ_X	J(A–B)	J(A–X)	J(B–X)	Ref.
F_5TeOH	−44·5	−44·7		±182·2	0	0	440
F_5TeOSO_2Cl	−48·4	−36·7		±177·1			440
F_5TeOSO_2F	−52·33	−40·33	+49·38	±178·9	±0·19[a]	∓2·95	440
$(F_5TeO)_2SO_2$	−51·62	−40·00		±177·7	1·0[b]	0[c]	440
$(F_5Te)_2O$	−48·1	−37·5		±176·3			440
$(F_5TeO)_2Xe$	−38·8	−43·8		192·9			441
$(F_5TeO)XeF$	−38·4	−44·6	−144·8	191·8			442
F_5TeOMe	−43·2	−56·6		188			443

[a] Not resolved in spectrum.
[b] J(B–B′).
[c] J(A–A′).

F_5TeOH, and it was suggested that this might be due to exchange catalysed by impurities. The authors[440] pointed out that this was the first report of a pentafluorotellurium compound in which the axial fluorine is less shielded than the equatorial, and a similar situation is found in the methoxy compound[443] and in the xenon compounds reported by Sladky.[441, 442] In contrast to the couplings in F_5SOSO_2F, J(A–X) and J(B–X) are of opposite sign in F_5TeOSO_2F.

† The authors of ref. 440 point out that the expressions $\Sigma\, 1,10 = \nu_0\delta - (5/2)J_{AB}$, $\Sigma\, 5,17 = \nu_0\delta + (5/2)J_{AB}$, where $\Sigma\, i,j$ is the sum of the separation of the ith and jth bands from the origin, should be used in the AB_4 analysis, rather than $\pm(2/5)J_{AB}$ as given by Emsley, Feeney, and Sutcliffe (*High Resolution* NMR *Spectroscopy*, Vol. 1, pp. 338, 340).

The reaction of methanol[443] with tellurium hexafluoride gave the methoxypentafluoro compound, and, under more vigorous conditions, the *cis*-dimethoxy compound [δ_{FA} −51·1, δ_{FB} −61·5, J(A–B) = 151 Hz]. Xenon difluoride reacted[441] with F_5TeOH to give xenon(II) bis-pentafluoro-orthotellurate; with more xenon difluoride this gave xenon fluoride pentafluoro-orthotellurate.[442] No coupling was observable in the latter between the AB_4 fluorines and that bonded to xenon, the chemical shift of which was somewhat to low field of those in xenon difluoride (δ_F −198·9).

Group VII

Bromine

A mixture of bromine pentafluoride and sulphur trioxide was reported[444] to give no observable $BrF_4^{\oplus}$, but to give instead $[BrF_2]^{\oplus}[SO_3F]^{\ominus}$ (δ_F −49·5 for the cation, −195·5 for the anion which was not resolved from polysulphuryl fluoride anions). A similar result was obtained from bromine trifluoride and sulphur trioxide and from BrF_3 and $Br(SO_3F)_3$; although earlier workers[445] found similar shifts for a 1:1 mixture of BrF_3 and $Br(SO_3F)_3$, they reported that the BrF chemical shift decreased when either more or less BrF_3 was present.

Iodine

The ^{19}F spectrum of the hexafluoroiodate ion $[IF_6]^{\ominus}$ was reported[446] to consist of two very broad bands at δ_F +1·5, −114·0. Broad-line studies of the hexafluoroiodonium ion $[IF_6]^{\oplus}$ have also been reported.[447] The signal obtained from a sample of $[IF_6]^{\oplus}[AsF_6]^{\ominus}$ was interpreted as a superposition of two lines of equal intensity but different widths, and, together with ^{127}I and ^{75}As resonance experiments, suggested a regular $[AsF_6]^{\ominus}$ octahedron with a distorted octahedron for $[IF_6]^{\oplus}$.

Group VIII

Xenon

Fluorinated derivatives of xenon have been discussed on p. 249 (xenon fluorosulphates) and p. 255 above (xenon orthopentafluorotellurates).

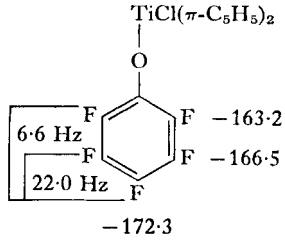
VII. TRANSITION METAL COMPLEXES OF FLUORINATED MOLECULES

In this section complexes formed between transition metals and fluorinated organic compounds or fluorophosphines are considered without regard to whether the ligand is π- or σ- bonded to the metal. Transition metal fluorides and their complexes with unfluorinated ligands are

considered in a later section (p. 286). In most cases the metals are considered in the order of the groups in the periodic table.

Titanium

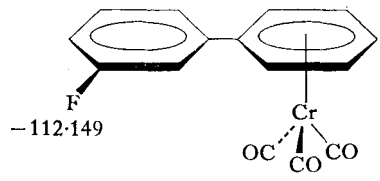
Titanocene dichloride reacted[222] with sodium pentafluorophenate to give the titanium phenoxide **539**, in which the *para*-fluorine absorbed to high field of the *meta*-fluorines as in the free phenol, and both were at higher field than in the free phenol although the metal usually deshields the ring fluorines, even when separated by a methylene group.



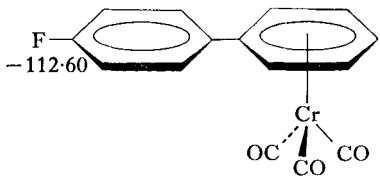
539

Chromium, molybdenum, tungsten

The ^{19}F shifts in 3′- and 4′-fluorobiphenyltricarbonylchromium (**540** and **541**) imply a significant increase in inductive withdrawal of electrons, but little change in the conjugative effect. The reasons for the large upfield shift in $C_6H_5F \cdot Cr(CO)_3$ (δ_F −135·05, *cf.* PhF, δ_F −113·15) were also discussed.[448]



540

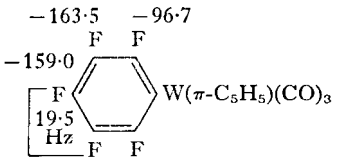


541

The ^{19}F spectra for some polyfluorophenyl complexes of π-cyclopentadienyltricarbonyltungsten, and the corresponding 4-substituted fluoropyridyl compounds, prepared by nucleophilic attack by the metal anion on the fluoroaryl ring, have been reported,[449] together with the corresponding pentafluorobenzoyl complex.

The deshielding of the fluorines *ortho* to the transition metal is obvious (compare **542** and **543**). No coupling of fluorine to ^{183}W (14·3% abund-

ance, $I=\frac{1}{2}$) could be resolved, but broadening of some of the signals suggested J (*ortho* F–W) might be *ca.* 0·5 Hz in **542.**



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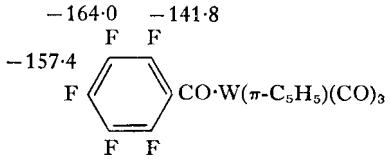

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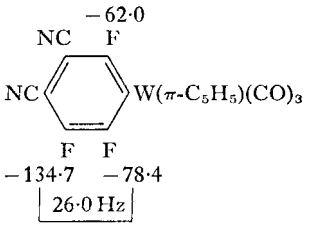
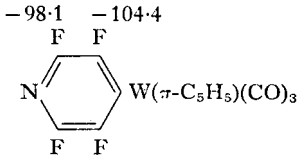


$J(F_2–F_5)$ = 12·3 Hz
$J(F_2–F_6)$ = 4·35 Hz

544



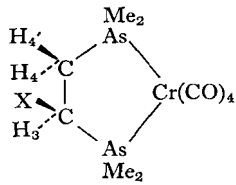
545

The *cis*- and *trans*-isomers of bis(trifluorophosphine)tetracarbonylchromium have been prepared,[450] and both gave $X_3AA'X_3'$ spectra (X = F, A = P) which are illustrated in the original paper. Analysis gave the shifts and coupling constants below.

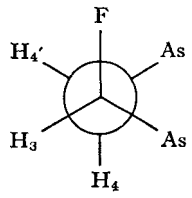
	δ_F	^1J(P–F)	^3J(P–F′)	^4J(F–F′)	^2J(P–P′)
cis	+0·2	−1312	+2·5	*ca.* 0	77·0
trans	−1·1	−1318	+11·5	2·6	34·0

It is noteworthy that ^2J(P–P′) is greater in the *cis*-isomer than in the *trans*, and of opposite sign, so that stereochemical assignment based entirely on NMR data becomes dangerous, particularly with chromium compounds.

The H–F couplings in the chelated tertiary diarsine complex **546a** suggested[451] a strong preference for the conformation with "axial" fluorine, although in the corresponding trimethylsilyl compound **546b**, the hydrogen took the axial position.



546a X = F
b X = $SiMe_3$



$^2J(F–H_3) = 49·6$
$^3J(F–H_4) = 48·7$
$^3J(F–H_4') = 15·7$

Manganese, (technetium), rhenium

A number of polyfluorophenyl and polyfluoropyridyl derivatives of manganese and rhenium compounds have been reported. Oliver and Graham[452] have given parameters for several compounds of the formula $C_6F_5Mn(CO)_nL_{5-n}$, prepared by displacement of carbon monoxide from the parent compound $C_6F_5Mn(CO)_5$. The parameters (Table XLII) followed the linear relationship established previously[453] for $\delta_{F_{para}}$ and J(F2–F4), which was $\leq 0·7$ Hz in all the compounds studied.

The *ortho*-coupling between F(3) and F(4) (19·1 to 19·5 Hz) was in the usual range for polyfluorophenyl compounds, but that between F(2) and F(3), as previously observed for transition-metal derivatives, was considerably larger (28·1 to 30·5 Hz). Coupling between phosphorus and *para*-fluorine (0·8 to 2·5 Hz) could be observed in many of the compounds containing phosphorus ligands, and between phosphorus and *meta*-fluorine in the triphenylphosphine (0·9 Hz) and triphenyl phosphite (1·4 Hz) derivatives.

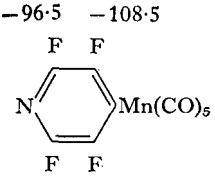
TABLE XLII

^{19}F shifts for pentafluorophenylmanganese compounds[452]

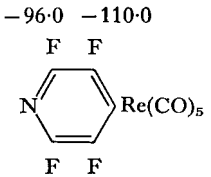
Compound	F2,6	F3,5	F4
$C_6F_5Mn(CO)_5$	−102·5	−162·4	−158·7
$C_6F_5Mn(CO)_4Pn\text{-}Bu_3$	−100·7	−162·6	−161·5
$C_6F_5Mn(CO)_4PPh_3$	−99·3	−162·6	−161·5
$C_6F_5Mn(CO)_4AsPh_3$	−99·0	−162·4	−160·2
$C_6F_5Mn(CO)_4SbPh_3$	−97·4	−162·1	−160·0
$C_6F_5Mn(CO)_4P(OPh)_3$	−100·1	−162·5	−160·0
$C_6F_5Mn(CO)_4NC_5H_5$	−106·5	−162·9	−160·2
$C_6F_5Mn(CO)_3(Pn\text{-}Bu_3)_2$	−97·5	−163·0	−162·6
$C_6F_5Mn(CO)_3[P(OEt)_3]_2$	−97·5	−164·6	−162·9
$C_6F_5Mn(CO)_3(Ph_2PCH_2\cdot)_2$	−95·6	−164·0	−162·3
$C_6F_5Mn(CO)_3(MeSCH_2\cdot)_2$	−105·3	−164·1	−161·3

Calculation of Taft σ_I and σ_R° parameters from the observed shifts led to unexpected substituent parameters (e.g. strong inductive withdrawal of electrons by $Mn(CO)_5$ was implied), and the authors concluded that the use of equations derived from parameters for "common" organic substituents is invalid. However, for monofluorophenyl derivatives (^{19}F shifts for some twenty of which were reported[294]), more reasonable values were obtained. The transition metal donates π-electrons by a conjugative mechanism whatever its nature or substituents, but may donate or withdraw electron density inductively.

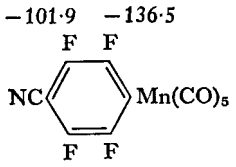
The pentacarbonylrhenium anion displaced $F^\ominus$ from active polyfluoroaromatic compounds,[454] and had very similar effects on δ_F to those of pentacarbonylmanganese (e.g. in **547** and **548**); ^{19}F shifts for 4-carboxy- and 4-ethoxycarbonyl- tetrafluorophenylpentacarbonylmanganese **549** were also reported.[454] The assignment of the bands for **548** and **549** given



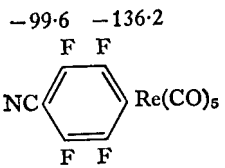
547a



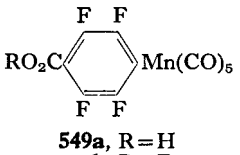
547b



548a



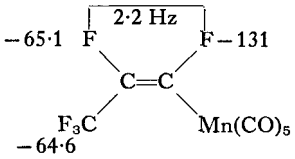
548b



549a, R=H
b, R=Et

in the paper (and shown above for **548**) was based on similar compounds reported previously, but interchange of the assignments gives a better fit with the shift parameters suggested by Bruce[455] for these substituents.

Parameters for pentafluoropropenylpentacarbonylmanganese (**550**), prepared by the reaction of perfluoropropene with $Me_3Sn{\cdot}Mn(CO)_5$, have been reported,[456] the configuration being assigned from the magnitude of the coupling constants.



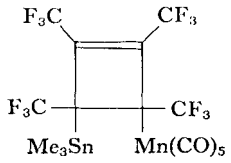
$J(CF_3\text{–}F\textit{trans}) = 13$ Hz

550

The photochemical reaction of $Me_3SnMn(CO)_5$ with perfluorobut-2-yne at room temperature gave a product tentatively identified as the 1:1-adduct **551**; the two ^{19}F signals showed no fine structure. At 77°, the product was the cyclobutene derivative **552**; ^{19}F shifts and splittings were quoted,[456] but not assigned (δ_F −51·0, *q* 19 Hz; −56·9, *q* 20 Hz, poorly resolved; −53·8, −57·0, singlets, width 17 Hz).

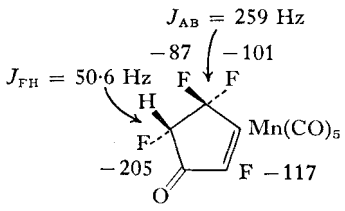
$Me_3Sn \cdot C(CF_3):C(CF_3) \cdot Mn(CO)_5$
δ_F −49·7, −50·9

551



552

The reaction of hydridopentacarbonylmanganese with perfluorocyclopentadiene[111] at room temperature gave a ketonic complex **553**, and three crystalline 1:1 adducts, **554** to **556** which were all characterised by degradation and by spectroscopic methods, the ^{19}F spectra being particularly useful. At low temperatures a further 1:1-adduct **557**, and a second ketonic complex **558** were obtained. Parameters are given with the formulae, and may be compared with those for polyfluorocyclopentenes in Table VI (p. 136). The low-field shift previously observed in fluoroalkyl derivatives of transition metals for the α-fluorine was also apparent in these rigid structures for vicinal fluorines *cis* to the transition metal.



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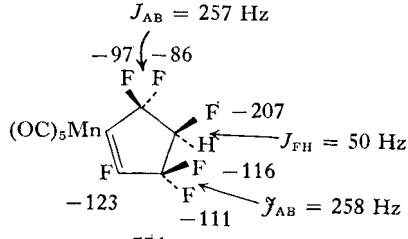

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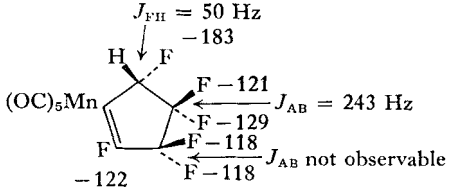

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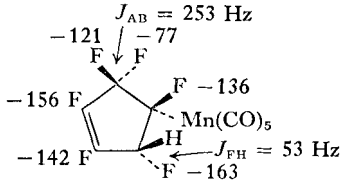

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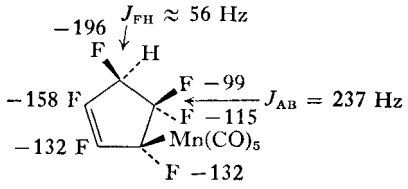
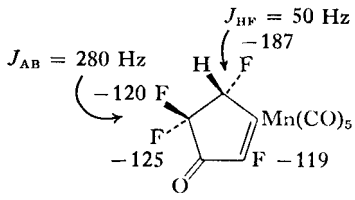


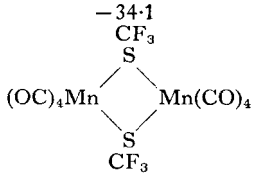
557



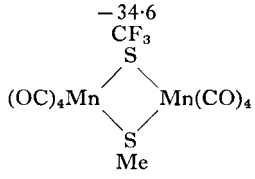
558

Thus the chemical shift difference for F5 (*trans* to manganese) and F5′ (*cis* to manganese) in **556** was large, and the fluorine of the CHF-group was also some 40 p.p.m. to low field of the position expected. Unfortunately, with the exception of **553**, the fine structure of the bands was too complex for complete analysis, and only the geminal fluorine-fluorine and fluorine-hydrogen couplings could be obtained.

The reaction of decacarbonyldimanganese with perfluorodimethyl disulphide gave[457] compound **559** with two bridging SCF_3 groups. The unsymmetrical disulphide MeS_2CF_3 gave also the unsymmetrically bridged compound **560**.



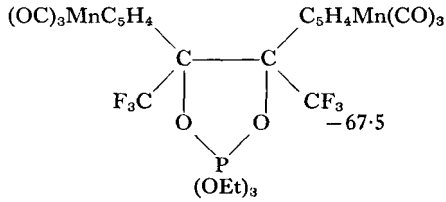
559



560

The reaction of nitrosyltetracarbonylmanganese with trifluorophosphine gave[458] a series of compounds $Mn(NO)(PF_3)_x(CO)_{4-x}$. The shift of the mono-substituted compound was reported as $\delta(CFCl_3)$ 6·53, with $J(P–F) = 1337$ Hz, and remained unchanged as the temperature was lowered to −120°. Both the di- and the tri- substituted compounds were reported to have mirror-image ^{19}F patterns characteristic of equivalent PF_3 groups and the IR spectra showed that the equivalence was a time-average effect. The ^{19}F spectrum of the di-substituted compound broadened at *ca.* −20°, and resharpened at lower temperature, with some differences in the minor peak separations, but remained qualitatively the same. No parameters were given for the tri-substituted compound, but for the di-substituted compound $N[= J(P–F) + J(P–F')]$ was 1319 Hz, and remained constant over the temperature range studied, but the coupling between the phosphorus nuclei changed from 87 Hz to 137 Hz at low temperature.

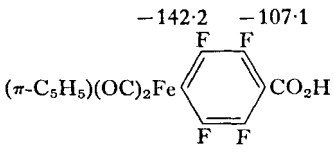
The reaction of trifluoroacetylcyclopentadienyltricarbonylmanganese with triethyl phosphite gave a compound formulated as **561**, the ^{19}F spectrum showing that all the fluorine atoms were equivalent.[459]



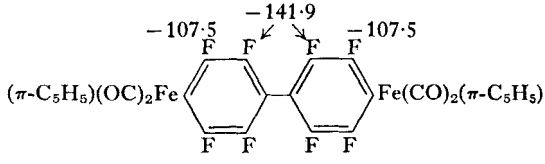
561

Iron, ruthenium, osmium

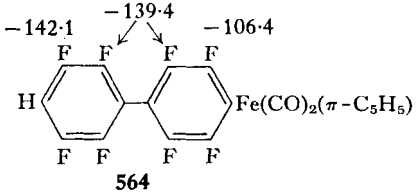
The cyclopentadienyldicarbonyliron anion displaced fluoride ion from a number of polyfluoroaryl compounds, and with pentafluorobenzoic acid[454] gave **562**. As noted with compounds **548** and **549**, reversal of the assignment shown here gives a better fit with Bruce's substituent parameters.[455] Similar reactions with perfluorobiphenyl,[152] gave compound **563** and a mixture identified as **564** and **565**.



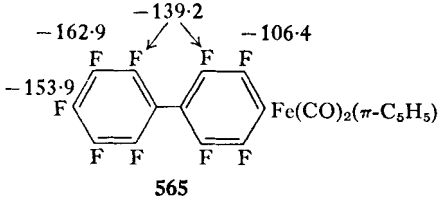
562



563



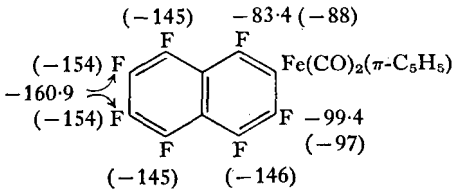
564



565

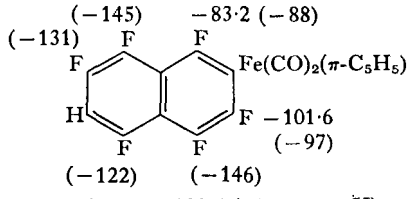
The reaction with octafluoronaphthalene also gave a mixture of two compounds, identified by mass spectrometry and NMR as **566** and (tentatively) **567**, although in the latter case clear distinction between the structure shown and the 7H-compound was not possible. ^{19}F shifts were calculated[152] on the basis of substituent constants established for the C_6F_5 series, with the assumption that deshielding by a substituent in one ring would be only a few p.p.m. for any position in the other ring, and are

shown in parentheses; bands which could not be specifically assigned are shown below the formulae.



δ_F −146·5, −149·4, −152·8

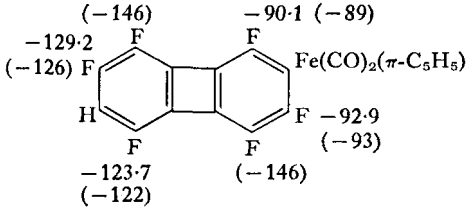
566



δ_F −119·7, −123·5 (adjacent to H)

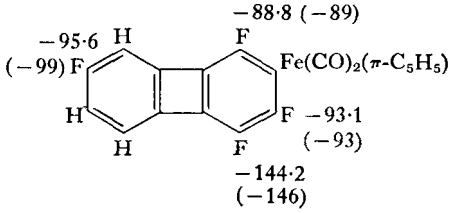
δ_F −139·8, −153·0

567



δ_F −148·2, −154·9

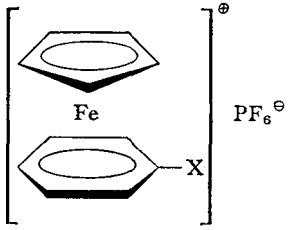
568



569

The reaction with octafluorobiphenylene[152] gave a mixture, even under mild conditions, and the structures of the products could not be firmly established. Some calculated values and observed ^{19}F shifts are shown in formulae **568** and **569**.

Arenecyclopentadienyliron compounds **570** have been prepared by Russian workers.[460] From the ^{19}F shifts in **570b** and **c** Taft σ_i and σ_r°



570

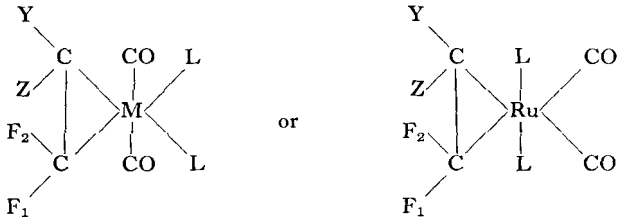
570a X = F, δ_F −134·20
b X = $C_6H_4F(p)$, δ_F −110·70
c X = $C_6H_4F(m)$, δ_F −111·06

parameters were calculated and showed that the arenecyclopentadienyl-iron group may be regarded as an electron-accepting substituent.

Fluoro-olefin complexes of carbonyliron[461] and its derivatives[462] and of substituted carbonylruthenium[462] have been prepared by two groups by UV irradiation of the olefin with an appropriate carbonyl compound, or by displacement of carbon monoxide from an olefin carbonyl complex. ^{19}F shifts and geminal coupling constants for some such complexes are given in Table XLIII. Although F_1 and F_2 in the complexes may be interchanged, so that it is not possible to identify the *cis*- and *trans*-fluorine-fluorine coupling constants with certainty, the large coupling constant in these complexes is the geminal fluorine-fluorine coupling rather than $J(F\text{–}F_{trans})$. This was shown unambiguously[461] by the spectrum of the complex from pentacarbonyliron and $CF_3 \cdot CH{:}CF_2$, and

TABLE XLIII

^{19}F parameters for olefin-metal complexes

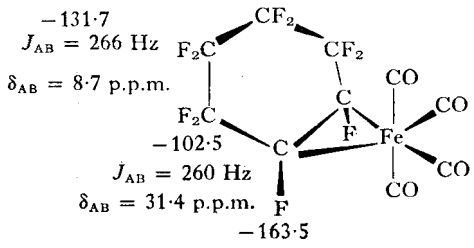


(I) (II)

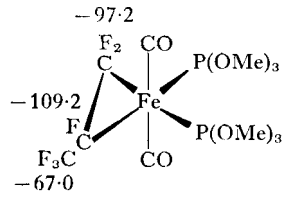
Compound				Chemical shifts				$J(F\text{–}F_{gem})$ (Hz)	Ref.
L	M	Y	Z	δ_{F1}	δ_{F2}	δ_Y	δ_Z		
I CO	Fe	F	F	−110·5	−110·5	−110·5	−110·5	..	461
I CO	Fe	Cl	Cl	−84·5	−84·5	..	..	.	461
I CO	Fe	F	CF_3	−93·5	−96·5	−183·5	−68·5	141	461
I CO	Fe	F	Cl	−99·5	−94·5	−116·5	..	130	461
I CO	Fe	F	Br	−97·9	−88·9	−113·7	..	126	461
I CO	Fe	CF_3	H	−72·6	−88·5	−55·7	..	113	461
I $(MeO)_3P$	Ru	F	F	−113·2	−113·2	−113·2	−113·2	180 ± 20	462
I $(MeO)_3P$	Ru	F	Cl	−95·7	−104·8	−122·0	..	163·0	462
I $(MeO)_3P$	Ru	F	H	−95·0	−104·1	−208·6	..	170·0	462
I $(EtO)_3P$	Ru	F	H	−94·5	−104·6	−206·7	..	166·0	462
I TMP[a]	Ru	F	H	−97·5	−104·6	−209·0	..	164·0	462
I $(MeO)_3P$	Fe	F	F	−112·0	−112·0	−112·0	−112·0	..	462
I $(EtO)_3P$	Fe	F	F	−113·0	−113·0	−113·0	−113·0	..	462
II PMe_2Ph	Ru	F	F	−115·2	−115·2	−115·2	−115·2	..	462
II PMe_2Ph	Ru	F	H	−98·5	−105·3	−211·0	..	170·0	462

[a] TMP = $C_2H_5C(CH_2O)_3P$.

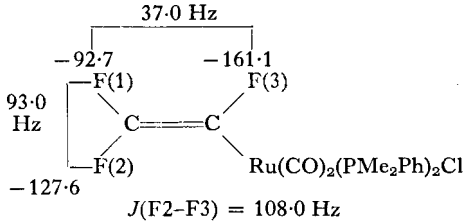
by regeneration of the original olefin on pyrolysis of the complex. This change implies a drastic change in hybridisation at carbon and suggests that the complexes are reasonably drawn in valence bond terms with C–M σ-bonds, e.g. **571**, **572**. The complexes from cyclic olefins (C_4F_6,[461,462] C_5F_8,[461] C_6F_{10}[461]) all showed AB quartets for the geminal pairs of fluorines as in **571**.



571



572



573

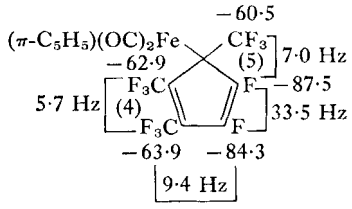
UV irradiation of *trans*-(bisdimethylphenylphosphine)dicarbonylruthenium[462] with chlorotrifluoroethylene, in contrast, gave the trifluorovinyl compound **573**.

UV irradiation of $Me_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ with hexafluorobut-2-yne gave[456] the 1:1-adduct **574** at room temperature, but the cyclopentadienyl compound **575** at elevated temperature, together with minor amounts of **576**. In the similar products formed from 3,3,3-trifluoropropyne **577a**, **b** the hydrogen was clearly *cis* to the trifluoromethyl group, but the direction of addition was not established with certainty.

Irradiation of tetrafluoroethylene[463] with nonacarbonyldi-iron or a mixture of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ gave good yields of the known heterocyclic compound **578**, and a number of derivatives have been obtained by ligand displacement reactions; their ^{19}F shifts are given in

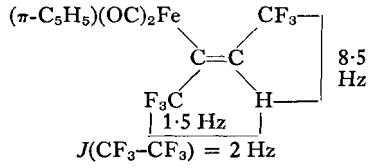
$Me_3Sn(CF_3)C{:}C(CF_3)[Fe(CO)_2(\pi\text{-}C_5H_5)]$
δ_F −49·4, −50·4

574



$J[CF_3(4)–CF_3(5)] = 3·2$ Hz

575

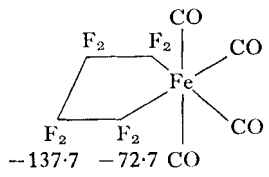


576

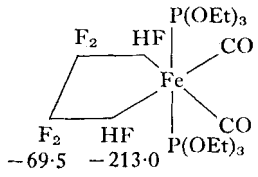
$Me_3MCH{:}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$

577a M = Si, δ_F −60·1, J(H–F) = 2 Hz
b M = Ge, δ_F −59·4, J(H–F) = 2 Hz

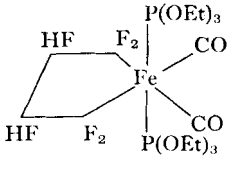
Table XLIV. Irradiation of trifluoroethylene with bis(triethylphosphite) tricarbonyliron gave a similar compound, formulated[462] as **579**. The authors stated that the alternative symmetrical structure with CF_2 groups adjacent to iron (**580**) cannot be excluded, and comparison with the ^{19}F shifts of the bis(triethyl phosphite) derivative of **578** suggests that **580** might be preferred.



578



579



580

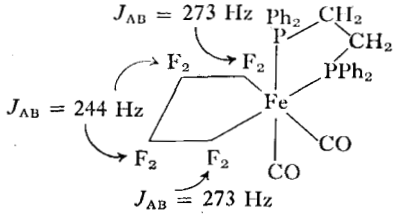
TABLE XLIV

^{19}F shifts for $(CF_2)_4Fe(CO)_{4-n}L_n$[463]

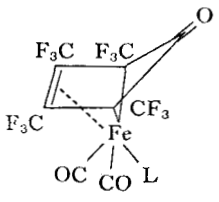
Compound	α-CF_2(1)	α-CF_2(2)	β-CF_2
$(CF_2)_4Fe(CO)_3PPh_3$	−74·1[a]	−81·3[b]	−139·3
$(CF_2)_4Fe(CO)_3AsPh_3$	−65·4	−71·1	−131·4
$(CF_2)_4Fe(CO)_3SbPh_3$	−70·5	−71·2	−137·8
$(CF_2)_4Fe(CO)_3P(OPh)_3$	−75·7[c]	−79·1	−138·5
$(CF_2)_4Fe(CO)_3P(OEt)_3$	−77·1[d]	−80·3[e]	−138·9
$(CF_2)_4Fe(CO)_2[P(OEt)_3]_2$	−82·3	−82·3	−138·9

[a] J_{PF} = 17 Hz.
[b] J_{PF} = 9 Hz.
[c] J_{PF} = 29 Hz.
[d] J_{PF} = 30·5 Hz.
[e] J_{PF} = 18 Hz.

It was suggested[463] that α-CF_2(1) in Table XLIV was probably *trans* to the substituent, since coupling of the fluorines to the *trans*-phosphorus would be expected to be stronger than to the *cis*. The complex formed by replacement of two carbon monoxide ligands by the chelating ligand 1,2-bis(diphenylphosphino)ethane appeared from its ^{19}F spectrum to have the unsymmetrical structure **581**, since geminal non-equivalence of the fluorines was observed.

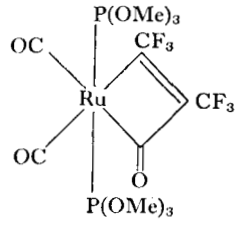


581



582

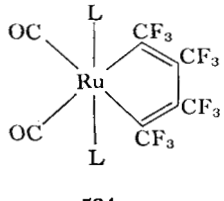
582a L = $PhMe_2P$; δ_F −52·7, −54·0
b L = $(EtO)_3P$; δ_F −52·6, −54·9



583

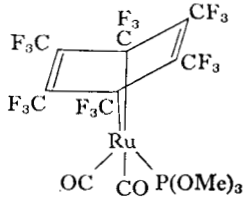
δ_F −58·0, −64·2
J(F–F) = 9·0 Hz

583



584

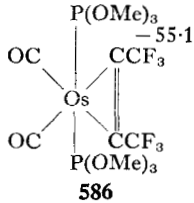
584a L = $(MeO)_3P$; δ_F −52·3, −54·6, J(F–F) = 3·5 Hz
b L = $PhMe_2P$; δ_F −50·2, −65·6



585

δ_F −49·2, −53·3, −56·9

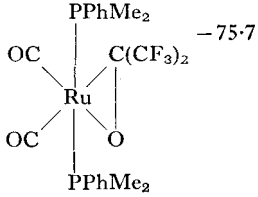
585



586

UV irradiation of hexafluorobut-2-yne with $Fe(CO)_3L_2$ ($L = (MeO)_3P$ or $PhMe_2P$) gave only the cyclopentadienone complexes **582**, but variation of the reactant ratios with the corresponding ruthenium compounds allowed the isolation of a number of metal complexes **583** to **585**.[464] In contrast,[464] irradiation of hexafluorobutyne and $Os(CO)_3[P(OMe)_3]_2$ gave only complex **586** under all the conditions studied.

With hexafluoroacetone, $Ru(PhPMe_2)_2(CO)_3$ readily gave[462] a complex **587**, but with the cyclopentadienyldicarbonyliron anion[222] a derivative of hexafluoroisopropanol (**588**) was formed.



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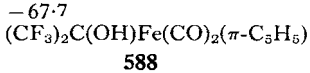
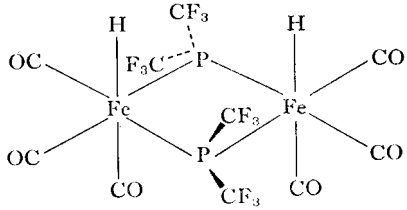


588

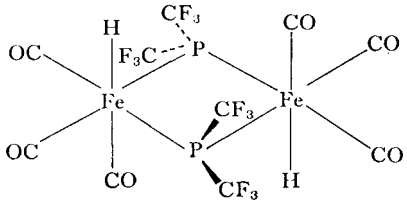
Heptafluoro-2-iodopropane reacted readily[461] with pentacarbonyliron to give $(CF_3)_2CF \cdot Fe(CO)_4I$, which showed the expected septet [J(F–F) = 11 Hz, δ_F −156·1) and doublet (δ_F −70·1).

The reaction of bis(trifluoromethyl)phosphine with pentacarbonyliron gave[465] a mixture of geometric isomers containing bridging phosphine groups formulated as **589a** and, in view of the $X_6AA'X_6'$ pattern observed, **589b**. The bridged phosphine complex **590** was reported to show 3 doublets in its ^{19}F spectrum, but no splittings were given.[466]



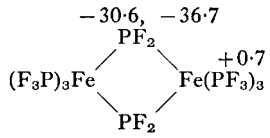
δ_F −58·5, −56·3
J(F–F) = 8·5 Hz

589a



δ_F −57·1
^2J(F–P) = 55·0 Hz
^4J(F–P′) ≈ 1·0 Hz
^2J(P–P′) = 175 Hz

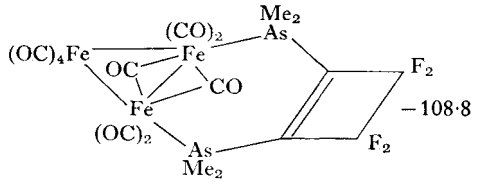
589b



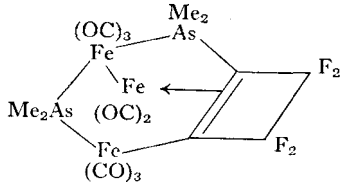
590

Butadienetricarbonyliron reacted with trifluorophosphine with successive replacement of the carbonyl groups.[467] The mono-substituted compound showed two sharp bands, [J(P–F) = 1300 Hz], which showed a slight shift to lower field when the sample was cooled to −100°, but no other change. At 30° the disubstituted compound showed a sharp peak and a broad unresolved peak separated by some 1300 Hz from their mirror image, as might be expected for equivalent PF_3 groups. When the temperature was reduced to −107° the spectrum (illustrated in the original paper) was resolved into a pair of 10 Hz doublets, separated by 150 Hz, with a mirror image pattern still 1300 Hz away, indicating that at low temperature the exchange between non-equivalent sites was no longer rapid on the NMR time scale.

1,2-Bis(dimethylarsino)tetrafluorocyclobutene and the corresponding phosphine-compound formed a number of transition-metal compounds, often of complex structures which required X-ray analysis. Parameters for some of the compounds reported[468, 469] are given in formulae **591** to **593**, and in Table XLV. The 8 lines reported for **592** are presumably a pair of AB quartets, and each band reported was stated to be "poorly resolved, showing four lines", which is presumably due to coupling to the methyl groups.

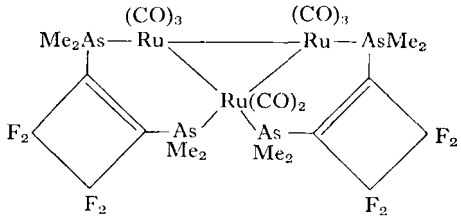


591



δ_F −93·6, −95·7, −99·1, −101·2, −101·8, −104·0, −105·2, −107·6

592

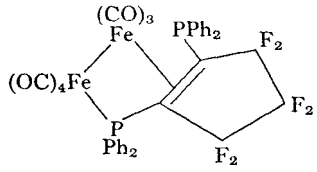


δ_F −107·8 Symmetrical pattern of 14 peaks

593

The similar diphosphinocyclopentene also formed complexes such as that formulated as **594**, which showed three AB quartets (δ_A −99·4, δ_B −110·9, J_{AB} = 264 Hz; δ_A −106·8, δ_B −111·4, J_{AB} = 272 Hz; and

δ_A −124·4, δ_B −128·6, J_{AB} = 238 Hz), indicating a lack of symmetry both in the plane of the ring and in the plane perpendicular to it.



594

TABLE XLV

Complexes with fluoro-cyclobutene and -cyclopentene arsenic and phosphorus ligands[468,469]

Compound	^{19}F shift and pattern
$C_4F_4(Me_2As)_2Ru_3(CO)_{10}$	−108·4 singlet
$C_4F_4(Me_2As)_2Ru_2(CO)_6$	−92·9, −94·8, −108·2, −110·0. Complex symmetrical pattern.
$C_4F_4(PPh_2)_2Ru_3(CO)_{10}$	−109·1 singlet
$C_4F_4(PPh_2)_2Ru_2(CO)_6$	−85·2, −87·1, −105·8, −107·8. Complex symmetrical pattern.
$C_4F_4(PPh_2)_2Ru(CO)_3$	−109·6 singlet
$C_5F_6(PPh_2)_2Ru(CO)_3$	−129·6 quintet (≈6·4 Hz) −108·0 triplet (≈6 Hz)
$C_5F_6(PPh_2)_2Ru_2(CO)_6$	−65·2, −103·3, −114·0, −122·2 doublets of multiplets.

Cobalt, rhodium, iridium

Polyfluorophenyl derivatives of cobalt[454] and rhodium[470,471] have been prepared and the parameters reported are given in Table XLVI.

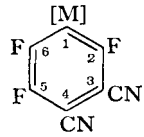
The reactions of fluorobut-2-ynes with cobalt carbonyl compounds gave a wide range of products; thus with hexafluorobut-2-yne dodecacarbonyltetracobalt gave[472] an alkyne complex $Co_4(CO)_{10}(CF_3C_2CF_3)$ which showed two singlets of equal intensity at δ_F −47·2, −52·1, suggesting that the C–CF_3 bonds were no longer colinear. Octacarbonyldicobalt and bis(triphenylphosphine)hexacarbonyldicobalt both gave alkyne complexes with trifluorobut-2-yne (δ_F −53·09, −45·8 respectively). The arrangement of substituent groups in the "flyover structures" **596** was deduced[473] from ^{1}H and ^{19}F NMR. The shifts lay in narrow ranges,

TABLE XLVI

^{19}F shifts for polyfluorophenyl-cobalt and -rhodium compounds

Compound	Chemical shift				
	F(2)	F(3)	F(4)	F(5)	F(6)
$(C_6F_5Rh(\pi\text{-}C_5H_5)Cl)_2$	−111·4	−164·9	−161·8	−164·9	−111·4
$C_6F_5Rh(\pi\text{-}C_5H_5)(C_5H_5N)Cl$	−114·3	−163·8	−160·8	−163·8	−114·3
$C_6F_5Rh(\pi\text{-}C_5H_5)(PPh_3)Cl$	−104·8	−164·6	−160·5	−164·6	−104·8
$C_6F_5Rh(\pi\text{-}C_5H_5)(en)Cl$[a]	−116·7	−166·5	−162·4	−166·5	−116·7
$C_6F_5CORh(Ph_2PMe)_2(acac)Cl$[b]	−140·5	−164·2	−160·5	−164·2	−140·5
$C_6F_5SO_2Rh(Ph_2PMe)(acac)Cl$	−134·6	−160·6	−157·3	−160·6	−134·6
595a	−69·65	..	..	−136·8	−86·78
595b	−70·7	..	..	−136·1	−88·3
595c	−69·0	..	..	−138·0	−87·5

[a] en = ethylenediamine; spectrum in EtOH/HCl.
[b] acac = acetylacetonate.



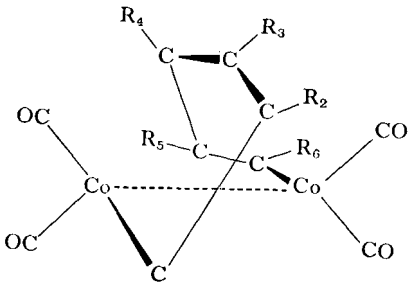
595a M = $Co(CO)_2[P(OPh)_3]_2$
b M = $Co(CO)_2[P(OCH_2)_3CEt]_2$
c M = $Co(CO)[P(OCH_2)_3CEt]_3$

and adjacent CF_3 groups coupled (*J ca.* 10 Hz), but adjacent hydrogen and CF_3 did not. Parameters for some compounds identified on this basis are given in Table XLVII.

TABLE XLVII

^{19}F shifts and splitting patterns in compounds 596[473]

Compound	R_1	R_2	R_3	R_4	R_5	R_6
$Co_2(CO)_4(CF_3C_2CF_3)_3$	−52·0q	−55·3sept	−59·1q	−59·1q	−55·3sept	−52·0q
$Co_2(CO)_4(CF_3C_2CF_3)_2$ (CF_3C_2H)	−57·6s	Hs	−61·8q	−59·5sept	−55·4sept	−52·2q
$Co_2(CO)_4(CF_3C_2CF_3)$ $(CF_3C_2H)_2$	−58·4s	Hs	−62·4s	−62·4s	Hs	−58·4s
$Co_2(CO)_4(CF_3C_2CF_3)$ $(CF_3C_2H)_2$	−57·8s	Hs	−64·0s	Hs	−61·4q	−51·1q
$Co_2(CO)_4(CF_3C_2H)_3$	−58·6s or −58·9s	Hs	−64·8s	Hs	Hs	−58·9s or −58·6s
$Co_2(CO)_4(CF_3C_2Me)$ $(CF_3C_2H)_2$	−57·25s	H	−57·32	Me	H	−60·85s



596

Cyclopentadienone derivatives have also been prepared; thus $(\pi\text{-}C_5H_5)Co(C_4(CF_3)_4CO)$ showed two bands at δ_F −60·6, −56·4. Two isomers were formed from 1,1,1-trifluorobut-2-yne. The singlet (δ_F −56·6) was assigned to that with both CF_3 groups β to the carbonyl, and the two bands at δ_F −53·0, −55·8 to the isomer with one α- and one β- CF_3 group. The cyclopentadienone derivative formed[474] from decafluorotolan and $(\pi\text{-}C_5H_5)Co(CO)_2$ showed six sharp lines, indicating the presence of two types of C_6F_5 but was stated to be too insoluble for measurement of parameters. The corresponding compound from pentafluorotolan showed four bands at δ_F −131·3 (4 *ortho* fluorines), −150·3 (t, $J \approx 20$ Hz, 1 *para* fluorine), −152·3 (t, $J \approx 20$ Hz, 1 *para* fluorine), and −159·9 (4 *meta* fluorines), in accord with a structure containing one α- and one β- C_6F_5 group, and the rhodium complexes $\{RhCl[(CO)(C_6F_5C_2C_6H_5)_2]\}_2$ and $(\pi\text{-}C_5H_5)Rh[(CO)(C_6F_5C_2C_6H_5)_2]$ were similarly formulated.

The reaction of hydridotetracarbonylcobalt with chlorotrifluoroethylene gave[475] the fluoroalkyl complex **597**, the spectra of which are illustrated in the paper.

$$\underset{\quad -116\cdot6 \quad -69\cdot7}{CHF_2\text{—}CFCl\text{—}Co(CO)_4}$$

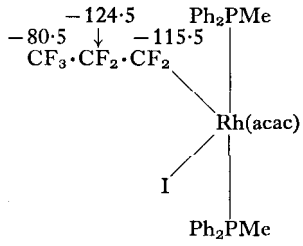
$^2J(F\text{–}F) \approx 275$ Hz†
$^2J(H\text{–}F) = 60\cdot1, 56\cdot9$ Hz
$^3J(F\text{–}F) = 11\cdot8, 20\cdot4$ Hz
$^3J(H\text{–}F) = 3\cdot4$ Hz

597

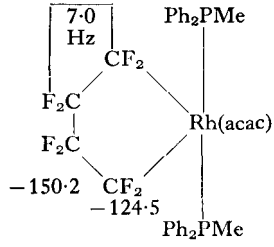
Several rhodium complexes have been prepared[471] by the reaction of acetylacetonatobis(methyldiphenylphosphine)rhodium and related rhodium compounds with fluoroalkyl iodides, fluoro-olefins, ketones, and

† Estimated from the illustration in ref. 475.

imines, and some structures and parameters are shown in formulae **598** to **606**.



598



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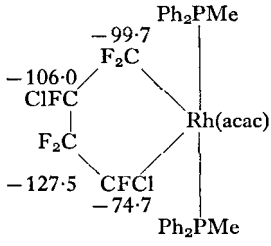

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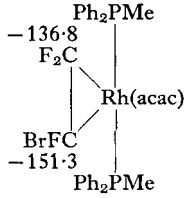

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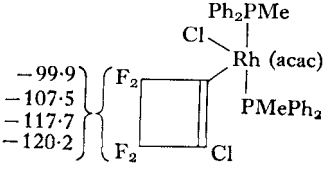

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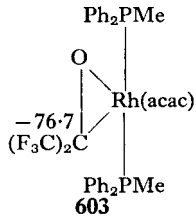

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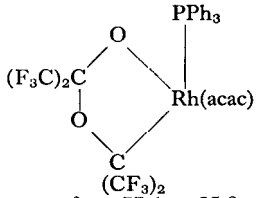
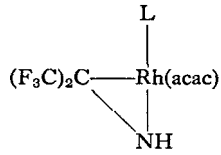
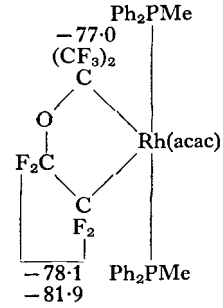


δ_F −77·6, −85·9

604



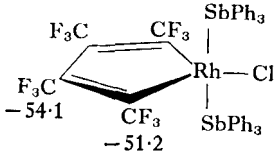
605a L = PPh_2Me, δ_F −76·0
605b L = PPh_3, δ_F −69·1



606

Parameters similar to those shown for **598** were reported for a number of perfluoropropylrhodium compounds. Rhodium-fluorine coupling was reported[470] for the compound $CF_3Rh(\pi\text{-}C_5H_5)(NC_5H_5)I$ [δ_F −26·4, $J(Rh–CF_3) = 11·7$ Hz], but was not observed for other compounds.

The structure of compound **607** has recently[476] been established by X-ray analysis, and parameters for the similar iridium complexes **608**, in which the α-CF_3 groups are non-equivalent because of the chlorine and carbonyl group also being in the equatorial plane, and **609** have also been reported.[477]



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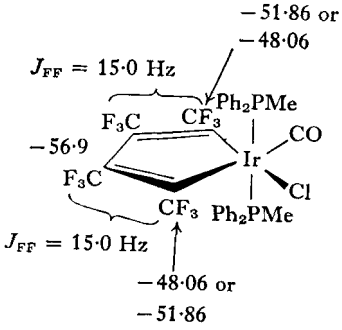

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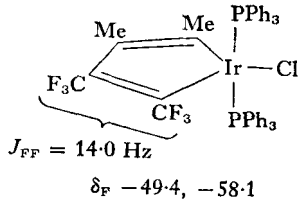


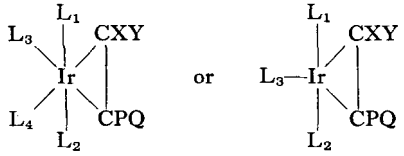
δ_F −49·4, −58·1

609

The parameters for a number of iridium complexes of fluoro-olefins and an acetylene are collected in Table XLVIII.

TABLE XLVIII

^{19}F parameters for fluoro-olefin and -acetylene iridium complexes



Compound						
L_1	L_2	L_3	L_4	Olefin or acetylene	Chemical shifts	Ref.
CO	Cl	PPh_2Me	PPh_2Me	C_2F_4	−155·5, −166·0	477
Ph_3P	Ph_3P	Cl	..	C_2F_4	−94·5	477
Ph_3P	Ph_3P	Ph_3P	Cl	C_2F_4	−100·5	477
CO	Cl	PPh_3	PPh_3	*trans* $CF_3C(CN):C(CN)CF_3$	−53·5, −58·0	478
CO	Cl	PPh_2Me	PPh_2Me	*trans* $CF_3C(CN):C(CN)CF_3$	−53·1, −57·9	478
PPh_2Me	PPh_2Me	CO	Cl	$CF_3C{:}CCF_3$	−51·7, −54·4[a]	477
Ph_3P	Ph_3P	Cl	..	$CF_3C{:}CCF_3$	−55·9	477

[a] J_{FF} = 15·0 Hz.

Fluoroalkyl-rhodium complexes analogous to hydroformylation intermediates have been reported by Wilkinson and his co-workers,[479] and parameters are shown below.

	F_α	F_β	J(H–F_α)	J(H–F_β)
$Rh(C_2F_4H)(CO)(PPh_3)_2$	−88·07	−128·70	9	56
$Rh(C_2F_4H)(CO)_3PPh_3$	−49·7	−122·00	5	60
$Rh(C_2F_4H)(SO_2)(CO)(PPh_3)_2$	−79·0	−134·3	8	55

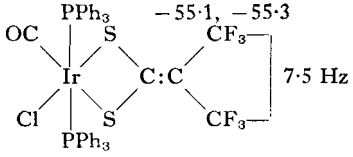
Some "nitrene complexes" of iridium and rhodium have been prepared[480] by the reaction of a fluoroalkyl azide with (e.g.) $(Ph_3P)_2Ir(CO)Cl$, and parameters are given with formulae **610** and **611**. The reaction of $IrCl(CO)(PPh_3)_2$ with the bis(trifluoromethyl)thioketen precursors gave[481] the chelated complex **612**, together with an inseparable mixture of isomers assigned the structures **613a** and **b**. Both the bands observed (centred at δ_F −57·5, −61·3) consisted of overlapping quartets [J(F–F) = 7·5 Hz].

$(Ph_3P)_2Ir(CO)Cl(N{\cdot}CF_2{\cdot}CHF{\cdot}CF_3)$ $(Ph_3P)_2RhCl(N{\cdot}CF_2{\cdot}CHF{\cdot}CF_3)(CO(CF_3)_2)$

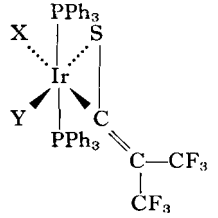
−139·5 ↑ −74·3 −140·1 ↑ −75·9 −78·1

−152·4 −153·0

610 **611**



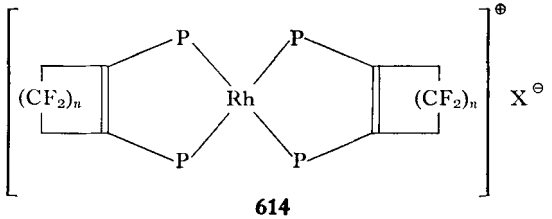
612



613a X = CO, Y = Cl

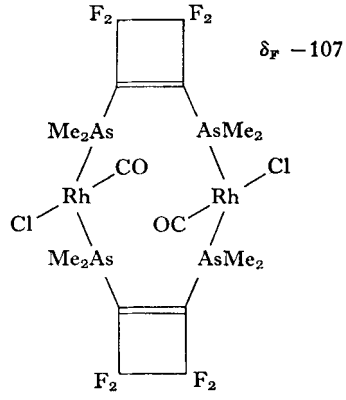
b X = Cl, Y = CO

The chelating diphosphine complexes 1,2-bis(diphenylphosphino)-perfluorocyclo -butene and -pentene formed ionic complexes on reaction[482] with dichlorotetracarbonyl dirhodium, and the products were formulated as the symmetrical structures **614**.



614

614a n = 2, X = [*cis*-$Rh(CO)_2Cl_2$]; δ_F −110 (singlet)
b n = 3, X = [*cis*-$Rh(CO)_2Cl_2$]; δ_F −108 (triplet), −128 (quintet)
c n = 3, X = BPh_4; δ_F −109 (triplet), −129 (quintet)



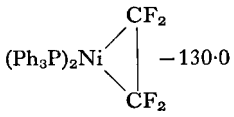
615

The corresponding reaction with 1,2-bis(dimethylarsino)tetrafluorocyclobutene, however, gave a complex in which single ^{1}H and ^{19}F signals indicated a symmetrical structure which was formulated as **615**.

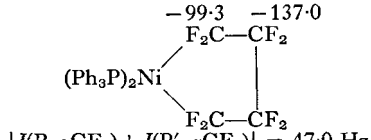
The reaction of tris(trifluoromethyl)phosphine with nitrosyltricarbonylcobalt gave a compound $\{[(CF_3)_3P]_2Co(NO)(CO)\}_3$, which was formulated[483] as a cobalt cluster with bridging carbonyls and terminal nitrosyls and phosphines. The ^{19}F spectrum consisted of a doublet ($J_{PF}=91{\cdot}3$ Hz, δ_F -59), indicating a symmetrical structure.

Nickel, palladium, platinum

The olefin complex **616** reacted[484] readily with tetrafluoroethylene to give the five-membered ring compound **617**, and a number of similar complexes (L = phosphine, phosphite, or pyridyl ligands) had the α-CF_2



616



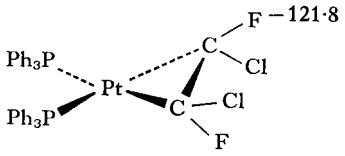
$|J(P\text{-}\alpha CF_2)+J(P'\text{-}\alpha CF_2)| = 47{\cdot}0$ Hz

617

groups in the region of δ_F -103 p.p.m. with the β-CF_2 group at δ_F -138 p.p.m. Hexafluoropropene complexes of nickel have also been prepared, and parameters reported[485] are given below. The assumption that F2 and F3 were *trans* was stated in the paper; the assignment of signals to the individual fluorines appears to have been made on the assumption that the nickel will affect each fluorine by a similar amount. This assignment leads to a large geminal coupling in the nickel complexes as shown[461] for the corresponding iron complexes.

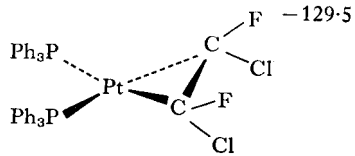
	F(3)F(4)C:C(F(2))CF$_3$(1)						
	$\delta_{F(1)}$	$\delta_{F(2)}$	$\delta_{F(3)}$	$\delta_{F(4)}$	$J(1, 2)$	$J(2, 3)$	$J(3, 4)$
C_3F_6	−72·0	−192·0	−107·0	−93·0	13·0	120·0	57·0
1,5-cyclo-octadiene Ni(C_3F_6)	−66·2	−209·0	−116·8	−112·1	..	79·0	168·0
$(Et_3P)_2Ni(C_3F_6)$	−65·0	−214·8	−122·6	−111·1	14·0	76·0	193·6

Olefin complexes of platinum, **618** to **620** have also been prepared.[478, 486] These readily rearranged to give the corresponding vinyl compounds and parameters for these and for some other vinyl compounds are given below.[478, 486]



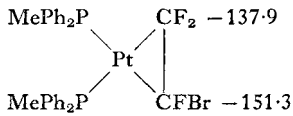
^2J(Pt–F) = 168·0 Hz
$|J$(P–F)+J(P′–F)$|$ = 57·0 Hz

618

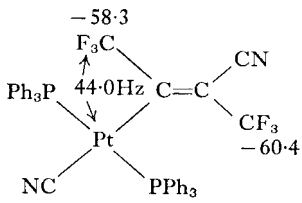


^2J(Pt–F) = 204 Hz
$|J$(P–F)+J(P′–F)$|$ = 44·0 Hz

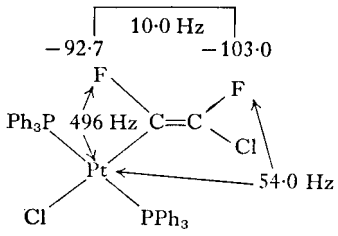
619



620

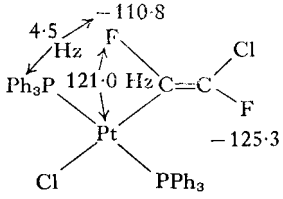


621



^3J(P–F) = 6·0 Hz
^4J(P–F) = 2·0 Hz

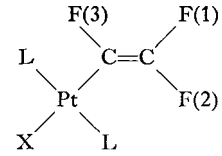
622



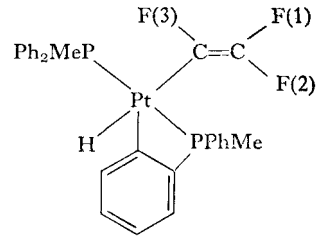
J(F–F) = 123·0 Hz

623

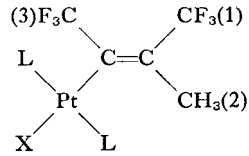
The difference in the values for the platinum-fluorine coupling constants for **624** and **625** is in accord with the different oxidation states for platinum. The complexes **626a** to **e** were formed[487] by addition to hexafluorobut-2-yne, and the value of the coupling constant between the two trifluoromethyl groups was used as evidence for the stereo-



624a X = Br, L = Ph_2PMe
b X = OAc, L = Ph_2PMe
c X = OAc, L = Ph_3P



625

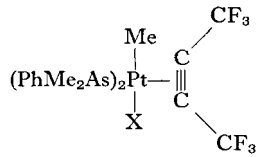


626a L = $PPhMe_2$, X = Cl
b L = $PPhMe_2$, X = Br
c L = $PPhMe_2$, X = I
d L = $AsPhMe_2$, X = Cl
e L = $AsMe_3$, X = Cl

	624a	**624b**	**624c**	**625**	**626a**	**626d**
δF(1)	−100·7	−97·6	−97·5	−101·0	−61·0	−60·6
δF(2)	−128·3	−128·9	−128·1	−128·2	..	..
δF(3)	−148·2	−151·1	−147·8	−147·8	−50·8	−51·5
J_{12}	100·0	101·0	96·0	103·0	..	..
J_{13}	33·0	30·0	31·0	32·0	15·0	15·0
J_{23}	108·0	108·0	108·0	106·0	1·7	2·0
J(P–F1)	6·0	6·5	7·0	6·0	..	..
J(P–F2)	4·0	4·0	..	..	..	..
J(Pt–F1)	62·0	60·5	69·5	121·0	6·2	3·5
J(Pt–F2)	45·5	59·5	60·0	101·0	..	..
J(Pt–F3)	425·0	565·0	579·0	283·5	128·3	128·5

chemistry shown. Parameters for **626b**, **c** and **e** were similar to those given here for **a** and **d**.

Acetylene complexes of platinum(IV) (**627**) have been prepared[488] by the oxidative addition of hexafluorobutyne to the platinum(II) compound.

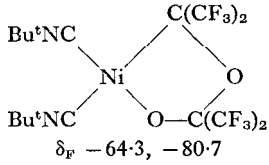


627

a X = Cl, δ_F −55·3 *J*(Pt–F) = 41·0 Hz
b X = I, δ_F −55·5 *J*(Pt–F) = 40·5 Hz

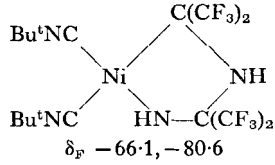
In contrast to the reactions of hexafluoroacetone with NiL_4 (L = Et_3P,

Ph_2PMe, or $L_2 = 1,5$-cyclo-octadiene), in which the 3-membered ring compounds are formed, when L is Bu^tNC, five-membered rings are formed[484] with both hexafluoroacetone and hexafluoroisopropylideneimine (**628, 629**).



δ_F −64·3, −80·7

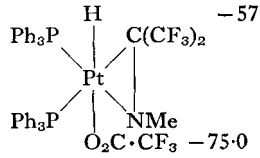
628



δ_F −66·1, −80·6

629

3-Membered rings from four-co-ordinate nickel and platinum complexes and hexafluoroisopropylideneimine and the *N*-methyl-compound all showed[489] a single ^{19}F absorption at δ_F *ca.* −60. Whether the CF_3-groups are equivalent in the complexes because changes in hybridisation at the nitrogen make the N–R bond coplanar with the ring, or whether rapid inversion at nitrogen takes place could not be determined. The six-co-ordinate platinum complex **630**, however, showed inequivalent geminal CF_3-groups.



630

Parameters for a number of fluoroalkyl-platinum(II)[486,487,490] and platinum(IV)[490] compounds have been reported, and are summarised in Tables XLIX and L. Fluorine nuclei adjacent to platinum were deshielded considerably as expected, and platinum-fluorine couplings were high both in Pt(II) and Pt(IV) compounds, decreasing with distance from the platinum. The platinum-fluorine coupling constants reported for the two compounds *trans* $PtI(CF_3)(PMe_2Ph)_2$[490] and *trans* $PtI(CF_3)(PPh_2Me)_2$[486] differ so widely as to suggest either that one must be in error or that a structure has been mis-assigned.

The ^{19}F shifts for bis(fluorophenyl)bis(triethylphosphine)platinum and the arsenic and antimony analogues have been reported.[491] Although the significance of the results was still not entirely clear, the difference

TABLE XLIX

^{19}F parameters for platinum(II) complexes

Compound	δ_F	J(P–F)	J(Pt–F)	Assignment
trans $PtI(CF_3)(PMe_2Ph)_2$	−12·2	20·5	753	αCF_3
trans $PtI(C_2F_5)(PMe_2Ph)_2$	−75·7	27·5	445	αCF_2
	−80·5	2·3	54	βCF_3
trans $PtI(C_3F_7)(PMe_2Ph)_2$	−72·4	28	442	αCF_2
	−114·8		105	βCF_2
	−79·6		25	γCF_3
trans $PtI(C_3F_7)(PPh_2Me)_2$	−76·0	38·0		αCF_2
	−114·7			βCF_2
	−79·9			γCF_3
trans $PtI(CF_3)(PPh_2Me)_2$	−11·99	10·2	17·9	αCF_3
trans $PtCl(COC_3F_7)(PPh_2Me)_2$	−111·6			βCF_2
	−127·5			γCF_2
	−81·4			δCF_3
trans $PtCl(CF_2 \cdot CF_2 \cdot CH_3)(PPhMe_2)_2$[a]	−68·3	29·2	480	αCF_2
	−94·5		66	βCF_2
trans $PtCl(CF_2 \cdot CF_2 \cdot CH_3)(AsMe_3)_2$	−67·4		474	αCF_2
	−95·3		106·5	βCF_2
trans $PtMe(CF_2 \cdot CF_2 \cdot CH_3)(PPhMe_2)_2$	−69·0	28·7	475	αCF_2
	−95·8			βCF_2

[a] Parameters for a number of other tetrafluoropropyl platinum(II) compounds are similar to those given here and are recorded in ref. 487.

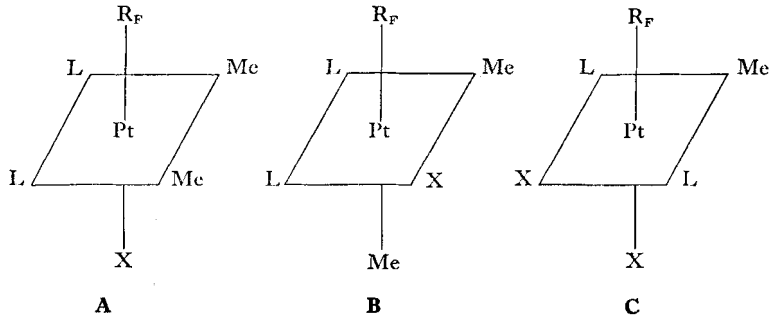
between δ_F (*meta*) and δ_F (*para*) appeared to indicate a slight gradation in the electronic properties in the series. Parameters are given below.

Compound	δ(*meta* F)	δ(*para* F)
cis $(Et_3P)_2Pt(C_6H_4F)$	−115·90	−123·55
cis $(Et_3As)_2Pt(C_6H_4F)$	−115·90	−123·35
cis $(Et_3Sb)_2Pt(C_6H_4F)$	−115·45	−122·85
trans $(Et_3As)_2Pt(C_6H_4F)$	−116·40	—

The parameters for a number of other nickel[484] and platinum[222,481,492] compounds are shown with formulae **631** to **636**.

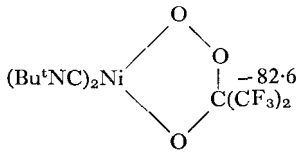
TABLE L

^{19}F parameters of platinum(IV) complexes

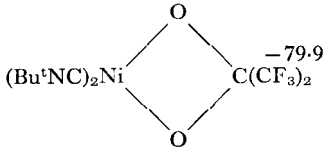


Structure	L	X	R_F	δ_F	J(P–F)	J(Pt–F)	Assignment
A	PMe_2Ph	I	CF_3	−19·3	14	517	αCF_3
A	PMe_2Ph	I	C_2F_5	−69·1	33	273	αCF_2
				−78·7	..	12	βCF_3
A	PMe_2Ph	I	n-C_3F_7	−66·1	30	260	αCF_2[a]
				−120·7	..	..	βCF_2
				−79·8	..	22	γCF_3
A	PMe_2Ph	Br	n-C_3F_7	−66·2	31	260	αCF_2[a]
				−119·3	..	..	βCF_2
				−79·3	..	21	γCF_3
A	PMe_2Ph	I	n-C_7F_{15}	−65·5	..	285	αCF_2
				−81·4[b]			CF_3
B	PMe_2Ph	I	CF_3CH_2	−54·1	..	100	βCF_3[c]
B	PMe_2Ph	I	$C_2F_5CH_2$	−110·4	..	48	βCF_2[d]
				−86·4	..	20	γCF_3
A	$AsMe_2Ph$	I	CF_3	−17·6		539	αCF_3
A	$AsMe_2Ph$	I	C_2F_5	−67·0		277	αCF_2
				−79·3		13·5	βCF_3
A	$AsMe_2Ph$	I	C_3F_7	−64·3		274	αCF_2[e]
				−119·7			βCF_2
				−79·8		20·5	γCF_3
A	$AsMe_2Ph$	I	CF_3CH_2	−53·4		94	βCF_3[c]
A	$AsMe_2Ph$	I	$C_2F_5CH_2$	−107·8		..	βCF_2
				−86·1		19	γCF_3
C	PMe_2Ph	I	CF_3	−17·0	14·5	505	αCF_3
C	PMe_2Ph	I	C_2F_5	−74·2	22	364	αCF_2
				−76·1	..	..	βCF_3

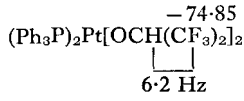
[a] $J(F\alpha–F\gamma)$ = 14 Hz.
[b] 5 other signals at δ_F −114·7, −120·7, −122·2, −123·0, −126·5.
[c] $J(H\alpha–F\beta)$ = 15 Hz.
[d] $J(H\alpha–F\beta)$ = 25 Hz.
[e] 2 quartets, separation 7 Hz.



631



632



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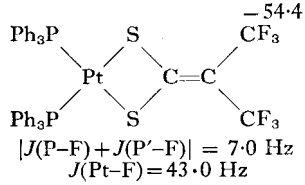

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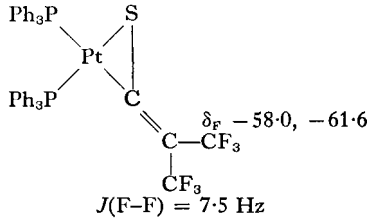

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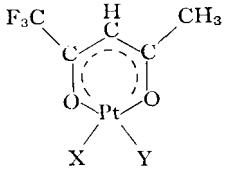


636a X = Cl, Y = olefin, δ_F −74·67
b X = olefin, Y = Cl, δ_F −75·55

Parameters[481] for the Ph_2PMe analogue of **634** are almost identical to those shown. The low-field band in the spectrum of **635** showed[481] phosphorus-fluorine coupling of 7·5 Hz, but the high-field band showed two different phosphorus couplings (6·0 and 1·5 Hz) and platinum-fluorine coupling (26·5 Hz).

The ^{19}F spectra of a series of fluorophosphine[493] complexes of nickel have been partially analysed as $[AX_n]_4$(tet) systems,[494] and the results are given in Table LI.

Similar parameters obtained[493] for dialkylaminofluorophosphine nickel carbonyl compounds are given in Table LII. The values for $NiL(CO)_3$ and $NiL_3(CO)$ were obtained from an old sample of $NiL_2(CO)_2$ which had disproportionated.[495] Spectra of fresh and old samples of $Ni(CO)_2[F_2PN(CH_2)_5]_2$ are illustrated in the paper.[495]

Tetrakis(chlorodifluorophosphine)nickel showed[466] a complex doublet *ca.* 1300 Hz wide at δ_F −12·8, and phosphinetris(trifluorophosphine)-nickel a complex doublet at δ_F −19·8.

TABLE LI

^{19}F parameters for tetrakis(fluorophosphine)nickel(0) compounds[493]

Compound	δ_{PF}	^1J(P–F)	^3J(P–F)	^2J(P–P)	^4J(F–F)
$Ni(PF_3)_4$	−16·8	−1347	+32·1	3	5·6
$Ni(CF_3PF_2)_4$	−72·1	−1207	+37	≪5	≪5
$Ni(CCl_3PF_2)_4$	−58·0	−1221	+31·5	21	2·3
$Ni(CH_2ClPF_2)_4$	−62·0	−1140±10	38±2	12±5	<10
$Ni(Me_2NPF_2)_4$	−50·0	−1125	+31	≪10	≪10
$Ni[(CF_3)_2PF]_4$	−159·2	−1005±10	+38±2	<5	<5

TABLE LII

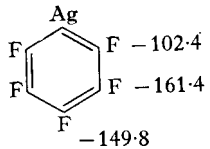
^{19}F parameters for $L_nNi(CO)_{4-n}$ complexes[493]

L		L_3NiCO	$L_2Ni(CO)_2$	$LNi(CO)_3$
Me_2NPF_2	^1J(P–F)	−1137	−1149	−1157
	^3J(P–F)	+27	+23	
	δ_F	−41·6	−43·3	−44·8
Et_2NPF_2	^1J(P–F)	−1134	−1145	−1150
	^3J(P–F)	+29	+23	
	δ_F	−40·6	−42·2	−43·62
$C_5H_{10}NPF_2$	^1J(P–F)	−1136	−1148	−1157
	^3J(P–F)	+27	+23	
	δ_F	−41·5	−43·09	−44·5
Me_2NPF	^1J(P–F)	−1024·6	sum[a] 1039	
	^3J(P–F)	+26·0		
	δ_F	−64·0	−68·7	

[a] $|^1J(P–F)+{}^3J(P–F)|$.

Silver and gold

The preparation of hexafluoroisopropylsilver, $AgCH(CF_3)_2$ has been reported.[496] The room temperature spectrum consisted of a doublet [J(H–F) = 13·5 Hz] at δ_F −51·26; at −40° in a mixture of methylene chloride and pyridine the spectrum consisted of a doublet [J(H–F) = 13·5 Hz] of doublets [^3J(F–Ag) = 20 Hz] assigned to the monomer, together with a second doublet [J(F–H) = 13·0 Hz] ascribed to an aggregate $nR_FAg.m$ pyridine. Pentafluorophenylsilver[497] and pentafluoropropenylsilver[498] have also been prepared, and the chemical shifts are shown with formulae **637** and **638**. The *ortho* fluorines in **637** are deshielded by the silver to a greater degree than are those of the gold complexes (shown below) which have also been reported.[499]



637

$-48{\cdot}4 \qquad -50{\cdot}5,\ -60{\cdot}9$

$CF_3 \cdot CAg : CF_2$

638

		δ_F(*ortho*)	δ_F(*meta*)	δ_F(*para*)
$(C_6F_5)_3Au.PPh_3$[a]	*cis*	−120·0	−161·0	−157·4
	trans	−122·0	−161·0	−156·4
$(C_6F_5)AuBr_2PPh_3$		−123·2	−160·9	−157·7
$(C_6F_5)AuPPh_3$		−116·0	−162·4	−158·3

[a] *Ortho* and *para* fluorines each appear as two sets of signals with relative intensities 2:1, ascribed to the C_6F_5 groups *cis* and *trans* to PPh_3.

The values of σ_I and σ_R calculated from the ^{19}F shifts for $C_6F_5Au.PPh_3$ (+0·29, −0·19) did not agree with those obtained[500] from *meta*- and *para*-fluorophenyl(triphenylphosphine)gold(I). The authors suggested[499] that this may be due to a through-space interaction between the *ortho*-fluorines and the metal, leading to a decrease in charge density at the fluorine. This in turn could result in an enhanced −M effect by the more negative gold on the *para*-fluorine, and, by a through-space interaction of the *ortho*- with the *meta*- fluorines, a downfield shift for the latter and hence an apparent increase in σ_I. Whatever the cause of the anomaly, it is clear that there may be difficulties in using ^{19}F shifts of pentafluorophenyl compounds for the calculation of σ parameters.

The ^{19}F shifts of *m*- and *p*- fluorophenylgold complexes with tertiary phosphines have been measured[501] in order to estimate the π-acceptor character for the various phosphines, a small value for the difference in shift of *meta*- and *para*- fluoro-compounds indicating good π-acceptor properties. Thus for $Et_3PAuC_6H_4F$, the shifts for the *meta*- and *para*-fluoro-compounds were δ_F −115·40 and −117·19 respectively, and the corresponding shifts for $(PhO)_3PAuC_6H_4F$ were −115·25 and −115·75. The π-acceptor order thus deduced ($Bu_3P \approx Et_3P \approx PhMe_2P <$ $(p\text{-}MeC_6H_4)_3P \approx Ph_2EtP \approx Ph_3P < C_6F_5Ph_2P < (PhO)_3P$) agrees well with the generally held ideas that electron-withdrawing substituents on the phosphorus increase the π-acceptor strength.

The gold complex $MeAuPPh_3$ reacted[502] with hexafluorobut-2-yne to give a compound $(Ph_3PAu)_2C_2(CF_3)_2$ for which the ^{19}F spectrum

consisted of the X part of an $X_3AA'X'_3$ pattern with δ_F −54 and the only identifiable coupling constant [either J(A–A′) or J(X–X′) from the analysis] *ca.* 50 Hz; the magnitude indicated that it is J(A–A′).

VIII. TRANSITION METAL FLUORIDES AND THEIR DERIVATIVES

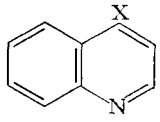
Scandium

The ^{19}F spectrum of an aqueous solution of $[ScF_6]^{3\ominus}$ appeared[503] as an octet of equal intensity bands [δ_F −70·9, $J(^{45}Sc–F) = 172$ Hz, $I^{45}Sc = 7/2$] which, above 25°, were of equal width. Below 10°, a symmetrical variation in line width was observed, and was attributed to a combination of quadrupolar relaxation and chemical exchange involving species of lower symmetry than the octahedral $[ScF_6]^{3\ominus}$ ion, e.g.,

$$[ScF_6]^{3\ominus} \rightleftharpoons [ScF_7]^{4\ominus} + [ScF_5]^{2\ominus}$$

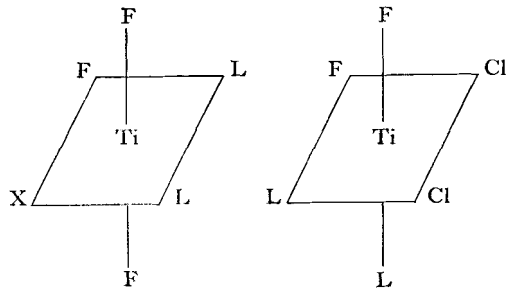
Titanium

Adducts formed from titanium tetrafluoride with two equivalents of amine oxide (4-substituted pyridine-*N*-oxide, 4- and 6- substituted quinoline-*N*-oxides) all showed[504] two triplets for the *cis*-isomer and some of the quinoline-*N*-oxide adducts also showed singlets for the *trans*-isomer close to the high-field triplet. Parameters obtained at −40° for the 4-substituted quinoline-*N*-oxides are shown below as representatives.

Substituent in 	*cis*-isomer δ_1	*cis*-isomer δ_2	*cis*-isomer J(F1–F2)	*trans*-isomer δ
X = OMe	126·2	145·5	37	123·2
X = Me	127·8	152·4	37	126·1
X = H	129·9	156·6	36	127·7
X = Cl	133·5	163·0	36	..
X = CN	138·9	176·9	36	..

Several chlorofluorotitanates have been detected[505] by ^{19}F NMR spectroscopy amongst the products of the reaction between titanium tetrafluoride, the tetrachloride, and tetrahydrofuran, and the stereochemistry of some of them has been deduced. Some parameters taken from spectra at −60° are given below.

	δ_F	J(F–F)	Structure assigned
cis-TiF_4.2THF	+223, +163	38	**A**
$TiClF_3$.2THF	+267, +200	33	**B**
$TiCl_2F_2$.2THF	+304, +228	45	**C**
	+232		Not assigned
$TiCl_3F$.2THF	+253		F *trans* to Cl or to THF not distinguished



A X = F
B X = Cl

C

L = tetrahydrofuran

Like the hexafluorogermanium(IV) ion, the hexafluorotitanium(IV) ion showed[297] marked solvent dependence of its chemical shift (δ_F +77·5 in MeOH, +75·5 in EtOH, +76·2 in Pr^nOH, +75·6 in Bu^nOH, and +71·0 in $CHCl_3$). Monocarboxylatopentafluorotitanium(IV) complexes had a relatively narrow range for the ^{19}F shifts of F^{2-5} (see formula **346** on p. 210 for numbering) (δ_F +82·2 to +88·7), but the fluorine *trans* to the carboxylato ligand (F6) changed more markedly (δ_F +128·1 to +96·1), and the fluorine-fluorine couplings (36 to 44 Hz) were rather smaller than in the corresponding germanium complexes. In contrast, the alkoxide complexes $[Ti(OR)^1F_5]^{2\ominus}$ had ^{19}F shifts in the range $\delta_{F^{2-5}}$ +50·2 to +43·6, and δ_{F^6} −15·9 to −24·6, with J(F–F) somewhat larger than in the corresponding germanium complexes. Parameters for some chelated complexes corresponding to the silicon and germanium complexes (see pp. 209 and 211) are also given in the paper.[297]

Chromium

Chromyl trifluoroacetate and other polyfluorocarboxylates have been prepared[506] by the reaction of chromium trioxide with the appropriate acid anhydride. The only ^{19}F parameter reported was δ_F −75 for the trifluoroacetate in solution in carbon tetrachloride.

Tungsten

Tungsten hexafluoride reacted readily with alkyl(alkoxy)silanes to give the trialkylfluorosilane and mixtures of alkoxytungsten compounds, which have been shown by their ^{19}F NMR spectra to be monomeric in solution. Some parameters reported by Noble and Winfield[507] are given below.

Compound	δ_{F1}[a]	δ_{F2}[a]	J(F–F)	$J(^{183}W–F)$
WF_5OMe	118·5	89·5	66	43 (F1), 33 (F2)
cis-$WF_4(OMe)_2$	63·5	44·0	66	46 (F1), 25 (F2)
trans-$WF_3(OMe)_3$	37·0	13·0	62	
cis-$WF_3(OMe)_3$		18·5		18
trans-$WF_2(OMe)_4$	−16·0			
cis-$WF_2(OMe)_4$		−39·5		14
cis-$WF_4(OEt)_2$	60·5	44·5	68	
WF_5OPh	126·5	112·0	65	39 (F1)
cis-$WF_4(OPh)_2$	84·0	76·0	68	
cis-$WF_3(OPh)_3$[b]		52·3		

[a] F1 is *trans* to F, F2 is *trans* to ligand.
[b] Tentative assignment only.

Handy and Brinckman[508] also reported the successive replacement of fluorine by methoxyl, and gave parameters in accord with those reported by Noble and Winfield,[507] together with a shift for the pentamethoxy-compound (δ_F −42·5). The only discrepancy between the two sets of parameters is that Handy and Brinckman obtained only one tetramethoxy-compound (δ_F −15·1) to which they assigned the *cis*-stereochemistry.

Noble and Winfield also reported the formation of a tetrafluoro-oxotungsten(VI)-dimethyl ether complex (δ_F 62·8, J(W–F) = 68 Hz) which also appeared to be monomeric. Other peaks found in the spectrum [at δ_F 60·3; J(F–F) = 58 Hz, J(F–W) = 72 Hz and δ_F −146; J(F–F) = 58 Hz, J(F–W) = 51 Hz; ratio of intensities ≈ 8:1], and also[509] in the spectrum of the WF_6 complex formed in the reaction with dimethyl sulphoxide, are thought to be due to the fluorine-bridged anion $[F_4(O:)WFW(:O)F_4]^{\ominus}$. The compound tentatively assigned[509] the structure $WF_6 \cdot Me_2SO$ showed a singlet (δ_F +144) with partially resolved tungsten satellites [J(F–W) = 40 Hz]. Parameters have been reported[509] for anionic pentafluoro-oxotungsten compounds **639**, **640**, which appeared as AX_4 systems, and also for the complex of tetrafluoro-oxotungsten(VI) **641**. The parameters for the latter were consistent

with either a monomeric hexaco-ordinate species, or a polymeric species with fast intermolecular exchange in which the $=WF_4OP(OMe)_2Me$ grouping remained intact.

	Compound	δ_A	δ_X	J(F–F)	J(F–W)
639	$[(MeO)_3PMe]^{\oplus}[WOF_5]^{\ominus}$	−84·2	+49·8	53	72 (X)
640	$[Pr_4N]^{\oplus}[WOF_5]^{\ominus}$	−82·8	+49·4	53	70 (X)
641	$Me(MeO)_2PO \cdot WOF_4$[a]		+60·1		70

[a] J(F–P) = 1·7 Hz.

A series of tungsten(VI) chloride fluorides has been prepared,[510] and the parameters reported are shown below.

Compound	$\delta_{F_{eq}}$[a]	$\delta_{F_{ax}}$[a]	J(F–F)	J(F–W)
WF_6	+164·5			44
WF_5Cl	+180·5	+125·1	73	25
trans-WF_4Cl_2	+189·5			20
cis-WF_4Cl_2	+197·5	+134·5	66	[b]
mer-WF_3Cl_3	+207·5	+137·5	62	[b]
fac-WF_3Cl_3		+142·5		[b]
trans-WF_2Cl_4	+218·5			[b]
cis-WF_2Cl_4		+150·5		[b]
$WFCl_5$		+156·5		[b]

[a] At −20°, ±5 p.p.m., dependent on composition of mixture, converted from WF_6 = 0.
[b] Not observable.

The authors noted that the tungsten-fluorine couplings were much lower than those of other tungsten(VI) compounds previously reported, but they are in accord with those reported for tri- and tetra- methoxy compounds.[507, 508]

Niobium

^{19}F studies of some compounds of niobium pentafluoride with organic donor molecules have been reported.[511] With pyridine or dimethyl sulphoxide, the compounds NbF_5L_2 were obtained, in agreement with previous work; although similar stoichiometry appeared to hold with tetrahydrothiophen, the nature of the compound could not be determined, but the ^{19}F parameters (δ_F +116·7, +151·6, in ratio 1:4) suggested a 1:1 adduct. 1:1-Adducts were obtained from diethyl sulphide (a single line, half-width at room temperature 175 Hz, further broadened at −40°, with the appearance at +70° of a second line, 28·3 p.p.m.

upfield) and also from diethyl ether (broad line at room temperature, further broadened at $-30°$). ^{19}F spectra of liquid samples of mixed chloride fluorides of niobium of formulae $(NbCl_2F_3)_x$, $(NbCl_{1\cdot6}F_{3\cdot4})_x$, $(NbCl_{2\cdot2}F_{2\cdot8})_x$, and $(NbClF_4)_x$ showed only one signal at δ_F +182 because of rapid exchange.[512]

Tantalum

The ^{19}F spectrum of $KTaF_6$ in anhydrous hydrogen fluoride showed[513] only HF and $[TaF_6]^{\ominus}$ fluorine environments, with no evidence for $[TaF_7]^{2\ominus}$ in detectable amounts. Chemical shifts for $[TaF_6]^{\ominus}$ under a range of conditions (e.g. $K^{\oplus}[TaF_6]^{\ominus}$ in anhydrous hydrogen fluoride, δ_F +31·9; $[Bu_2NH_2]^{\oplus}[TaF_6]^{\ominus}$ in methylene chloride, δ_F +38·2) were reported; δ_F +39·5 was reported independently[512] for $[Et_4N]^{\oplus}[TaF_6]^{\ominus}$, the signal being broadened by ligand exchange. The mixed halide $(TaClF_4)_x$ showed[512] only a single line at δ_F +117·5 because of exchange between monomer and polymer. Other mixed halides ($[TaCl_2F_3]_x$ and $[TaCl_{1\cdot7}F_{3\cdot3}]_x$) gave signals at δ_F +111·5 and δ_F −58·5 assigned, on the basis of relative intensities, to terminal and bridging fluorines respectively.

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Nuclear Magnetic Resonance Spectroscopy in the Study of Carbohydrates and Related Compounds

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I. INTRODUCTION

SINCE THIS subject was last reviewed in this series[1] there have been many important developments in the application of NMR spectroscopic techniques to carbohydrate chemistry. There has been an increasing use of ^{19}F measurements and papers have appeared in which PMR studies of compounds containing ^{15}N and ^{31}P have been described. Probably more significantly there has been an explosion of ^{13}C NMR studies and quite obviously the potential of this technique to carbohydrate chemists is considerable. A greater awareness that factors other than the magnitude of the dihedral angle can affect the coupling constants between vicinal

protons has resulted in more careful and more detailed analyses of the relationship between coupling constants and conformation, and in conformational studies increasing use has been made of information provided by geminal and long-range coupling constants and of chemical shift effects. Examples of detailed conformational studies in rigid molecules and of the application of the results obtained to conformationally mobile molecules will be given in this review. This review essentially covers the period 1968–1970 and is concerned with those papers that further our understanding of the NMR characteristics of carbohydrates while at the same time describing the structural information NMR studies provide. As in the previous review no attempt has been made to cover all the reports in which NMR spectroscopy was used routinely to establish the primary structure of carbohydrates.

II. CONFORMATIONAL STUDIES OF PYRANOID SYSTEMS

Considerable emphasis has been placed on the use of NMR in the study of conformational equilibria—rather than simply in establishing preferred conformations. Thus the conformational equilibrium between the 1C(D) and C1(D) conformers of β-D-ribopyranose tetraacetate (**1**) was measured by (a) the method of averaging spin coupling, (b) the

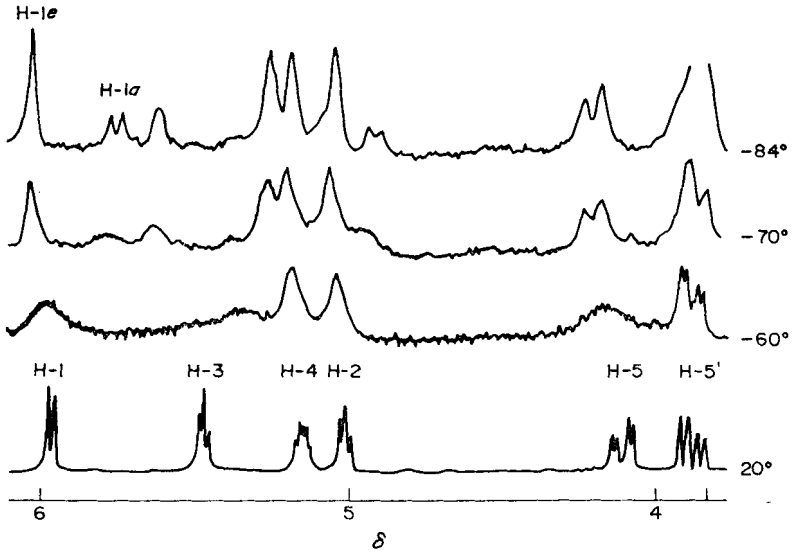
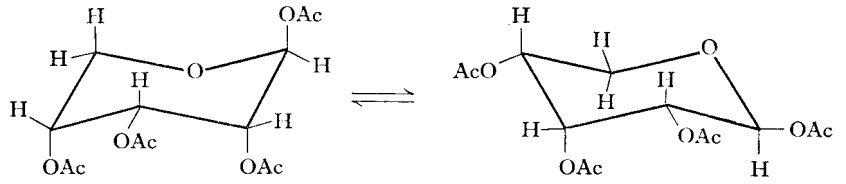


FIG. 1. The low-field portion of the 220 MHz spectrum of β-D-ribo-pyranose tetraacetate (**1**) in acetone-d_6 at 20, −60, −70 and −84°. (From Durette *et al.*[2])

method of averaging chemical shifts and (c) direct integration of the two conformers below the temperature of conformational freeze out.[2] The 220 MHz spectrum of **1** in deuterioacetone at various temperatures is shown in Fig. 1. Direct integration of the anomeric proton signals of the two conformers at $-84°$ indicated that the 1C:C1 ratio was 2:1. However, comparison of the $J_{1,2}$ coupling (4·8 Hz) at 20° with the $J_{1e,2e}$ coupling (1·0 Hz) and the $J_{1a,2a}$ coupling (8 Hz) at $-84°$ indicated that the 1C:C1 ratio was 1:1·2. On the other hand the method of averaging chemical shifts suggested that at 20° the 1C conformation preponderated. That the method of averaging chemical shifts was unreliable for estimating conformational equilibria was illustrated by reference to β-D-



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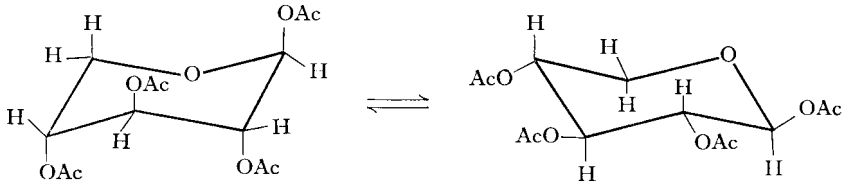

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xylopyranose tetraacetate (**2**). For **2**, $J_{1,2}$ increased from 6·9 Hz at room temperature to 8·1 Hz at $-85°$ and further decrease in temperature caused no further increase in $J_{1,2}$. Since no other anomeric proton signal was detected it was assumed that at $-85°$ **2** existed as a pure C-1 conformer. The chemical shift data showed that as the temperature was lowered H-1 shifted to lower field. Since axial protons usually resonate at higher field than equatorial protons a shift to higher field at lower temperatures would have been expected. The applicability of the method of averaging chemical shifts has also been discussed by Eliel and Martin.[3] From the results of their studies it was concluded by Horton and his coworkers[2] that the method of averaging spin couplings was the most satisfactory method for estimating conformational equilibria for

those systems where one conformer has a pair of vicinal protons in diaxial orientation provided that (a) the signal of one of these protons was clearly visible and (b) that at least 5 to 10% of the less favoured conformer was present. Although the method of integration below the temperature of conformational freeze out provides convincing evidence of conformational equilibria its use was restricted to those examples having substantial proportions of both conformers at low temperatures.

The results obtained by Horton and his coworkers[2] also provided direct evidence that the energy barrier for chair-chair interconversion in pyranoid sugar derivatives is small enough for a time-averaged spectrum to be observed at room temperature thereby confirming many other results where the NMR parameters appeared to be intermediate between those expected for the separate chair forms.

The method of averaging spin coupling constants has been used to estimate the conformational equilibria of eight D-aldopentopyranose tetraacetates in deuteriochloroform or deuterioacetone at room temperature.[4] The relevant NMR parameters for the eight aldopyranose acetates measured at 100 MHz are listed in Table I. Conformational

TABLE I

Conformational equilibria of D-aldopentopyranose tetra-acetates in perdeuterioacetone

Configuration	Temperature	$J_{1,2}$	$J_{4,5}$	$J_{4,5'}$	Equilibrium constant K = C1/1C
α-D-*ribo*	28°	3·7	9·1	4·6	4·0
β-D-*ribo*	20°	4·8 (8·0)	3·3	5·8	1·2
α-D-*arabino*	28°	6·3 (7·5)	3·5	1·8	0·23
β-D-*arabino*	28°	2·7	1·2	1·8 (1·5)	0·03
α-D-*xylo*	28°	3·5 (3·5)	5·4 (5·4)	11·0 (11·0)	> 50
β-D-*xylo*	25°	6·9 (8·1)	4·7	8·6 (10·5)	4·0
α-D-*lyxo*	28°	2·9	4·3	8·6	2·9
β-D-*lyxo*	28°	2·0	3·1	5·3	0·67

Values in parentheses are limiting values observed at low temperature (~ −85°). The C-5 proton resonating at lower field is designated H-5 and that resonating at higher field is designated H-5′.

populations at room temperature were determined from the observed coupling of H-4 with the *trans*-disposed proton at C-5, taken in conjunction with values for $J_{4e,5e}$ and $J_{4a,5a}$ that had been obtained for model compounds. The $J_{4,5'}$ value for α-D-xylopyranose tetraacetate was 11·0 Hz and $J_{2,3}$ was 9·7 Hz. These values remained unchanged as

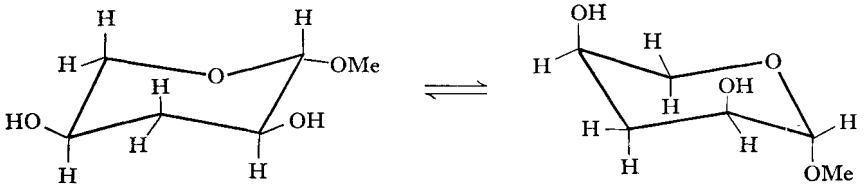
the temperature was lowered to $-50°$ and it was concluded that **2** was essentially all in the C1(D) conformation. Thus $11{\cdot}0 \pm 0{\cdot}5$ Hz was taken as the magnitude of $J_{4a,5a}$ for each compound. For the β-D-arabinose derivative the $J_{4,5'}$ value (1·8 Hz) decreased to a lower limit at $-25°$ and thus the value of $1{\cdot}5 \pm 0{\cdot}5$ Hz was used throughout as the magnitude of $J_{4e,5e}$. For the β-D-*ribo*-, α-D-*arabino*-, β-D-*xylo*- and α-D-*lyxo*- compounds the conformational populations could also be measured from the time-averaged $J_{1,2}$ values in conjunction with values of $J_{1a,2a}$ of $8{\cdot}0 \pm 0{\cdot}5$ Hz and $J_{1e,2e}$ of $1{\cdot}0 \pm 0{\cdot}5$ Hz as determined from β-D-ribopyranose tetraacetate (**1**). The conformer populations estimated from $J_{4,5}$ values and $J_{1,2}$ values were in fair agreement. It must be pointed out that some error in this approach using model compounds is unavoidable since the precise magnitude of the coupling constants (e.g. $J_{4,5}$) in the present instance will depend on whether the 4-*O*-acetate group is axial or equatorial. Nevertheless, the methods outlined above certainly provide much valuable information and enable the effects of different solvents on conformational equilibria to be compared. More recently the approach has been used to examine the conformational equilibria of a wide range of peracetylated aldopentopyranosyl derivatives.[5]

The method of averaging spin coupling has also been used to estimate the conformational equilibrium in a series of 2-alkoxy-tetrahydropyrans.[6] For these compounds, since their spectra were not first order, calculations were based on the magnitude of the distance ($J°$) between the outside peaks in the H-2 quartet using the equation:

$$N_a = \frac{J_B - J°}{J_B - J_A}$$

where N_a is the percentage of conformer A, J_A is $J_{a,a} + J_{a,e}$ and J_B is $J_{e,e} + J_{a,e}$. *cis*-4-Methyl-2-methoxytetrahydropyran and methyl 2-deoxy-α-D-glucopyranoside were used as model compounds, from which the parameters J_A and J_B were derived.

Lemieux and Pavia have successfully employed NMR to demonstrate



1C(D) ⇌ C1(D)

3

that changes with solvent in the optical rotations of pyranoid derivatives are caused by conformational changes.[7,8] The changes in $J_{1,2}$ coupling constant and rotation of methyl 2-deoxy-α-D-*erythro*-pentopyranoside (**3**) with solvent are shown in Fig. 2. It will be appreciated that whereas in D_2O **3** exists in the 1C conformation, in $CDCl_3$ the Cl conformation preponderates.

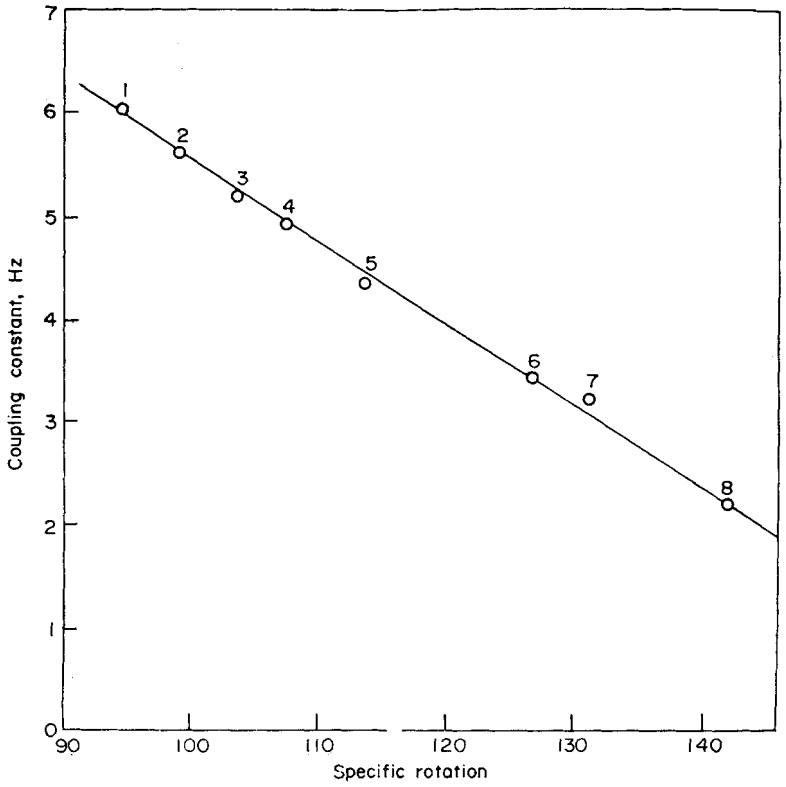


FIG. 2. Relationship between specific rotation ($[\alpha]_D^{25}$) and the coupling constant at 35° for H^1 and H^2 of methyl 3-deoxy-β-L-erythro-pentopyranoside (**3**) with change in solvent at concentrations (g/100 ml) of 9 ± 1 (except for acetonitrile and pyridine, 7 ± 1):1, D_2O; 2, $(CD_3)_2SO$; 3, 6·4 g $(CD_3)_2SO$/g $CDCl_3$; 4, 2·57 g D_2O/g $(CD_3)_2CO$; 5, C_5D_5N; 6, CD_3CN; 7, $(CD_3)_2CO$; 8, $CDCl_3$. (From Lemieux *et al.*[8])

Other conformational changes have been examined in order to investigate the mechanisms by which conformational equilibria are influenced by solvation effects.[9] For this purpose 4,4,5,5-tetradeuterio-2-methoxy-

tetrahydropyran was prepared and the magnitude of $J_{2,3}$ and $J_{2,3'}$ measured in different solvents. Model compounds used to obtain the individual coupling constants were the anomeric pair of methyl 2-deoxy-D-*arabino*-hexopyranosides in which $J_{aa} = 9{\cdot}9$ Hz, $J_{ae} = 1{\cdot}9$ Hz and $J_{ea} = 3{\cdot}9$ Hz and $J_{ee} = 1{\cdot}4$ Hz. The results obtained suggested that the molecular rotation was influenced not only by the position of the chair-chair equilibrium but also by the particular orientation adopted by the methoxy group. ^{13}C NMR spectroscopy was used subsequently to examine the validity of this latter conclusion.

Evidence, based on NMR measurements has also been presented to show that, in addition to solvation effects, small changes in substituents can have a profound effect on conformational equilibria.[10] For example, in a series of methyl 3-deoxy-β-L-*erythro*-pentopyranosides, the 2,4-di-*O*-acetyl, 2,4-di-*O*-benzoyl, 2,4-di-*O*-mesyl and 2,4-di-*p*-nitrobenzoyl derivatives adopted a C-1 conformation in various solvents whereas the 2,4-di-*O*-methyl derivative preferred the 1C conformation. The conformations of the 2-*O*-acetyl-4-*O*-methyl derivative and the 4-*O*-methyl derivative varied with the nature of the solvent.

Among papers that are important because detailed NMR data were presented as evidence for a particular conformation are reports that α-D-iodopyranose tetraacetate exists preponderantly in the C1(D) conformation[11] and that fully chlorosulphated α- and β- D-xylopyranosyl and lyxopyranosyl chlorides adopt conformations in which the halide takes up an axial orientation.[12] Both reports use evidence from long-range and geminal couplings as well as from vicinal couplings in support of the configurational assignments.

It was found in a detailed 220 MHz NMR study of some 2-substituted 1,3-dioxanes that, where the 2-substituent was methyl, *isopropyl*, *tert*-butyl, phenyl and *p*-chlorophenyl, there was no significant difference between the vicinal couplings of the protons on C-4, C-5 and C-6, thereby showing that the nature of the substituent had little effect on ring geometry.[13]

Although not strictly relevant to this section a conformational study of the 1,3-dioxepan ring in 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol has been reported.[14] The 2,5-*O*-methylene protons were magnetically equivalent in thionyl chloride from ambient temperature down to $-82°$. It was concluded that either the 1,3-dioxepan ring was undergoing a fast ring inversion or that it existed in a conformationally stable (probably twist chair) form.

A general review of the composition and conformation of sugars in solution has presented much information of the NMR characteristics of sugars in solution.[14a]

III. THE STEREODEPENDENCE OF GEMINAL, VICINAL AND LONG-RANGE COUPLING CONSTANTS

It will be of interest to carbohydrate chemists that the $J_{1e,2e}$ and $J_{1a,2e}$ values for protons are not identical. Thus in 1,1:2,2:3,3:4,4-octadeuteriocyclohexane the following values were obtained:[15] $J_{1,1} = -13{\cdot}05$ Hz; $J_{1a,2a} = +13{\cdot}12$ Hz; $J_{1a,2e} = 3{\cdot}65$ Hz and $J_{1e,2e} = +2{\cdot}96$ Hz. From these values it was calculated from the equation[16]

$$J = A(\cos^2\theta + n\cos\theta)$$

that θ, the dihedral angle between vicinal protons was 57° (as compared to the 55° value suggested by electron diffraction data).

In an admirable review article Hall and Manville[17] have discussed factors which affect the magnitude of vicinal coupling constants. For example it is now well known that J_{ae} is smaller when an electronegative substituent is *trans* to a vicinal coupling proton (Fig. 3b) than when *gauche* to a vicinal coupling proton (Fig. 3a). Thus in pyranoid derivatives

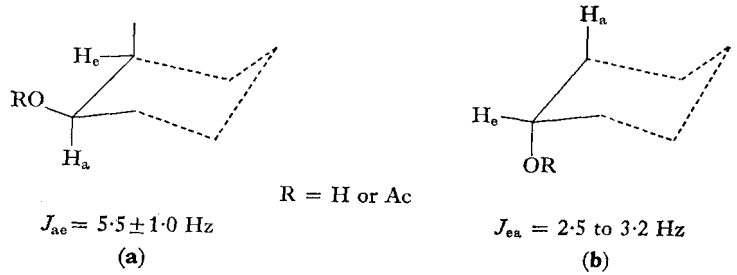


FIG. 3.

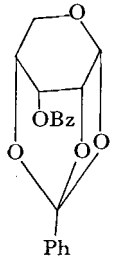
$J_{1e,2e}$ (*ca.* 1·5 Hz) is smaller than J_{ae} (2 to 2·4 Hz) and $J_{e,a}$ (3·5 to 3·6 Hz) couplings. Despite the fact that the factors which affect vicinal coupling constants are complex, the Karplus equation and its modifications continue to be used in conformation studies of fused ring systems with the general treatment becoming more and more refined. For example, Coxon has discussed the conformations of two 1,2-*O*-benzylidene- and four 1,2:3,5-di-*O*-benzylidene-α-D-glucofuranose derivatives[18] and a series of 1,2:4,6-di-*O*-benzylidene-α-D-glucopyranose derivatives.[19]

Coupling constants, obtained by first-order analysis, were refined by iterative procedures and related to the magnitude of the proton-proton dihedral angles by an explicit form of the Karplus equation:

$$\Theta = \cos^{-1}\left[\frac{0{\cdot}5 \pm (0{\cdot}25 + 36\{J + 0{\cdot}28\})^{1/2}}{18}\right]$$

Hall and Manville[17] provided evidence to support previous reports that geminal couplings were smaller (less negative) when an adjacent electronegative substituent was orientated between the methylene protons (i.e. an equatorial substituent) than when orientated externally (i.e. an axial substituent). Thus for pentopyranose derivatives: axial OR_4, $J_{5a,5e} = 13{\cdot}3 \pm 0{\cdot}3$ Hz; equatorial OR_4, $J_{5a,5e} = 11{\cdot}2 \pm 0{\cdot}5$ Hz. In 2-deoxy-D-*arabino*-hexopyranose derivatives the $J_{2a,2e}$ coupling constants were 13·8 Hz and 12·4 Hz for axial and equatorial anomeric substituents respectively.

One of the most interesting studies of a fused ring system and one in which many stereospecific dependencies are illustrated has been Coxon's[20] analysis of the NMR spectrum of 3-*O*-benzoyl-1,2,4-benzylidyne-α-D-ribopyranose (**4**). This compound is locked in the skew conformation shown (**5**). Measured geminal, vicinal and long-range coupling constants



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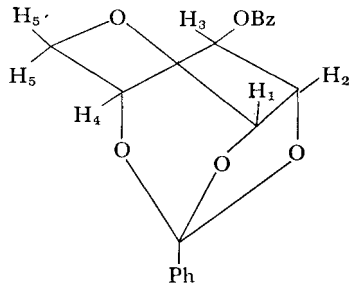

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were correlated with the stereochemistry of the locked skew conformation and used to test the reliability of equations which relate coupling constant to dihedral angle. The spectrum of **4** is shown in Fig. 4 and the calculated parameters, obtained by ABX analysis of H-3, H-2 and H-4 with H-1 decoupled and by ABX analysis of H-5, H-5′ and H-4 are listed in Table II. Little difference was observed for these parameters and the subsequent parameters refined by iterative techniques and from which the theoretical spectrum was calculated. In Table III the dihedral

angles measured from a Dreiding model are given, together with values calculated from the observed vicinal coupling constants and the Karplus equation described above. The values to be expected if **4** adopted a symmetrical C_2 skew conformation are also given. The mean deviation of

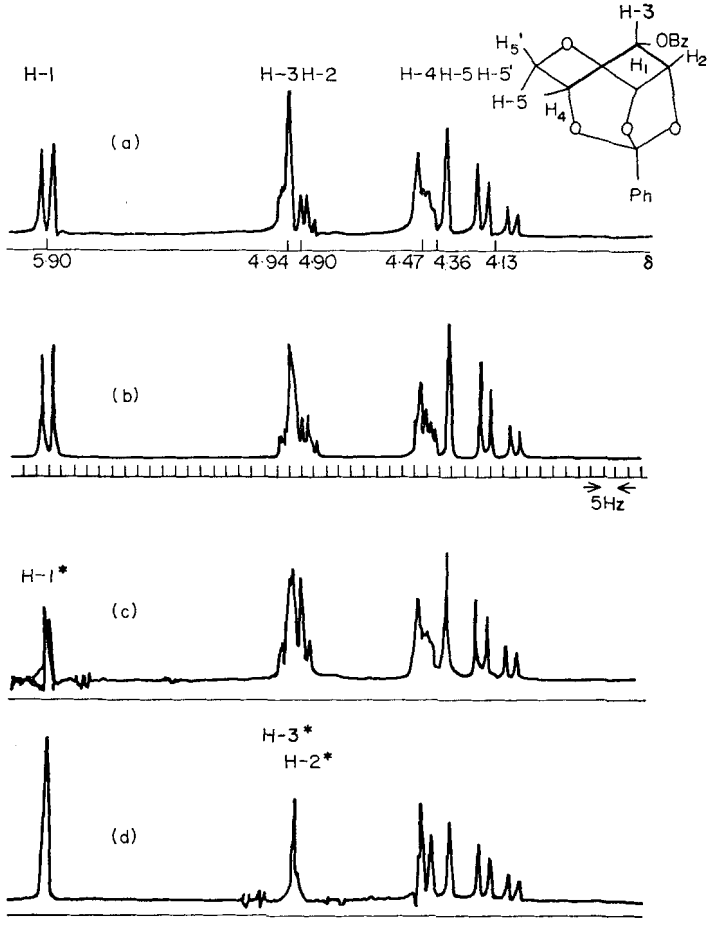


FIG. 4. PMR spectra of 3-*O*-benzoyl-1,2,4-*O*-benzylidyne-α-D-ribopyranose in chloroform-*d* at 100 MHz; the signals of the aromatic protons are not shown. (a) Single resonance spectrum, (b) theoretical spectrum from iterative analysis, (c) irradiation of H-1, and (d) irradiation of H-2 and H-3. (From Coxon.[20])

the approximate proton-proton dihedral angles as calculated from a Karplus equation and from those measured in the molecular model was 11°.

TABLE II

PMR spectral parameters (Hz) of 3-*O*-benzoyl-1,2,4-*O*-benzylidyne-α-D-ribopyranose (4) at 100 MHz

Parameter	Initial	Refined (13 iterations)
ν_1	590·32	590·31 ± 0·02
ν_2	489·99	489·77 ± 0·04
ν_3	495·36	495·34 ± 0·04
ν_4	440·72	440·62 ± 0·03
ν_5	435·68	435·79 ± 0·03
$\nu_{5'}$	412·43	412·64 ± 0·03
$J_{1,2}$	4·50	5·22 ± 0·05
$J_{1,3}$	0	−0·54 ± 0·05
$J_{1,4}$	0	−0·06 ± 0·03
$J_{1,5}$	0	0·05 ± 0·03
$J_{1,5'}$	0	−0·14 ± 0·04
$J_{2,3}$	3·37	3·58 + 0·03
$J_{2,4}$	2·27	2·45 ± 0·03
$J_{2,5}$	0	0·04 ± 0·03
$J_{2,5'}$	0	−0·04 ± 0·04
$J_{3,4'}$	1·08	1·33 ± 0·04
$J_{3,5}$	0	−0·18 ± 0·05
$J_{3,5'}$	0	−0·02 ± 0·05
$J_{4,5}$	0·30	0·27 ± 0·04
$J_{4,5'}$	3·30	4·09 ± 0·04
$J_{5,5'}$	−11·69	−11·71 ± 0·03

TABLE III

Approximate proton-proton dihedral angles (ϕ, degrees) in 3-*O*-Benzoyl-1,2,4-*O*-benzylidyne-α-D-ribopyranose

Angle	Proton orientations[a]	From molecular models[b]	Calculated from J	For C_2 twist form[c]
$\phi_{1,2}$	e, q	22	36 (139)[d]	33
$\phi_{2,3}$	q, a	50	47 (129)	33
$\phi_{3,4}$	a, e	72	63 (113)	71
$\phi_{4,5}$	e, q	100	103 (74)	87
$\phi_{4,5'}$	e, q	20	44 (132)	33

[a] Equatorial (e), axial (a), quasi (q).

[b] Dreiding.

[c] Pyranoid ring in idealised symmetrical twist form with ring-atom dihedral angles of 33° or 71°

[d] The figures in parentheses are the alternative values of ϕ calculated from the Karplus equation.

The value of the geminal coupling constant ($J_{5,5'} = 11{\cdot}7$ Hz) in **4** was intermediate between values reported previously (10·8 to 10·9 Hz and 13·4 to 14·0 Hz) for the α- and β- D-anomers or ribopyranose derivatives that were in the C1 and 1C conformations respectively. Although the magnitude of this coupling constant was nearer to that found in compounds with a C1 conformation, the geometry of the skew form was closer to the 1C form where the ring oxygen atom has *trans* and gauche relationships with H-5′ and H-5. It was pointed out that the magnitude of geminal coupling constants in non-chair systems may be influenced by factors other than the orientation of vicinal electronegative substituents and thus the use of geminal coupling constants in conformational assignments must be used with caution.

The strong coupling (2·4 Hz) between H-2 and H-4 in **4** is one of the largest couplings that has been observed over four saturated bonds, and its positive sign was in agreement with calculations based on an indirect "through bond" coupling mechanism. In the conformation **5** the dihedral angles θ' (of H-2 and C-4 about the C-2–C-3 bond) and θ''' (of H-4 and C-2 about the C-3–C-4 bond) are 170° and 171° respectively. Substitution of these values in the equation:[21]

$$^4J = \mathrm{A}\cos^2\theta'\cos^2\theta''' - \mathrm{B} \qquad (1)$$

[where B = 0·35 and A = 0·31 for $0° \leqslant \theta', \theta''' \leqslant 90°$; $1{\cdot}07 \leqslant \theta' \leqslant 90° \leqslant \theta''' \leqslant 180°$ and 3·61 for $90° \leqslant \theta', \theta''' \leqslant 180°$] gave the value of 3·07 Hz for $J_{2,4}$, which was in close agreement with the observed value.

Another equation:

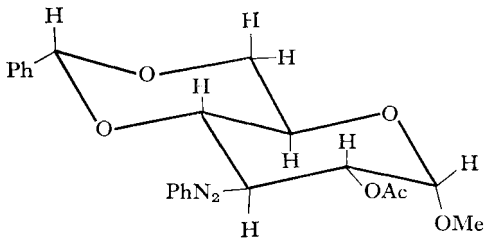
$$^4J = 0{\cdot}7\,(\cos^2\theta^1 + \cos^2\theta''') - 0{\cdot}3 \qquad (2)$$

gave much poorer agreement between observed and calculated couplings. However, it must be pointed out that for 1,6-anhydro-β-D-mannopyranose triacetate the observed and calculated long-range $J_{1,3}$ and $J_{3,5}$ couplings were in much better agreement when equation (2) rather than equation (1) was used.

The conformations of some 4-amino-2,3-unsaturated sugars have been deduced from detailed analysis of geminal, vicinal and long-range coupling constants.[20a]

Hall and Manville[22] have presented an excellent account of the use of both "selective irradiation" and the "spin tickling" methods for determining the relative signs of proton-proton coupling constants of carbohydrate derivatives. Also a simple model has been discussed which correctly predicts that if by definition $J(^{13}\mathrm{C–H})$ is positive, geminal and vicinal H–H couplings for protons on sp^3 hybridised carbon atoms should be negative and positive respectively. This result means that in com-

puted spectra geminal and *trans*-vicinal couplings cannot be confused. Unfortunately the simple model also predicts incorrectly that long-range H–H couplings over four bonds will all be negative in sign. Other mechanisms of long-range couplings have suggested that if the sole mechanism for long-range coupling is *via* the bonding electrons $^4J_{ee}$ and $^4J_{ae}$ couplings should both be positive in sign whereas $^4J_{aa}$ couplings should be negative in sign. Hall and Manville have demonstrated that $^4J_{ee}$ couplings are positive (for the compounds studied the range was $+0{\cdot}8$ to $+1{\cdot}6$ Hz) and $^4J_{ea}$ couplings were negative in sign ($-0{\cdot}2$ to $-0{\cdot}7$ Hz). It was pointed out that this inversion of sign should provide an extremely valuable extension of the selection of stereospecific dependencies which are available for configurational and conformational assignments and that it should be particularly valuable for studies of those derivatives that show ^4J coupling whose magnitudes lie between those normally found for $^4J_{ee}$ and $^4J_{ea}$ couplings. It was also observed that the magnitudes of the long-range coupling constants listed by Hall and Manville were somewhat smaller than found in strained-ring systems. No definite $^4J_{aa}$ coupling constants were reported by Hall and Manville, although possibly a $^4J_{2,4}$ coupling of $+0{\cdot}75$ Hz had been detected in methyl-β-D-glucopyranuronate. However, an example of a long-range $^4J_{aa}$ coupling was provided[23] by analysis of the NMR spectrum of methyl-2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucopyranoside (**6**). The analysis of the skeletal protons was conducted as a



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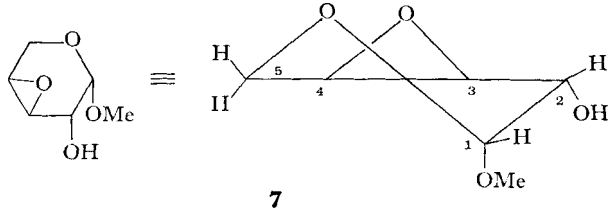
general 7-spin system. From the calculations it emerged that couplings across four saturated bonds, i.e. $J_{1,3}$ ($-0{\cdot}16$ Hz), $J_{2,4}$ ($-1{\cdot}2$ Hz) and $J_{3,5}$ ($-0{\cdot}28$ Hz) were all negative in sign. The negative $J_{1,3}$ coupling, which is a J_{ea} coupling, is consistent with the results of Hall and Manville whereas the negative $^4J_{aa}$ couplings ($J_{2,4}$ and $J_{3,5}$) were opposite in sign to that of the possible $^4J_{aa}$ coupling detected by Hall and Manville.

It is of interest to compare these results with those reported following an analysis of the spectrum of methyl 3,4-anhydro-β-L-arabinopyrano-

side[24] (**7**) which had the following coupling constants (Hz): $J_{1,2}$, 3·88; $J_{1,3}$, 0·49; $J_{1,5'}$, 0·57; $J_{2,3}$, 0·65; $J_{2,4}$, 0·65; $J_{3,4}$, 4·38; $J_{3,5}$, 1·0; $J_{3,5'}$, 0·04; $J_{4,5}$, 0·87; $J_{4,5'}$, 1·72; $J_{5,5'}$, −13·53. $J_{2,4}$ and $J_{3,4}$ possessed the same sign which was almost certainly positive and the signs of $J_{3,5'}$ and $J_{1,5'}$ could be related. Only with the signs shown were the computed values consistent with the observed spectrum. The positive sign of the $J_{3,5}$ coupling was in accordance with the sign expected for a $^4J_{ee}$ coupling but not for an allylic equatorial-equatorial coupling (if the epoxide carbons behave as if they were sp^2 hybridised) and the sign of the $J_{3,5'}$ coupling was consistent with expectation for a $^4J_{ea}$ coupling or for a equatorial-axial allylic coupling. The sign of the $J_{1,5'}$ coupling, apparently positive was opposite to that suggested by Hall and Manville for $^4J_{ea}$ couplings. These results indicate that, although the signs of long-range coupling constants will undoubtedly be of value in stereochemical analysis, much more work is needed before routine use is made of sign determinations.



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Another example of studies of the signs of coupling constants is the work of Pachler and Wessels[25] who showed that long-range couplings occur so widely in furanoid derivatives that it is seldom possible to resolve and observe them directly and that in 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranurononitrile all the ^4J values were negative. Also Hall and Manville reported an interesting variation in the signs of geminal coupling constants. In 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose, $J_{6,6'}$ was +4·85 Hz whereas for 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene β-L-idofuranose the geminal $J_{6,6'}$ coupling was −1·45 Hz. That is, in the former case the coupling was typical of a sp^2 hybridised system and in the latter case the coupling was typical of a sp^3 hybridised system. In this connection it is of interest that, whereas the epoxide showed long-range couplings similar to those observed in 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose, the episulphide showed no such long-range coupling constants.

Of some value to carbohydrate chemists are the studies of Fraser and his coworkers on the stereodependence of vicinal H–C–O–H coupling constants.[26] An exact analysis of the ABC type absorption arising from

the CH_2OH group of 3-β-acetoxy-5β,6β-oxidocholestan-19-ol provided two vicinal H–C–O–H coupling constants. From these values, and other literature data, a modified Karplus equation was proposed for vicinal H–C–O–H constants:

$$J_{HCOH} = 10{\cdot}4 \cos^2 \theta - 1{\cdot}5 \cos \theta + 0{\cdot}2$$

It should be noted that J_{HCOH} constants can change with solvent but whether this change reflected only a change in rotamer population or also a change in coupling with fixed dihedral angle was not established.

A long-range coupling involving a hydroxyl proton has been observed in the spectrum of 2,2-anhydro-2-*C*-hydroxymethyl-1,3:4,6-di-*O*-isopropylidene sorbitol.[27] The 5-OH proton coupled not only with H-5 ($J_{5,OH}=7$ Hz) but also with H-6 ($J_{6,5\,OH}=0{\cdot}7$ Hz).

IV. CHEMICAL SHIFTS OF PYRANOID RING PROTONS AND SUBSTITUENTS

A number of papers have reported on the relationship between substituent resonances with substituent position and configuration. Horton and Lauterback have assigned the individual acetoxy resonances in methyl α-D-glucopyranoside tetraacetate by use of specific deuterioacetylation procedures.[28] The results (Table IV) showed that the 6-acetoxy group resonated at lower field than the other acetoxy groups in chloroform-*d*, pyridine-d_5 and benzene-d_6.

TABLE IV

Chemical shifts of methoxyl groups and acetoxyl groups as assigned by synthesis of specifically deuterated derivatives of methyl-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside

Solvent	OMe	2-OAc	3-OAc	4-OAc	6-OAc
$CDCl_3$	3·42	2·071	2·005	2·025	2·093
C_5D_5N	3·35	1·971	2·021	2·032	2·035
C_6D_6	3·00	1·641	1·743	1·719	1·743

The absorption ranges have been deduced for axial and equatorial *O*- and *N*- acetyl resonances in cyclitol and aminocyclitol polyacetates, and the scope and limitation of the diagnostic use of such resonances in configurational and conformational assignments have been discussed.[29]

Tulloch and Hill have examined the spectra of ten new partially acylated derivatives of methyl β-D-glucopyranosides which all had acyl

groups at C-6.[30] It was shown that in compounds with OH-4 acylated the H-6 signals were at higher field (by 0·1 to 0·3 p.p.m.) than when OH-4 was not acylated. Acylation of OH-3 had little effect on the chemical shift of the H-6 protons. When a trimethylsilyl group was introduced at C-4 the chemical shift difference between the H-6 protons was increased markedly. Estimations of J_{BX} and J_{AX} (where B was the H-6 proton at higher field and X was H-5) from the spectra obtained in pyridine-d_5 and acetone-d_6 showed that $J_{BX} < J_{AX}$ when there was an acyl group at C-4 but that $J_{BX} > J_{AX}$ when there was no acyl group at C-4. The above observations were useful in locating acyl groups in naturally occurring sophorosides.

NMR assignments for the ten signals derived from the methyl groups in methyl 2,3,4,6-tetra-*O*-methyl-α- and β- D-glucopyranoside have been given, based on experiments in which the various groups were selectively deuterated.[31] The information was then used to analyse the products of hydrolysis of tri-*O*-methyl cellulose and to assess the pattern of methylation in partially methylated methyl β-D-glucopyranoside. Similar studies have been reported for partially methylated D-galactopyranose derivatives.[32]

An alternative means of determining substituent position may result from studies in dimethyl sulphoxide of the chemical shifts of free OH resonance.[33] For example, it has been shown that the chemical shifts of the hydroxyl protons of α-D-glucopyranosides varied in the order 1-OH (low field), 2-OH, 3-OH, 4-OH and 6-OH with the anomeric proton resonating between the 1-OH and 2-OH groups. Previous results had suggested that the 2-OH and 4-OH resonances were reversed.

A survey of nearly 300 methyl glycosides has shown that of 209 axial or pseudoaxial methoxy substituents, 93% had chemical shifts in the range δ 3·30 to 3·48 p.p.m.[34] Of 74 compounds with equatorial or pseudo-equatorial methoxy substituents, 76% had chemical shifts in the range δ 3·50 to 3·64 p.p.m.

Attention has been drawn to the observation that in 6-deoxy-pyranoses the 6-deoxy group resonates at higher field in α-anomers than in β-anomers.[35] Thus, where both anomers are available, information about the anomeric configuration in complex molecules may be obtained and it was suggested that the method might have some application in configurational assignments of disaccharide derivatives.

In a previous review[1] attention was drawn to the fact that chemical shift data, as well as coupling constant data, was able to aid configurational and conformational assignments in carbohydrate chemistry. A detailed paper has now appeared in which many of the various factors which affect chemical shifts have been summarised with particular

reference to glucose and mannose derivatives.[36] Complete first-order analyses of compounds **8a** to **8i** were reported and the following conclusions arrived at. In addition to the well-known generalisations that axial protons resonate at higher field than equatorial protons and that H-1 shifts to lower field as the electronegativity of the C-1 substituent increases, attention was drawn to the fact that the chemical shift of the anomeric protons also depends on the orientation and electronegativity of the C-2 substituent. Thus, as illustrated in Fig. 5, H-1e resonates at

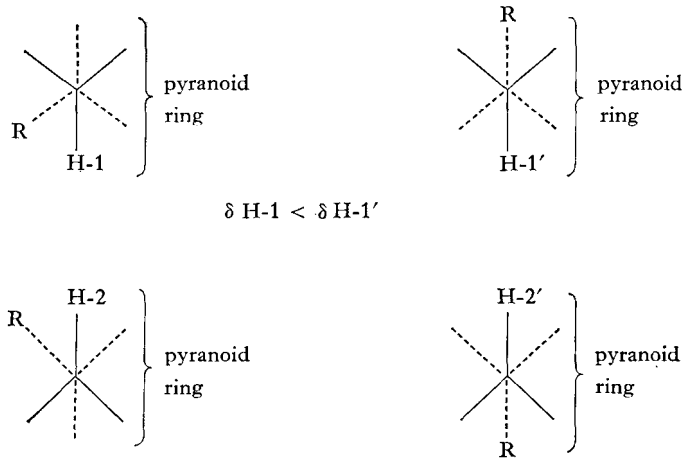
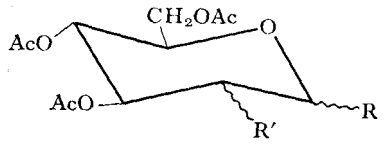


FIG. 5.

lower field when the 2-substituent is equatorial than when the 2-substituent is equatorial, whereas H-1a resonates at lower field when there is an axial rather than equatorial 2-substituent. In other words, H-1a and H-1e have higher chemical shifts respectively when the 2-substituent is *trans* coplanar with the anomeric proton. A similar relationship holds for H-2 (Fig. 5). These observations may be important in cases where the magnitude of the $J_{1,2}$ coupling does not establish the anomeric configuration of pyranoid derivatives which are known to exist in C-1 chair forms. It must be pointed out that the magnitudes of the vicinal coupling

constants of the β-D-glucopyranosyl and β-D-mannopyranosyl halides leave no doubt that these compounds take up a normal chair form unlike the aldopentopyranosyl halides in which the halogen substituent takes up an axial orientation in all recorded instances. The results for the glucose and mannose derivatives (**8a**) to (**8i**) also showed that, in accordance with other results, electronegative axial substituents have a deshielding effect on 1,3-axially orientated axial protons.



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8a R = R′ = H
8b R = OH, R′ = Cl
8c R = $OCOCH_3$, R′ = Cl
8d R = R′ = $OCOCH_3$
8e R = OCH_3, R′ = $OCOCH_3$
8f R = Br, R′ = $OCOCH_3$
8g R = $OCOCH_3$, R′ = H
8h R = R′ = Cl
8i R = OCH_3, R′ = Cl.

The generalisations reported by Lemieux and Stevens[37] for the chemical shifts of ring protons in pyranose derivatives have been shown to apply to methyl 2,3-anhydropyranosides.[38] Thus (a) the chemical shifts of the *quasi*-equatorial protons were independent of the position of the epoxide oxygen, (b) the *quasi*-axial H-4 was shielded less (0·24 p.p.m.) when the epoxide oxygen was *trans* than when it was *cis* (a hydroxyl group causes a similar shift) and (c) the axial H-5 was deshielded (by 0·2 p.p.m.) when the epoxide ring was *cis* to it (a hydroxy group causes deshielding by 0·35 p.p.m.).

The spectra of a series of sulphated monosaccharide derivatives have been measured.[39] The H-1e protons were deshielded by (a) 0·27 p.p.m. by a *cis*-equatorial 2-sulphate and (b) by 0·06 p.p.m. by an equatorial 3-sulphate; H-1a protons were deshielded by 0·18 p.p.m. by an equatorial 2-sulphate.

In acetylated 1-*O*-acyl-D-glucopyranoses containing aryl or indolylacetyl groups at C-1, the C-2 acetyl group appeared at unusually high fields (δ 1·57 to 1·82), a result which may be explained in terms of the anisotropy of the aromatic ring.[40]

The chemical shifts observed for H-2a, H-2e, H-4a and H-4e in some 1,6-anhydro-2,4-di-*O*-toluene-*p*-sulphonyl-β-D-hexopyranos-3-uloses were effected as expected by the anisotropy of the carbonyl group.[40a]

V. THE EFFECT OF SOLVENTS AND OTHER COMPOUNDS ON CHEMICAL SHIFTS

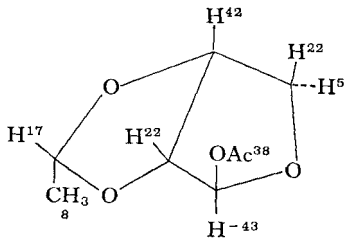
Although the effects of solvents and other compounds on the chemical shifts of carbohydrate ring protons are not fully understood their use in simplifying otherwise complex spectra is invaluable. A number of papers have been concerned with the chemical shifts induced in carbohydrates by aromatic solvents. Thus large aromatic solvent induced shifts (ASIS) have been observed in a series of acetylated monosaccharides and acetylated methyl glycosides.[41,42] The model, used by Williams and his co-workers[43,44] to explain anisotropic shifts in aromatic solutes was adapted to account for anisotropic factors in the ASIS of acetylated saccharides. In all cases the acetoxymethyl resonances occurred from 0·3 to 0·45 p.p.m. to higher field in benzene than in chloroform-*d* but the solvent shifts of the ring protons were both to higher and lower fields.

The effect of aromatic solvents, other than benzene, on carbohydrate proton shifts has also been examined.[45] For example in pentafluorobenzene only small acetoxymethyl proton chemical shifts (compared to values in chloroform-*d*) were observed. The ring proton shifts in pentafluorobenzene were usually positive. It is of interest that the largest ring proton shifts were observed in pyridine. These observations may be of some value in directing the choice of solvent for simplifying the spectra of compounds which give complex patterns.

The effects of aromatic solvents on the chemical shifts of ring protons and other groups of protons in methyl glycosiduloses have also been described.[46] It was concluded that the ASIS of the pyranoid ring protons in a number of compounds depends on the position of the carbonyl group with respect to the ring proton but that the methoxy protons at C-1 were much less affected by the position of the carbonyl group.

The relative position of protons may be reversed in benzene. Thus, it was shown by use of specifically deuterated compounds that in pyridine-d_5 and in chloroform-*d* the axial C-2 proton in methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexapyranosid-3-ulose resonated at lower field than the equatorial proton but in benzene-d_6 the axial proton was at higher field than the equatorial proton.[47]

Information provided by consideration of benzene-induced chemical shifts has been used to provide proof of configuration of the acetal carbon in 1-*O*-acetyl-2,3-*O*-ethylidene-β-D-erythrofuranose (**9**).[48] From the shielding parameters [numbers are $\delta . 10^2$ p.p.m.] it was apparent that benzene associated with **9** from the "top" (convex) side. Only the anomeric proton was deshielded from the specific association of benzene with the acetate carbonyl group. The shielding values for the *exo*



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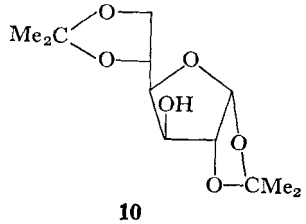
(0·22 p.p.m.) and *endo* (0·05 p.p.m.) C-4 methylene protons supported the configurational assignment at the ethylidene carbon atom; that is the *exo* methine proton was shielded more strongly than the *endo* methyl protons (0·17 and 0·08 p.p.m. respectively).

Of interest to carbohydrate chemists is a long paper in which considerable use was made of benzene-induced solvent shifts for conformational assignments to forty-four 1,3-dioxan derivatives.[49]

The mechanism by which tetramethylammonium salts cause deshielding effects on the H-1, H-3 and H-5 protons when added to solutions of tetra-*O*-acetyl-β-D-glucosyl halides or phenoxides in acetonitrile has been considered in detail.[50] The deshielding effects were not observed when halide salts were added to solutions of the same substrates in strongly solvating media such as chloroform-*d* and no specific deshielding effects were observed for penta-*O*-acetyl or α-D-tetraacetates. These observations were in accord with a simple electrostatic model which was constructed to describe the nature of the complexes of anions with tetra-*O*-acetyl-D-glucopyranosyl halides. It was considered that in favourable circumstances an NMR method, such as described by Lemieux and his coworkers, might be used as a probe for electrophilic regions in molecules.

An important paper[51] has described the simplifying effect of europium tris(dipivaloylmethane) on the 100 MHz spectrum of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**10**); the spectra are shown in Fig. 6. Although the induced shifts were dependent on temperature and con-



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centration, undoubtedly the europium reagent will be of considerable value to carbohydrate chemists in the future.

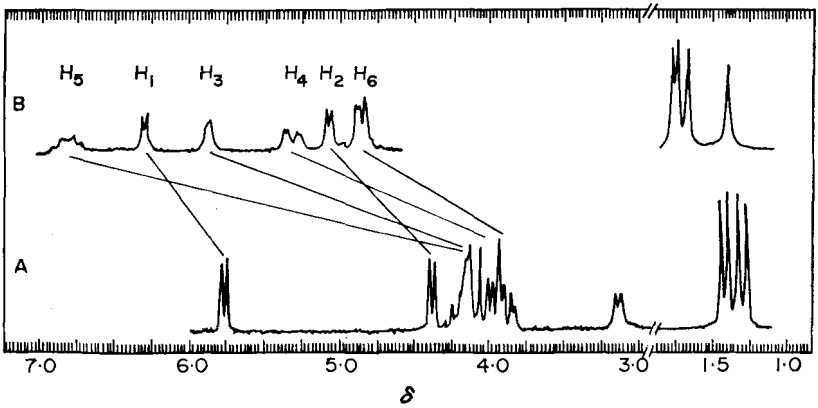


FIG. 6. Proton magnetic resonance spectra (100 MHz) of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**10**) in carbon tetrachloride solution (0·102 g in 0·5 ml). A, the normal spectrum: B, the spectrum of the same solution after the addition of europium tris(dipivaloylmethane). (From Armitage and Hall.[51])

VI. FURANOID DERIVATIVES

Fletcher and Stevens have discussed the NMR spectra of a number of pentofuranose derivatives in considerable detail.[52] They showed that $J_{1,2}$ was usually *ca.* 4·5 Hz when H-1 and H-2 were *cis* and that $J_{1,2}$ was usually less than 1·5 Hz when H-1 and H-2 had a *trans*-relationship. Attention was drawn to the fact, however, that *trans* vicinal protons in furanoid rings need not necessarily have a small coupling constant (i.e. $< 1{\cdot}5$ Hz) and that when $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ couplings were considered, *cis* couplings were in the range 4·3 to 6·8 Hz, and *trans* couplings ranged from $< 0{\cdot}5$ Hz to 7·2 Hz. The considerable overlap between these two ranges of coupling constants obviously precludes the assignment of *cis* or *trans*-relationships between neighbouring hydrogens in a five-membered ring when the coupling constant between those hydrogens is greater than about 4 Hz. On the other hand it would appear that a coupling constant less than about 4 Hz may be ascribed to neighbouring *trans*-hydrogens.

Chemical shifts were also shown to be diagnostic of configuration. Thus, for an anomeric pair of compounds H-1 is at lower field when the substituents at C-1 and C-2 are *cis* than when *trans*. For pairs of compounds isomeric at C-4, when the C-4 substituent is on the same side of the ring as H-3, this hydrogen is shielded compared with the other isomer

but, otherwise, no simple consistent shielding effect of substituent groups upon H-2 and H-3 was evident.

In the course of their studies Fletcher and Stevens observed what they considered to be a virtual long-range coupling effect which involved a hydroxyl proton. Thus the NMR spectrum of 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose, measured in acetone solution, showed H-1 and H-3 as multiplets, whereas in chloroform H-1 and H-3 gave the expected doublet and quartet respectively. However, whereas in chloroform HO-2 gave a distinct signal in acetone there was only a small chemical shift between H-2 and HO-2 giving rise to the observed virtual long-range coupling.

An excellent survey of furanoid ring conformations has been provided by Hall and his coworkers[53] who have pointed out that, since there is a low-energy barrier between many furanoid conformers, conformational inversion will be fast on an NMR time scale and consequently NMR methods are automatically limited to the determination of conformations which are to a greater or lesser extent time-averaged. From a detailed analysis of relationships between coupling constants and dihedral angles of protons and fluorine atoms in furanoid rings Hall and his coworkers reached the conclusion that it was possible to decide which segment of the pseudorotational cycle was significantly populated and which of the many possible conformations could be definitely precluded. A similar, but much less well-defined, approach had been described previously.[54]

The conformations of the furanose ring in a number of nucleoside derivatives and other furanoid derivatives [55 to 60] have been analysed by NMR procedures which have utilised coupling constants in conjunction with the Karplus equation often in conjunction with specific chemical shift effects. One such study utilised 220 MHz measurements.[60a]

An attempt has also been made to use Karplus-type relationships between dihedral angles and H-^{19}F vicinal coupling constants in addition to normal H–H vicinal coupling constant data to establish the conformations of furanoid rings.[61] In this study particular attention was focused on correlations between substituent electronegativity and vicinal coupling constants and chemical shifts.

Cushley and his coworkers have demonstrated that specific chemical shift effects, such as those caused by hydrogenation of double bonds in pyrimidine nucleosides (Vol. 2, page 72) which were diagnostic of anomeric configuration, are also apparent in purine nucleosides.[62]

The NMR spectra of aqueous solutions of uracil, uridine, deoxyuridine and other compounds have been studied as a function of electrolyte concentration.[63] Factors which effect conformational changes have been discussed and the possible effect of changes such as those involving

the orientation of the uracil base about the glycosidic bond on chemical shifts and coupling constants have been outlined. It was observed that for uridine and uridine 5′-monophosphate the observed changes in the H'_1–H'_2 coupling constant could be correlated with salt-induced H_6 shifts. The absence of a detectable conformation change in the furanose rings of deoxyuridine and uridine 3′-monophosphate was attributed to a greater rigidity of the furanose moiety in these cases.

Using the basic principles described in Vol. 2 (page 50), NMR has been widely used in configurational and conformational studies of 1,3-dioxolans[63a] and to distinguish between two 1,2:5,6-di-*O*-bromoethylidene-D-mannitols.[63b] In dioxolan derivatives with phenyl substituents the proton shifts induced by the aromatic nucleus have also been shown to be diagnostic of both configuration and conformation.[63c]

VII. ACYCLIC SUGAR DERIVATIVES

There has been considerable recent interest in the conformations adopted in solution by acyclic sugar derivatives. For example, Horton and Wander[64] have measured the NMR spectra of some peracetylated aldosethioacetals, the coupling constants of some of which are listed in Table V. On the assumption that vicinal anti-parallel protons show spin-spin coupling of 8 to 9 Hz and that vicinal protons having a dihedral angle of *ca.* 60° are coupled by 3 to 4 Hz, the observed coupling data were interpreted in terms of the favoured conformation of the sugar chain. Thus from Table V it will be seen that the D-arabinose, D-lyxose, L-rhamnose and L-fucose derivatives existed in zig-zag conformations with only *trans* or *gauche* vicinal proton interactions. On the other hand,

TABLE V

First-order coupling-constants for acetylated aldose diethyl dithioacetals

Configuration	Coupling constants, Hz						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$
ribo	6·2	5·7	3·6	3·1	7·7	12·0	
arabino	8·3	2·8	7·9	2·9	6·0	12·3	
xylo	5·2	5·9	4·2	4·3	6·6	11·8	
lyxo	4·2	7·9	2·0	4·9	7·6	11·5	
galacto	8·2	1·8	9·1	2·2			6·5
manno	4·7	7·7	1·8	8·4			6·3

as a result of deviation from the zig-zag conformation because of interactions between pairs of parallel eclipsed acetoxy groups at C-2 and C-4, the coupling constant data of the D-ribose and D-xylose derivatives were consistent with sickle arrangements for these compounds. The sickle arrangements were derived by rotation about the C-3-C-4 bond in the D-ribose derivative and about the C-2–C-3 bond in the D-xylose derivative.

From the above results it was concluded that the planar zig-zag conformation, which results from maximum staggering of small - medium - large sets of groups about each carbon-carbon bond, is adopted by polysubstituted alkane derivatives as the favoured arrangement provided that this arrangement does not lead to a parallel 1,3-interaction of substituent groups (analogous to a 1,3-diaxial interaction in 6-membered rings). Other workers have reached a similar conclusion for other acyclic sugar derivatives. Thus the *arabino-* and *lyxo-* isomers of methyl 2,3,4,6-tetra-*O*-acetyl-5-hexulosonates adopt a planar zig-zag conformation whereas the *xylo-* and *ribo-* isomers have distorted shapes[65] and the conformations adopted by the tetra-acetates of *aldehydo*-D-ribose, -D-arabinose, -D-xylose, -D-lyxose and 6-deoxy-D-galactose and the diphenyldithioacetals of tetra-*O*-acetyl-D-lyxose and 6-deoxy-L-mannose show a similar pattern.[66]

It has been pointed out [67] that for some 3,4,5,6-tetra-acetoxy-*trans*-1-nitro-1-hexenes, $O_2N\cdot{}^1CH=^2CH\cdot{}^3CH(Oac)\cdot{}^4CH(OAc)\cdot{}^5CH(OAc)\cdot{}^6CH_2OAc$, the NMR spectra were consistent with a planar zig-zag conformation of the carbon skeleton (C2-C6) for the D-*arabino* isomer but not for the D-xylo and D-ribo isomers for the same reasons as described above. For the *ribo*-isomer measurement at 220 MHz was necessary to give a spectrum which could be analysed conveniently. Attention was drawn to the fact, however, that the observed coupling constants did not *prove* the assigned conformations because solution of the Karplus equation always gives two possible values, although one solution can usually be discounted. Attention was also focused on the finding that the H-2, H-3, H-4 ABX systems in some of the tetra-acetoxy-*trans*-1-nitro-1-hexenes gave deceptively simple spectra.[67]

Lee and Scanlon[68] have also studied the conformations of acyclic carbohydrate derivatives in solution and shown that 1,3-eclipsed interactions are more important than 1,2-gauche interactions in determining relative conformer populations. In their experiments 9·2 Hz was considered to be a standard *trans*-coupling constant and 4·2 Hz a standard *gauche* coupling constant; also it was considered that at higher temperatures $J_{obs}=(J_t+2J_g)/3=4{\cdot}5$ Hz. It was demonstrated that for 2(L-*arabino*-tetra-*O*-acetylbutyl)4-*p*-bromo-phenyl-1,3-thiazole, the coupling constants were close to the expected 9·2 Hz and 4·2 Hz at low

temperatures, but tended towards 4·5 Hz in accordance with expectation as the temperature was increased. The results, which are summarised in Table VI, show that the energy differences became more important as the temperature was raised and the conformer population tended to a statistical average.

TABLE VI

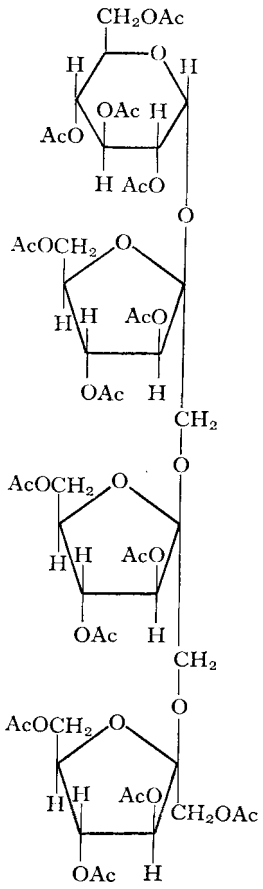
Variation of coupling-constants (Hz) with temperature of 2(L-*arabino*-tetra-*O*-acetylbutyl)4-*p*-bromophenyl-1,3-thiazole

	Temperature				
	Chloroform-*d*			DMSO-d_6	
	−60°	−10°	+30°	+30°	+150°
$J(H_2–H_3)$	2·1	3·0	3·3	3·3	4·5
$J(H_3–H_4)$	9·5	8·9	8·4	8·4	6·5
$J(H_4–H_5)$	..	3·0	3·0	3·5	4·0
$J(H_4–H_{5'})$	..	5·0	5·0	5·5	5·5

The polyhydroxylalkyl chains in some sugar osotriazoles were also shown to adopt planar zig-zag conformations except where such an arrangement led to eclipsed 1,3-interactions of hydroxyl groups.[69] For these compounds with free OH groups measurements were made in dimethyl sulphoxide-d_6.

VIII. OLIGOSACCHARIDES

A number of very interesting studies of the use of NMR for structural investigations of oligosaccharide derivatives have been reported. For example, Binkley, Horton and Bhacca[70] have measured the NMR spectra of the peracetates of sucrose, 1-kestose and nystose in benzene-d_6, chloroform-*d* and acetone-d_6 and shown that, by use of the appropriate solvent, detailed first-order analyses of oligosaccharides containing up to at least four sugar residues may be obtained. Both peracetylated sucrose and 1-kestose gave satisfactory first-order spectra in benzene-d_6 at 100 MHz, whereas nystose tetradecaacetate only gave a satisfactory first-order spectrum at 220 MHz. The low-field portion of the spectrum of nystose tetradecaacetate (**11**) in benzene-d_6 is shown in Fig. 7. By comparison with the results obtained for the more simple methyl α-D-glucopyranoside tetraacetate, sucrose octaacetate and 1-kestose hendecaacetate the signals arising from H-1, H-2 and H-4 of the glucopyranosyl moiety were assigned without difficulty. The H-3′ and H-4′ signals for



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the three D-fructofuranosyl residues in nystose were identified in the spectrum in benzene-d_6 as doublets at δ 6·04, 6·02 and 5·81 and as triplets at δ 5·73, 5·70 and 5·63. From coupling data and the absence of second-order effects the doublet at δ 5·81 and the triplet at δ 5·63 were assigned to the same D-fructofuranosyl residue (H-3a′ and H-4a′). The doublets at δ 6·04 and 6·02 had almost identical couplings so that correlation of each with the individual triplets at δ 5·73 and 5·70 (to differentiate the pairs H-3b′ and H-4b′ and H-3c′ and H-4c′) could not be made.

Of particular interest was the fact that the observation of a clear two-proton AB system near δ 3·7 (chloroform-*d*) in the spectrum of peracetylated 1-kestose and of two similar two-proton AB systems in

per-acetylated nystose established that there is a (2→1) linkage between the two D-fructofuranosyl residues in 1-kestose and that nystose is built up from kestose by (2→1) attachment of an additional D-fructofuranosyl group. This information had not been obtained previously by chemical or enzymatic methods.

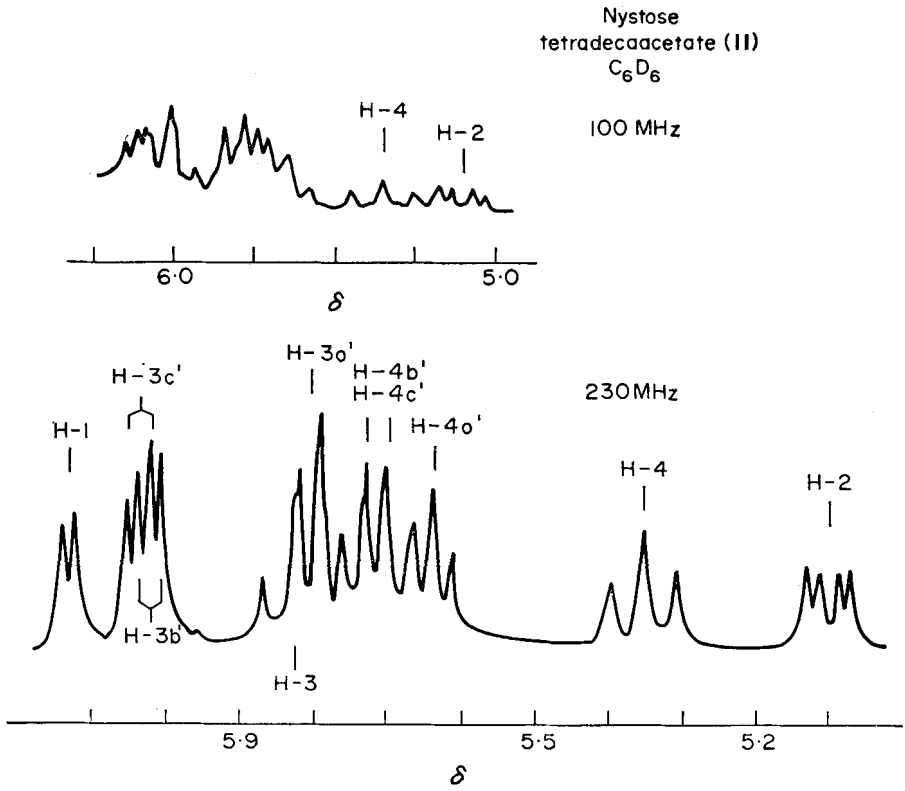


FIG. 7. The low-field portion of the NMR spectrum of nystose tetradecaacetate (**11**) in benzene-d_6 at 100 and 220 MHz. (From Brinkley *et al.*[70])

The anomeric region (*ca.* δ 5·5 p.p.m.) of the NMR spectra (recorded in D_2O at 70°) has been shown to be a useful region for fingerprinting mannans from different sources.[71] It has also been shown by studies with mannans with known structure and modifications that the nature of borate on the spectra of such mannans depends on the position and effect of the anomeric linkage and it has been suggested that the effects observed with borate may be diagnostic of structure. Thus whereas addition of

borate to methyl α-D-mannopyranoside and to the non-reducing end of α(1→2) linked D-mannopyranosyl oligosaccharide caused large (> 10 Hz) chemical shifts of the anomeric protons to lower field, the effect of borate on the anomeric protons of 3-*O*-α-D-mannopyranosyl-D-mannose was negligible. In Fig. 8 is illustrated the effect of borate on the anomeric proton chemical shifts of α-D-(1→2) linked mannotetraose, *T-aculeatum*-mannan and *R-glutinis*-mannan. In the mannotetraose the H-1 signal of the non-reducing end was shifted downfield by about 10 Hz, whereas the H-1 signals of the internal (1→2) units were essentially unaffected. Also addition of borate to *R-glutinis* mannans which gives two H-1 signals

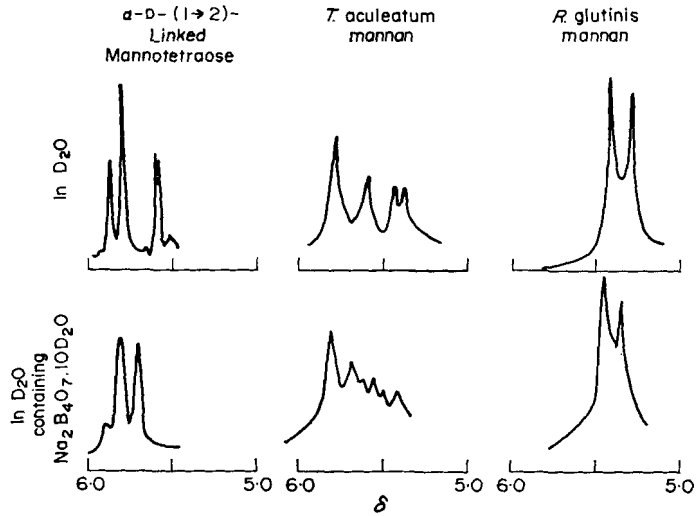


FIG. 8. Effect of sodium tetraborate on H-1 signals of mannopyranose derivatives. (From Gorin *et al.*[71])

[from alternate β-D-(1→3) and β-D-(1→4)-linked D-mannopyranosyl units] resulted in downfield shifts of the signals at δ 5·42 and 5·31 by 4 Hz and 7 Hz respectively. The results from these compounds of known structure and from other model compounds helped in the analysis of the spectrum of *T-aculeatum*-mannan. Four different H-1 signals were apparent in the spectrum of this polysaccharide before the addition of borate but after borate addition six anomeric proton signals were evident. The major H-1 signal at δ 5·80, assigned to (1→2) linked units, was shifted downfield by borate by only 2 Hz. On the other hand the two middle signals previously at δ 5·60 and δ 5·46 were shifted downfield by 8 Hz

and 9 Hz respectively. These signals presumably arose from 2,3-borate complexed units and corresponded to non-reducing end units or possibly 6-*O*-linked mannopyranosyl units. Another component of the δ 5·60 signal which possibly arose from H-1 of 2,6-di-*O*-substituted units appeared to be shifted downfield by only a few Hz on borate addition. Thus, it was possible to obtain many clues about the structure of *T-aculeatum*-mannan by analysis of the chemical shifts of its anomeric protons in the presence and absence of borate. Further studies[72] have also led to the conclusion that resemblances in the NMR spectra of mannose containing polysaccharides reflect similarities in chemical structure.

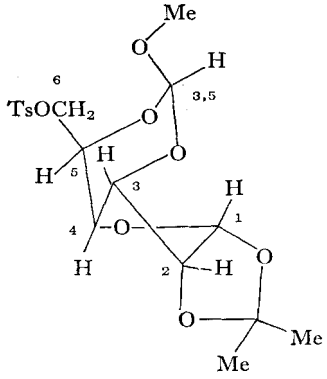
Studies of the conformation of amylose and the α- and β- cyclodextrins have been reviewed previously.[1] Casu[73] and his coworkers have recently reported the results of their studies on acetylated cyclodextrins, amylose and β-maltose. Significant changes in the chemical shifts of various ring protons were observed on going from β-maltose octa-acetate to more complex structures. Possible reasons for the changes in the chemical shifts of the ring protons and acetoxymethyl resonances were discussed. Other workers have shown that in peracetylated cyclodextrins the glucopyranose rings have the expected C-1 conformation.[74] The conformations of *O*-methylated amylose and cyclodextrins have also been investigated by NMR.[75]

Michell has studied the spectra of some cellulose oligosaccharides in DMSO.[76] In the spectra of cellobiose and cellotriose, in addition to signals at δ 6·62 arising from the HO-1 resonance of the β-D-anomers, there were signals near δ 6·30 arising from the HO-1 resonances of the α-D-anomers. However, the spectra of cellotetraose and cellopentaose showed only very weak unresolved signals near δ 6·62. In the spectra of deuterated cellobiose and cellotriose there were doublets at δ 4·88 ($J = 3{\cdot}0$ Hz) and doublets at δ 4·28 ($J = 7$ Hz) arising from the equatorial and axial H-1 resonances respectively. These results were considered to show that cellobiose and cellotriose were anomeric mixtures, the cellotriose and cellopentaose were essentially the β-D-anomers.

The configuration of the glycosidic linkage in pertrimethylsilylated oligosaccharides have been established by NMR procedures[77] and NMR has proved to be a powerful method for determining the anomeric configuration of sugars released during enzymic hydrolysis of some D-glucopyranosides and glucans.[78] It was possible to demonstrate that, with some polysaccharidases, hydrolysis occurred with retention of anomeric configuration, whereas with others inversion of anomeric configuration occurred. The utility of NMR in monitoring enzyme reactions remains to be fully explored.

IX. CONFORMATIONAL EVIDENCE FROM A NUCLEAR OVERHAUSER EFFECT

The configurations of the methylidene carbon (designated C3,5) in the diastereoisomeric 1,2-*O*-isopropylidene-3,5-*O*-(methoxymethylidene)-6-*O*-*p*-tolylsulphonyl-α-D-glucofuranoses (**12** and **13**) have been



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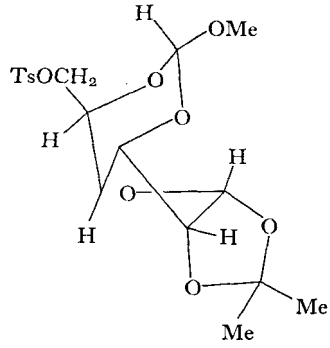


13

assigned by standard NMR methods and conformational information has been obtained from the observation of a Nuclear Overhauser Effect.[79] Evidence that **12** had the configuration depicted was first indicated because the lower chemical shift of H3,5 in **13** compared with **12** was more consistent with the axial orientation of this proton in **13**. Further, long-range (H-4 to H3,5) coupling (0·42 Hz) was only observed in **12** and it is well known that ^5J couplings occur most readily in 6-member rings when both the protons in the 1,4 relationship are equatorially attached. From a consideration of non-bonded interactions in **12** and **13** it was assumed that minimisation of strain energy would occur by a direction of the methyl group of the methoxyl group away from C-6 and H-3. Experimental evidence for this assumption was obtained from an intramolecular nuclear Overhauser experiment. Saturation of the methoxyl protons of **12** resulted in a 25% enhancement of the integrated intensity of its methylidene proton resonance signal when compared with a similar experiment in which the irradiating frequency was applied off resonance. However, a similar irradiation of the methyl protons of the *p*-tolylsulphonyl group in **12** produced only a 7% enhancement of the signal intensity of the methylidene proton. In view of previous work in which irradiation of methyl protons in 3,3-dimethylacrylic acid and *N*,*N*-dimethylformamide resulted in 17 to 18% enhancement of the signal intensity of a *cis* methine proton but no significant effects when the

methine proton was *trans* to the irradiated methyl group, the results from **13** suggest that the methoxyl protons are in a *cis*-relationship with H-3,5; that is with the *O*-methyl group orientated away from *syn*-axial H-3 and C-6.

X. ^{13}C NMR STUDIES

The potential utility of ^{13}C NMR for studies of carbohydrates was first demonstrated by Hall and Johnson[80] and by Perlin and Casu.[81] The former workers studied the natural abundance ^{13}C spectra of a number of free sugars and glycosides and were able to show that the chemical shifts of C-1 carbon atoms were distinctive. A more detailed analysis of α- and β- D-xylose was reported. Perlin and Casu[81] described studies of D-glucose in which each of the six carbons was isotopically enriched, approximately uniformly, to the extent of about 50%. In the PMR spectrum (Fig. 9) it was observed that whereas H-1β was a pair of

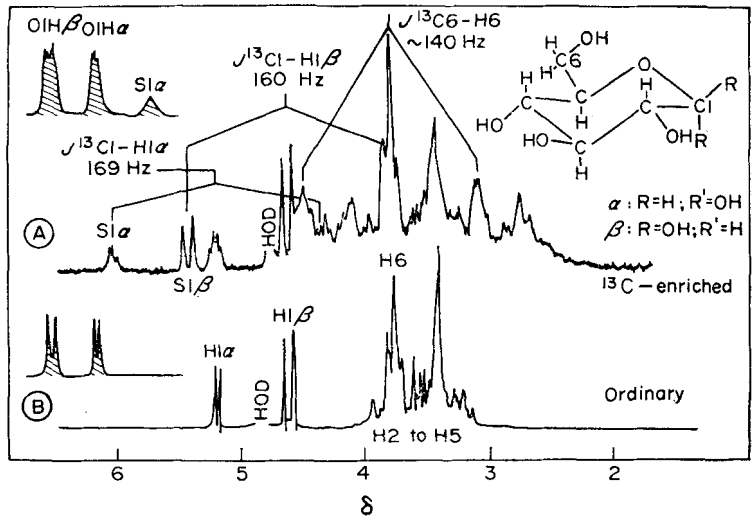


FIG. 9. PMR spectra of D-glucose in D_2O at 100 MHz. (From Perlin and Casu.[81])

doublets resulting from coupling with H-2 and C-1, H-1α showed further splitting presumably arising from couplings with C-2, C-3 and C-5. In this context, H-1α is orientated *trans* with respect to C-3 (across the C-1–C-2 bond) and to C-5 (across the C-1–O bond), whereas H-1β is *gauche* relative to both of them, which at least agrees qualitatively with calculated values of 7·8 and 0·7 Hz respectively for *trans* and *gauche* couplings in ^{13}C–C–C–H systems.[82] Similarly, spin-spin coupling of

about 4 Hz is to be expected for coupling between H-1 and ^{13}C-2 and presumably accounts in part for the multiplicity of the H-1α signal. However, since H-1β clearly did not interact appreciably with ^{13}C-2 the ^{13}C–C–H coupling must also be subject to steric influence. The ^{13}C spectra of D-glucose are shown in Fig. 10, which illustrates the typical range of ^{13}C chemical shifts in sugars and also illustrates the differences to be expected between enriched and natural abundance ^{13}C spectra. Of

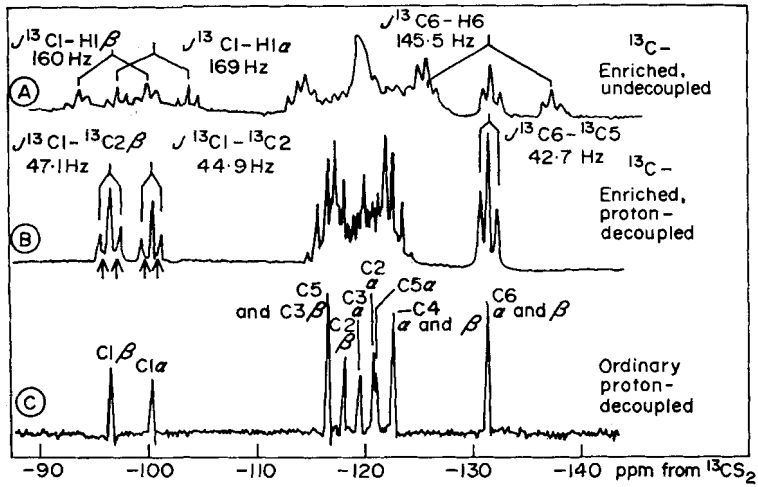


FIG. 10. ^{13}C NMR spectra of D-glucose in H_2O at 25·1 MHz. (From Perlin and Casu.[81])

interest is the fact that the C-1 and C-6 signals in the ^{13}C enriched D-glucose appear as singlets (due to the absence of ^{13}C-2 and ^{13}C-5) superimposed on doublets (from coupling with ^{13}C-2 or ^{13}C-5); these two signal components are of equal intensity in accord with the approximately equal probability that isolated ^{13}C and adjacent ^{13}C–^{13}C arrangements occur at positions 1 and 2, or 5 and 6.

Although spin-spin coupling data from ^{13}C carbohydrates is of considerable interest it is clear that in the immediate future most information will come from chemical shift data from natural abundance ^{13}C studies and recently a number of detailed natural abundance studies have been reported. For example, following studies of acyclic and alicyclic alcohols[83] and cycloalkanones,[84] Roberts and his coworkers have investigated inositol[85] and pyranose derivatives[86] and Perlin and his coworkers have discussed the influence of conformation and configuration on the chemical shifts of ^{13}C in carbohydrates.[87,88]

In Tables 7 and 8 are shown the chemical shift data obtained by Perlin, Casu and Koch.[89] The assignments were possible principally because *O*-methyl substituents have a large effect on the chemical shift of only the adjacent ^{13}carbon atom and because deuteration has a marked

TABLE VII

Carbon-13 chemical shifts for hexoses and their methyl glycopyranosides[a]

Compound	Carbon 1	2	3	4	5	6	CH_3
α-D-Glucose	−100·4	−120·9	−119·5	−122·8	−121·2	−131·4	..
-Glycoside	−92·9	−120·6	−118·9	−122·4	−120·9	−131·3	−137·2
β-D-Glucose	−96·5	−118·2	−116·6	−122·8	−116·6	−131·4	..
-Glycoside	−89·1	−119·1	−117·3	−122·5	−117·3	−131·1	−135·0
α-D-Galactose	−100·0	−123·5	−123·5	−123·8	−122·0	−131·2	..
-Glycoside	−93·0	−122·9	−122·6	−123·9	−121·6	−131·0	−137·2
β-D-Galactose	−95·8	−120·2	−119·5	−123·1	−117·3	−131·4	..
-Glycoside	−88·7	−121·6	−119·5	−123·7	−117·5	−131·4	−135·4
α-D-Mannose	−97·6	−121·0	−121·5	−124·9	−119·8	−130·7	..
-Glycoside	−91·8	−122·0	−122·7	−125·8	−120·1	−131·6	−137·5
β-D-Mannose	−98·2	−120·8	−118·7	−125·2	−115·9	−130·7	..
-Glycoside	−91·5	−122·2	−119·5	−125·7	−116·2	−131·4	−135·9
β-D-Allose	−99·0	−121·2	−121·4	−125·6	−119·0	−131·2	..
Methyl α-D-altroside	−91·7	−122·8	−122·8	−128·0	−122·8	−131·5	−137·4
Methyl α-D-idoside	−91·3	−121·9	−121·0	−122·5	−122·0	−132·6	−137·0

[a] In p.p.m. from carbon disulphide. Readers are reminded that high-field (low-frequency) shifts are negative.

TABLE VIII

Carbon-13 chemical shifts for pentoses and their methyl glycopyranosides[a]

Compound	Carbon 1	2	3	4	5	CH_3
α-D-Xylose	−100·0	−120·6	−119·2	−123·1	−131·1	..
-Glycoside	−94·2	−121·3	−119·3	−123·2	−131·8	−137·9
β-D-Xylose	−95·5	−118·0	−116·1	−122·8	−127·2	..
-Glycoside	−88·7	−119·8	−116·8	−123·2	−127·8	−135·9
β-L-Arabinose	−99·4	−123·6	−123·6	−123·8	−129·9	..
α-L-Arabinose	−95·3	−120·1	−119·7	−123·8	−126·1	..
α-D-Lyxose	−98·2	−122·1	−121·6	−124·7	−129·4	..
β-D-Lyxose	−98·2	−122·1	−119·6	−125·5	−128·3	..
α-D-Ribose	−98·9	−123·6	−122·0	−124·7	−129·4	..
β-D-Ribose	−98·4	−121·1	−121·1	−123·7	−129·4	..

[a] In p.p.m. from carbon disulphide.

impact on the signal of an adjacent ^{13}C nucleus. From the data listed in Tables VII and VIII and from theoretical considerations Perlin and his coworkers made the following observations.

(a) A comparison of chemical shifts with expected electron densities suggested that ^{13}C-2 and ^{13}C-4 experienced relatively stronger shielding than ^{13}C-1, ^{13}C-3 and ^{13}C-5, possibly because they oppose the ring oxygen.

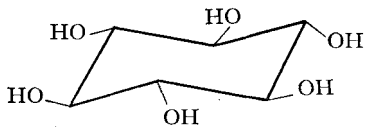
(b) The inversion of an equatorial O to an axial O was associated with increased shielding of the ^{13}C nucleus to which it was bonded, of adjacent ^{13}C nuclei and of those in the β-position (i.e. having an opposing axial H or O).

(c) Removal of a *gauche* O/O interaction was associated with ^{13}C deshielding.

In glucose, for example,[88] the transformation $\beta \rightarrow \alpha$-D—glucose was characterised by increased shielding at all carbons except C-4 and C-6 whereas the appended protons, except, H-4 and H-6, became less shielded. On the other hand the corresponding hydroxyl proton resonances (measured with dimethyl sulphoxide as solvent) were affected in parallel with those of ^{13}C nuclei, i.e. the difference between β- and α-D-glucose in the chemical shift of all hydroxyl protons, except OH-4 and OH-6, amounted to an increase in shielding. The importance of these observations is that they reflect changes in electron distribution which may be correlated with changes in the conformational stability of carbohydrate molecules, and these relationships have been discussed at length by Perlin and his coworkers.[87, 88, 89]

For the inositol derivatives, Roberts and his coworkers devised a system of empirical constants which could be used to estimate the spectra of inositols.[85] The treatment assumed that ^{13}C chemical shift differences in the inositols are associated with the variation in steric perturbation which must accompany epimerisation at any centre in the molecule. A reference point for the chemical shift of the α-carbon was adopted and the changes in its chemical shift were correlated with epimerisation of the hydroxyl groups on the remaining carbons from the equatorial to the axial configuration. It was assumed that such steric changes at the β, γ and δ carbons would be associated with an independent and additive constant representing the change in chemical shift in each case. Reference points adopted were *scyllo*-inositol (**14**) for carbons bearing equatorial OH groups and the C-2 resonance in *myo*-inositol (**15**) for cases in which the hydroxyl group at the α-carbon is axial. The symbols β, γ and δ were used to represent shifts associated with epimerisation at the β, γ and δ carbons respectively. On this basis the difference in

chemical shift between the C-1 resonance of *epi*-inositol (**16**) and the resonance of *scyllo*-inositol will be $\beta_e + \delta_e$ while the chemical shift differences between the C-2 resonances of *myo*- and *epi*- inositols can be represented by γ_a (the e and a subscripts denote that the reference carbon has an equatorial or an axial hydroxyl group respectively).



scyllo

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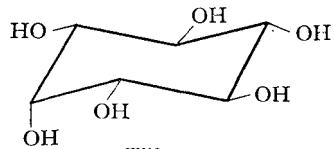

myo

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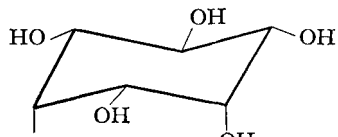

epi

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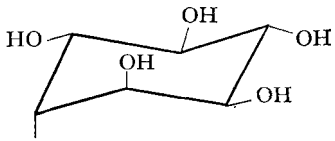

chiro

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The results of correlations based on the above assumptions are listed in Table IX. The best values for the constants were $\beta_e = 1{\cdot}7$, $\gamma_e = 2{\cdot}8$, $\delta_e = -0{\cdot}7$, $\beta_a = 0{\cdot}6$ and $\gamma_a = -2{\cdot}3$ p.p.m.

It was concluded that the substituent shifts derived for the above unsubstituted inositols were in accord with the general recognition that steric hindrance or a proximity effect is a very important factor in determining ^{13}C chemical shift differences in reasonably related compounds. The fact that the magnitudes of the γ_e and γ_a are the largest of the series of substituent constants reflects the importance of 1,3-diaxial interactions while the small and variable δ_e shifts show the expected attenuation of steric effects that would accompany increasing distance between interacting groups.

The results obtained by Dorman and Roberts[86] for pyranose derivatives were in general agreement with those obtained by Perlin and his coworkers[87] except that the assignments to C-2 and C-3 D-glucose were reversed. Koch and Perlin[88] have shown subsequently that C-2 resonates at higher field than C-3. Attempts[89] to derive a system of empirical constants for calculating the ^{13}C shifts in pyranose derivatives were less successful than with the inositols.

Other papers on ^{13}C NMR studies of particular interest to carbohy-

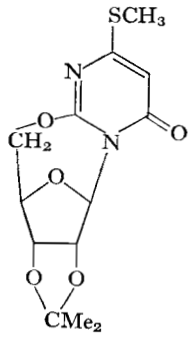
TABLE IX

Calculated and empirical ^{13}C chemical shifts in unsubstituted inositols

Compound	Carbon	Ref point	$\Delta\delta$[a]	δ_{calcd}[b]	δ_{exp}[b]	Error
Scyllo- (14)					−118·8	
Myo- (15)	5	−118·8	δ_e	−118·1	−118·2	−0·1
	1,3	−118·8	β_e	−120·5	−120·1	+0·4
	2				−120·3	
	4,6	−118·8	γ_e	−121·6	−121·4	+0·2
Chiro- (17)	3,4	−118·8	$\gamma_e+\delta_e$	−120·9	−119·7	+1·2
	1,6	−120·3	β_a	−120·9	−120·9	0
	2,5	−118·8	$\beta_e+\gamma_e$	−123·3	−122·0	+1·3
Epi- (16)	2,4	−120·3	γ_a	−118·0	−118·0	0
	1,5	−118·8	$\beta_e+\delta_e$	−120·9	−120·8	+0·1
	3	−118·8	$2\beta_e$	−122·2	−122·4	−0·2
	6	−118·8	$2\gamma_e$	−124·4	−125·7	−1·3

[a] Chemical shift measured in parts per million from the relevant reference point.
[b] Chemical shift measured in parts per million from external carbon disulphide.

drate chemists include studies of 1,3-dioxans,[90] studies of conformational effects on carbinyl carbon shielding in cyclohexanols and derivatives[91] and natural abundance ^{13}C studies of a number of pyrimidine nucleosides.[92] Distinctive ^{13}C chemical shift differences between the anhydronucleosides **18** and **19** permitted distinction that was not possible by PMR measurements to be made between these structures.[93]



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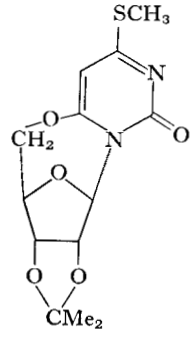

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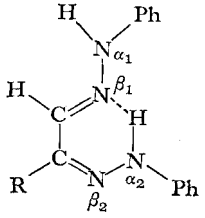
Additionally the first Fourier-transform spectra of polyols have been described.[94]

XI. CARBOHYDRATES CONTAINING ^{15}N

The spectra of 6-acetamido-6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose and its 6-^{15}N-derivative, obtained by measurements with pyridine-d_5 as solvent, have been compared.[94a] The former compound showed coupling constants of $^1J(^{15}N\text{–}H) = 1{\cdot}5$ Hz and $^2J(^{15}N\text{–}H_6) = 0{\cdot}5$ Hz.

Some information about the nature of the chelate in sugar osazones has been provided by ^{15}N NMR studies.[95] To decide between the five possible chelate structures of osazones the spectra at 60 MHz of osazones substituted separately with ^{15}N in the α and β positions have been measured. When substituted in the α-positions D-xylosazone gave two doublets for the ^{15}N–H signals; the chelated ^{15}N–H (position α_2), at 12·20 p.p.m. ($J = 94{\cdot}5$ Hz) and the free ^{15}N–H (position α_1), at 9·21 p.p.m. ($J = 93$ Hz). The observed equal values for $J(^{15}N\text{–}H)$ indicated that the two ^{15}N–H bonds were of the same nature and that rapid equilibration between the two forms **20** and **21** could be excluded. No



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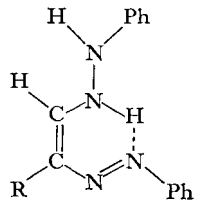

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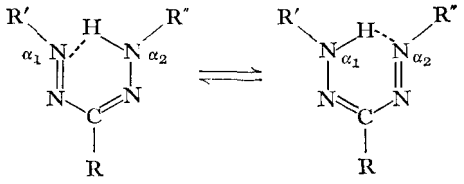
change was observed for the non-chelated N–H proton signal of D-xylosazone substituted by ^{15}N in positions β_1 and β_2. In contrast the chelated N–H peak appeared as a quadruplet ($J = 5{\cdot}0$ and 2·0 Hz) resulting from coupling with both ^{15}N atoms. Similar results were obtained with D-galactosazone. These results, although providing useful additional information about osazone structures did not permit unequivocal structural assignments.



22 **23**

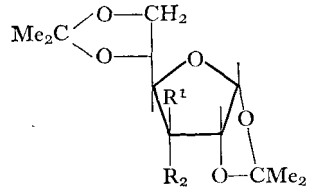
The NMR spectra of some ^{15}N-substituted sugar formazans have also been examined.[96] The chelated proton was a doublet with $J(^{15}N–H) = 46·5$ Hz when only one α position was substituted with ^{15}N and a triplet with $J(^{15}N–H) = 46·6$ Hz when both α-positions were substituted with ^{15}N. These results were consistent with the tautomeric equilibria **22**⇌**23**.

XII. CARBOHYDRATES CONTAINING ^{31}P

Hall and his coworkers[97] have reported preliminary NMR studies of carbohydrates containing phosphorus linked to the sugar ring by C–P bonds. For example, the coupling constants (Hz) for the C-3 epimers of dimethyl(1,2:5,6-di-*O*-isopropylidene-α-D-hexofuranose)3-C-phosphate (**24**) and (**25**) are:

	$J_{1,2}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J(P–H_2)$	$J(P–H_4)$
(**24**)	3·8	4·8	6·5	5·9	−8·3	7·8	29·7
(**25**)	3·7	2·5	..	..	..	<0·5	7·5

The vicinal $^{31}P–C–C–H$ couplings were in excellent agreement with the values expected on the basis of the known[98] angular dependence of vicinal $^{31}P–C–C–H$ couplings and on the assignment of the $^3T_2$ conformation to both derivatives. Particularly noteworthy was the near zero $J(P–H_2)$ coupling for (**24**) which should correspond to a dihedral angle of *ca.* 90° between the C-3–P and C-2–H-2 bonds.



(**24**) $R^1 = PO.(OMe)_2$, $R^2 = OH$
(**25**) $R^1 = OH$, $R^2 = PO.(OMe)_2$

In another report[99] of potential interest to carbohydrate chemists Hall has discussed the stereospecific dependencies of $^{31}P–H$ coupling constants of phosphate esters. The *trans* P–O–C–H couplings were found to be *ca.* 21 Hz and *gauche* P–O–C–H couplings were *ca.* 3 Hz.

XIII. STUDIES OF FLUORINATED CARBOHYDRATE DERIVATIVES

Hall and his coworkers, in an extensive series of publications, have studied the ^{19}F NMR and PMR spectra of a large number of carbohydrate derivatives with the intention of (a) providing fundamental NMR information, (b) establishing the structures of the fluorinated derivatives under study, and (c) using ^{19}F as an "amplifier" for studying conformational distortions and mobility in carbohydrates.

From a study of the ^{1}H and ^{19}F spectra of a series of hexopyranosyl fluoride derivatives it was shown[100] that the ^{19}F chemical shifts depend on the orientation of the fluorine substituent with respect to the pyranose ring and on the relative orientation of other substituents attached to the ring. For example, for a series of D-glucopyranosyl fluoride derivatives the fluorine substituent (equatorial) had a shift (ref. $CFCl_3$) within the range $-131{\cdot}8$ to $-137{\cdot}8$ p.p.m., whilst for corresponding axially orientated fluorine the shift range was $-147{\cdot}8$ to $-149{\cdot}9$ p.p.m. Thus, as for protons the equatorial resonance was at lower field than the axial resonance. It was also demonstrated that the ^{19}F–1 shifts are very sensitive to configurational changes at other points in the carbohydrate molecule. The induced shifts for an axially orientated fluorine substituent following inversion of a "remote" acetoxy substituent are shown in Table X. The chemical shift of the C-1 fluorine substituent in a series of 2-deoxy-2-halogeno hexopyranosyl fluorides also varied in a regular fashion with the nature of the halogen substituent at C-2.[101]

TABLE X

Induced shifts for an axially orientated fluorine substituent following inversion of a remote acetoxy substituent

Compound	Orientation of acetate at			δ	Induced shift p.p.m.
	C-2	C-3	C-4		
D-*gluco*	eq	eq	eq	−149·9	0·0
D-*manno*	ax	eq	eq	−138·8	+11·1
D-*allo*	eq	ax	eq	−146·0	+3·9
D-*galacto*	eq	eq	ax	−151·1	−1·2

The chemical shift of ^{19}F in primary fluoro-derivatives (i.e. those derivatives containing a $-CH_2F$ function) has been shown to be in the range -213 to -235 p.p.m. and thus significantly removed from the ^{19}F

shifts observed in glycosyl fluorides and "secondary" fluoro-derivatives.[102]

In glycosyl fluorides the vicinal ^{19}F–H couplings show the expected angular dependence. For example $J_{trans} = ca.$ 24 Hz, $J_{gauche} = 1{\cdot}0$ to $1{\cdot}5$ Hz for $J(F_a\text{–}H)$ and $J_{gauche} = 7{\cdot}5$ to $12{\cdot}6$ Hz for $J(F_e\text{–}H)$. The geminal ^{19}F-1–H-1 couplings depended on the orientation of the C-2 substituent. Thus $J(F_1\text{–}H_1)$ was *ca.* $53{\cdot}8$ Hz when the C-2 substituent was equatorial and *ca.* 49 Hz when the C-2 substituent was axial. At first sight this variation in magnitude is the reverse of that noted for geminal H–H couplings. However, since geminal ^{19}F–H couplings are positive and geminal H–H couplings are negative in fact the effect of an axial vicinal group is to reduce the magnitude of the geminal coupling in both cases. In accord with these observations, geminal H–^{19}F couplings at C-3 in galactopyranose derivatives were found[103] to be smaller (47 to 48 Hz) than in the corresponding glucopyranose derivatives (*ca* 51 Hz). However, a similar trend was not shown by geminal H–F couplings at C-2.[104]

The ^1H and ^{19}F spectra of the α- and β- anomers of 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-glucopyranosyl fluoride and the corresponding D-mannopyranosyl derivatives have been fully analysed.[104] In marked contrast with the usual observation that for vicinal H–H and ^{19}F–H couplings $J_{trans} > J_{gauche}$ and in contrast to the finding that ^{19}F–H couplings are absolutely positive in sign, the values of *trans* and *gauche* ^{19}F–^{19}F couplings were approximately the same magnitude (*ca.* 15 to 20 Hz) and absolutely negative in sign.

The magnitude of vicinal ^{19}F–H couplings (27 to 29 Hz) for 6-fluoro-D-glucopyranose derivatives indicated that the favoured rotamer about the C-5–C-6 bond has F-6 antiparallel to H-5 whereas in the corresponding galactopyranose derivatives the magnitude (15 to 18 Hz) of this vicinal coupling indicated that H-5 and H-6 had a *gauche* disposition.[101]

The ^{19}F parameters of 2-deoxy-2-halogeno hexopyranosyl fluorides showed the same angular dependence as that of vicinal H–H couplings in so far as, for each particular substituent at C-2, $J_{trans} > J_{gauche}$. Also the vicinal ^{19}F–H couplings appeared to have an approximately linear relationship with the Huggins electronegativity values of the substituents attached to C-1 and C-2.[101]

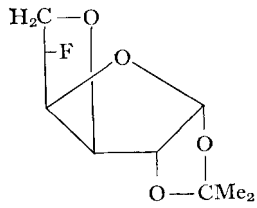
In acetylated pentofuranosyl fluorides the anomeric effect of fluorine is such that, no matter what the configuration of the pentose, the pentofuranosyl fluoride adopts a chair conformation in which the fluorine substituent has an axial orientation.[105] This conclusion was reached on the basis of observed vicinal and long-range coupling constants and from a consideration of the ^{19}F chemical shifts which could be calculated from previously formulated rules.

Some angular dependencies of long-range ^{19}F–H coupling constants

in pyranoid derivatives have been summarised.[106] In a series of 3-fluoro-pyranoid acetates the following couplings were observed: $J_{1e,3Fe}$ and $J_{5e,3Fe} = +3{\cdot}6$ to $+4{\cdot}2$ Hz, $J_{1Fe,3a} = -0{\cdot}8$ Hz and $J_{3Fe,5a} = 1{\cdot}1$ Hz. These results demonstrated that long-range ^{19}F–H couplings occur preferentially when the two nuclei have a 1,3-diequatorial relationship, or more generally when they form part of the planar W arrangement which is usually postulated as necessary for large ^4J(H–H) couplings. In accord with findings from H–H studies, the signs of $^4J(^{19}$F–H) couplings exhibited a configurational dependence; the $^4J_{e,e}$ couplings were absolutely positive and the $^4J_{e,a}$ couplings were absolutely negative in sign. Several derivatives exhibited long-range coupling across five bonds. Thus 3-fluoro-3-deoxy-β-D-glucose tetraacetate showed a coupling of 1·5 Hz between the equatorial 3-fluoro-substituent and one of the C-6 protons.

The fluorine substituent in 3,6-anhydro-5-deoxy-5-fluoro-1,2-*O*-isopropylidene-α-L-idofuranose (**26**) exhibited detectable spin coupling with all the ring protons except H-2.[107] In Fig. 11 the PMR spectra of **26** and its 5-*O*-benzoyl substituent are shown and in Fig. 12 the observed and computed ^{19}F spectra of **26** are illustrated. In studies[108] of several 3,6-*anhydro*-hexofuranosyl fluorides long-range couplings of 4·8 to 6·3 Hz between F-1 and H-3 were detected, but surprisingly although F-1 and H-5 have the same general relationship as F-1 and H-3, only a small coupling was detected between these nuclei.

Carbohydrates have been shown to be useful substrates for determinations of the signs of long-range $^4J_{F,F}$ couplings.[109] In the α- and β-anomers of 2,4,6-tri-*O*-acetyl-3-deoxy-3-fluoro-D-glucopyranosyl fluo-



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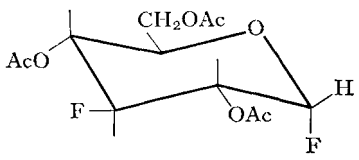

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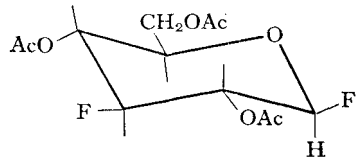

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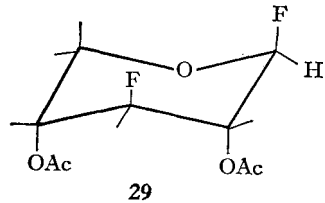

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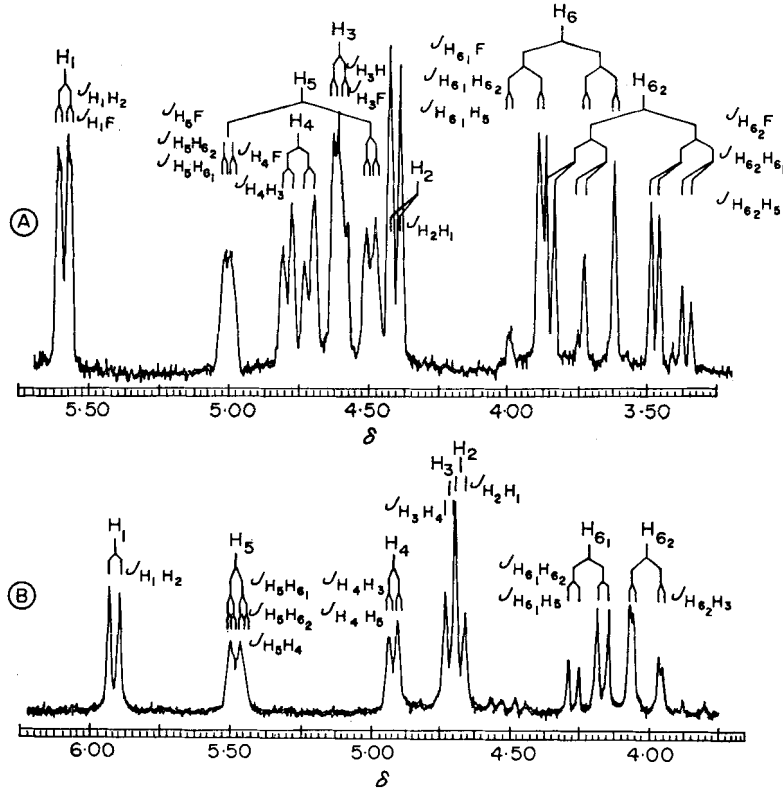


FIG. 11. Partial 100-MHz proton magnetic resonance spectra of: (A) 3,6-anhydro-5-deoxy-5-fluoro-1,2-*O*-isopropylidene-α-L-idofuranose (**26**) in benzene-d_6 solution; (B) 3,6-anhydro-5-*O*-benzyl-1,2-*O*-iso-propylidene-α-L-idofuranose in chloroform-*d* solution. First-order assignments are as indicated. The small peaks at δ 4·50 and 3·85 in the lower spectrum arise from residual impurities. (From Hall and Steiner.[107])

rides (**27**) and (**28**), and in 2,4-di-*O*-acetyl-3-deoxy-3-fluoro-β-D-xylopyranosyl fluoride (**29**) the following $^4J_{F,F}$ couplings were observed: $^4J_{a,a} = +10{\cdot}4$ Hz, $^4J_{a,e} = +1{\cdot}0$ Hz and $^4J_{e,e} = -3{\cdot}0$ Hz. From a com-

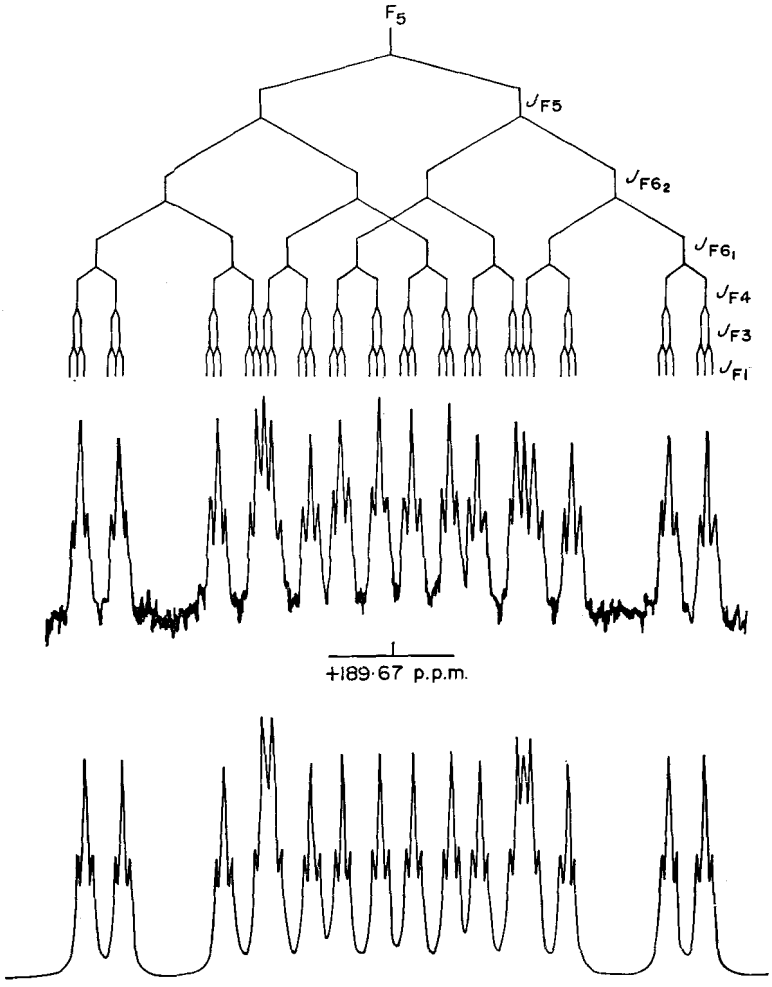
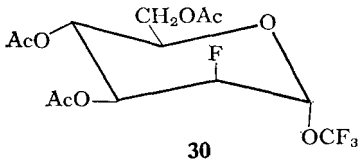


FIG. 12. ^{19}F NMR spectrum of 3,6-anhydro-5-dexoy-5-fluoro-1,2-*O*-isopropylidene-α-L-idofuranose (**26**) in benzene-d_6 solution. The simulated (lower) spectrum was obtained using the LAOCOON III programme and the SMASH plot routine. (From Hall and Steiner.[107])

parison of results with fluorinated cyclohexanes[110] ($^4J_{a,a} = +26$, $^4J_{a,e} = 0$ and $^4J_{e,e} = -10$ Hz) it was suggested that, since the magnitude of $^4J_{F,F}$ couplings clearly depend on the nature and relative orientations of nearby substituents, it is necessary to determine the sign as well as the magnitude of $^4J_{F,F}$ couplings if they are to be used for configurational and conformational investigations.

Other studies of ^{19}F NMR that have been reported include an investigation[111] of compounds such as (**30**) and (**31**) and an investigation of methyl 2,3-di-*O*-methyl-4-deoxy-4-fluoro-α-D-glucopyranoside in which a ^5J coupling of 3 to 4 Hz was observed between F-4 and H-1.[112]



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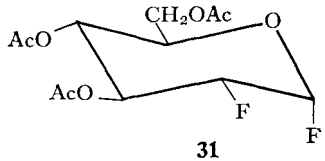

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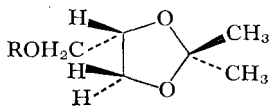

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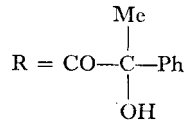

The ^{19}F spectra of anomeric pairs of trifluoroacetylated methyl glycosides have been compared. Assignments of the various CF_3 signals have been made and it has been suggested that ^{19}F NMR measurements may provide a simple and definitive method for determining anomeric configuration in glycosides.[113]

The observation[114] that in the mixture of diastereoisomeric esters from 2,3-*O*-isopropylidene-D-glycerol and racemic atrolactic acid (**32**) the acetal methyl group *cis* to the atrolactoyl group showed chemical shift non-equivalence of 2 Hz prompted a study of 2,3-*O*(trifluoromethyl)-ethylidene-D-glycerols as derivatising agents for optically active acids. Unfortunately no chemical shift non-equivalence was shown by the trifluoromethyl substituents.

A long-range spin-spin coupling has been observed between the anomeric proton (H-1′) and fluorine in fifteen 5-fluoropyrimidine nucleosides, which was not present in their non-fluorinated analogues.[115] The magnitude of the $J(H_{1'}–F)$ coupling was dependent on the anomeric configuration being $>1{\cdot}5$ Hz for the β-D-anomers and $<1{\cdot}5$ Hz for the α-D-anomers. It was concluded that the coupling was through bonds and not through space and possible through bond mechanisms for the couplings observed were discussed.

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Heteronuclear Magnetic Double Resonance

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I. INTRODUCTION

THIS REVIEW is intended to expand and bring up to date the earlier one on the same subject which appears in Volume 1 of this series.[1] Accordingly the same terminology and notation will be used as far as possible, the main difference being that SI units will be used throughout. Thus the main (polarising) magnetic field will be denoted by B_0, and oscillating r.f. fields by B_1, B_2, etc.; their units are tesla (kg s^{-2} A^{-1}, $\equiv 10^4$ gauss). However, since the numerical values of magnetogyric ratios differ by a factor of 10^4 in the c.g.s. and SI units, the quantity $\gamma B/2\pi$, which expresses the amplitude of a r.f. field in Hz, is numerically the same in the two systems. The reader who requires an account of NMR in SI units should consult Lynden-Bell and Harris's book.[2]

Heteronuclear double resonance experiments are now becoming quite widely used, and it is likely that the technique will soon become as important as homonuclear double resonance is now. Some typical

applications include: the simplification of ^{1}H or ^{19}F spectra by the removal of fine structure arising from spin coupling to a nucleus of another species; the removal of broadening which may arise when a nucleus such as ^{2}D or ^{14}N, with a nuclear quadrupole moment, is present; the determination of the chemical shifts of nuclei other than ^{1}H or ^{19}F with high precision and sensitivity; the determination of the signs of coupling constants between nuclei of different species; the production of INDOR spectra which can give the details of the fine structure of the spectra of many nuclei; and the improvement of signal-to-noise ratio in the spectra of nuclei other than ^{1}H and ^{19}F (notably ^{13}C) by removal of coupling to protons and nuclear Overhauser enhancement. In addition there are a number of double resonance techniques which so far have been applied largely to homonuclear systems, but which have considerable potential in the heteronuclear field. These include spin saturation studies of chemical exchange and the use of the nuclear Overhauser effect for the direct study of molecular geometry.

A number of review articles have appeared in recent years which have included sections on magnetic double resonance, and these are listed in references 3 to 8; the topic is also discussed in several books.[2,9,10]

II. THEORETICAL ASPECTS

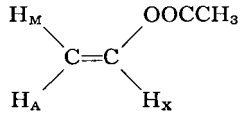
A. Decoupling

The normal effect of applying a sufficiently strong second r.f. field (ν_2) at the Larmor frequency of one nucleus in a spin system is to remove the scalar coupling to other nuclei, whose resonances are consequently simplified. This behaviour is conveniently discussed by transforming to a coordinate system which is rotating about the z-axis (i.e. the $-B_0$ direction) at a frequency ν_2. The effective polarising field is then $B_0 - 2\pi\nu_2/\gamma_X$, which will be small for the irradiated nucleus since ν_2 is close to its Larmor frequency ($B_0\gamma/2\pi$), but very large for the other nuclei in the system.[11] The resultant field acting upon the irradiated nucleus is the vector sum of the two perpendicular fields $B_0 - 2\pi\nu_2/\gamma_X$ and B_2, and so will lie along B_2 when this is large compared with the width of the resonance of the irradiated nucleus. B_2 will therefore be the direction of quantisation of the spins of the irradiated nuclei, but the spins of the other nuclei will be quantised along B_0 which is perpendicular to B_2. Thus the observed coupling, which is the scalar product $J_{AX}\mathbf{I}_A\mathbf{I}_X$ and is therefore proportional to the cosine of the angle between the two directions of quantisation, will vanish.

The foregoing description is adequate provided that the observed and irradiated nuclei are of different species, for then $B_0 - 2\pi\nu_2/\gamma_A$ will

always be very large and the spins of the observed nuclei will be quantised along the B_0 direction. However, in homonuclear experiments the chemical shift difference between the observed and irradiated nuclei may be insufficient for the former to remain unperturbed by the irradiating field, and consequently their direction of quantisation may not be along B_0. In the limit of $\gamma_X B_2/2\pi > \nu_A - \nu_X$ the spins of both types of nuclei will be quantised along the same direction at right angles to B_0 and the full coupling will return.[12]

This behaviour has been demonstrated experimentally with the olefinic proton resonance of vinyl acetate (**1**),[13] in which the chemical shift separation of the X and M resonances is 247 Hz at 100 MHz, and the X resonance extends over 20·4 Hz.



(1)

$J_{MX} = 14{\cdot}0$ Hz and optimum (but not totally complete) collapse of this coupling is achieved when X is irradiated with a field given by $\gamma B_2/2\pi =$ 44 Hz. When the irradiating field is increased beyond this value the splitting of the M resonance begins to reappear, and when the field is 100 Hz the *apparent* coupling is *ca.* 5 Hz. It is thus clear that considerable circumspection must be used in interpreting spectra which have been "simplified" by homonuclear decoupling. It is further evident that the differences between homonuclear and heteronuclear experiments are not merely instrumental, and that circumstances can arise in which the complete removal of certain splittings in a homonuclear system may be extremely difficult or even impossible.

A more detailed analysis of decoupling shows that even in heteronuclear systems multiplet collapse may not be complete unless the spin system is particularly simple. In fact in all but A_nX systems some residual splitting will remain, no matter how large the irradiating field. Furthermore, in many cases rather large couplings (often some hundreds of Hz) occur and it may be difficult technically to generate large enough r.f. amplitudes at the sample, and quite small errors in the choice of the decoupling frequency will lead to incomplete decoupling. These problems have been examined by Anderson and Nelson,[14] and by Ernst,[15] who find that modulation of the irradiating frequency can considerably alleviate the difficulties.

The normal result of using an inadequate decoupling field, or one which is offset from exact resonance, is to give a residual splitting in the

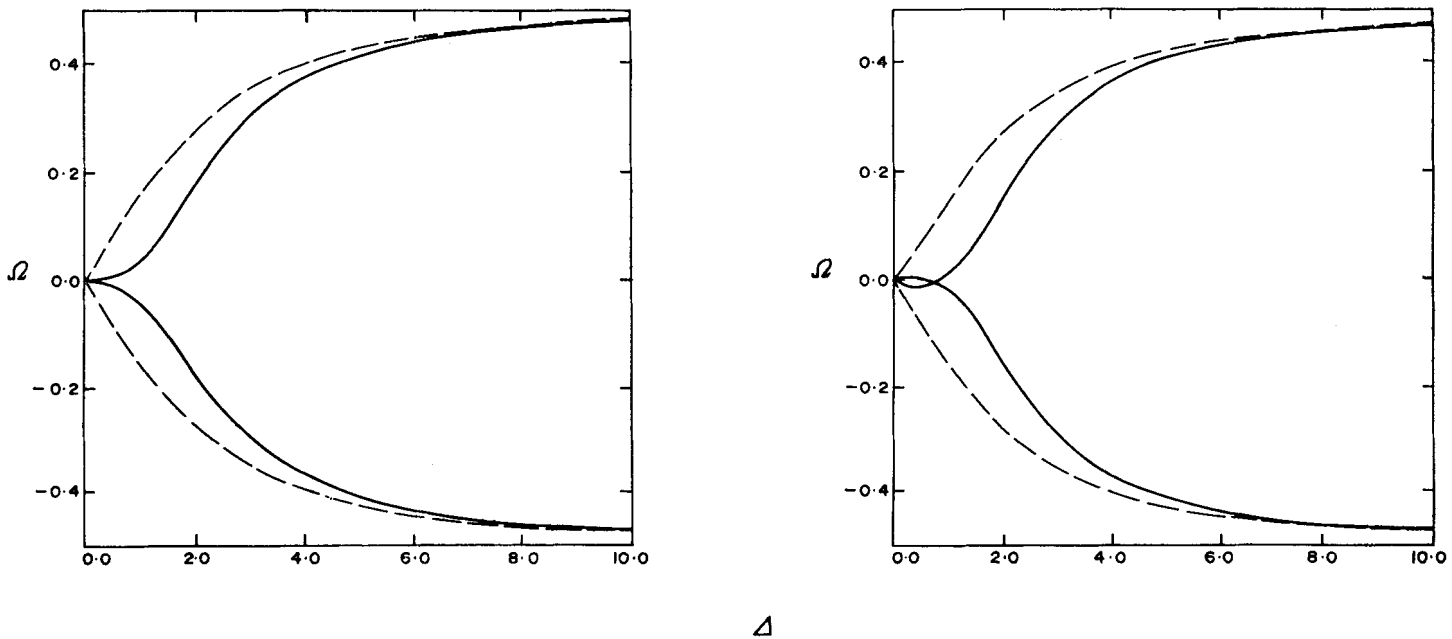


FIG. 1. Transition frequencies Ω of the A groups plotted against the offset parameter Δ for the strong lines of an AX system with $\gamma_X B_2/2\pi = 3J_{AX}$. The broken lines represent an unmodulated decoupling field and the solid lines the effect of modulating with a frequency given by (a) $\gamma_X B_2/2\pi$, (b) 1·1 $\gamma_X B_2/2\pi$. In each case the modulation index was 0·5. (From Anderson and Nelson.[14])

recorded spectrum. This manifests itself in the AX case as two symmetrically placed lines which coalesce at the centre of the spectrum as the irradiating power is increased or exact resonance is achieved. The positions of these lines are given by the broken lines in Fig. 1(a), in which the axes are calibrated in units of J_{AX} and the amplitude of the decoupling field is given by $\gamma B_2/2\pi = 3J_{AX}$. The residual splitting (i.e. the separation between the two halves of the curve) is zero only when exact resonance is achieved by the decoupling field, and increases rapidly as ν_2 is offset from this position. If the irradiating frequency is simultaneously frequency modulated with an audio frequency equal to $\gamma B_2/2\pi$ at a modulation index of *ca.* $\frac{1}{2}$ the positions of the lines are as indicated by the full curves of Fig. 1(a). It will be noticed that the initial rate of divergence for a small offset is much smaller than for the unmodulated case, and the residual splitting remains relatively unimportant until the offset exceeds J_{AX}. Furthermore, if the modulation frequency is increased by a few per cent, the curves appear as shown in Fig. 1(b) in which the range of negligible residual splitting is even greater, and there are two positions at which complete decoupling is achieved. Thus by modulating the irradiating frequency considerably more efficient use may be made of the available r.f. power.[14] More complicated spin systems can be treated by using a set of superposed curves placed so that a crossover point of one lies on a different crossover point of the next. In this way it can be shown that in addition to the simple AX_n case, for which modulation is not essential (although it may be beneficial), it is also possible to achieve complete decoupling in the following systems: A_2X_n, A_3X_n, AKX_n and AK_2X_n, where A and X are the observed and irradiated species respectively. For more complex cases some residual splitting will remain, but it will still be advantageous to use modulation.

This technique is most valuable when a small number of relatively large splittings have to be collapsed, and is illustrated in Fig. 2 which shows the proton spectrum of dimethyl phosphite, $(CH_3O)_2PHO$. In this molecule $^1J(^{31}P\text{–}H) = 690$ Hz and an attempt to collapse the P–H proton resonance to a singlet by irradiation at the centre of the phosphorus resonance with a field of amplitude $\gamma(^{31}P)\, B_2/2\pi = 500$ Hz lead to incomplete decoupling as shown in Fig. 2(b). However, when the irradiating frequency was frequency modulated with an audio-frequency of 510 Hz, essentially complete collapse was achieved as shown in Fig. 2(c). In experiments like this the choice of the modulation frequency is quite critical and is best made empirically.

It often happens that although the individual couplings are quite small it is nevertheless difficult to achieve satisfactory decoupling in heteronuclear work because the resonances of the irradiated species are

spread over a wide range by chemical shift differences. In these circumstances it is advantageous to modulate the decoupling frequency with random (white) noise of an appropriate band width; that is, to use an incoherent r.f. field. This approach was proposed by Primas and Ernst,[16] and was realised experimentally by Ernst.[15]

It is important to appreciate that for noise modulation to be effective the irradiating r.f. field must be of sufficient amplitude to collapse the largest splitting when properly centred in the absence of any modulation. That is $\gamma B_2/2\pi \gg J_{\max}$ where $J_{\max}$ is the largest coupling that is to be

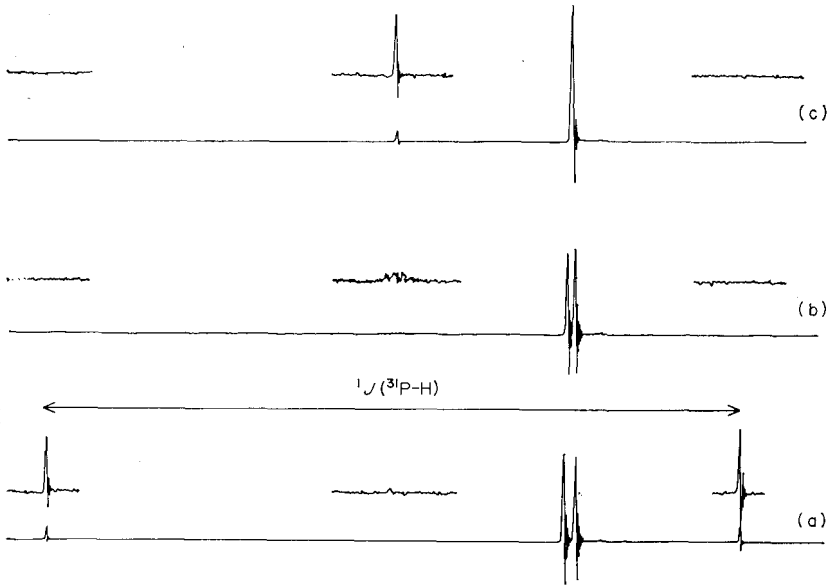


FIG. 2. ^{31}P decoupling experiments on dimethyl phosphite, $(CH_3O)_2PHO$. (a) Normal proton spectrum at 60 MHz. (b) Attempted decoupling with maximum power available at 24·28 MHz. (c) As for (b) but with modulation of decoupling r.f. at 510 Hz; the decoupling is essentially complete.

removed. The effect of noise modulation is then to distribute the available r.f. energy over a wide frequency range so as to permit a large spread of internal chemical shifts to be accommodated. The theoretical treatment[15] shows that for spin systems in which all the irradiated nuclei are of spin $\frac{1}{2}$ and are weakly coupled there is an equivalence between the effects of irradiation with an incoherent (i.e. noise modulated) r.f. source and of chemical exchange. Thus for an AX system an increase in the amplitude of the noise modulated r.f. field at the X resonance frequency leads to a

broadening of the two A lines, followed by their coalescence and ultimate collapse to a single sharp line. For systems in which there are sets of magnetically equivalent nuclei this is no longer true, and in particular it will be found that transitions associated with different symmetry classifications behave differently in the two cases. However, ultimate collapse to a single line will be achieved at sufficiently high amplitudes of B_2.

A theoretical comparison between the various methods of spin decoupling shows that even in the most favourable circumstances the necessary r.f. field is nearly ten times greater with unmodulated double resonance than for either of the two modulated versions. When the size of the various splittings is very small compared with the total spectral spread of the irradiated species it is found that noise modulation is greatly superior to modulation with a single coherent frequency. However, when the smaller splittings are less than *ca.* $J_{max}/3$ ordinary modulation becomes more effective; experiments performed on CHF_2CHCl_2 confirm these predictions.[15] The ^{19}F spectrum is a double-doublet with splittings of 8 and 55 Hz, and irradiation at the proton resonance frequency with an unmodulated r.f. field of amplitude given by $\gamma(^1H)B_2/2\pi = 1500$ Hz gave satisfactory decoupling over quite a narrow range. Modulation of the irradiating field at a frequency of 1500 Hz extended this range to ± 400 Hz (although there was a lack of uniformity in results obtained at intermediate offsets), and noise modulation extended the permissible offset to more than 600 Hz.

One major advantage of the noise modulation decoupling technique is that, as ν_2 need not be set accurately, it is possible to perform field-sweep experiments without continual readjustment of the decoupling frequency as the spectrum is recorded. The method is thus very suitable for use on unsophisticated spectrometers. Details of instrumentation and applications will be mentioned later.

B. Spin tickling

The theory of double resonance with weak irradiating fields was developed by Anderson and Freeman[12,17,18] on the assumption that relaxation effects could be neglected. It predicts that irradiation of a single transition will produce equal doublet splittings of connected transitions, irrespective of whether they are related progressively or regressively to the irradiated one, although there may be differential line-width effects. In fact the approximation that relaxation effects are unimportant is not wholly justifiable, especially when $\gamma_X > \gamma_A$ and very weak fields (comparable with the line width) are used. In these circumstances it is necessary to use density matrix theory[6] which takes into account all relaxation processes as well as the direct perturbation of the

nuclear energy levels by the irradiating field.[19 to 27] The broad conclusions are that provided $\gamma_X B_2/2\pi \gg (T_2)^{-1}$ then Anderson and Freeman's theory is adequate, but for smaller levels of B_2 near to the threshold of line splitting the full theory must be used. In particular the size of the splitting produced may differ from that predicted by the simpler theory and will depend upon whether the relationship to the irradiated transition is progressive or regressive. Commonly the wider splittings will be associated with the regressive relationship,[24] and since these lines are also the ones to be sharpened in tickling experiments they will be the most suitable to use in exact measurements. Additionally, when $\gamma_X > \gamma_A$ extremely anomalous line shapes may be obtained and inverted lines can occur.[25] However, when $\gamma_X < \gamma_A$ (this is the more common situation) these effects will be much less important.

In principle the details of the fine structure of the spectrum of a nucleus whose resonance is not observed directly can be mapped out by a series of tickling experiments. However, these may be very tedious to perform, and it is therefore of interest to seek a more rapid method of acquiring this information. One such method is to record the INDOR spectrum[28] by monitoring an appropriate line in the observed spectrum and sweeping the irradiating frequency through an appropriate range, but this places high demands upon instrumental stability and the interpretation may be complicated. An alternative is to use the technique for the "transfer of fine structure" developed by Freeman and Gestblom.[29] Consider a first order AMX spin system in which $J_{AM} = 0$ and the relative magnitudes of J_{AX} and J_{MX} are such that B_2 can fulfil the inequality (1).

$$|J_{AX}| \gg |\gamma_X B_2/2\pi| \gg |J_{MX}| \tag{1}$$

The X spectrum will be two widely separated doublets and the A spectrum will be two lines, each of which will be split by irradiating at the frequency of either component of the X spectrum. However, if the irradiating r.f. field is set at the centre of either of the doublets in the X spectrum no individual X transition will be at exact resonance and two offset parameters (cf. ref. 18 and ref. 1, p. 141) must be considered in each experiment. These are given by

$$\Delta = \pm \tfrac{1}{2} J_{MX} (\gamma_X B_2/2\pi)^{-1} \tag{2}$$

and Fig. 3 may be used to predict the resulting appearance of the A spectrum. Each A line is split into four rather than two lines and, provided the inequality (1) is satisfied, the fine structure of the X spectrum may be said to be "transferred" to the observable A lines. However, the magnitude of the splitting is reduced to half by this process, and small errors in the setting of ν_2 will have little effect upon this.

This treatment may be applied to more complex systems, and in general it is found that fine structure in the spectrum of the irradiated nucleus will be transferred faithfully to the observed spectrum with a halving of all splittings provided that B_2 is chosen to satisfy (1). The technique should be especially useful for examining the fine structure

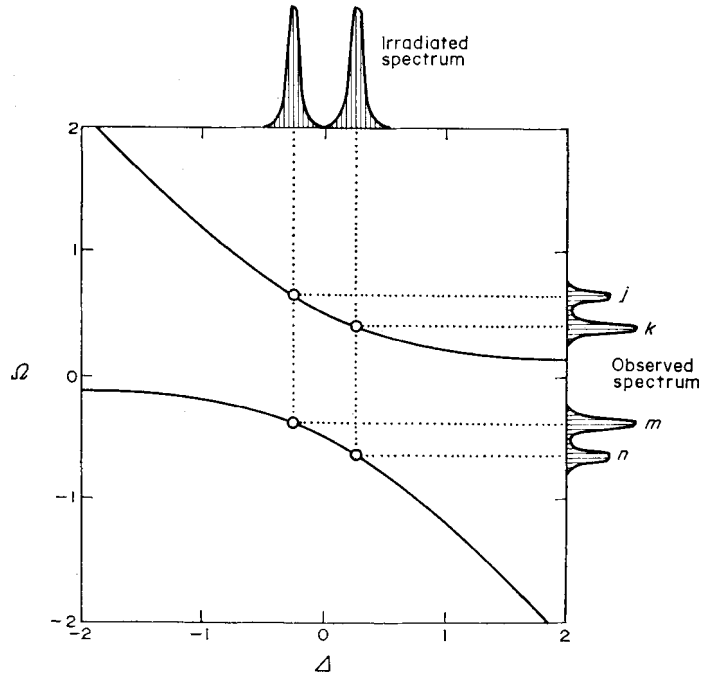


FIG. 3. Graphical illustration of the relation between the line frequencies observed in a spin-tickling experiment (Ω) and the offset of the second r.f. field from resonance (Δ). If the irradiating frequency is set at the centre of a doublet the observed spectrum contains four transitions, j, k, n and m: it is as if an additional splitting had been transferred from the irradiated line. This additional splitting is the separation between j and k or m and n. (From Freeman and Gestblom.[29])

of ^{13}C resonances by means of ^1H-$\{^{13}C\}$ experiments, and this application has been illustrated by determining $^2J(^{13}C\cdots{}^2D)$ (actually 1·5 Hz) in $H-C\equiv{}^{13}C-CD_3$ by transferring the splitting to the proton spectrum.[29] An example of the use of the method in organophosphorus chemistry is shown in Fig. 4 which illustrates experiments on di-*iso*propyl phosphite $[(CH_3)_2CHO]_2PHO$. From the proton spectrum it is easy to measure $^1J(^{31}P-H)=690$ Hz and $^4J(^{31}P\cdots H)=0$ Hz, but it is rather

more difficult to determine the size of the coupling between phosphorus and the methine protons since the resonance of the latter is further split by coupling to the methyl groups. However, when the high-field multiplet of the ^{31}P spectrum is irradiated with a field of amplitude given by $\gamma(^{31}P)B_2/2\pi = 50$ Hz the fine structure of the ^{31}P spectrum is transferred to the split-out components of the P–H doublet which therefore appear

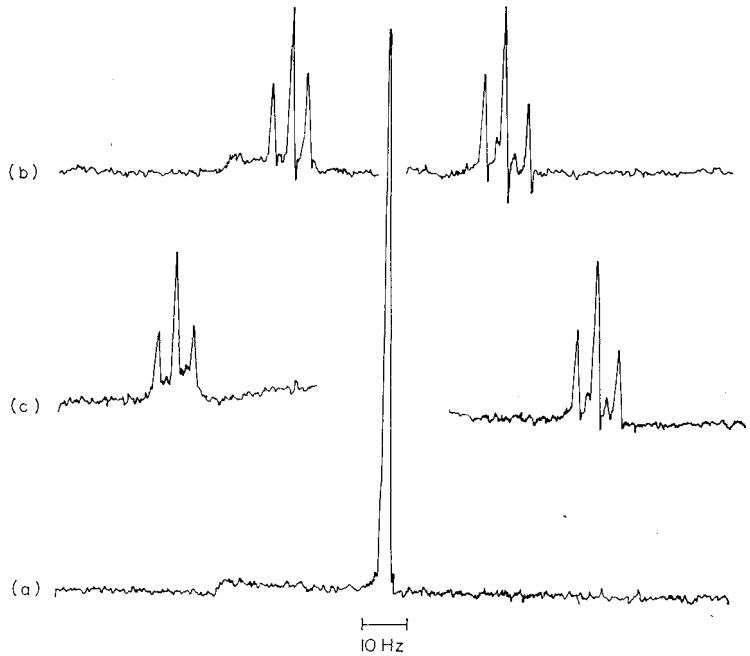


FIG. 4. Transfer of fine structure from the ^{31}P spectrum of di-isopropyl phosphite, $[(CH_3)_2CHO]_2PHO$, to the P*H*O proton resonance. (a) Unperturbed *high-field* component of proton doublet. (b) With simultaneous irradiation of high-field ^{31}P multiplet with $\gamma(^{31}P)\ B_2/2\pi = 50$ Hz. (c) As for (b) with $\gamma(^{31}P)\ B_2/2\pi =$ 100 Hz.

as triplets, and the coupling can be measured as $2 \times 4{\cdot}5 = 9$ Hz. When the irradiating field is increased to 100 Hz, as in Fig. 4(c), the separation between the two triplets increases, but the internal splitting is unchanged, and when the relationship between the observed and irradiated lines is progressive there is line broadening.

In many cases the requirement that $J_{AM} = 0$ will not be fulfilled strictly, and there will be a small splitting in the normal single resonance spectrum. In the double resonance experiment it will then be found that

this splitting is either increased or decreased, according to (a) whether the relationship between observed and irradiated transitions is progressive or regressive, and (b) the relative signs of J_{AX} and J_{MX}.

If the spectrum of the X nucleus displays broadening (say as a result of nuclear quadrupole relaxation or chemical exchange) rather than resolved fine structure, this may be transferred in a similar manner to the observed spectrum in a double resonance experiment.[30] In this case, provided that inequality (3) is satisfied, the broadening of the perturbed lines in the observed spectrum will be half that in the spectrum of the irradiated species. The technique is specially useful

$$J_{AX} \gg \gamma_X B_2/2\pi \gg \Delta\nu_X \tag{3}$$

when the cause of the broadening of the X spectrum has no apparent effect upon the appearance of the A spectrum and so cannot be studied directly. It has been used to examine the effect of the $^{35/37}Cl$ nuclear quadrupole moment upon ^{13}C relaxation in chloroform,[30] and Fig. 5 shows similar experiments upon the high-field ^{29}Si satellite ($I=\frac{1}{2}$, abundance = 4·6%) in the proton spectrum of trichlorosilane, $HSiCl_3$. The width at half-height of the unperturbed proton line is 0·5 Hz, whereas the perturbed components have widths of 2·5 Hz, indicating that the line width in the ^{29}Si spectrum is *ca.* 5 Hz as a result of $^{35/37}Cl$ quadrupolar relaxation.

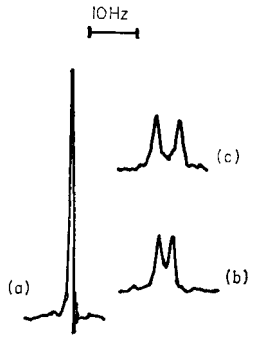


FIG. 5. Transfer of line-broadening in a double resonance experiment. (a) High-field ^{29}Si satellite in the single resonance proton spectrum of trichlorosilane, $SiHCl_3$. The line width at half-height is 0·6 Hz. (b) Effect of irradiating at the frequency of one of the two ^{29}Si transitions with an r.f. field of strength given by $\gamma B_2/2\pi = 3$ Hz. (c) $\gamma B_2/2\pi = 4{\cdot}5$ Hz. In (b) and (c) the width of the perturbed components of the proton line is *ca.* 2 Hz, and this is due to broadening in the ^{29}Si spectrum itself brought about by $^{35/37}Cl$ nuclear quadrupole relaxation.

The treatment of spin tickling by Freeman and Anderson[18] is directly applicable to systems in which the irradiated transitions are non-degenerate. If this condition is not fulfilled it remains true qualitatively that connected transitions will be perturbed in the experiments, but the quantitative description may be different. This has been investigated in some detail[31] in the case of the $NH_4^{\oplus}$ ion in which ^{14}N has spin $I=1$ and

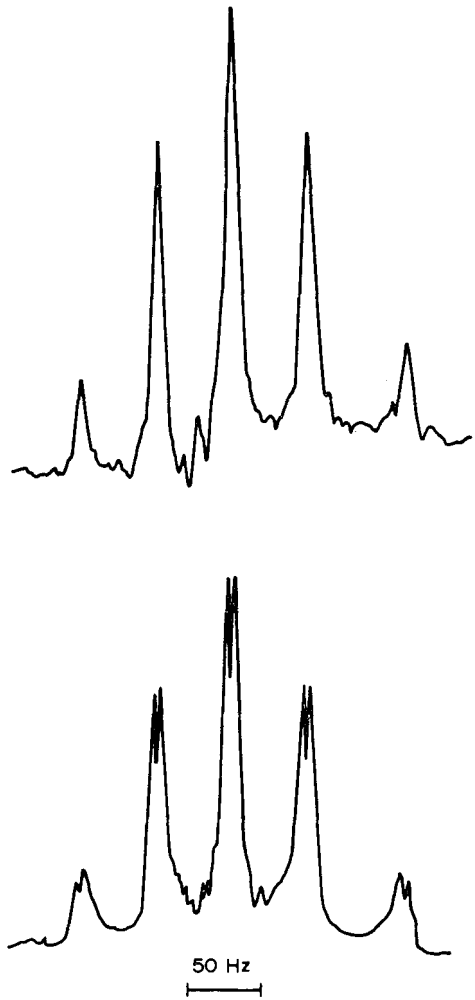


FIG. 6. ^{14}N INDOR spectra of $NH_4^{\oplus}$ obtained under identical conditions. (a) Central line of 1:1:1 proton triplet monitored. (b) Outer line of proton triplet monitored. (From McFarlane and Whiffen.[31])

quadrupolar effects are eliminated by the symmetry of the ion. Irradiation of a single line in the nitrogen quintet gives a splitting out of the expected fraction (e.g. 12/16 for the central line) of the central line of the 1:1:1 proton triplet, but the width of the splitting is $B_2\gamma(^{14}\mathrm{N})/2\pi$ and not half this amount as it would be in the all-spin $\frac{1}{2}$ case. Furthermore, when exact resonance is not achieved in the nitrogen spectrum the appearance of the proton pattern remains symmetrical but the two "perturbed" components lose intensity and move apart. The on-resonance behaviour of the outer lines of the proton triplet is similar except that the fraction affected in a particular experiment is only half what it would be in the case of the central line. The off-resonance behaviour is very different: up to seven lines may be observed in positions which depend upon the amplitude and offset of the irradiating field. An important consequence of this is that, whereas the central proton line has minimum height when exact resonance is achieved in nitrogen spectrum, the outer proton lines give a local maximum under these conditions. If ^{14}N INDOR spectra are plotted their appearance therefore depends upon which proton line is monitored: the central one gives a normal quintet, but either of the outer ones gives a quintet with a sharp hole in each peak, as shown in Fig. 6. Great care must therefore be taken in interpreting double resonance experiments which involve the irradiation of degenerate transitions.

C. Spin population and relaxation effects

At very low amplitudes of B_2 the predominant effects in double resonance experiments arise from spin population transfer and the true nuclear Overhauser effect (NOE). The former has been termed the "generalised Overhauser effect"[32] but recent developments have made it desirable to confine the use of the expression "Overhauser" to cases where there is a *direct* effect upon nuclear relaxation.[33] These effects are largest when $\gamma_X > \gamma_A$ so that for ^{1}H–{X} and ^{19}F–{X} (X $\neq$ H or ^{19}F) experiments they are relatively unimportant.

The intensity of the signal given by a nucleus depends upon the degree of magnetic polarisation achieved, and normally this is governed by the Boltzman distribution. However, in an AX system in which the X resonance is continuously irradiated by a decoupling field the ratio of the magnetic polarisation of the A spins is given by equation 4.

$$\langle M_z(A)\rangle = \langle M_z(\mathrm{A})\rangle_0 + \frac{W_2 - W_0}{2W_1(A) + W_2 + W_0}\left(\frac{\gamma_X}{\gamma_A}\right)\langle M_z(A)\rangle_0 \qquad (4)$$

$\langle M_z(A)\rangle_0$ is the polarisation in the absence of the decoupling field, and

the W's are the transition probabilities defined in ref. 34. These transition probabilities depend upon the relaxation mechanisms affecting the two nuclei and it will be noticed that the enhancement of magnetic polarisation, and hence of signal intensity, is independent of the relaxation of the X spins provided that saturation of *both* X transitions is achieved. If the mutual dipole-dipole interaction dominates the relaxation of the system it can be shown that

$$W_2 : W_1(A) : W_0 = 1 : 1/4 : 1/6 \tag{5}$$

so that

$$M_z(A) = \langle M_z(A) \rangle_0 + 0{\cdot}5\left(\frac{\gamma_X}{\gamma_A}\right)\langle M_z(A) \rangle_0 \tag{6}$$

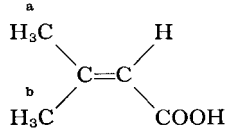
and an intensity enhancement of $(\gamma_X/\gamma_A).50\%$ is possible.† When other mechanisms contribute to the relaxation of the A spins, $W_1(A)$ will be larger and so the observed enhancement will be less. This phenomenon is the nuclear Overhauser effect.

These predictions have been tested quantitatively by ^{13}C–$\{^1H\}$ experiments on enriched formic acid, $H^{13}COOH$, in which irradiation of the proton resonance increased the ^{13}C intensity by a factor of $2{\cdot}98 \pm 0{\cdot}15$, which may be compared with the theoretical value of 2·998.[35] Equation 6 also applies to more complex spin systems, and the improvement of signal-to-noise ratio in ^{13}C spectra in this way is now an established technique which is dealt with in more detail later (p. 377).

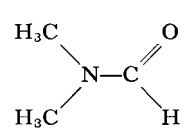
In ^1H–$\{^1H\}$ (and other homonuclear) double resonance experiments the theoretical enhancement factor is 50% and in practice contributions from other relaxation processes make it rare to observe enhancements exceeding 30%. The dipole-dipole interaction is proportional to the inverse sixth power of the separation between the interacting nuclei, and so the nuclear Overhauser effect may be used to determine which nuclei are physically close. In the case of protons the effect is negligible when the distance exceeds the van der Waals diameter (*ca.* 240 m^{-12}) and so NOE studies can be very valuable for establishing molecular geometry.[36,37] A complete account of applications of the NOE to homonuclear systems would be out of place here, but in view of the potential value of heteronuclear experiments a few illustrative results will be considered. In β,β-dimethyl acrylic acid (**2**) irradiation of the methyl group resonance at higher field increased the intensity of the α proton resonance by 17%

† An interesting consequence of equation 6 is that if one nucleus has a negative γ the "enhancement" will be negative.

while irradiation of the methyl resonance at lower field had a negligible effect. The high-field methyl resonance is therefore assigned to CH_3(a) which is close to H-α. Similarly in *N,N*-di-methyl formamide (**3**) where



(2)



(3)

partial double bond character between nitrogen and the carbonyl group leads to a planar structure the intensity of the formyl proton resonance is affected only when the high-field methyl resonance is irradiated.[36] If the temperature of (**3**) is raised the rate of internal rotation about the C–N bond will increase and at about 120° the two methyl peaks coalesce to a singlet. However, at somewhat lower temperatures (*ca.* 90°) two separate resonances are observed, but irradiation of *either* of these enhanced the intensity of the formyl proton resonance by *ca* 28%. This behaviour occurs because at 90° the lifetime of an individual rotamer is short compared with the time required for the decay of the saturation of a particular methyl group (T_1—of the order of seconds) but is long compared with $(\nu_0 \cdot \Delta)^{-1}$ (less than 0·1 s), so that spin saturation is transferred from one site to another.[38] Clearly, caution must be used in applying the NOE to conformationally mobile systems.

Other examples of the NOE applied to structural determinations in all-proton systems are to be found in references 39 to 45, while recently ^1H-$\{^{19}F\}$ effects have been reported in fluoroaromatic compounds.[46] Experimental points are that paramagnetic materials (e.g. dissolved oxygen) should be removed from the sample as this will affect the relaxation of the observed nucleus, and solvents containing nuclei of high magnetic moment should be avoided. This rules out protonated and halogenated solvents and leaves carbon disulphide and deuterium oxide. Since the nuclear Overhauser enhancement is often accompanied by normal decoupling it is important to use peak areas to assess intensity changes. If an adiabatic fast passage is made through a resonance immediately prior to recording the spectrum the populations of the irradiated spins will be inverted rather than just equalised, and the foregoing intensity changes will be doubled. Such experiments can often be performed quite easily by setting the irradiating frequency a few Hz off exact resonance (in the appropriate direction) and recording the spectrum in the field-sweep mode.

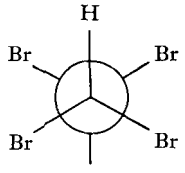
The nuclear Overhauser effect may also be used for more detailed studies of relaxation behaviour, and in particular it is often possible to

distinguish between the effects of dipole-dipole and spin-rotation interactions in this way.[47] Thus in work[48] on liquid trifluoromethane at low temperatures both pulsed and steady-state techniques were used, and it was found that the spin-rotation mechanism was important only for the relaxation of the fluorine nuclei. Similar studies have been made of 1,1-difluoroethylene[49] and ethyl fluoride,[23] and double resonance experiments have been used to study relaxation in systems containing quadrupolar nuclei.[50, 51]

Double resonance experiments may be used to extend the range of lifetimes over which chemical exchange processes can be studied by NMR. Again most of this work applies to homonuclear systems and so is considered only briefly here. If the resonance of an exchanging nucleus at one site is saturated this saturation will be transferred to the other site provided that the lifetime at the irradiated site is shorter than T_1. Thus the intensity of the resonance at the second site will be seen to decrease when the first site is irradiated, and this may be used to demonstrate that exchange is indeed occurring.[52] A more subtle aspect of this phenomenon is that the resonance of a third nucleus which is not exchanging with the irradiated one may also be saturated if it is tightly coupled to the second nucleus. Thus in the AB + X spin system given by a mixture of diphenyl carbinol and *t*-butyl alcohol under appropriate conditions, saturation of the OH resonance of the second component reduced the intensities of both the OH *and* the CH resonances of the first, provided that the internal chemical shift difference was small.[54] This behaviour arises because the strong coupling between A and B permits them to exchange their spin states relatively freely (in the limit $\delta_{AB} = 0$ A and B are equivalent magnetically and the spin exchange is completely free) and so saturation of A (*via* its exchange with X) produces partial saturation of B. It has been shown that this type of "indirect spin saturation" may be transmitted along a chain of mutually coupled protons (e.g. in almost equivalent methylene groups) and can also be brought about by saturating a double quantum transition.[55, 56]

When the interchange of a pair of nuclei occurs as a result of internal rotation, rather than true chemical exchange, the effects of spin saturation can give the relative signs of coupling constants *in different conformers*. Thus the ^{19}F spectrum of 1,1,2,2-tetrabromofluoroethane at low temperatures consists of two doublets given by the *trans* and *gauche* rotamers (**4**) and (**5**) respectively in which $^3J(H \cdots F) = 24{\cdot}0$ and $1{\cdot}7$ Hz. In a homonuclear experiment it was found that selective saturation of the high-field component (corresponding to a particular proton spin state) of the doublet given by the *trans* isomer also saturated the high-field *gauche* line. Since nuclear spin states are conserved during internal rotation this

indicates that the H–F coupling constant has the same sign in each rotamer.[57]



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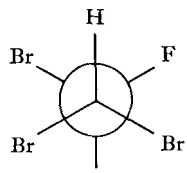

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D. Other topics

Govil and Whiffen[58] have presented the theory of magnetic double resonance in a form suitable for handling by an electronic computer, and have applied their program to the calculation of the double resonance spectrum of crotonaldehyde obtained with simultaneous irradiation with a moderate r.f. field in the neighbourhood of the aldehyde resonance. Excellent agreement was obtained between theory and experiment. This type of program may be used for checking the results of spectral analysis of second-order systems, and is specially valuable when two or more calculated first-order spectra are very similar. It has also been used to predict the spin tickling behaviour of weakly coupled systems and to give the relative signs of coupling constants.[59]

The theory of triple resonance with weak r.f. fields in systems *without* degenerate energy levels has been presented,[60] and confirmed[61] experimentally. Of course most of the situations in which triple resonance experiments are necessary involve degeneracy of either energy levels or transitions.

Pulsed magnetic double resonance can be valuable when relaxation processes are of interest, and a density matrix treatment of the theory has been presented.[62] Experiments of this type can be used to discriminate between spin population changes and spin-tickling effects. By using Fourier transform spectroscopy the entire spectrum can be accumulated very rapidly (typically in less than 1 s) and so the effects of time-dependent phenomena can be largely eliminated. Thus by removing the irradiating field (B_2) prior to applying the exciting pulse (B_1) any splitting into sub-multiplets will be removed, and the relaxation behaviour of individual transitions can be investigated.[63]

Double resonance tickling experiments have also been used in the assignment of transitions in the complex spectra given by molecules partially oriented in a liquid crystal solvent.[64]

III. APPLICATIONS

A. Instrumentation

Several manufacturers of NMR spectrometers now offer facilities for performing heteronuclear double resonance experiments. In the more sophisticated systems a constant relationship is maintained between the various radio frequencies by means of phase-locking circuitry and quite delicate experiments may be performed. However, if work on more than three or four different nuclei is contemplated it is probably more economical to purchase a basic NMR spectrometer and a commercial frequency synthesiser. In addition to the normal output of the synthesiser it is usually possible to obtain certain auxilliary fixed frequencies and it is worth while selecting a model in which one of these bears a simple relation to the spectrometer oscillator frequency. In the author's laboratory a 20-MHz output from a Schlumberger FS 30 frequency synthesiser is multiplied by three and then used to drive the 60-MHz transmitter of the spectrometer. This gives an internal stability for the whole system of better than 10^{-9} for indefinite periods. Charles[65] has described a circuit for phase-locking a Varian HA 100 spectrometer to an harmonic of a 100-kHz crystal.

Systems which are somewhat less stable than the foregoing but which are adequate for many purposes can be made at much lower cost. These are usually based on a crystal-controlled radio frequency oscillator which is modulated by a variable audio frequency. The resulting energy spectrum contains the centre band and two side bands, and although it is possible to extract only a single side band electronically this is seldom necessary, as it can usually be arranged that only one of the side bands falls near a transition. In a reasonably stable environment the frequency drift of such a system will be better than 10^{-6} h^{-1}. A versatile spin decoupler of this type has been described by Hopkins[66] and similar equipment is available commercially.† Other workers have used similar arrangements.

Modifications of the spectrometer probe to permit it to accept a second radio frequency have been described by several workers:[67 to 70] for single-coil instruments it is best to wind an extra coil at right angle to the first, while for crossed-coil spectrometers another coil may be added or the transmitter coil can be double-tuned. In ^{19}F–$\{^1H\}$ decoupling experiments it was found sufficient to supply both radio frequencies to the transmitter coil which was tuned to the ^1H resonant frequency to optimise the decoupling effect.[71]

In his original work on noise decoupling Ernst[15] used a pseudo-random noise generator based on a 10-stage shift register to produce

† From N.M.R. Specialties Inc.

noise of known characteristics; Fig. 7 is a block diagram of the arrangement used. The effect of the phase modulation is very similar to that of

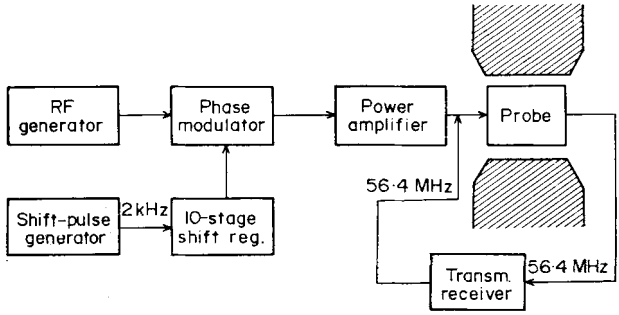


FIG. 7. Schematic diagram of instrumentation of equipment for noise decoupling. In this case the spectrometer operates at a frequency of 56·4 MHz. (From Ernst.[15])

true frequency modulation and has the advantage that no modification of the radio frequency oscillator is necessary. This arrangement is the basis of the Varian noise decoupler, but for many purposes it is sufficient to use a low-frequency square or triangular wave since these contain a large number of different sinusoidal components. One group of workers has found that amplitude modulation with cacophonous music is very effective.[70]

B. Decoupling experiments

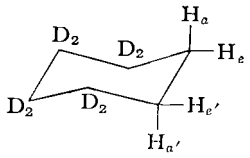
This section describes experiments of which the main object is to achieve spectral simplification by the elimination of spin-spin splittings or quadrupole broadening. The most commonly observed nucleus is the proton, although the technique is now much used in the direct study of ^{13}C resonances. The selection of examples is intended to be illustrative rather than comprehensive.

(a) **^1H–{^2D}**: Spin coupling between protons and deuterons never exceeds a few Hz (except in HD itself) and the effect of the deuterium ($I=1$) quadrupole moment is usually slight, so quite moderate levels of the irradiating power suffice. Much of the work involves the measurement of spectral parameters in compounds which have been partially deuteriated in order to simplify the spectrum of the remaining protons. Unfortunately this leads to an overall broadening, especially if deuteriation is extensive, and ^2D decoupling is then necessary to give sharp lines.

Although the interproton coupling constants in many derivatives of cyclohexane are known, those in the parent molecule can only be ob-

tained by studying a partially deuteriated molecule such as (**6**). At $-103°$ a sharp AA'BB' spectrum was obtained under conditions of deuterium decoupling and analysis of this gave the parameters

$J_{ae} = -13{\cdot}05$ Hz, $J_{aa'} = 13{\cdot}12$ Hz
$J_{ee'} = 2{\cdot}96$ Hz, $J_{ae'} = 3{\cdot}65$ Hz.



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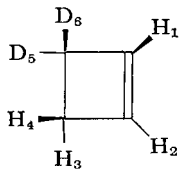
A deuterium isotope shift of 0·0209 p.p.m. upfield was also noted.[72] The increase in line height brought about by the deuterium decoupling made it possible to record the ^{13}C satellites at good signal-to-noise ratio, and their fine structure confirmed the results of the foregoing analysis.

The proton spectrum of cyclobutene consists of two sharp lines which have been accounted for in various ways. Examination[73] of the spectra of the deuteriated derivatives (**7**) to (**9**) under conditions of deuterium decoupling gave results which agreed with those obtained from a study of the ^{13}C satellite spectra and showed the coupling constants to be:

$J_{1,2} = +2{\cdot}85$ Hz, $J_{1,3} = +1{\cdot}00$ Hz, $J_{1,5} = -0{\cdot}35$ Hz,
$J_{3,4} = -12{\cdot}00$ Hz, $J_{3,5} = +4{\cdot}65$ Hz, $J_{3,6} = +1{\cdot}75$ Hz.



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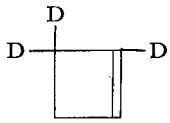

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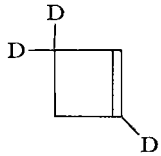

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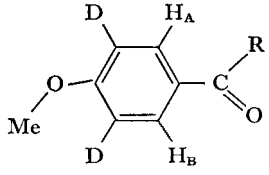
Many of the spacings in the proton spectra were very narrow and it would have been quite impossible to conduct the analysis without the aid of deuterium decoupling.

Partial double bonding between the aldehydic carbon atom and the aromatic ring in (**10**) (R = H or CH_3) leads to restricted rotation which



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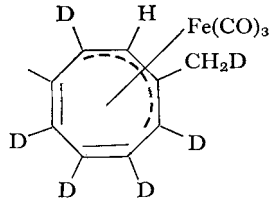
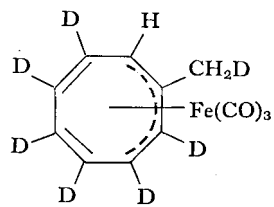
makes H_A and H_B magnetically inequivalent.[74] At low temperatures these protons gave a characteristic AB spectrum in which deuterium decoupling was needed to permit a line-shape analysis for the evaluation of the thermodynamic parameters. These were found to be sensitive to both temperature and solvent.

The spectra of certain cyclic olefins bound to transition metals are abnormally simple as a result of rapid intramolecular valence tautomerism. The spectrum given by the ring proton of (**11**) is broad, but with deuterium decoupling a sharp singlet is obtained at temperatures down to $-100°$. Below $-145°$ two sharp singlets are obtained.[75] This indicates that **11A** and **11B** are the only tautomers to be present to any appreciable extent, and the sharpness of the lines obtained with deuterium decoupling makes it possible to estimate accurately the energy of activation for the inter-conversion of the two forms. Without ^2D irradiation this would be quite impossible.



11a

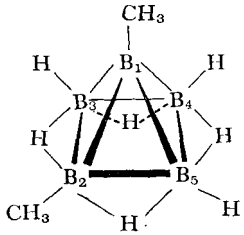


11b

Simultaneous ^2D and ^{14}N decoupling were used in a study of deuteriated pyrrole.[76]

(b) ^1H–{^{11}B}: The natural isotopic abundance of ^{11}B ($I=3/2$) is 81% and as a result of its electric quadrupole moment the proton spectra of molecules containing direct B–H bonds are normally very broad. (For most purposes the presence of ^{10}B with $I=3$ and an abundance of 19% may be neglected). A great improvement may therefore be effected by boron decoupling and much work has been done in this field by Onak's group. Their study of the proton spectrum of 1,2-$(CH_3)_2B_5H_7$ (**12**) is typical.[77] The terminal protons attached to B_3, B_4 and B_5 give a 1:1:1:1 quartet with $J(^{11}B–H)=156$ Hz at low field. Irradiation at an ^{11}B frequency corresponding to the chemical shift of these three boron atoms collapsed the quartet to a singlet and also sharpened the high-field part of the bridging proton resonance, which can therefore be assigned to H(3-4) and H(4-5). Irradiation at the frequencies of B_1 and B_2 sharpened the high- and low-field methyl resonances respectively thus giving the assignment of these peaks. Finally, simultaneous irradiation at three

different ^{11}B frequencies gave five reasonably sharp proton lines which arise from the terminal protons, the two different methyl groups, and the two types of bridging proton. In a study of the $B_3H_8^{\ominus}$ ion at low temperatures ^{11}B irradiation had no effect upon the appearance of the proton spectrum, and it was concluded that the rate of quadrupole relaxation was high enough to have given essentially complete decoupling.[78]



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(c) **^{1}H–{^{14}N}**: The 99·6% abundant isotope ^{14}N has a small magnetogyric ratio so quite high levels of radio frequency power are often necessary to give complete decoupling and eliminate quadrupole broadening effects unless noise modulation facilities are available. The dielectric heating may therefore be quite marked and it is often necessary to use a temperature control unit to maintain a reasonable sample temperature. It should be stressed that the common method of monitoring the sample temperature by means of a thermocouple in the cooling gas stream may not be valid in these circumstances as the heat is generated within the sample itself. When there are no protons directly bound to nitrogen (or when the effect of any such is eliminated by chemical exchange) quite moderate power levels are often sufficient, and Fig. 8 shows normal and decoupled spectra of methyl pyridinium iodide.[79] In (b) with ^{14}N decoupled a large amount of additional fine structure is visible, and (d) with both the *N*-methyl group and ^{14}N decoupled shows that this is due to coupling between the *ortho-* and *meta-* protons and the methyl group. ^{14}N decoupling has been used in detailed analyses of the proton spectrum and its protonated cation.[80] Several groups of workers have examined the *N*-decoupled spectra of pyrrole and its derivative and have obtained essentially concordant results.[81, 82, 75] In work on pyrrole itself the parameters obtained were

$$J_{1,2} = 2{\cdot}60 \text{ Hz}, J_{1,3} = 2{\cdot}45 \text{ Hz}, J_{2,3} = 2{\cdot}69 \text{ Hz},$$
$$J_{2,4} = 1{\cdot}44 \text{ Hz}, J_{2,5} = 1{\cdot}87 \text{ Hz}, J_{3,4} = 3{\cdot}34 \text{ Hz}.$$

and without the aid of ^{14}N decoupling it would have been impossible to obtain the coupling constants involving the 1-proton attached to nitro-

gen. The results were checked by examining various deuteriated derivatives (with simultaneous deuterium decoupling) and by recording the ^{13}C satellites.[75] All of these coupling constants were shown to be of the same sign (presumably positive) by triple resonance experiments involving simultaneous ^{14}N decoupling and homonuclear proton tickling.[82]

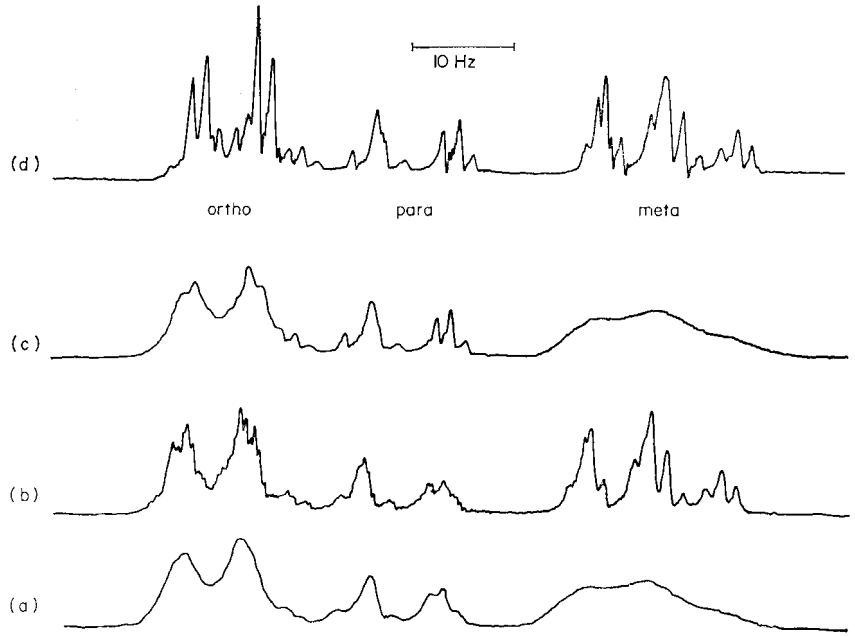


FIG. 8. Decoupled proton spectra of methyl pyridinium iodide (aromatic region.) (a) Normal spectrum. (b) With ^{14}N decoupled. (c) With Methyl protons decoupled. (d) With ^{14}N *and* methyl protons decoupled.

(d) **^{1}H–{^{19}F}**: Appreciable ^{19}F–^{1}H coupling often extends over four or five bonds, so the presence of fluorine can add materially to the complexity of proton spectra. The simplification that results from ^{19}F decoupling is especially valuable when the proton spectrum exhibits second-order features, and may provide the key to an otherwise insoluble problem. The proton spectrum of benzotrifluoride when ^{19}F decoupled is that of an AA'BB'C system, and analysis by means of an iterative computer program gave the proton chemical shifts and coupling constants. These values were then used in conjunction with trial values of the three ^{19}F–^{1}H coupling constants to facilitate a computer analysis of the full AA'BB'CX_3 spin system associated with the undecoupled spectrum.[84] Excellent agreement between computed and experimental

spectra was obtained. A similar approach was adopted[85] in the analysis of the ^{1}H and ^{19}F spectra of 1,2,4-trifluorobenzene, in which data from the ^{19}F decoupled proton spectrum (an ABC spectrum) were invaluable for selecting trial parameters. In this work the total spread of the fluorine spectrum (over 2·5 kHz) necessitated noise modulation of the irradiating frequency to achieve decoupling from all three types of ^{19}F nucleus at once.

^{19}F decoupling can also be used to establish that a particular splitting is indeed due to coupling to fluorine for example in work on "through space" coupling, and may also aid in the measurement of unresolved splittings. For example, in methyl trifluorobenzene $CH_3C_6F_5$ the coupling between the methyl protons and the *meta* ^{19}F nuclei is very small, but was estimated as $0{\cdot}2 \pm 0{\cdot}03$ Hz by comparing $^{19}F_{meta}$-decoupled and normal experimental spectra with computed ones.[85] The decoupled spectra were needed to give an accurate estimate of the line-width.

(e) **^{1}H–{^{31}P}**: As with ^{19}F decoupling the principal applications are the simplification of complex proton spectra and the demonstration that observed splittings actually are due to coupling to phosphorus. Fig. 2 shows the normal and decoupled proton spectra of dimethyl phosphite, $(CH_3O)_2PHO$. In this case the large value of $^{1}J(^{31}P–H)$ (690 Hz) necessitated audio modulation of the decoupling frequency, but for many applications this is unnecessary as the spread of the phosphorus spectrum is normally much narrower.

Experiments involving complete decoupling of other nuclei are rare because fairly low natural abundance prevents serious modification of the proton spectrum.

(f) **^{19}F–{X}**: These experiments are of comparable value to ^{1}H–{X} ones, but in practice are much less common. Fig. 9 shows the results of ^{10}B and ^{11}B decoupling experiments on the $BF_4^{\ominus}$ ion in which quadrupole broadening is eliminated by the symmetrical structure. The detailed fine structure in the ^{10}B species is well resolved when ^{11}B is decoupled, and the isotope effect upon the ^{19}F chemical shift is clearly visible.

Several groups have studied the ^{19}F spectra of pentafluoro-phenyl derivatives but were unable to give complete analyses when the substituent contained magnetic nuclei.[86 to 88] For C_6F_5H, $C_6F_5CH_3$ and C_6F_5CHO proton decoupling removed these difficulties and complete analyses were then possible.[85] In the last compound the chemical shift difference between the fluorine nuclei *ortho* and *para* to the substituent was very small and the decoupling experiments aided the assignments by

showing which lines were associated with a large $J(F_o–H)$ or small $J(F_p–H)$ coupling with the proton. In work on partially deuteriated fluorobenzenes proton decoupling was used to simplify the ^{19}F spectrum, and also gave a large gain in signal-to-noise ratio as all the intensity was concentrated in the 1:1:1 triplet produced by coupling to deuterium ($I=1$).[89]

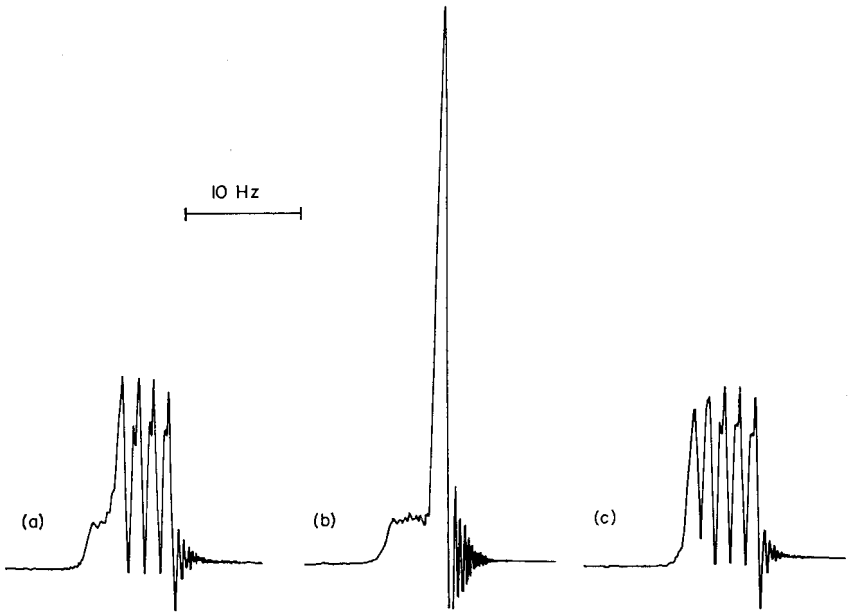


FIG. 9. ^{11}B and ^{10}B decoupling experiments on the $BF_4^{\ominus}$ anion. (a) Normal ^{19}F spectrum. (b) With ^{11}B decoupled. (c) With ^{10}B decoupled.

(g) **^{13}C–{^{1}H}**: Developments in this area have transformed the value of ^{13}C spectra, and direct ^{13}C work is now assuming an importance that is comparable with proton work in the study of many types of organic molecule. Proton decoupling leads to a substantial gain in signal-to-noise ratio because the many lines resulting from spin coupling to neighbouring protons are all collapsed into a single peak, and there is also a large nuclear Overhauser effect (p. 365). Unless another magnetic nucleus such as ^{19}F or ^{31}P is present the spectra contain only chemical shift information (the abundance of ^{13}C is so low that with non-enriched samples molecules containing more than one ^{13}C nucleus may be neglected) is obtained, but this is not as serious a limitation as was once feared. Further sensitivity can be achieved by spectral accumulation,

and when this is allied to the Fourier transform technique the time used is quite small. Three of the main manufacturers of NMR spectrometers now offer ^{13}C Fourier transform systems complete with wide band

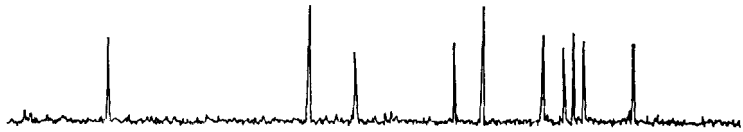
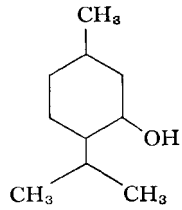


FIG. 10. Proton decoupled Fourier transform ^{13}C spectrum of menthol (**13**) (16 Scans). The pulse repetition interval was 20 s. and the differences in peak intensities arise from variation in ^{13}C relaxation times. (By courtesy of JEOL.)

proton decoupling and a small dedicated computer. Fig. 10 shows the natural abundance ^{13}C Fourier transform spectrum of menthol (**13**) obtained with complete proton decoupling. Sixteen pulses were used and the total spectrometer time was *ca.* 300 s. Clearly problems of assignment arise when the molecule contains many different carbon atoms and two methods have been devised for distinguishing quaternary carbon atoms from the others.[90 to 92]



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When a carbon atom is attached to at least one proton its resonance will extend over 125 Hz or more owing to spin coupling, and quite high decoupling power will be needed to produce collapse to a single line. However, the resonances of quaternary carbon atoms cover a much narrower range (usually less than 10 Hz) and so complete decoupling can be effected with much less power or with an off-resonance setting of the irradiating field. Thus a comparison of ^{13}C spectra obtained with the proton decoupling field exactly on resonance, and with it set a few hundred Hz off-resonance, will identify the quaternary carbon atoms and so materially aid assignment. By a judicious choice of the setting and amplitude of the decoupling field it is also possible to determine the number of protons attached to the other carbon atoms in many cases.[90, 91]

The relaxation and in particular the nuclear Overhauser effect behaviour of quaternary ^{13}C atoms differ from those of others. For protonated carbon atoms the relaxation is dominated by dipole-dipole interaction with the attached proton(s) owing to the small internuclear distance; there is a substantial nuclear Overhauser effect and the relaxation time is short. However, for a quaternary carbon atom the relaxation is much less efficient (i.e. T_1 is longer) and may not be dominated by dipole-dipole interaction with neighbouring protons, as these are relatively far away. Consequently the nuclear Overhauser effect enhancement may be much less and the intensities of the resonances given by non-protonated carbon atoms are often abnormally low in proton decoupled spectra. A study of pyrene, acenaphthene, acenephthalene and fluoranthene[92] confirmed these predictions, and it was found that carbon nuclei without attached protons gave much weaker lines. Clearly, care must be used in the interpretation of relative intensities in ^{13}C spectra. The effect of the longer relaxation time of quaternary carbon atoms is also important in ^{13}C spectra obtained by the Fourier transform technique. The ^{13}C nuclei are subjected to a series of intense r.f. pulses at intervals of a few seconds and if relaxation is not completed within the pulse interval the intensity of the response will be affected. Fig. 11 shows natural abun-

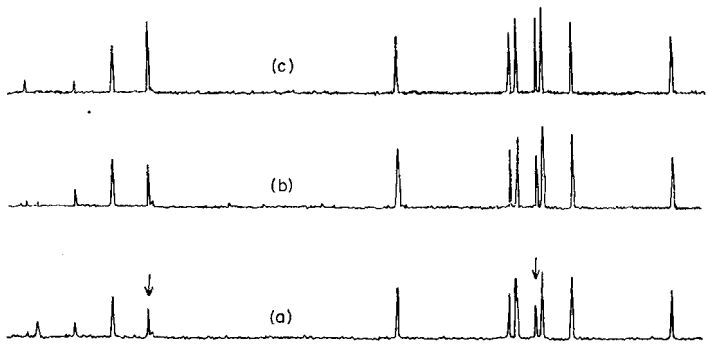
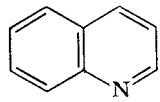


FIG. 11. Proton decoupled Fourier transform ^{13}C spectra of quinoline (**14**) (16 scans each), with different pulse repetition intervals. (a) 7·5 s. (b) 15 s. (c) 30 s. (By courtesy of JEOL.)

dance ^{13}C Fourier transform spectra (16 scans each with protons noise decoupled) of quinoline (**14**) obtained with different pulse repetition intervals. This has little effect upon the intensities of most of the lines, but the two indicated by vertical arrows increase rapidly as the pulse interval is lengthened. These are the resonances of the two carbon nuclei at the points of ring fusion.

The spin-coupling information that is normally lost by the proton decoupling may be retained if the decoupling field is switched off immediately prior to recording the ^{13}C spectrum. In this way some of the nuclear Overhauser effect enhancement is retained provided that the spectrum is swept at a sufficiently rapid rate (*ca.* 100 Hz s^{-1}). If this technique were allied to Fourier transform spectroscopy in which all of the spectrum is examined in a very short time the nuclear Overhauser effect would retain its normal value.[93]

The foregoing techniques have now been applied to many organic molecules, especially in the natural product and biochemical fields, and references 94 to 112 contain typical examples of this work. ^{13}C–$\{^{19}F\}$ decoupling experiments are of potential value in the study of fluorinated



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materials as the nuclear Overhauser signal enhancement should be almost as great as with proton decoupling, but little work has been done in this area yet. The decoupling of the protons naturally leaves couplings to other nuclear species unaffected and data on ^{13}C–X coupling in a range of compounds has been obtained in this way.[113]

(h) *Other decoupling experiments*: Proton decoupling is of use in the direct study of ^{31}P and ^{119}Sn, both of which are often coupled to many protons,[114] however, little has been done in this field. A ^{7}Li–$\{^{13}C\}$ experiment was used in a study of ^{13}C enriched methyl lithium.[115]

IV. THE DETERMINATION OF CHEMICAL SHIFTS

^{1}H–$\{X\}$ (or ^{19}F–$\{X\}$) experiments for the determination of the chemical shift of X have the following advantages. (a) Convenience—a single modified spectrometer can be used for all nuclei. (b) High sensitivity to NMR detection of the observed nucleus. (c) High potential precision. (d) A single *internal* reference can be used. (e) The relation of lines in the proton (^{19}F) and X spectra is obtained unequivocally. A disadvantage is that the measurement may be rather time-consuming and it may be difficult to observe the appropriate lines if the proton spectrum is complex. Thus while ^{1}H–$\{^{13}C\}$ experiments are ideal for determining ^{13}C chemical shifts in relatively simple molecules containing methyl groups, the ^{13}C–$\{^{1}H\}$ technique is better suited to the study of natural products.

For many purposes it is adequate to know the chemical shift to within one p.p.m. and in this case quite large magnitudes of B_2 may be used and the choice of proton reference is not particularly important. However, as work[116] on ^{13}C and ^{29}Si shielding in TMS in various solvents shows, when detailed solvent studies are contemplated considerable thought should be given to the choice of reference compound. In view of the general acceptance of TMS as a reference in proton work it seems reasonable to use this compound in heteronuclear double resonance experiments and suggestion in reference 1 of "correcting" all frequencies to a field strength corresponding to a TMS proton resonance at exactly 100 MHz offers a convenient way of presenting the data. For comparative studies of a range of compounds this is of course unnecessary. The chemical shifts of other nuclei can also be related to the proton resonant frequency of TMS by X–{^{1}H} experiments if the chemical shift of the decoupled protons is known, but this procedure tends to be less accurate.

Work on various nuclei is now considered.

(a) $^{10/11}$**B**: Quadrupole broadening normally restricts studies to molecules containing direct B–H bonds and as the gain in sensitivity is not particularly high for ^{11}B (the more abundant isotope) relatively little work has been done. The technique was useful in the assignment of the *proton* spectrum of a boron hydride derivative.[77] A comparative study of the ^{10}B and ^{11}B resonant frequencies in the tetrahedral ions $BH_4^{\ominus}$ and $BF_4^{\ominus}$ showed[117] that any primary isotope effect (that is a dependence of the boron chemical shift upon the isotopic mass of the boron atom) was less than 0·01 p.p.m.

(b) ^{13}**C**: A substantial amount of work has been done on this nucleus and some very elegant INDOR spectra have been produced, particularly by Olah and his coworkers.[118 to 120] They have studied carbonium ions and by establishing the relationship between lines in the proton and ^{13}C spectra were able to assign structures unequivocally. The fine structure resolved in the INDOR spectra shows how many protons are associated with a particular carbon atom and, for example, the structure of the norbornyl cation in SbF_5-SO_2 at $-70°$ was assigned from the observation of a quintet (produced by four *effectively* equivalent protons) in the INDOR spectrum.[118] Horsley and Sternlicht[121] have similarly obtained ^{13}C chemical shifts in enriched amino acids and peptides and have given details of their instrumentation. Spin-tickling experiments were used to give ^{13}C shieldings to closer than 0·1 p.p.m. in a range of organophosphorus compounds,[122] and a solvent study of *N*,*N*-dimethylformamide indicated that a chemical shift difference of *ca.* 5 p.p.m.

between the methyl groups could not be accounted for by magnetic anisotropy.[123] Work[124] on the methyl groups in esters showed a correlation between ^{13}C shielding and the pK_a of the acid.

(c) **^{14}N**: The double resonance technique is very valuable for this nucleus which has almost 100% abundance but a very low sensitivity to NMR detection. Owing to the quadrupole moment the experiments normally aim at removing a broadening in the proton spectrum and the accuracy is not particularly high. Also in a fair proportion of molecules the ^{14}N nucleus is relaxing too fast for there to be any observable effect in the proton spectrum. This does not usually apply to compounds with direct N–H bonds. Successful studies have been made of thioamides,[125] benzthiazoles,[126], 1-phenylazo-2-naphthols[127] and hydroxyquinolines.[128] Nitrogen shielding has also been studied in compounds enriched in ^{15}N. As this nucleus has no quadrupole moment the lines are sharp and high precision can be attained.[129 to 131] At present it appears that any differences between ^{14}N and ^{15}N chemical shifts are slight.

(d) **^{19}F**: The double resonance technique offers advantages in the study of temperature and solvent effects upon ^{19}F shielding;[132] otherwise direct observation is satisfactory.

(e) **^{29}Si**: ^{19}F–{^{29}Si} experiments were used to determine ^{29}Si chemical shifts with considerable precision in fluorosilanes.[68] Spin-tickling experiments on the ^{29}Si satellites in the proton spectra of the three series of compounds $(CH_3)_nSi(OOCR)_{4-n}$ $(n=1,2,3)$ show that the silicon shielding depends upon the pK_a of the parent acid.[133]

(f) **^{31}P**: Data on ^{31}P chemical shifts are often obtained as a bonus in double resonance experiments aimed at determining the signs of coupling constants.[122,134,135] Although high-quality ^{31}P spectra can now be obtained directly, double resonance experiments on the proton spectra of unseparated reaction mixtures can be very illuminating. This was demonstrated elegantly in a study of the reaction between *tert*-C_4H_9MgCl and CH_3PSBr_2 when the proton spectrum of the crude mixture was found to contain many lines.[136] The double resonance experiments showed which lines were associated with a particular compound and gave its ^{31}P chemical shift, and the INDOR spectra which were plotted showed that a *tert*-C_4H_9 group was attached to phosphorus in all four species present.

(g) **^{77}Se**: Preliminary studies of this nucleus indicate that trends in

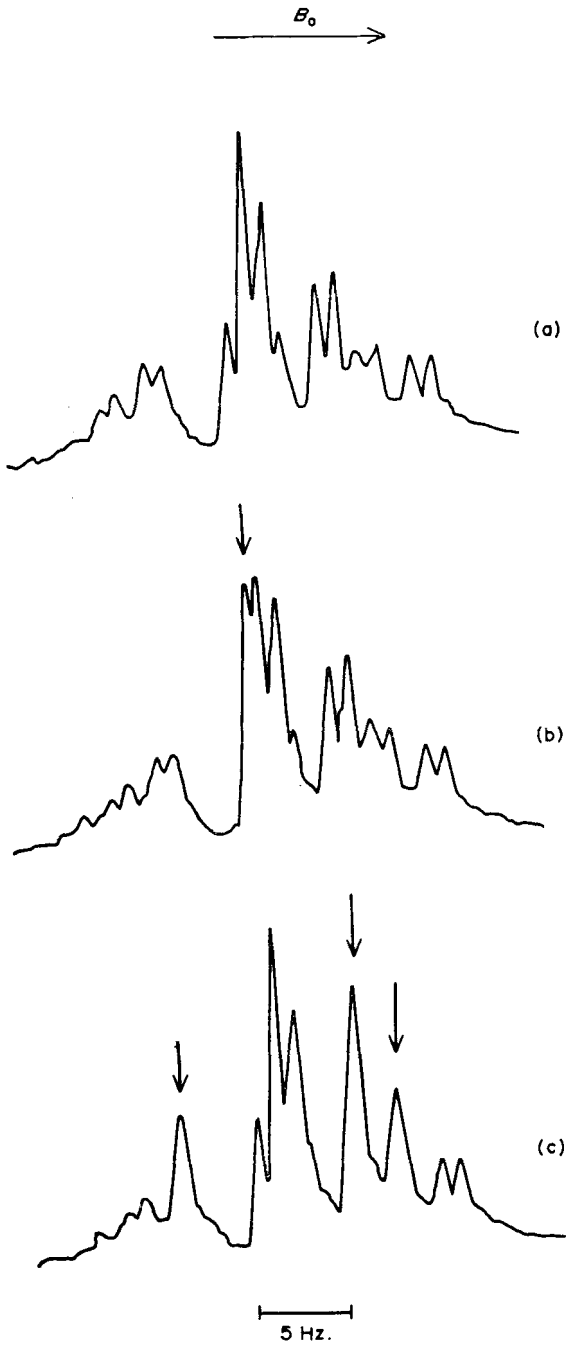
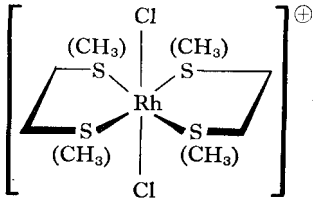


FIG. 12. ^{103}Rh decoupling experiments on the complex ion (**15**). (a) Normal methyl proton spectrum. (b) With irradiation at a single ^{103}Rh frequency: a pair of lines is collapsed to a singlet at the point indicated by the vertical arrow. (c) With irradiation at another ^{103}Rh frequency; three doublets are collapsed, these arise from different methyl groups in the same ion. (From McFarlane.[142])

chemical shifts are similar to those found for phosphorus,[137, 138] although the overall range is much greater. In selenols the chemical shift is sensitive to the degree of association and the high precision of the method permits detailed studies of hydrogen bonding in these materials.[139]

(h) ^{103}**Rh**: The sensitivity of this nucleus to NMR detection is extremely low and $^{31}P-\{^{103}Rh\}$ experiments have been used to measure rhodium chemical shifts in a series of phosphine complexes.[141, 142] The shifts depend upon the oxidation state of rhodium and the electronegativity of the ligands, and are not dominated by the ΔE term in the Ramsey equation. The cation (**15**) exists in five different configurations which give separate methyl signals in their proton spectra. Each of these is split into a doublet by coupling to rhodium, and the associated ^{103}Rh frequencies cover a chemical shift range of over 80 p.p.m.[142] The rhodium shielding is also temperature dependent. Figure 12 illustrates two rhodium decoupling experiments on this cation.



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(i) ^{119}**Sn**: The double resonance method has been used extensively in studies of organo-tin compounds,[143] and the ability to relate lines in the proton and the tin spectra has been invaluable in the study of mixtures.

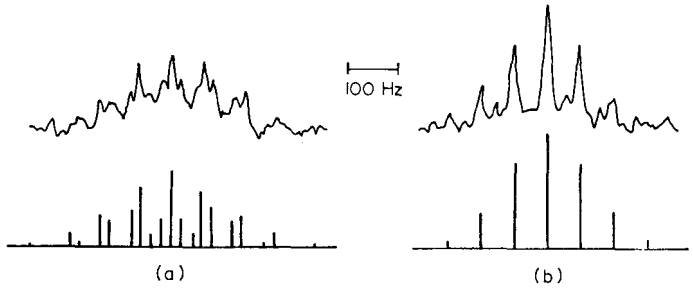
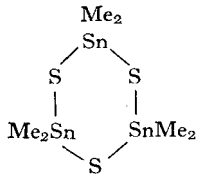


FIG. 13. ^{119}Sn INDOR spectra obtained by monitoring the appropriate methyl group satellites in the proton spectra of a mixture of **16** and **17**. (a) Tin environment printed in bold in **18**. (b) Species **16**. The lower stick spectra are calculated using parameters from the proton spectra.

Fig. 13 shows ^{119}Sn INDOR spectra of species found to be present in a mixture of (**16**) and (**17**) which are actually the molecules (**16**) and (**18**) which is formed by intermolecular exchange. An important result that has arisen from these studies is that an increase in the coordination number of the tin atom from four to five or six can shift the ^{119}Sn resonance several hundred p.p.m. to higher field.[143] This has been utilised in the study of equilibria involving tin atoms with different coordination numbers, such as distannoxanes and tin alkoxides.[144,145]



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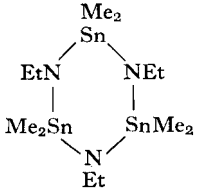

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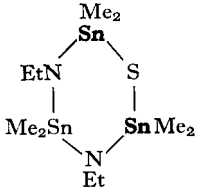

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Work on ^{117}Sn can be done with almost equal facility, but offers no advantages except in doubtful cases when the tin satellites in the proton spectrum are partially obscured.

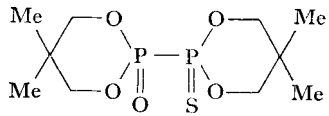
(j) ^{183}**W**: As with ^{103}Rh the sensitivity to NMR detection of this nucleus is very low, and additionally the abundance is only 14%, so double resonance experiments are especially valuable. ^{19}F–{^{183}W} experiments have shown[146] that the tungsten shifts are dominated by the $(\Delta E)^{-1}$ term in a series of derivatives of tungsten hexafluoride.

(k) ^{195}**Pt**: Although a fair amount of direct platinum work has been reported in the literature there can be no doubt that the double resonance method offers considerable advantages in most cases.[147] Thus studies[148] of solutions of *cis* and *trans* $(Me_2S)_2PtCl_2$ in dimethyl sulphoxide have shown that the solvent can replace part or all of the sulphide ligand, and intermediate species have been identified in mixtures of platinum complexes.[149]

V. THE DETERMINATION OF THE SIGNS AND MAGNITUDES OF COUPLING CONSTANTS

A. Simple spin systems

Most of the molecules examined fall into this class in that the results of the double resonance experiments can be interpreted by considering the different sub-spectra associated with the various nuclear spin orientations. Much work has been done on spin coupling between the nuclei of directly bound elements for which reasonably well developed theory is available.[150 to 152] It has been found that reduced coupling constants between the proton and other directly bound nuclei are positive;[153, 154] while couplings between ^{19}F and other nuclei, apart from H and B (in BF_3), are negative.[155 to 157] Coupling constants between carbon and other nuclei are positive unless the element is of high electronegativity,[122, 158 to 160] e.g. Se, Te or F. With phosphorus ^1K(P–C) depends upon the valency of phosphorus: it is normally positive except in P^{III} derivatives where the sign is sensitive to the phosphorus hybridisation.[161] Other coupling constants between directly bound elements that have been studied by heteronuclear double resonance include ^1K(N–P), negative in $(CF_3)_2PNH_2$;[162] ^1K(Se–Pt) and ^1K(P–Pt), positive in complexes of Pt^{II};[163] ^1K(P–Si) and ^1K(P–Sn), both negative in P^{III} compounds;[164] and ^1K(P–P), positive in (**19**).[165]



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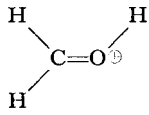
Most of the foregoing work also gave information about the signs and magnitudes of geminal and longer range coupling constants; there have also been investigations specifically aimed at elucidating these parameters, which are often sensitive to bond angles at the intervening atom(s). Partially deuteriated samples were used to study ^2J(H···H) in Group IV hydrides,[166] and this coupling was found to become more positive (it is −12·4 Hz in methane) as the mass of the central atom increased. The geminal ^{13}C–X–H coupling in the methyl derivatives was found to increase similarly. The long-range coupling constant ^4J(H···H), which can be observed with the aid of ^{13}C satellites, in $(CH_3)_nZ$ (Z = C, O, CO, SO, Si, Hg) is positive, although its magnitude depends upon Z and possibly the conditions of measurement.[167 to 169] Samples enriched in ^{13}C were used to determine geminal C–C coupling constants in several of

these molecules.[170] All the H–H and C–H coupling constants in protonated formaldehyde (**20**) except $^2J(^{13}C\cdots H)$ are positive.[171] Couplings



20

between protons and X in vinyl derivatives $(CH_2CH)_nX$ (X = N, Si, Sn, Pb) are positive,[172,173] as are the couplings in phenyl derivatives of phosphorus[174] and mercury.[175]

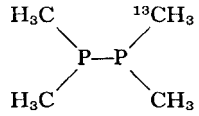
The sign of $^2J(^{31}P\cdots H)$ usually changes from positive to negative on quaternisation of the phosphorus atom,[122] although this may depend upon the absence of geometrical constraints,[176] but this behaviour is exceptional for $^2J(^{31}P\cdots{}^{19}F)$. However, this coupling constant has opposite signs in $CF_2{:}CFPCl_2$ and $CF_2{:}CFPF_2$.[177] The magnitude and sign of the geminal coupling constant between protons attached to phosphorus are very sensitive to the other substituents, and appear to depend upon the bond angles at phosphorus; these parameters were studied in partially deuteriated molecules.[178] The signs of H–F and F–F coupling constants have been determined by double resonance experiments in fluorinated aromatic compounds and carbohydrates.[179,180]

B. Complex spin systems

Studies of this type of system are not common, and it is important to remember that Freeman and Anderson's tickling rules[18] may not apply directly if degenerate transitions are irradiated (see p. 364). In the analysis of single resonance spectra of AA'XX' spin systems it is not possible to distinguish $J_{AA'}$ and $J_{XX'}$ unless second-order features or differential relaxation effects are taken into account. However, tickling experiments can distinguish between transitions belonging to the symmetric and antisymmetric sets and so permit a full analysis.[175] In a study of the AA'MM'X spin system, given by the aromatic nuclei of *para*-$NH_2C_6F_4H$, it was shown that all the coupling constants could be obtained by ^1H–$\{^{19}F\}$ tickling experiments, although a triple resonance experiment was needed to distinguish the symmetric and antisymmetric sets of ^{19}F transitions.[181]

The spin system $AA'X_nX'_n$ with $J_{XX'} = 0$ occurs commonly in organophosphorus compounds with $A = {}^{31}P$ and $X = {}^1H$. It has been shown[182] that $|J_{PP}|$ can be determined from the positions of certain very weak lines in the proton spectrum, and if the effective symmetry is lowered by considering lines due to molecules containing ^{13}C as in (**21**) then the sign

of this coupling constant may be determined by normal tickling experiments. This technique has been used in studies of $^2J_{PP}$ in a large number of transition metal complexes with phosphorus-containing ligands.[134, 135]



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A disadvantage of the foregoing procedure is that very weak lines in the proton spectrum must be observed and so it is necessary to use concentrated solutions; this is especially so when J_{PP} is large. However, consideration of the phosphorus spectrum shows that this too contains weak lines whose positions may be used to give J_{PP}, and since these are connected with *strong* lines in the proton spectrum, ^1H–$\{^{31}P\}$ experiments can give the sign and magnitude with very dilute solutions. Experimental tests have shown that this approach can give a precision of better than 0·2 Hz and a further advantage is that the molecule need not contain carbon.[183]

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Nitrogen NMR Spectroscopy

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I. GENERAL ACCOUNT OF NITROGEN NMR

THE ELEMENT NITROGEN in its natural occurrence has two isotopes, ^{14}N and ^{15}N, with the latter being present in only a minute amount

(Table I). The nuclei of both possess magnetic moments; consequently both give nuclear magnetic resonance spectra and additionally may effect the spectra of other nuclei. From the NMR point of view the important characteristics of the nitrogen nuclei are given in Table I. The differences

TABLE I

Important NMR properties of nitrogen nuclei

Isotope	^{14}N	^{15}N
Natural abundance	99·635%	0·365%
Gyromagnetic ratio[a]	0·072 236 749	−0·101 330 447
relative to that of ^{1}H	±0·000 000 010	±0·000 000 010
Magnetic quantum number	+1 0 −1	$+\frac{1}{2}$ $-\frac{1}{2}$
Electric quadrupole moment ($e \times 10^{-24}$ cm^2)	$7{\cdot}1 \times 10^{-2}$[b]	0
NMR frequency at a field corresponding to a ^{1}H frequency		
of 60 MHz	4·335 MHz	6·081 MHz
of 100 MHz	7·225 MHz	10·135 MHz
NMR sensitivity relative to that of a ^{1}H at the same field	0·001 01	0·001 04

[a] For $^{14}NH_4^{\oplus}$ and $^{15}NH_4^{\oplus}$; see ref. 35.

[b] From *Varian Associates NMR Tables*, Fifth Edition, 1965; previous editions quote a value of 2×10^{-2}.

in nuclear properties of the isotopes are apparent from the NMR spectra. The low natural abundance and small magnetic moment of ^{15}N has so far made almost impossible any application of ^{15}N NMR spectroscopy without isotopic enrichment. This is costly, very often laborious, and must be planned in advance. Whereas ^{14}N NMR spectra are obtained without enrichment, but even here the small magnetic moment results in low sensitivity. The non-zero electric quadrupole moment of ^{14}N gives rise to a broadening of ^{14}N resonance signals via quadrupolar relaxation (Section III). This may obscure small chemical shifts and disturb the appearance of spin-spin coupling between ^{14}N and other nuclei in the molecule. The broadening may also adversely effect the detection of ^{14}N resonance signals. However, it is sometimes possible to obtain information about the electron distribution around the nitrogen nucleus from quadrupole broadened ^{14}N signals.[1 to 10]. This complication is absent from the spectra of ^{15}N and nuclei coupled to ^{15}N.

The opposing signs of the gyromagnetic ratios for ^{14}N and ^{15}N, result in opposite signs for the corresponding coupling constants. Since

the magnitudes of the gyromagnetic ratios are also different, owing to the difference in the magnetic moments of ^{14}N and ^{15}N, a quantity called the reduced coupling constant is particularly useful in nitrogen NMR spectroscopy (Section VII).

It is interesting to note that the ^{14}N resonance shift between $NH_4^{\oplus}$ and $NO_3^{\ominus}$, reported in 1950,[11] was one of the first "chemical shifts" to be discovered in NMR spectroscopy. Relatively little work was performed between 1950 and 1964 on nitrogen NMR,[1, 2 and 11 to 43] and many of the results obtained suffer from the use of inaccurate techniques and standards, which are reflected in the validity of the conclusions which may be drawn from the experimental data. Most of the early work has been summarised and supplemented by Herbison-Evans and Richards[44] who have published an extensive tabular presentation of ^{14}N shifts, which has been widely quoted in later papers. It is still a very useful guide to the general location of nitrogen resonance signals for various classes of molecules. However, the data quoted therein must be accepted with caution, since in many instances they have been demonstrated to be rather inaccurate, and even misleading, as shown for amines and ammonium ions,[45] nitroalkanes,[46, 47] pyridine[48] and some cyanides and isocyanides.[49]

Improvements in experimental techniques have produced a remarkable surge of research interest in nitrogen NMR since 1964, for both ^{14}N and ^{15}N nuclei. In ^{14}N NMR spectroscopy, it has been possible to detect subtle changes in chemical shifts within various groups of molecules by direct measurement of the ^{14}N resonance signal.[7, 9, 45 to 60] Double resonance techniques have been introduced in systematic ^{14}N investigations in favourable cases[29, 30, 33, 34, 43 and 61 to 76] and spin-spin couplings involving ^{14}N nuclei have been observed.[7, 17, 18, 20, 27, 31, 33, 35 to 37, 39 to 41, 45, 48, 50, 61, 62, 68 to 70, 73, 75, 77 to 96] Much other work on ^{14}N spectra has also been published.[3, 4, 8, 10, 76, 97 to 127] Additionally the NMR spectra of ^{15}N have been examined on a more extensive scale by direct methods[128 to 140] and by double resonance methods including the observation of ^{15}N spin-spin couplings from proton spectra.[5, 6, 43, 78, 91, 130, 131, 141 to 179] Attempts at a detailed interpretation of nitrogen chemical shifts have been made [9, 45, 48, 49, 51, 120, 180 to 187] in terms of the general theory of chemical shifts. (Section II). Similar attempts have been made to account for nitrogen spin-spin coupling constants[130, 132, 142, 151, 152, 157, 166, 188] (Section VII). Most of the work reported up to 1967 has been discussed by Mooney and Winson in Volume 2 of this series.[189] This review will deal essentially with the work published between 1967 and 1970, but where necessary will also refer to earlier reports.

The experimental techniques used in nitrogen NMR may be generally

divided into direct methods, employing the measurement of nitrogen (^{14}N or ^{15}N) resonance signals, and indirect methods which make use of spin coupling with other nuclei. The direct methods may involve either the frequency sweep technique[3,7,44] for ^{14}N NMR or, more commonly, the field sweep technique which may employ audio-frequency modulation with a frequency smaller[51,59,108,190,191] or larger than the ^{14}N signal width.[9,45 to 48,52 to 54,57,107,121 to 123] A convenient technique of the latter kind has recently been reported,[48] which involves the recording of the ^{14}N spectrum at a high radio-frequency power level and both the central band and side bands are examined. This makes possible the simultaneous recording of broad ^{14}N resonances at a suitable signal-to-noise ratio in the central band and narrow signals with no saturation effects in either side band. The side bands may also be used to calibrate the spectra. The scope of this method may be extended by using a spectrometer with a field-lock system and a time-averaging computer, as reported for some work on nitrogen-containing metal complexes.[122,123] In this case the magnetic field is locked on to a proton resonance signal, it may also be locked on to a sufficiently sharp ^{14}N signal such as that of tetranitromethane.[7] A combination of the pulse method in sample irradiation and signal detection, field-sweep via a proton lock, and spectrum accumulation has been used in a series of ^{14}N measurements on nitroalkanes and their salts,[58,192] nitramines,[60] and in ^{14}N quadrupole relaxation studies of pyridine and aniline derivatives.[8,10] The method is equally applicable in ^{15}N resonance spectroscopy.[140,193 to 196]

^{15}N NMR spectra of samples enriched in ^{15}N may be measured quite simply by the direct method, since they usually exhibit small (~ 1 Hz) line widths. So far there has been only one report of a ^{15}N measurement in a natural abundance sample[128] but the recent employment of precise digital frequency-sweep[197,198] methods combined with spectrum accumulation may improve the situation in this field.

The indirect methods, based on double resonance, may be employed for both ^{15}N and ^{14}N nuclei. The nitrogen chemical shifts may be measured as differences between the optimum decoupling frequencies as observed in the spectra of nuclei, usually ^{1}H, spin coupled to nitrogen. This is relatively simple for ^{15}N shifts,[43,91,168,169,179] but it is more difficult for ^{14}N because of the quadrupole relaxation effects (Section IV). However, a considerable number of ^{14}N chemical shifts have been obtained in this manner.[29,30,35,63,65 to 67,71 to 74,91] A variety of double-resonance techniques, including spin-decoupling spin-tickling and INDOR have been employed for ^{15}N,[35,91,141,157,167,169,175] and in favourable cases for ^{14}N,[61,62,64,68,70,73,75,94] for the determination of nitrogen coupling constants and their signs (Section VII).

The question of the calibration of nitrogen chemical shifts is still open. Many investigators use standards which are convenient in a particular problem, but have little value for general application. Standards for the calibration of nitrogen chemical shifts may be either internal (dissolved in the sample experiencing the same average magnetic field as the molecules examined), or external (usually contained in a system of coaxial tubes). The most popular external standard that has so far been used is the ammonium ion in aqueous NH_4NO_3 or the nitrate ion in acidified aqueous NH_4NO_3.[44, 51, 57, 63, 65 to 67, 71 to 74, 99, 128, 190] Other external standards have occasionally been used, such as 70% HNO_3,[50, 129] nitrobenzene,[134] acetonitrile,[109] liquid ammonia,[136, 137] nitromethane,[7, 59] gaseous trimethylamine,[139] $(CH_3)_2NNO$,[59, 191] aqueous $NaNO_3$[121] and $NaNO_2$.[123]

A universal scale for nitrogen chemical shifts based on an internal reference system has been proposed by Witanowski and Januszewski,[107] (Table II).

TABLE II

Internal standards for nitrogen chemical shifts

CH_3NO_2	0 p.p.m.	Primary internal standard for general use with organic solvents and mineral acids.
$NO_3^{\ominus}$	0 p.p.m.	Primary internal standard for general use in aqueous solutions, neutral or basic, but not acidic.
$C(NO_2)_4$	−48 p.p.m.†	Secondary internal standard for nitrocompounds.
$(CH_3)_2NCHO$	−276 p.p.m.†	Secondary internal standard for aromatic nitrocompounds and nitrogen heterocycles.

† Editorial Note: Attention is drawn to the convention of chemical shift scales—high-field shifts are negative.

The zero chemical shift between CH_3NO_2 and $NO_3^{\ominus}$ was first based on a series of experiments in which acetonitrile was used as an intermediate standard.[107] However, more recently it has been reported that the shift for nitromethane is about 3 p.p.m. to low frequency of the signal of the $NO_3^{\ominus}$ ion, but no experimental details were given.[189] Also two peaks separated by about 4 p.p.m. have been observed for the solution of CH_3NO_2 and NH_4NO_3 in methanol at +65°C. The latter result is not directly comparable with the shift measurements[107] of KNO_3 versus CH_3NO_2 owing to the nature of the ammonium cation, and appears to cast some doubt on the suitability of NH_4NO_3 as a standard. We have

recently checked[199] the CH_3NO_2–$NO_3^{\ominus}$ shift using acetonitrile-nitromethane and aqueous acetonitrile-KNO_3 solutions as well as those of nitromethane and KNO_3 respectively, in a 2:1 v/v mixture of dimethylformamide and water. The former series of experiments indicate concentration shifts which, in the extreme, might reach a 3 p.p.m. difference in the observed shifts of acetonitrile relative to that of the two standards. Measurements carried out in the same medium, namely dimethyl formamide and water, show that the shift between CH_3NO_3 and $NO_3^{\ominus}$ is 1 ± 1 p.p.m., or just within the experimental error. It seems that for all practical purposes the shift may be considered as zero. Nitromethane has also been employed as an internal standard for acidic aqueous solutions[45] in which it is moderately soluble. The experiment involved the measurement of the ^{14}N shift of tetramethylammonium chloride in concentrated HCl relative to a trace of nitromethane and that of tetramethylammonium chloride in neutral aqueous solution relative to KNO_3. The shifts were found[45] to be $-333{\cdot}5 \pm 0{\cdot}5$ p.p.m. and $-334{\cdot}5 \pm 0{\cdot}5$ p.p.m.,† respectively, which is within the experimental error. A large number of ^{14}N chemical shifts have been reported which refer to the internal reference scale described above.[9, 45 to 49, 52 to 56, 107]

A further method of internal calibration of nitrogen chemical shifts is based on a proton chemical shift being used as reference, usually that of TMS. This may be carried out either by means of heteronuclear double resonance (see also p. 353), with exact monitoring of the decoupling frequency,[64, 179, 181] or by a field-lock on the proton resonance of TMS and exact measurement of the resonance frequencies in the nitrogen spectra.[169] If the resonance of TMS occurs at frequency F (e.g. 60 000 000 Hz or 100 000 000 Hz) plus the modulation frequency f (a few kHz, commonly used for obtaining the field-locking sideband) and the decoupled proton resonance is shifted by D Hz from TMS then the observed resonance frequencies for the nitrogen nuclei, X_{obs}, in the double resonance experiment may be recalculated to correspond to the field at which the TMS resonance occurs by:

$$X\,(\text{TMS scale}) = FX_{obs}/(F+f-D) \qquad (1)$$

The double resonance method of calibration depends on the existence of a measurable coupling. The TMS scale of nitrogen chemical shifts may include non-specific solvation effects which, while being very useful for solvation studies, may become a nuisance for the comparison of nitrogen chemical shifts of various molecules.

† Editorial Note. Readers are requested to refer to p. xii regarding the convention for chemical shifts used in these volumes.

There have been some attempts[120,141] at setting up an "absolute" scale of nitrogen chemical shifts, which refers to the resonance of a bare nitrogen nucleus. The latter has not so far been experimentally accessible, but has been deduced from theoretical calculations of the magnetic shielding in the N_2 molecule.[141,200] The calculated "absolute" shift of the N_2 resonance is about 103 p.p.m. to high frequency. The reported N_2 shift[14] has been used[141] for relating the calculated position of the resonance of the bare nucleus to the shifts found in a variety of molecules. Unfortunately, the experimental shifts used[14] are very inaccurate on the whole, particularly dubious is the reported N_2 shift of 14 p.p.m. to low frequency of $NO_3^{\ominus}$. The value reported later by Kent and Wagner[51] is 70 p.p.m. This result has been used recently[120] in a further attempt at finding the absolute resonance shifts of nitrogen nuclei in various molecular structures. However, the results of Kent and Wagner[51] are based on the external standard technique with aqueous NH_4NO_3 as the reference in a system of coaxial tubes. It is not clear how the shift for liquid N_2 was obtained in this way. The large divergence of results for N_2 and the uncertainty of the molecular beam experiment (± 20 p.p.m.) do not afford much more than a rough estimate of the absolute scale.

Recently Becker[201] has reviewed the system of references and scales that has been used for expressing nitrogen chemical shifts. He has proposed that both ^{14}N and ^{15}N chemical shifts should be quoted relative to tetramethylammonium iodide as an internal reference. The shifts can then be readily referred to the proton resonance of TMS by means of double resonance techniques.

II. THEORY OF NITROGEN CHEMICAL SHIFTS

The NMR spectra of nitrogen nuclei may provide an important contribution to the development of the general theory of chemical shifts [202] by allowing a rigorous check of current theories. This arises from the variety of nitrogen valence states occurring in molecules including more or less "non-bonding" electron pairs, many types of bonds of varying polarity and hydrogen-bonding, as well as the common occurrence of nitrogen atoms in both neutral and ionic species. So far there has been no adequate theory of nitrogen chemical shifts, which can successfully account for the shifts of more than a selected group of molecules.[9,45,49,51 to 53,119,132,180,182 to 187,203] Usually, the results of calculations are in much better agreement with experimental data for ^{13}C nuclei than for nitrogen, as shown in recent work on azines[183] and a number of nitrogen-containing molecules.[187] However, the difficulties

encountered in the explanation of nitrogen chemical shifts should serve the purpose of stimulating new theoretical solutions.

The general expression for the nuclear screening parameter for nucleus A, σ_A, may be split into diamagnetic, paramagnetic and long-range terms[204 to 207] according to equation (2).

$$\sigma_A = \sigma_A^{dia} + \sigma_A^{para} + \sum_B \sigma_{AB} \text{ (long-range)} \tag{2}$$

The long-range screening effects, which are usually not larger than a few p.p.m., may be considered unimportant when compared with the experimental range of nitrogen chemical shifts which is about 900 p.p.m. in diamagnetic compounds (Sections V and VI). An example of this is the low-frequency shift of the ^{14}N resonance in nitrobenzene and other nitroaromatic compounds,[48, 52] relative to that of some nitroalkanes[46, 48] which is in the opposite direction to that produced by the deshielding effect operating in the plane of the benzene ring. No long-range effects have so far been considered in calculations of nitrogen chemical shifts.

The diamagnetic term, σ_A^{dia}, represents the shielding caused by a spherical distribution of electron charge, and may be expressed[203] by:

$$\sigma_A^{dia} = \frac{e^2}{3mc^2} \sum_i \rho_{ii} \langle r_i^{-1} \rangle \tag{3}$$

where $\langle r_i^{-1} \rangle$ is the mean reciprocal of the distance of the ith electron from the nucleus, ρ_{ii} is the orbital population, and the summation is over all occupied orbitals. The values of $\langle r_i^{-1} \rangle$ for nitrogen may be calculated by means of equations (4) to (7).

$$\langle r_i^{-1} \rangle = \frac{Z_i}{n^2 a_0} \tag{4}$$

$$Z_{1s} = 6{\cdot}6 - 0{\cdot}1(P_{2s2s} + P_{2p_x2p_x} + P_{2p_y2p_y} + P_{2p_z2p_z}) \tag{5}$$

$$Z_{2s} = 5{\cdot}65 - 0{\cdot}35P_{2s2s} - 0{\cdot}2(P_{2p_x2p_x} + P_{2p_y2p_y} + P_{2p_z2p_z}) \tag{6}$$

$$Z_{2p} = 5{\cdot}35 - 0{\cdot}5P_{2s2s} - 0{\cdot}35(P_{2p_x2p_x} + P_{2p_y2p_y} + P_{2p_z2p_z}) \tag{7}$$

where n is the principal quantum number, a_0 is the Bohr radius, and Z_i is the effective nuclear charge expressed in terms of electron charge densities P_{jj}.

Generally speaking, the diamagnetic term provides an increase in screening resulting in a shift of the resonance signal to lower frequencies as the electron density around nucleus A increases. The contribution of the diamagnetic term to the total nuclear screening constant for nitrogen seems to be rather insignificant. Experimental data on many groups of compounds, including those with trigonally hybridized nitrogen atoms,[48]

isonitriles,[7,49] ammonium ions and amines,[45] pyridine and the pyridinium ion,[44,48,180,203] show resonance shifts which are in the opposite direction to those expected from changes in the diamagnetic term. However, this argument alone is not sufficient for dismissing this term from calculations aimed at a quantitative or semi-quantitative correlation of the theoretical and observed nitrogen chemical shifts. The σ_A^{dia} term has been omitted in many considerations of the theory of nitrogen resonance shifts,[9,48,49,51,180,182,184,185,203] and some justification for this may be found in recent calculations involving all valence electrons.[183,186,187] The calculations for pyridine, pyrazine, pyrimidine and pyridazine[183] show that the variation in the diamagnetic term is less than 0·5 p.p.m., while the chemical shifts differ within a range of about 100 p.p.m. A recent consideration[186] of the nitrogen chemical shift between pyridine and the pyridinium ion in terms of all valence electron calculations gives the following contributions to the shift:

		^{14}N Py–PyH$^{\oplus}$ shift
Calculated	σ_A^{para}	128·8 p.p.m.
	σ_A^{dia}	−10·8
	Total	118·0
Observed		113 ± 2 p.p.m. (ref. 48)

which provides very good agreement with the experimental data. The contribution from changes in the diamagnetic term is of an order of magnitude smaller than the corresponding contribution from the paramagnetic term. The values given above are corrected for an arithmetic error found in the original paper,[186] and are compared with more recent experimental results.[48] The agreement is even better than originally reported.

Chemical shift calculations including all valence electrons for ^{13}C, ^{14}N and ^{17}O in simple molecules[187] have also indicated that changes in the diamagnetic term are not significant for a considerable number of structures including pyramidal, tetragonal, planar and linear systems of bonds at the nitrogen atom.

In view of these results, the calculation of the diamagnetic corrections to the nitrogen screening constants recently reported by Grinter and Mason[120] are probably not valid. They have employed an additive scheme of diamagnetic shielding without consideration of the molecular wavefunctions, and obtained very large values for the contribution of σ_A^{dia} to the nitrogen chemical shifts. This contribution has been used as a

correction to the experimental chemical shifts in order to obtain the paramagnetic contribution. Apart from the obvious inconsistency of their results with the calculations quoted above,[183, 186, 187] a comparison with experimental data indicates that the directions of the experimental shifts and the calculated diamagnetic corrections are not only opposite in sign, but the latter is of a higher order of magnitude (Table III).

TABLE III

Comparison of some relative experimental nitrogen chemical shifts and reported diamagnetic contributions

	Relative observed chemical shift† (ref. 45) p.p.m.	Relative diamagnetic term contribution reported by Grinter and Mason (ref. 120) p.p.m.
NH_3 (liquid)	0	0
$MeNH_2$	5	−30
Me_2NH	12	−59
Me_3N	18	−88
$NH_4^{\oplus}$	0	0
$NMe_4^{\oplus}$	21	−117

† Editorial Note: Attention is drawn to the convention of chemical shift scales—ow field shifts are positive.

Experimentally, a regular change of about +5·5 p.p.m. per methyl group is observed, while the claimed diamagnetic contribution is about −29 p.p.m. It seems highly improbable that regular changes in the observed shifts will contain such regular and large contributions of opposite sign.

The paramagnetic term, σ_A^{para}, which has been discussed theoretically by Ramsey,[204] has also been expressed by Pople[205 to 207] in terms of a linear combination of gauge invariant orbitals:

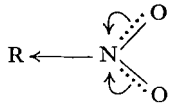
$$\sigma_A^{para} = -\frac{2e^2\hbar^2}{3m^2c^2}\langle r_{2_p}^{-3}\rangle \sum_i^{occ.}\sum_j^{unocc.} (\Delta E_{i\to j})^{-1}$$
$$\times[(C_{i,x_A}C_{j,y_A} - C_{i,y_A}C_{j,x_A})\sum_B (C_{i,x_B}C_{j,y_B} - C_{i,y_B}C_{j,x_B})$$
$$+(C_{i,y_A}C_{j,z_A} - C_{i,z_A}C_{j,y_A})\sum_B (C_{i,y_B}C_{j,z_B} - C_{i,z_B}C_{j,y_B})$$
$$+(C_{i,z_A}C_{j,x_A} - C_{i,x_A}C_{j,z_A})\sum_B (C_{i,z_B}C_{j,x_B} - C_{i,x_B}C_{j,z_B})] \qquad (8)$$

where the summation over B involves all atoms including A, the C terms are the coefficients of the corresponding $2p$ orbitals in the molecular orbitals i and j and $\langle r_{2p}^{-3} \rangle$ is the mean value of the reciprocal cube of the $2p$-orbital radius, sometimes called the orbital expansion term. The latter is usually calculated from equation (9)

$$\langle r_{2p_i}^{-3} \rangle = \frac{1}{3}\left(\frac{Z_{2p}}{2a_0}\right)^3 \tag{9}$$

which is analogous to equation (4). It is important to realise how this contribution affects the paramagnetic term and the screening constant for nitrogen nuclei since much controversy has arisen over the significance of changes in this contribution for nitrogen chemical shifts.[9, 48, 49, 51, 180, 182 to 185, 187, 191, 203, 208] An increase in the electron density at atom A decreases the value of $\langle r_{2p}^{-3} \rangle$, and thus decreases the absolute magnitude of the paramagnetic term. Since the latter is negative the overall effect is to increase the shielding and to shift the resonance to lower frequencies. Thus, this part of the paramagnetic term acts in the same direction as does the diamagnetic term. Qualitatively then, the same arguments as those against the significance of the diamagnetic term for changes in nitrogen chemical shifts could apply here.

It has been shown experimentally[45 to 49, 53, 56] for many molecules of the type R–X, where X is a group containing a nitrogen atom (NO_2, NC, NH_2, $NH_3^{\oplus}$, NCO, NCS, N_3) directly bonded to R, that the nitrogen resonance shifts to lower frequency with increasing electronegativity of R, i.e. in the opposite direction to that expected from changes in $\langle r_{2p}^{-3} \rangle$. The same discrepancy has been observed for the nitrogen resonance shift between pyridine and the pyridinium ion.[48, 180, 203] One might argue that if the nitrogen atom in group X constitutes part of a multiple-bond



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system, then the increasing electro-negativity of R should result in an increased π-electron density at the nitrogen atom, as in **1**, and thus explain the low-frequency shift in terms of a decrease in $\langle r_{2p}^{-3} \rangle$. Such arguments have been used in the literature.[191, 208] The fault of this explanation is that the perturbation of the electron distribution in X, upon increasing the electronegativity of R, results from an inductive loss of electron charge at N, and the net effect should be an increase in $\langle r_{2p}^{-3} \rangle$

rather than a decrease. This becomes more apparent when one considers that the more closely bound 2*s* electrons provide an important contribution to the effective nuclear charge Z_{2p}, equation (7).[48,180,187,203] An experimental suggestion that the actual 2*p*-electron charge density at N tends to decrease with increasing electronegativity of R in R–NO_2 and $(R–NO_2)^{\ominus}$ may be found[9,48] from the decreasing width of the corresponding ^{14}N resonance signals. Much of the misunderstanding here may have arisen from the method of calculating $\langle r_{2p}^{-3} \rangle$, and particularly from those methods employed in the evaluation of the effective nuclear charge Z_{2p}. If Slater's rules are used, the resulting equation for Z_{2p} is

$$Z_{2p}\,(\mathrm{N}) = 3{\cdot}90 + 0{\cdot}35(n - q_{\mathrm{N}}^{\pi}) \qquad (10)$$

where q_{N}^{π} is the π-charge density at the nitrogen atom, and n is the number of electrons supplied by the nitrogen atom to the π-electron system. Equation (10) suggests that variations in the orbital expansion term play a major role in changes in $\sigma_{\mathrm{A}}^{\mathrm{para}}$. This arises mainly from the neglect of changes in the σ-bond core. Kent and Wagner[51] have employed equation (10) for linear triatomic molecules and ions but the correlation they obtained requires the assumption of two different values for the mean excitation energy in equation (12). The N_2 molecule deviates from the correlation and, as is shown in other reports,[16,48,57] the $NO_2^{\oplus}$ ion is also not predictable with a chemical shift of about -130 p.p.m. from $NO_3^{\ominus}$ instead of the value of -46 p.p.m. reported by Kent and Wagner.[51] The same equation has been used by Ting Kai Wu[182,184] for calculations of nitrogen chemical shifts in heterocyclic systems, but it is difficult to estimate the significance of these calculations because they contain an error in the expression for the paramagnetic term. Apparently, the error has been transmitted to the calculations carried out by Hendrickson and Kuznesof[185] on some small nitrogen containing ions.

Other investigators[48,180,203] have suggested that the experimental data do not support the proposal that changes in the orbital expansion term play a dominant role and have looked for an explanation of nitrogen chemical shifts in terms of the remaining part of the paramagnetic term.

Recent calculations on azines[183] have shown that if both σ- and π-electrons are considered, by the method of Bene and Jaffe,[209] the resulting contributions of the orbital expansion term and of the other part of the paramagnetic term are comparable in magnitude and sign. Since the correlation with experimental data is worse for ^{14}N resonance shifts than for those of ^{13}C, it is difficult to draw conclusions as to the relative significance of the components of the paramagnetic term.

Velenik and Lynden-Bell,[187] in their recent all-valence electron calculation of chemical shifts for ^{13}C, ^{14}N and ^{17}O in a large number of

simple molecules, have criticised the use of Slater orbitals in the expression for $\langle r_{2p}^{-3} \rangle$ since these are unreliable close to the nucleus. Instead they have used SCF functions of neutral atoms and ions, giving

$$\langle r_{2p}^{-3} \rangle_N = 3{\cdot}009 - 0{\cdot}732Q \tag{11}$$

where Q is the total local charge density at the nitrogen nucleus. Variations in the term $\langle r_{2p}^{-3} \rangle$ are not found to be large when compared to those in the remaining part of the paramagnetic term.

Thus it seems that caution is necessary in calculating the orbital expansion term, also the contribution of the latter to experimental nitrogen chemical shifts appears to be rather small, contrary to the conclusions derived from the simplified model represented by equation (10).

The summation in the expression for the paramagnetic term, equation (8), is over all excited states so that the exact evaluation of the sum is rather difficult. A very popular method of circumventing this difficulty is to use the closure approximation and express the sum in terms of the average excitation energy, ΔE_{av}, and ground state molecular orbitals. This is called the AEE approximation. The paramagnetic term is then expressed[205 to 207] by equations (12) and (13).

$$\sigma_A^{para}(\text{AEE}) = -\frac{e^2\hbar^2}{2m^2c^2} \langle r_{2p}^{-3} \rangle (\Delta E_{av})^{-1} \sum_B Q_{AB} \tag{12}$$

where the summation over B includes atom A, and

$$Q_{AB} = \frac{4}{3}\delta_{AB}(P_{x_Ax_B} + P_{y_Ay_B} + P_{z_Az_B}) - \frac{2}{3}(P_{x_Ax_B}P_{y_Ay_B} + P_{x_Ax_B}P_{z_Az_B} + P_{y_Ay_B}P_{z_Az_B}) + \frac{2}{3}(P_{x_Ay_B}P_{x_By_A} + P_{x_Az_B}P_{x_Bz_A} + P_{y_Az_B}P_{y_Bz_A}) \tag{13}$$

where δ_{AB} is the Kroenecker delta ($\delta_{AB} = 1$ if $A = B$, otherwise $\delta_{AB} = 0$) and the P's are the elements of the charge density and bond-order matrix for the atomic orbitals in the LCAO molecular orbitals. One should note that in two cases[182, 185] of theoretical estimates of nitrogen chemical shifts a minus sign was erroneously used for the last term of the sum in equation (13). Since this term has a non-zero contribution to the shift, if sigma-bond polarisation is considered, the results obtained should be recalculated.

The usefulness of the AEE method is limited to cases where ΔE_{av} may be assumed constant for a number of molecules or where a reasonable estimate may be made from some experimental data. The former assumption may be experimentally checked by comparison of the cal-

culated and observed shifts; this has been done for several groups of nitrogen-containing molecules.[9,48,49,183] The latter estimate involves either the adjustment of ΔE_{av} in order to obtain a general correlation for different types of molecules, if there are any correlations within each type,[51] or looking for a relationship between the wavelength of the lowest energy transitions and the chemical shifts.[59,132,180,182,184,191] However, there is no sound evidence that such transitions actually represent a major portion of ΔE_{av}, which is an artificial quantity. As can be seen from equation (8) the contribution of the lowest excited states depends not only on ΔE but also on the atomic orbital coefficients of the corresponding wave functions, and the latter may be much more critical. There is some evidence[45] that in the relatively simple case of amines, an obvious discrepancy is observed between their ^{14}N shifts and the lowest $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transition frequencies.

The AEE approximation with the assumption of negligible effects from changes in the orbital expansion term and the average excitation energy gives a qualitative agreement with changes in nitrogen chemical shifts within such groups of compounds as nitroalkanes, nitramines and alkyl nitrates,[48] alkyl cyanides and isocyanides,[49] alkyl isocyanates, isothiocyanates and azides[48] and nitrocarbanion systems.[9] The AEE approximation with the inclusion of $\langle r_{2p}^{-3} \rangle$ and the assumption of two different values of ΔE_{av} shows a correlation with the ^{14}N shifts for linear triatomic molecules and ions.[51] Similar methods have been used by Ting Kai Wu for some heteroaromatic compounds[182,184] and by Hendrickson and Kuznesof[185] for some small nitrogen containing ions, but their calculations contain an error, as mentioned earlier in this section.

The AEE approximation may be compared with equation (8) by means of the different excitation energy (DEE) method[183] which incorporates the lowest known excited states according to equation (8), but uses ΔE_{av} for the remaining excited states. Such methods have been employed by Gil and Murrell[180] and by Emsley[203] in their calculations on the pyridinium ion–pyridine nitrogen chemical shift. They have used the AEE method for the pyridinium ion but the DEE approximation for pyridine with neglect of the factor containing $\langle r_{2p}^{-3} \rangle$, with moderate success, and indicate that the inclusion of the latter factor leads to a complete discrepancy between the calculated and experimental shifts. The DEE approximation has been employed on a larger scale by Tokuhiro and Fraenkel[183] for pyridine and some diazines. The results give reasonably good agreement with the experimental ^{13}C shifts but are less satisfactory for ^{14}N.

More sophisticated methods, which reject the AEE approximation have been applied recently to calculations on simple nitrogen-containing

molecules[187] and on pyridine and the pyridinium ion.[186] Velenik and Lynden-Bell[187] have obtained results which are less satisfactory for ^{14}N than for ^{13}C chemical shifts. They have been obliged to assume different correction factors for each arrangement of bonds at the nitrogen atom (pyramidal, tetragonal, planar 2- and 3- coordinate, linear-end, linear-centre).

Recently calculations have been reported for some nitrogen-oxygen-halogen compounds using equation (8) directly.[192] With a few exceptions the correlation between the experimental and theoretical chemical shifts is good.[57] It appears that changes in ^{14}N chemical shifts may be dominated either by changes in excitation energy or molecular wavefunctions or both. Consequently it is unwise to attempt to ascribe chemical shift changes exclusively to either of these effects.

There is still much to be done in the theoretical explanation of nitrogen chemical shifts. No general method has so far been devised, in spite of the limited success of various approximations. It seems that a method which may be considered as generally valid must be first checked against the subtle shifts observed within groups of similar molecules where the arbitrariness of assumptions is greatly reduced.

III. QUADRUPOLAR EFFECTS ON ^{14}N NMR SPECTRA

It is well known that the ^{14}N nucleus has an electric quadrupole moment (Section I) and that this is frequently responsible for producing broad-line NMR spectra.[189, 208] Broad lines often occur both in the spectrum of the ^{14}N nucleus and in the spectrum of any nucleus spin coupled to the nitrogen nucleus which may preclude the detection of any spin-spin coupling between these nuclei (Section IV).

Abragam[210] has described an extreme narrowing approximation occurring when,

$$\tau \ll \frac{1}{\omega_0} \tag{14}$$

where τ is a molecular correlation time and ω_0 is the nuclear Larmor frequency.[2, 3, 5, 6] The inequality given by equation (14) is frequently obeyed in practice.[2, 3, 5, 6, 208] Under these conditions the influence of the quadrupole moment on the nuclear relaxation times is given by,[3]

$$\frac{1}{T_Q} = \frac{1}{T_{1N}} = \frac{1}{T_{2N}} = \frac{3}{8}\left(1+\frac{\epsilon^2}{3}\right)\left(\frac{eq\,eQ}{\hbar}\right)^2 \tau \tag{15}$$

where T_{1N} is the nuclear spin-lattice relaxation time, T_{2N} is the nuclear spin-spin relaxation time, T_Q is the quadrupolar relaxation time, $(eq\,eQ/\hbar)$

is the quadrupolar coupling constant dependent upon the electric field gradient at the nucleus, eq, and the nuclear quadrupole moment, eQ. The factor ϵ describes the deviation of the electric field gradient from axial symmetry. When equation (15) is obeyed the quadrupolar relaxation time, T_Q, may be derived from the full line-width at half-height, ΔN, of the ^{14}N resonance signal, by

$$\frac{1}{T_Q} = \pi \Delta N \tag{16}$$

when spin-spin coupling between ^{14}N and protons occur T_Q may also be determined by a line shape analysis of the proton signal[6] (Section IV).

From equations (15) and (16) it is apparent that the line-width of a ^{14}N resonance signal will depend upon the product of the quadrupole coupling constant and the correlation time. Since the value of eQ is known and ϵ may often be obtained from a knowledge of molecular symmetry, measurement of ΔN provides an estimate of either eq or τ if the other is already known.

By considering τ to be the correlation time for the rotation of a sphere in a viscous medium an expression for τ may be obtained from Stokes' formula,

$$\tau = \frac{V\eta}{kT} \tag{17}$$

where V is the volume of the sphere, η is the viscosity of the medium, k is Boltzmann's constant and T is the temperature in °K. Expressions similar to equation (17) are available for more realistic liquid models[3] showing the same dependence upon η and T. It follows from these expressions that the ^{14}N line width may be decreased by increasing the temperature and by decreasing the viscosity of the medium.

By using estimated values of the quadrupole coupling constant for CH_3CN, $CH_2{=}CHCN$ and pyridine, Herbison-Evans and Richards[3] have predicted values of τ from measurements of ΔN for these compounds. The experimental values of τ are found to be shorter than anticipated from equation (17), better agreement is obtained by the introduction of a microviscosity factor.

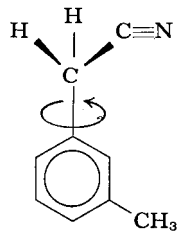
It follows from equations (15), (16) and (17) that, for a series of chemically similar molecules at a given temperature the ratio of ΔN to η should be proportional to the product of the molecular volume and the quadrupole coupling constant.

For a series of 4-halo-nitrobenzenes the ratio is found to increase in the order 4-F < 4-Cl < 4-Br < 4-I. The increase in volume is not thought to make a significant contribution to this ordering. The order is claimed

to be indicative of an increase in conjugation across the ring between the nitro group and the 4-halo group.[3] An analogous increase in the ratio, in the order 2-halo < 3-halo < 4-halo, may be interpreted in a similar manner.

The principal electric field gradient axes about a given nucleus are essentially fixed relative to the direction of the bonds to this nucleus. Consequently if a bond direction changes with respect to the rest of the molecule both the internal rotation producing this change, and the overall molecular rotation is capable of causing the electric field gradient axes to reorientate relative to the direction of the applied magnetic field.

Both of these rotation processes may thus effect the ^{14}N NMR line width by means of quadrupolar relaxation. If these occur at a comparable rate then it is possible to study the internal rotation by line width measurements.[4,115] The 2-, 3- and 4- methylbenzyl cyanides provide an application of this, **2**.



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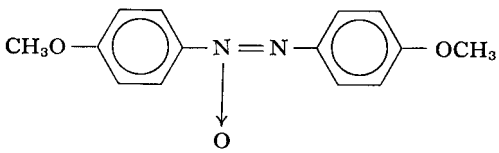
The internal rotation of the $-CH_2CN$ group relative to the benzene ring produces a reorientation of the bond to the nitrogen atom relative to the direction described by the applied magnetic field. By using an independent measure of the molecular rotation rate, the ^{14}N relaxation time, determined from line-width studies, permits an estimate of the internal rotation rate to be made.[115] The results obtained for 3- and 4-methylbenzyl cyanide are physically reasonable and in satisfactory agreement with data from dielectric relaxation measurements on similar molecules.

In a crystalline solid the nuclear quadrupole moment is expected to produce a splitting of the ^{14}N NMR signal. Expressions for the nuclear energy levels of a quadrupolar nucleus have been derived by assuming that the quadrupolar interaction is weak compared to the Zeeman interaction with the applied field.[211] These show that if the ^{14}N nuclei are in equivalent lattice sites the ^{14}N NMR signals will be split into two component lines. For non-equivalent sites two components arise from each type of site. The splitting depends upon the quadrupole moment

and the electric field gradient. Consequently, by using a known value for the former, it is possible to obtain information concerning the shape of the latter and its orientation with respect to the crystallographic axes. In some cases it is possible to derive information concerning the crystal structure and chemical bonding from a single crystal specimen (Section VI). Polycrystalline samples do not usually yield structural information but some details of chemical bonding are often still available.

Providing that the orientation factor is sufficiently small for the quadrupolar interaction to be much weaker than the Zeeman interaction, it is possible to observe two peaks for each nitrogen site in the ^{14}N spectrum of a molecule in the nematic phase of a liquid crystal solution. Although the ^{14}N signal is weaker than that from protons, the ^{14}N NMR spectrum may be advantageous in studying liquid crystals. The number of inequivalent nitrogen atoms is usually small and many of the static and dynamic effects observed in proton spectra are often dominated by the quadrupolar effects of the ^{14}N nucleus. Consequently the ^{14}N NMR spectrum of a liquid crystal is frequently easier to interpret in terms of molecular orientation than is the corresponding proton spectrum.

The ^{14}N NMR spectrum of the nematic phase of the liquid crystal *para*-azoxyanisole **3** shows four lines.[212] This reflects the difference in



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the electric field gradients at the two ^{14}N sites arising from the fact that only one of the two nitrogen atoms in *para*-azoxyanisole is bonded to an oxygen atom. By heating the sample until the isotropic phase is obtained the four lines coalesce. The width of the resulting single line has been interpreted in favour of an ordering factor, arising from the magnetic field, of less than 3×10^{-4} at 9·7 kG for the isotropic phase.[212]

In the nematic phase of poly-γ-benzyl-L-glutamate, the ^{14}N spectra of acetonitrile, nitromethane and nitrobenzene give two reasonably sharp peaks, with line widths from 0·7 to 2·3 kHz.[213] From the peak separations the quadrupolar coupling constants are reported as $3{\cdot}60 \pm 0{\cdot}10$ MHz, $1{\cdot}45 \pm 0{\cdot}05$ MHz and $1{\cdot}76 \pm 0{\cdot}07$ MHz respectively. For acetonitrile this provides reasonable agreement with the value of 3·738 MHz obtained from solid-phase measurements and poorer agreement with the gaseous-phase value of 4·35 MHz.

In general it appears that values of ^{14}N quadrupole coupling constants determined from measurements on liquids and liquid crystals are close to those obtained from solid phase measurements, and smaller than the corresponding values in the gaseous phase.[2,76,125,212] Gas phase measurements on HN_3 have shown that both positive and negative ^{14}N field gradients exist in this molecule. Consequently it is not surprising that a simple account of the electronic structure of $N_3^{\ominus}$ is insufficient to provide an entirely satisfactory description of the relative ^{14}N line widths as determined from solution NMR spectra.[3]

Semi-empirical MO calculations of the electric field gradient at a nucleus have been reported.[214 to 216] It is considered that the field gradient may be of either sign since it involves the sum of two contributions arising respectively from the nuclei and electrons. In general, the semi-empirical method, involving an extended Hückel type of calculation with charge iteration, has been found to give a satisfactory description of ^{14}N electric field gradients in a number of representative molecules.[215]

In principle the magnitude of an electric field gradient at a nucleus is expected to reflect the molecular symmetry. Consequently narrow ^{14}N NMR lines are observed for the ammonium ion and for the tetramethyl, and other similarly substituted, ammonium ions. Since the field gradient depends upon the inverse cube of the average separation of the nucleus and the surrounding electronic charge density, the presence of substituents such as methyl and benzyl together in an ammonium ion do not appreciably broaden the ^{14}N signal.[18]

Relatively narrow ^{14}N NMR lines may be obtained from species with low molecular symmetry such as the pyridinium ion[32] and some alkyl isonitriles.[31,40] These examples may be taken to demonstrate the short-range nature of an electric field gradient.

By considering two substituted ammonium ions, $NX_2Y_2^{\oplus}$ and $NX_1Y_3^{\oplus}$ to have C_{2v} and C_{3v} symmetry respectively, where X and Y are chemically different groups, it is readily shown that the ratio of the electric field gradients at the nitrogen nuclei in the two cases is 1·155:1. This is in agreement with the experimental ratio of the ^{14}N line-widths in $(CH_3)_2NH_2^{\oplus}$ and $(CH_3)_3NH^{\oplus}$ and supports the conclusion that the observed lines represent the natural line-widths uninfluenced by spin-spin coupling between the protons and nitrogen nuclei.[18]

IV. NMR SPECTRA OF NUCLEI SPIN-COUPLED TO THE ^{14}N NUCLEUS

The electric quadrupole relaxation process of the ^{14}N nucleus may

influence the NMR spectra of nuclei which are spin-coupled to it. The most frequently encountered example is the N–H coupling.

Theoretical line shapes for the spectrum of a proton spin-coupled to a ^{14}N nucleus, in the absence of proton exchange, have been reported.[217,218] Under these circumstances the shape of the proton signal depends upon the dimensionless parameter ζ:

$$\zeta = 10\pi T_{1N} J(\text{N–H}) \tag{18}$$

where T_{1N} is the spin-lattice relaxation time for the ^{14}N nucleus and J(N–H) is the spin-spin coupling constant between the proton and ^{14}N nucleus. By assuming that $4\pi^2 T_{1N}^2(\nu_N - \nu_H)^2$ is much greater than unity, where ν_N and ν_H are the resonance frequencies of the ^{14}N and ^{1}H nuclei, the relative intensity of absorption $I(x)$ is given by

$$I(x) = \frac{2\zeta}{\pi J(\text{N–H})}\left[\frac{45+\zeta^2(5x^2+1)}{225x^2+\zeta^2(34x^4-2x^2+4)+\zeta^4(x^6-2x^4+x^2)}\right] \tag{19}$$

where the dimensionless parameter x gives the frequency relative to the centre of the absorption band,

$$x = \frac{\nu - \nu_H}{J(\text{N–H})} \tag{20}$$

The form of equation (18) for a series of values of ζ is shown in Fig. 1. In the absence of quadrupolar relaxation the proton spectrum is expected to consist of three equally intense lines. For large values of ζ the quadrupolar relaxation mechanism is relatively slow and the proton lines are

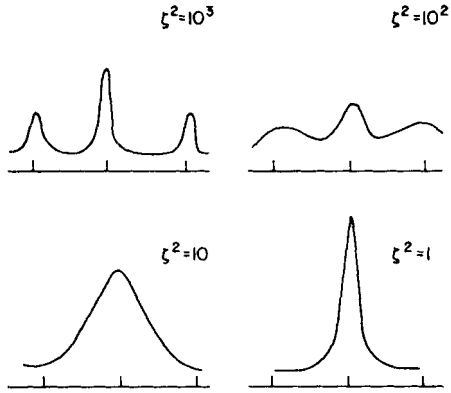


FIG. 1. Theoretical line-shapes for the spectrum of a spin-half nucleus coupled to a ^{14}N nucleus. The vertical lines indicate the position of the triplet in the absence of quadrupolar relaxation. (From Pople.[217])

slightly broadened, the two outside lines being broader than the central line. If the quadrupolar relaxation rate becomes sufficiently rapid, the proton triplet collapses into a single broad line. A further decrease in ζ leads to a sharpening of the proton line, and a corresponding broadening of the single line in the ^{14}N spectrum, so that now the two nuclei are effectively decoupled.[217] A recently reported example of very rapid quadrupolar relaxation producing a narrow N–H proton line, is that of some *N*-acyl-glycosylamines, *N*-acetyl-2-amino-2-deoxy-D-glycoses and 1,1-bis(acylamido)-1-deoxy-glycitols, where line-widths at half-height of 3·5 to 4·0 Hz have been observed.[219]

A labile proton spin coupled to a ^{14}N nucleus, may become effectively decoupled if the exchange rate K is such that

$$2\pi K \gg J(\text{N–H}) \tag{21}$$

Hence, it may be difficult to decide whether the shape of the proton signal is determined by exchange or by quadrupolar relaxation. Since the ^{15}N nucleus has no quadrupole moment its substitution is expected to be useful in studying N–H exchange processes.

The overall band shape for the resonance of a group of magnetically equivalent spin-$\frac{1}{2}$ nuclei, coupled to other magnetically equivalent groups of spin-$\frac{1}{2}$ nuclei and to a ^{14}N nucleus in a first-order spin system, has been shown to be given by a direct superposition of equation (18) centred at the resonant frequencies calculated in the absence of the ^{14}N nucleus.[220] This derivation has been made with the assumption that the extreme narrowing approximation given by equation (14) is applicable.

If the electric field gradient at the ^{14}N nucleus is small, as in the case of isocyanides, J(N–H) may be measured directly.[31, 61, 64, 96] Consequently T_{1N} may be obtained, by means of equations (18), (19) and (20), from a measurement of the half-widths of the components of the proton spectrum.[217, 221] On the other hand the quadrupolar relaxation rate could be very rapid ($\zeta^2 \ll 1$) such that only a single sharp line appears in the proton spectrum. The single Lorentzian line has relative intensity 3, compared to the unit intensity of each line of the proton triplet which appears when T_{1N} is long, and has an effective relaxation time T_{2H} given by:

$$\frac{1}{T_{2H}} = \frac{8\pi^2}{3} J^2(\text{N–H}) T_{1N} \tag{22}$$

Under these conditions J(N–H) may be measured by studying the field dependence of T_{1H} and T_{2H}.[221] This relies upon the fact that in this case the spin-spin coupling between protons and nitrogen becomes a relaxation mechanism of the second kind for the protons.[210]

Systems between the two extremes of very slow and very rapid quadrupolar relaxation have been investigated by means of spin-echo and high-resolution studies.[5, 6, 222]

From equation (22) it is apparent that the proton spectrum with a Lorentzian shape will only yield the product of T_{1N} and J(N–H) whereas detectable departures from this shape may provide values for both T_{1N} and J(N–H) by fitting the observed spectrum to equation (19). If $\zeta^2 < 10$ then deviations from the Lorentzian shape are reported to be undetectable,[222] this is exemplified by some fluoropyridines.[221, 222] In this case, in order to unambiguously determine J(N–F) and T_{1N}, additional experimental data are required. Such data may be obtained by observing the ^{15}N satellite lines in the ^{19}F spectrum which yields a value for $J(^{15}\text{N–F})$ from which $J(^{14}\text{N–F})$ may be found and consequently T_{1N} from equation (22).[222] Alternatively, in the case of rapid quadrupolar relaxation, T_{1N} may be obtained directly from the ^{14}N NMR spectrum.

If two different types of magnetically equivalent spin-$\frac{1}{2}$ nuclei, A and B, are coupled to the ^{14}N nucleus then the ratio of the coupling constants, J(N–A) and J(N–B), may be determined from the half-widths ΔA, ΔB of the Lorentzian lines in the spectra of A and B. From equation (22) it follows that:

$$\frac{\Delta A}{\Delta B} = \frac{J^2(\text{N–A})}{J^2(\text{N–B})} \tag{23}$$

Hence, if either J(N–A) or J(N–B) is previously known, from independent data, the other may be determined from equation (23).

It follows from equations (15) and (17) that high temperatures and low-viscosity solvents will effectively reduce the rate of quadrupolar relaxation. This has been used in a study of some ^{14}N–^{1}H systems which give unresolved lines at room temperature.[6, 15] Resolution of overlapping ^{14}N spectra of some pyridine derivatives has been obtained at elevated temperatures.[8, 10] An algorithm for the numerical decomposition of such overlapping spectra, assuming a Lorentzian line shape, has recently been published.[127]

Conversely, the use of low temperatures and more viscous solvents tends to increase the rate of quadrupolar relaxation. This leads to a sharpening of proton lines which are broadened owing to the incomplete removal of ^{14}N–^{1}H spin-spin coupling by ^{14}N quadrupolar relaxation. In a study of the spectra of the protons in the α position to the nitrogen atom in pyridine, thiazole, isothiazole, isoxazole and quinoline the use of low temperatures and more viscous solvents has led to the resolution of ^{1}H–^{1}H spin-spin coupling which is otherwise not observed owing to line-broadening.[5] It was concluded from this study that the broadening

of the α proton line arises from the incomplete removal of ^{14}N–^{1}H coupling by quadrupolar relaxation of the nitrogen nucleus rather than a shortening of the proton relaxation time which might arise from a ^{1}H–^{14}N interaction.[5]

In the presence of ^{1}H–^{14}N spin-spin coupling, analysis of the proton line shape could lead to an estimate of the quadrupolar relaxation time of the nitrogen nucleus.[6, 221] By performing the line-shape analysis as a function of temperature, the temperature dependence of the quadrupolar relaxation time may be obtained. Since the quadrupolar correlation time, τ_Q, depends upon intramolecular rotational motions, a study of the temperature dependence of τ_Q leads to the related activation parameters for molecular reorientation. If the temperature dependence follows the Eyring equation then,

$$\frac{1}{\tau_Q} = \frac{fKT}{\hbar} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{24}$$

where K is Boltzmann's constant, f is a frequency factor which may be taken to be unity and $\Delta G^{\ddagger}$ is the free energy of activation for molecular reorientation. Equation (24) has been employed in a study on dimethylnitramine and methyl nitrate, which have relatively long quadrupolar relaxation times, and the activation parameters for molecular reorientation have been evaluated.[6] A similar analysis of the ^{19}F line-shape of a series of compounds exhibiting ^{19}F–^{14}N spin-spin coupling has been reported together with an estimate of effective activation energies.[221 to 223] In general, ^{19}F spectra of perfluorinated molecules are preferable to the corresponding proton spectra for line-shape studies, since the smaller N–H coupling constants cause the quadrupolar and inhomogeneity broadening to be comparable. Additionally proton spectra may show small second-order effects which invalidate the use of equation (19).[221]

A complete proton line-shape analysis for a series of nitro compounds of the type X–NO_2, where X = C, N or O, has been reported.[6] The analysis yields values for the quadrupolar relaxation times from which the ^{14}N quadrupolar coupling constants have been estimated. The results indicate that the electron distribution at the nitrogen atom in the nitro grouping becomes more symmetrical as X changes from C to O to N. This trend has been accounted for in terms of the Townes and Daily[224] model for quadrupolar interactions. Small electric field gradients at the site of the nitrogen atom are found to largely arise from the inductive removal of electron population, from the sigma orbital forming the X–NO_2 bond, by the electronegative X substituents.[6]

Spin coupling between the nitrogen nucleus and protons may also be

removed by heteronuclear magnetic double-resonance.[43,69] This technique has been successfully used for measuring the chemical shifts of ^{14}N nuclei directly bonded to protons (Section V). By observing the proton signal and simultaneously irradiating the sample at the ^{14}N resonance frequency, removal of fine structure or a sharpening of the signal indicates when spin-decoupling has occurred. The value of the r.f. field required to achieve this yields the ^{14}N chemical shift. Since this technique involves the observation of a proton signal it is more sensitive than the direct observation of the ^{14}N signal. However, it is limited to those cases in which the proton and ^{14}N nucleus are spin coupled. Hence it is important that the proton and ^{14}N nuclei should not previously be effectively decoupled by either a short ^{14}N quadrupolar relaxation time or by proton exchange, if a labile proton is involved.

^{1}H–$\{^{14}N\}$ spin tickling measurements have been used to provide the first determination of the anisotropy of the ^{14}N screening tensor. The measurements were made on methyl isocyanide in a nematic liquid crystal.[76] The anisotropy of the screening tensor provides a chemical shift anisotropy of 360 ± 73 p.p.m. The same experiment has produced a value of 272 ± 2 kHz for the ^{14}N quadrupole coupling constant which is in reasonable agreement with values reported from ^{14}N NMR line-width measurements.[50,76] However, the value obtained is only 57% of that reported (483 ± 17 kHz) from measurements on the gaseous phase. Perhaps a measurement on the solid phase would produce closer agreement with the value obtained from the liquid crystal measurement[2,125,212] Semi-empirical MO calculations provide approximate agreement with the values of both the ^{14}N chemical shift anisotropy and the quadrupole coupling constant determined from the ^{1}H–$\{^{14}N\}$ spin-tickling data.

V. SOME EXAMPLES OF NITROGEN CHEMICAL SHIFTS IN ORGANIC MOLECULES

With the exception of experimental errors and non-uniformity of calibration techniques there is so far no convincing evidence that the nitrogen chemical shifts observed in ^{14}N magnetic resonance spectra differ from those obtained from ^{15}N spectra. In some early work on nitrogen NMR, Ray[128] presented a comparison of ^{15}N and ^{14}N shifts which are equal within experimental error. However, three exceptions were noted: ethyl nitrate, dimethyl formamide and hydrazine where the differences were ascribed to hindered internal rotation in these molecules. Later work has shown that these differences are essentially non-existent.[48,208,225] The ^{14}N shift for ethyl nitrate, which according to Ray[128] should be a few p.p.m. from nitromethane, has subsequently

been found to be 37 p.p.m.[48] and the ^{15}N shift between methyl formamide and dimethyl formamide is reported to be 15 p.p.m.[208] instead of about 200 p.p.m. given by Ray.[128] An apparent discrepancy between the ^{14}N data on aromatic nitro compounds[52] and the corresponding ^{15}N shifts[134] has recently[138] been shown to arise from an error in the original ^{15}N data.[134] The latest investigation of isotope effects on nitrogen chemical shifts[225] has been carried out for ^{14}N and ^{15}N nuclei in tetramethylammonium iodide, benzyl isocyanide, methyl nitrate and dimethylnitramine by precise double-resonance methods. These studies have shown that the ratio of $^{15}N/^{14}N$ resonance frequencies is $1{\cdot}402\ 756\ 95 \pm 8 \times 10^{-8}$ so that there is no significant contribution from isotope effects to the shielding of the nucleus. The only isotope effect that has so far been observed in nitrogen NMR is the low-frequency shift of about 0·3 p.p.m. for each deuterium substituted in $^{14}NH_4^{\oplus}$.[68,85]

Extensive systematic studies have recently been reported on nitrogen chemical shifts for large groups of organic molecules. These will be reviewed here together with the inclusion of some earlier data.

A. The nitro group

^{14}N chemical shifts of nitroalkanes have been published in a number of papers.[46,47,53] It has been shown[46] that the ^{14}N resonance of the NO_2 group in R–NO_2 is shifted to lower frequencies as the electronegativity of the group R increases, also that nitromethane, primary-, secondary-, and tertiary nitroalkanes may be distinguished by means of their nitrogen chemical shifts. Simple additivity rules are reported for the nitrogen chemical shifts of nitroalkanes.[47] A rather good correlation of these shifts with the Taft constant for the group R has also been reported[53] Recently the nitrogen shifts of nitroalkanes were rationalised[48] in terms of changes in the nuclear shielding calculated by the AEE approximation (Section II). A relationship[55] between the chemical shifts and the antisymmetrical vibration frequencies, ν_{as}, of the NO_2 group has been reported. Where ν_{as} is expressed in cm^{-1} by:

$$\nu_{as}\,(NO_2) = 1573 + 1{\cdot}147\delta_N\,(NO_2) \qquad (25)$$

with a correlation coefficient of 0·935. The nitrogen shift data for polynitroalkanes have recently been extended[56] and a linear relationship between the ^{14}N shifts and the Taft σ^* constants of substituents has been reported:

$$\delta_N\,(\text{polynitroalkane}) = -25{\cdot}0 + 13{\cdot}8\sigma^*\ (\text{p.p.m.}) \qquad (26)$$

with a correlation coefficient of 0·994. The calculations carried out[56] on

TABLE IV

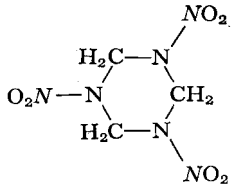
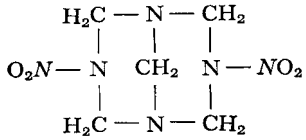
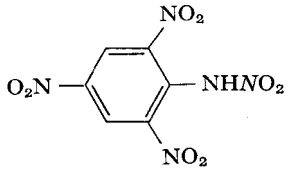
^{14}N chemical shifts of some nitroalkanes and related compounds. All shifts are referred to nitromethane as internal standard, shifts to low frequency are taken to be negative

Substance	Chemical shift p.p.m. (±1 or better)	Half-height width Hz	Reference
$MeNO_2$	0	24	46
$EtNO_2$	12	30	46
	10·8	30	53
n-$PrNO_2$	10	35	46
	9·5	..	53
n-$BuNO_2$	10	49	46
$Me(CH_2)_4NO_2$	10	56	46
$Me(CH_2)_5NO_2$	10	57	46
i-$PrNO_2$	24	38	46
nitrocyclohexane	20	92	46
t-$BuNO_2$	30	43	46
$MeCH(NO_2)_2$	−11	28	47
	−10·5	24	53
$MeCH_2CH(NO_2)_2$	−11	35	47
$Me_2C(NO_2)_2$	0	34	47
$CH(NO_2)_3$	−35·5	11	46
$MeC(NO_2)_3$	−26·2	11	53
$C(NO_2)_4$	−48	10	46
$C_2(NO_2)_6$	−46·5	6	56
$PhCH_2NO_2$	7·5	163	46
$HOCH_2CH_2NO_2$	10·8	30	53
$MeCHClNO_2$	5·5	30	47
$MeCH_2CHClNO_2$	4·5	50	47
	2·6	..	53
$MeCH_2CHBrNO_2$	4	75	47
$Me(CH_2)_3CHClNO_2$	4·5	67	47
Me_2CClNO_2	13	35	46
$MeCH_2CCl_2NO_2$	−1	31	47
$CFCl(NO_2)COOH$	−16	78	56
$CHF(NO_2)_2$	−24	10	56
$MeCCl(NO_2)_2$	−13·5	21	56
$MeCBr(NO_2)_2$	−13	25	56
$CF(NO_2)_3$	−39	5	56
$CCl(NO_2)_3$	−36	8	56
$CBr(NO_2)_3$	−33	6	56
$HOCH_2C(NO_2)_3$	−30	10	53
CF_3NO_2	(−23)[a]	(100)	191
$C_3F_7NO_2$	(−23)[a]	(100)	191
CCl_3NO_2	(−15)[a]	(110)	191
CBr_3NO_2	(−13)[a]	(115)	191
$CF_2ClCFClNO_2$	(−3)[a]	(110)	191

[a] The data in parentheses were obtained with a wide-line spectrometer, with Me_2NNO external standard; the accuracy quoted was ±10 p.p.m. or better.

TABLE V

^{14}N chemical shifts of some nitramines and nitrates. All shifts are referred to nitromethane as internal standard unless stated otherwise

Substance	Chemical shift p.p.m.	Half-height width Hz	Reference
$H_2NCONHNO_2$	-40 ± 1	30	48
	$-36{\cdot}5 \pm 1$	35	46
	$-27{\cdot}0 \pm 0{\cdot}5$	30	46
	$-34{\cdot}5 \pm 1$	32	48
$MeNHNO_2$	$-23{\cdot}2 \pm 0{\cdot}5$	10	60
$O_2NNHCH_2CH_2NHNO_2$	$-25{\cdot}7 \pm 0{\cdot}5$	20	60
$EtOOCNHNO_2$	-42 ± 10[a]	..	191
Me_2NNO_2	-23 ± 10[a]	..	191
	$-21{\cdot}8 \pm 1{\cdot}5$[b]	..	73
$NCCH_2CH_2HNNO_2$	-28 ± 10[b]	..	73
$HOOCCH_2NHNO_2$ (di-K salt)	-21 ± 4[b]	..	73
$EtOOCCH_2NHNO_2$ (K salt)	$-21 + 7$[b]	..	73
$H_2NCOCH_2NHNO_2$	-24 ± 3[b]	..	73
$HOOCCH_2NMeNO_2$	-26 ± 4[b]	..	73
$NCCH_2NMeNO_2$	-24 ± 3[b]	..	73
$MeCHNHNO_2$ | $MeCHNHNO_2$	-26 ± 7[b]	..	73
N_2O_5 (CCl_4)	-60 ± 1	80	48
($CHCl_3$)	-48 ± 2[c]	..	57
$HONO_2$ 97%	$-47{\cdot}5 \pm 0{\cdot}5$	17	48
$EtONO_2$	$-37 \pm 0{\cdot}5$	17	48
myoinositol hexanitrate	-60 ± 4	370	48
$ClONO_2$	$-43{\cdot}6$[c]	..	57

[a] Results obtained with Me_2NNO external standard.
[b] From proton spectra by double-resonance method, referred to external $NO_3^{\ominus}$.
[c] Referred to external NH_4NO_3 by sample replacement method.

previous data[46,47,53] for some mono-nitroalkanes also give a good correlation:

$$\delta_N \text{ (mono-nitroalkane)} = -0{\cdot}6 + 103\sigma^* \qquad (27)$$

with a correlation coefficient of 0·981.

Since the data on the nitrogen chemical shifts of the NO_2 group in nitroalkanes are now fairly comprehensive and are based on the uniform scale of chemical shifts referred to internal nitromethane, the entire collection is given in Table IV. There is an indication[48] that if the C–NO_2 system is replaced by N–NO_2 or O–NO_2, then the NO_2 resonance is shifted to lower frequencies. This is in agreement with qualitative predictions based upon the electronegativity of group R in R–NO_2. A number of ^{14}N chemical shifts for systems involving nitramines and nitrates have been reported.[46,48,60,73,191] (Table V).

The anions derived from nitroalkanes[9,58,140,194] and nitramines[60] have also been investigated by ^{14}N and ^{15}N resonance methods. The results are given in Table VI. Whereas the anions derived from the *C*-nitro structures show an appreciable difference in their ^{14}N chemical

TABLE VI

Nitrogen chemical shifts of some salts of nitroalkanes and nitramines. All shifts are referred to internal KNO_3 or $NaNO_3$, 0 p.p.m., or to internal dimethylformamide −276 p.p.m. unless stated otherwise

Substance	Solvent	^{14}N Chemical shift p.p.m.	Half-height width Hz	Reference
$(CH_2NO_2)^{\ominus}Na^{\oplus}$	20% NaOH	−79 ± 2	450	9, 48
$(MeCHNO_2)^{\ominus}Na^{\oplus}$	20% NaOH	−79 ± 3	660	9
$(Me_2CNO_2)^{\ominus}Na^{\oplus}$	20% NaOH	−88 ± 4	660	9
$[HC(NO_2)_2]^{\ominus}K^{\oplus}$	20% NaOH	−20 ± 0·5	46	9, 140
	DMF	−20 ± 0·5	50	9
$[MeC(NO_2)_2]^{\ominus}K^{\oplus}$	20% KOH	−24 ± 1	40	9
	DMF	−18 ± 1	56	9
$[MeC(NO_2)_2]^{\ominus}NH_4^{\oplus}$	DMF	−26 ± 1	87	9
$[EtC(NO_2)_2]^{\ominus}Na^{\oplus}$	20% NaOH	−30 ± 1	250	9
$[C(NO_2)_3]^{\ominus}K^{\oplus}$	20% NaOH	−27 ± 0·5	25	9, 140
	DMF	−36 ± 1	36	9
$(MeNNO_2)^{\ominus}Na^{\oplus}$	H_2O	−26 ± 1[a]	43	60
$(O_2NNCH_2CH_2NNO_2)^{2\ominus}2Na^{\oplus}$	H_2O	−28 ± 1[a]	103	60

[a] Referred to external nitromethane.

shifts relative to the parent compounds, only a slight change is observed for the corresponding anions derived from the nitramines. The nitrogen chemical shifts of the anions of nitroalkanes are ordered differently from

TABLE VII

Nitrogen chemical shifts of the NO_2 group in some nitroaromatic compounds. All ^{14}N shifts are referred to nitromethane as internal standard

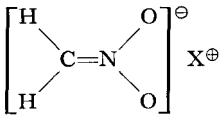
Substance	^{14}N Chemical shift (52) p.p.m. ±1	Half-height width Hz	^{15}N shift[a] (138) p.p.m.
Nitrobenzene	−8	60	(−8)
Aminonitrobenzene, *p*-	..	..	−7·7
Nitrophenol, *o*-	−7	70	..
m-	−9	140	..
p-	−7	110	..
Nitroanisole, *o*-	−6	70	..
m-	−8	90	..
p-	−7	100	−8·2
Nitrotoluene, *o*-	−7	50	..
m-	−8	90	..
p-	−7·5	85	..
Fluoronitrobenzene, *p*-	..	..	−9·1
Chloronitrobenzene, *p*-	..	..	−10·3
Bromonitrobenzene, *p*-	..	..	−10·7
Cyanonitrobenzene, *p*-	..	..	−11·3
Nitrobenzaldehyde, *o*-	−11	75	..
m-	−12	100	..
p-	−12·5	95	..
Dinitrobenzene, *o*-	−12	35	..
m-	−13	63	..
p-	−13	70	−12·6
1,3,5-Trinitrobenzene	−18·5	63	..
2,4,6-Trinitrotoluene	−14	100	..
2,4,6-Trinitrophenol	−18	128	..
2,4,6-Trinitrobenzoic acid	−19	125	..
2,4,6,*N*-Tetranitroaniline(C–NO_2)	−22[b]	85	..
Trimethylsilylnitrobenzene, *o*-	−7[c]	100	..
m-	−9[c]	139	..
p-	−12[c]	182	..

[a] ^{15}N Shifts referred originally to nitrobenzene, the data given here are recalculated to refer to internal nitromethane.

[b] Reference 48.

[c] Reference 54.

those of the nitroalkanes themselves. This has been accounted for in terms of changes in the mobile bond orders at the nitrogen atom.[9] The ^{14}N spectra suggest that an increase in the number of nitro groups attached to the carbon atom causes the structure of the anion to change from being similar to that of the classical formula of the aci-nitroalkane salt (**4**) to more closely resemble a true nitrocarbanion, e.g. $C^{\ominus}(NO_2)_3$.[9]



4

The proposal that the NO_2 groups in the salts of dinitromethane and trinitromethane are equivalent[9] has been supported by variable temperature (+25°C to −75°C) measurements[140] of the ^{15}N spectra of $C(^{15}NO_2)_3^{\ominus}K^{\oplus}$ in dimethyl formamide, acetone and methanol, and $HC(^{15}NO_2)_2^{\ominus}Na^{\oplus}$ in dimethyl formamide. A single resonance is observed in all cases throughout the entire temperature range; the signal of the latter molecule is a doublet with a spacing of 6 Hz arising from proton-coupling.

The nitrogen resonance of the NO_2 group attached to an aromatic ring occurs at a lower frequency than that of mono-nitroalkanes.[52, 54, 189] The signal moves to lower frequencies as the electronegativity of the substituents in the benzene ring increases but no appreciable differences between the *ortho*, *meta* and *para* isomers are observed.[52] Hence, any important contributions from the mesomeric effect are excluded. A comparison of recent values of nitrogen chemical shifts derived from ^{14}N and ^{15}N data is presented in Table VII.

There is no indication of any significant hydrogen-bonding effect in the ^{14}N spectra of nitrophenols.[52] It should also be noted that there seems to be no "hyperconjugation effect" such as suggested by Bose, Das and Chatterjee[99] for the nitrotoluenes. They have reported an 11 p.p.m. difference between the *o*- and *p*- nitrotoluene shifts, apparently on the basis of erroneous experimental data.

B. The nitroso group

Much less systematic work has been done in nitrogen NMR on the nitroso group,[59, 132] which exhibits broader ^{14}N signals than the nitro group. There seems to be a rough correlation of the shifts with the wavelength of the lowest energy electronic absorption band.[59] The available results are given in Table VIII.

TABLE VIII

Nitrogen chemical shifts of some nitroso compounds. All shifts from ^{14}N data[59] referred to nitromethane as external standard unless stated otherwise

Substance	Chemical shift p.p.m. ± 10	Half-height width Hz
Me_2NNO	158	355
MeO NO	188	265
CF_3SNO (−85°)	342	1140
EtSNO	412	455
CF_3NO (−90°)	427	450
C_3F_7NO	487	?
PhNO (ether)	489	1120
$Ph^{15}NO$ (ether)	532[a]	..
PhNO (acetone)	530[b] ± 4	750

[a] Referred to external NH_3, recalculated to external $NO_3^{\ominus}$, ref. 132.

[b] From CH_3NO_2 internal standard, unpublished results of M. Witanowski and G. A. Webb.

C. Nitrogen oxides, oxyhalides and related species

There has been a fair amount of experimental ^{14}N data reported recently on these molecules and ions[48,57,59,190,191] which should be classified as inorganic, but will be considered here because of their structural relationship with organic nitro- and nitroso- compounds (Table IX).

The ^{14}N shift of $NO_3^{\ominus}$ has been used as one of the primary internal standards in a unified scale of nitrogen chemical shifts.[107] It has been included in the general correlation between ^{14}N shifts and the calculated electronic structure of nitroalkane anions.[9] The shift of the nitrite ion, $NO_2^{\ominus}$, is in qualitative agreement with the trend in shifts shown by the nitroalkanes[48] if the electron pair on the nitrogen atom is considered to be the least electron-attracting "substituent" R in $R–NO_2$.

The shift for the nitronium ion, $NO_2^{\oplus}$, was recently reported[57] to be about −130 p.p.m. from $NO_3^{\ominus}$, in good agreement with the early work of Ray,[16] and differing from the value of −46 p.p.m. reported by Kent and Wagner.[51]

It has been shown[57] that the compounds of the $X–NO_2$ and X–NO type have nitrogen chemical shifts which follow the general trend previously observed for various alkyl derivatives[46 to 48] whereby the resonance is shifted to lower frequency as the electronegativity of X increases.

TABLE IX

Nitrogen chemical shifts of some nitrogen-oxygen-halogen molecules and ions. All shifts from ^{14}N data are referred to external $NO_3^{\ominus}$ unless stated otherwise

Molecule or ion	Solvent	^{14}N Shift p.p.m.	Half-height width Hz	Reference
$NO_3^{\ominus}$	H_2O	0	12	48
$NO_2^{\ominus}$	H_2O	237 ± 4[a]	520	48
$NO_2^{\oplus}$	HSO_3F	-129 ± 5	v. broad	57
		-125 ± 10		16
$NO^{\oplus}$	H_2SO_4	-5 ± 10	v. broad	59
$ONNO_2$	neat ($-50°$)	67 ± 10[b]	300	191
$ONNO_2$	neat ($-50°$)	302 ± 10[b]	745	59
N_2O_4	CCl_4	-15 ± 3	?	57
		-10 ± 10[b]	400	191
	HSO_3F	-89 ± 5	?	57
N_2O_5	CCl_4	-60 ± 1[c]	80	48
	$CHCl_3$ ($-25°$)	-48 ± 2	?	57
ClNO	neat ($-20°$)	224 ± 5	?	57
BrNO	neat ($-20°$)	352 ± 5	?	57
FNO	neat ($-78°$)	116 ± 5	?	57
	neat ($-68°$)	101 ± 10[b]	270	59
FNO_2	neat ($-110°$)	-82 ± 5	?	57
	neat ($-65°$)	-69 ± 10[b]	155	191
$ClNO_2$	neat ($-20°$)	-68 ± 5	?	57
	neat (0°)	-63 ± 10[b]	95	191
F_3NO	neat ($-110°$)	-131 ± 5	?	57

[a] Referred to internal $NO_3^{\ominus}$.
[b] From external nitromethane.
[c] From internal nitromethane.

The ^{14}N NMR spectra of N_2O_4 and N_2O_3 indicate the structures O_2N-NO_2 and $ON-NO_2$, respectively.[190] It has been suggested that amongst the various possible equilibria existing in mixtures of NO and NO_2 the most significant ones are **5**[190] rather than those involving the

$$N_2O_3 \rightleftarrows NO + NO_2$$
$$2NO_2 \rightleftarrows N_2O_4$$

5

species ON–O–NO, $ON-ONO_2$ and O=N–N=O. The low frequency nitrogen chemical shift indicates that the $NO_2^{\oplus}$ ion is formed when N_2O_4 is dissolved in HSO_3F, however the ^{14}N spectrum does not reveal any $NO^{\oplus}$ resonance signal possibly on account of its broadness.

The ^{14}N shifts of some nitrogen fluorides have been reported[57] together with the recalculated shifts for the two isomers of difluorodiazine taken[36] from an earlier work (Table X).

TABLE X

^{14}N chemical shifts of some nitrogen fluorides[57] All shifts referred to $NO_3^{\ominus}$ as external standard

Substance	Chemical shift (p.p.m.)
NF_3 (−152°C)	−8
N_2F_4 (−110°C)	−35
cis-N_2F_2	5·3
trans-N_2F_2	67·2
$N_2F_3^{\oplus}$ (in anh. HF)	22

It may be concluded from a comparison of the data in Tables IV to IX that nitrogen NMR provides a satisfactory means of distinguishing between the nitro and nitroso structures in both inorganic and organic molecules and ions.

D. The cyano and isocyano groups

The ^{14}N resonance of the cyano group in R–CN has been shown to shift towards higher frequencies as the electronegativity of R increases, whilst a shift in the opposite direction has been observed for the isocyano group in R–NC.[49] The difference in the trends for the nitrogen chemical shifts of these groups has been explained in terms of the average excitation energy approximation.[49] The isocyano group resonance occurs at a lower frequency (about −200 p.p.m. from nitromethane) than that of the cyano group (about −130 p.p.m. from nitromethane), and the signal width of the former is much smaller at least in simple molecules for which it may be less than 1 Hz. Recent high-resolution measurements of the shifts for isonitriles[7, 225] are in good agreement with previous values obtained by the direct method,[49] but differ considerably from the value of −240 p.p.m. for CH_3NC quoted by Herbison-Evans and Richards,[44] from previous work.[21] The recent data are presented in Table XI. One should note that the direction of the shifts within the group of isonitriles is the same as that observed for nitroalkanes, nitramines and alkyl nitrates.[48] ^{14}N spectra may be helpful in the identification of nitriles and isonitriles in mixtures such as that resulting from the reaction of AgCN with alkyl halides.[49]

TABLE XI

Nitrogen chemical shifts of the cyano and isocyano groups.[49] All shifts from ^{14}N data are referred to nitromethane as internal standard unless stated otherwise

Substance	Chemical shift p.p.m.	Half-height width Hz
Me_3CCN	-139 ± 1	190
EtCN	-137 ± 1	122
MeCN	-137 ± 1	88
CH_2ClCN	-126 ± 1	175
CCl_3CN	-122 ± 1	220
BrCN	-124 ± 1	165
$CH_2(CN)_2$	-128 ± 2	280
$NC(CH_2)_2CN$	-134 ± 2	370
$NC(CH_2)_3CN$	-136 ± 2	400
$MeCH(CN)_2$	-132 ± 2	420
HO CH_2CH_2CN	-136 ± 2	370
$MeOOCCH_2CN$	-130 ± 3	460
$CH_2{=}CHCH_2CN$	-133 ± 1	166
$CH_2{=}CHCN$	-124 ± 1	110
PhCN	-124 ± 2	390
$PhCH_2CN$	-133 ± 3	300
$CN^{\ominus}$ $K^{\oplus}$ (H_2O)	-99 ± 1[a]	52
MeNC	$-218 \pm 0{\cdot}5$	7·5[b]
	$-219{\cdot}6 \pm 0{\cdot}1$[c]	0·26
EtNC	$-203 \pm 0{\cdot}5$	8[b]
	$-205{\cdot}1 \pm 0{\cdot}1$[c]	0·31
Me_3CNC	-184[d]	..
EtSCN	-103 ± 2	140

[a] Referred to internal $NO_3^{\ominus}$.

[b] Apparent width if no effort to maintain high-resolution conditions is made; actually the signals display a multiplet pattern due to spin-spin coupling.

[c] High-resolution, field-lock ^{14}N spectra, external CH_3NO_2 reference; data from ref. 7, referred to internal TMS, recalculated by assuming -218 for MeNC.

[d] Double resonance method; data from ref. 64.

The nitrogen chemical shift of the $CN^{\ominus}$ ion is to high frequency of that observed both for nitriles and isonitriles. It should be mentioned that the difference between MeCN and $CN^{\ominus}$ of about 38 p.p.m. is much larger than the value of 5 p.p.m. reported by Bramley, Figgis and Nyholm[109] in their study of transition metal complexes.

E. Cyanates, isocyanates, isothiocyanates and azides

A few ^{14}N chemical shifts have recently been reported[48, 226] for simple molecules in these groups and their corresponding anions. There is an obvious difference between the ^{14}N chemical shifts of cyanates and isocyanates (Table XII). This difference has been used to indicate the type of bonding occurring in complexes of the $NCO^{\ominus}$ ion.[226] (Section VI). The nitrogen resonance of alkyl isocyanates occurs at a very low frequency (about −350 p.p.m. from nitromethane), whilst that of the alkyl isothiocyanates is found at about −280 p.p.m. Simple alkyl azides give three distinct ^{14}N signals corresponding to the three non-equivalent nitrogen atoms in the molecule. The trends observed in the shifts for molecules of the type R–N=X=Y are similar to those found in nitro-

TABLE XII

Nitrogen chemical shifts of some cyanates, isocyanates, isothiocyanates and azides.[48] All shifts from ^{14}N data are referred to nitromethane or KNO_3 as internal standard unless stated otherwise

Substance	Chemical shift p.p.m.	Half-height width Hz
EtOCN	-222 ± 1[a]	45
PhOCN	-208[b]	
n-PrNCO	-346 ± 1[a]	70
Ph–NCO	-330 ± 3[a]	50
H–NCO (ether)	-351 ± 2[a]	35
MeNCO	$-363 \pm 0{\cdot}5$	50
EtNCO	-346 ± 1	72
$(NCO)^{\ominus}$ $K^{\oplus}$ (H_2O)	$-300 \pm 0{\cdot}5$	13
MeNCS	-291 ± 1	40
EtNCS	-273 ± 1	55
$(NCS)^{\ominus}$ $K^{\oplus}$ (H_2O)	-168 ± 1	147
MeN_3 (R–N)	-320 ± 1	101
(central)	$-128 \pm 0{\cdot}5$	17
(terminal)	$-170{\cdot}5 \pm 0{\cdot}5$	19
EtN_3 (R–N)	-305 ± 1	122
(central)	$-129{\cdot}5 \pm 0{\cdot}5$	22
(terminal)	$-167{\cdot}5 \pm 0{\cdot}5$	28
$N_3^{\ominus}Na^{\oplus}$ (central)	$-128 \pm 0{\cdot}5$	20
(terminal)	-277 ± 1	60

[a] Data taken from ref. 226, recalculated with respect to external $NO_3^{\ominus}$ from external KNCO.

[b] Data taken from ref. 121.

alkanes and isonitriles where the resonance is shifted to lower frequencies as the electronegativity of R increases. This effect is helpful in assigning the R–N resonance in the ^{14}N spectra of alkyl azides, whilst the shifts observed for the $N_3^{\ominus}$ ion make it possible to assign the remaining two nitrogen atoms.[48] The ^{14}N shifts of the corresponding anions are always at a higher frequency than those of the alkyl derivatives. This is in agreement with the direction of the shift for $NO_2^{\ominus}$ and $CN^{\ominus}$ relative to the corresponding alkyl derivatives.

F. Nitrogen heterocyclic compounds

Relatively little experimental work on nitrogen NMR of these compounds has been published in recent years.[45, 48] Most of the earlier data are found in the collection of Herbison-Evans and Richards[44] and in the work of Hampson and Mathias on hydroxyquinolines[65] and benzthiazoles.[67] The recent data are presented in Table XIII. An investigation

TABLE XIII

^{14}N chemical shifts of some heteroaromatic ring compounds. All shifts are referred to nitromethane as internal standard

Substance	Chemical shift p.p.m.	Half-height width Hz	Reference
Pyridine	-68 ± 2	260	48
Pyridinium ion	-181 ± 1	20[a]	48
Quinoline	-71 ± 3	650	48
Quinolinium ion	-185 ± 2	50[a]	48
Isoquinoline	-68 ± 4	680	48
Isoquinolinium ion	-188 ± 2	55[a]	48
2-Aminopyridine	-128 ± 4	650	45
3-Aminopyridine	-88 ± 4	680	45
4-Aminopyridine	-105 ± 4	680	45

[a] Doublet, J(N–H) = 68 ± 1 Hz.

of the possible hydrogen-bonding effects on the ^{14}N resonance of pyridine has shown[48] that, contrary to earlier reports,[98] there is hardly any significant effect on the shift, but the signal width is influenced (Table XIV).

The nitrogen chemical shift difference between pyridine and the pyridinium ion measured by a uniform internal reference method, and

based on a spectrum of the ion which reveals a doublet,[73] thus excluding any significant contribution to the shift from signal averaging arising from chemical exchange, is found to be 113 ± 2 p.p.m. (Table XIII).

TABLE XIV

Solvent effects on the pyridine ^{14}N resonance[48]

	Chemical shift from internal CH_3NO_2 p.p.m.	Half-height width Hz
Pyridine + DMF	-68 ± 2	260
Pyridine + DMF + $CHCl_3$ (2:1:2) mole ratio	-68 ± 2	275
Pyridine + DMF + MeOH (2:1:2)	-73 ± 2	320
Pyridine + DMF + MeCOOH (2:1:2)	-70 ± 4	550

Earlier values of 131 ± 10 p.p.m.[30] and 116 ± 5 p.p.m.[44] have been reported. This shift has been subject to several theoretical considerations[48,180,186,203] (Section II).

G. Amides and related compounds

The ^{14}N resonance signals of amides and thioamides are usually quite broad. Systematic investigations of their chemical shifts are based on double-resonance methods.[63,66] This work has already been reviewed.[189] The characteristic range of amide nitrogen shifts is -240 to -285 p.p.m. to low frequencies of $NO_3^{\ominus}$, and -210 to -240 p.p.m. for thioamides. Recently, the investigations have been extended to include ureas and thioureas.[72] The corresponding ^{14}N signals occur at lower frequencies than those of amides and thioamides respectively. The introduction of a phenyl group on a nitrogen atom in ureas, thioureas, amides and thioamides results in a high frequency resonance shift. The effect of *N*-alkylation is negligible with methyl groups, but with the ethyl and larger groups it is found to be about 15 p.p.m. to high frequencies. The values of the chemical shifts are given in Table XV. Kamei[74,227] has reported solvent effects on the ^{14}N shifts of formamides measured by double-resonance techniques from their proton spectra (Table XVI). These solvent effects are attributed to a hydrogen bonding interaction which involves the carbonyl oxygen atom of the formamide grouping.

TABLE XV

^{14}N chemical shifts of some amides,[63] thioamides,[66] ureas[72] and thioureas.[72] All shifts are referred to ($NO_3^{\ominus}$) as external standard

Substance	Chemical shift (p.p.m. ± 2)	
	NH_2	NH
$HCONH_2$	−268	
$MeCONH_2$	−270	
$EtCONH_2$	−273	
n-$PrCONH_2$	−272	
i-$PrCONH_2$	−273	
$CH_2ClCONH_2$	−279	
$CHCl_2CONH_2$	−281	
CCl_3CONH_2	−283	
$PhCH_2CONH_2$	−274	
$Ph_2CHCONH_2$	−273	
$CH_2{=}CHCONH_2$	−276	
$PhCH{=}CHCONH_2$	−277	
$PhCONH_2$	−282	
MeCONHMe		−269
MeCONHEt		−253
MeCONHPr-*n*		−247
MeCONHBu-*n*		−249
EtCONHMe		−270
HCONHMe		−264
HCONHEt		−249
HCONHPh		−235
MeCONHPh		−243
EtCONHPh		−244
PhCONHPh		−252
$MeCSNH_2$	−239	
$PhCH_2CSNH_2$	−229	
$PhCSNH_2$	−239	
MeCSNHPh		−211
PhCSNHPh		−217
$PhCSeNH_2$	−235	
NH_2CONH_2	−299	
$MeNHCONH_2$	−303	−303
MeNHCONHMe		−305
$EtNHCONH_2$	−303	−283
EtNHCONHEt		−284
i-PrNHCONH Pr-*i*		−284
n-$BuNHCONH_2$	−306	−284
$PhNHCONH_2$	−305	−275
PhNHCONHPh		−270
NH_2CSNH_2	−267	
$MeNHCSNH_2$	−272	−270
MeNHCSNHMe		−275
$EtNHCSNH_2$	−275	−252
n-$PrNHCSNH_2$	−276	−250
$PhNHCSNH_2$	−272	−250
PhNHCSNHPh		−250
NH_2CSeNH_2	−259	
$PhCSeNH_2$	−235	

TABLE XVI

Solvent effects on the ^{14}N chemical shifts of some formamides

Substance	Chemical shift from external $NO_3^{\ominus}$ (p.p.m.) Neat	Acetone inf. dilution	Methanol inf. dilution
$HCONH_2$	$-265{\cdot}5 \pm 0{\cdot}4$	-274 ± 2	$-268 \pm 1{\cdot}5$
HCONHMe	$-266{\cdot}4 \pm 0{\cdot}7$	-272 ± 2	$-267 \pm 1{\cdot}5$
HCONHEt	$-247{\cdot}1 \pm 0{\cdot}7$	-253 ± 2	$-245 \pm 1{\cdot}5$
$HCONMe_2$	$-272{\cdot}3 \pm 0{\cdot}5$	$-273 \pm 1{\cdot}5$	$-264 \pm 1{\cdot}5$
$HCONEt_2$	$-246{\cdot}5 \pm 0{\cdot}5$	$-247 \pm 1{\cdot}5$	$-237 \pm 1{\cdot}5$

H. Amines and ammonium ions

Recently, a systematic study of the ^{14}N chemical shifts of amines and ammonium ions has been published.[45] The resonance signals of alkylamines occur at -320 to -380 p.p.m. from internal CH_3NO_2, while the resonances of the corresponding ammonium ions are found at higher frequencies by 5 to 30 p.p.m. There is a regular shift of the ^{14}N resonance to higher frequencies as the alkyl groups are changed in the order H < Me < Et < *i*-Pr < *t*-Bu.

This occurs both in the amines and the alkylammonium ions, and is analogous to the trend observed for nitroalkanes, isonitriles, isocyanates, isothiocyanates and azides. There is also a high frequency shift upon increasing the number of alkyl groups attached to the nitrogen atom of amines and ammonium ions. The order of ^{14}N shifts in alkylamines is quite different[45] from that expected from increases in the wavelength of the lowest energy n–σ^* transition in their electronic spectra. The experimental data are presented in Tables XVII and XVIII. The results for neat amines are essentially the same as those obtained in dioxane solutions so that only the former are given in Table XVII. There is an appreciable difference in the shifts for aqueous NaOH solutions of alkylamines and those for neat amines or for solutions in dioxane. One should note that the shifts quoted in Table XVII are in many instances different from the early data quoted by Herbison-Evans and Richards.[44]

The nitrogen resonance signals of aromatic amines are shifted to high frequency of the signals of alkylamines (Table XIX). It is interesting that there is a low-frequency shift of the anilinium ion resonance compared to that of neat aniline. This is in the opposite direction to the shifts observed for alkylammonium ions relative to their parent amines.

Solvent effects on the ^{15}N chemical shift of ammonia, referred to

TABLE XVII

^{14}N chemical shifts of some amines.[45] All shifts are referred to nitromethane or KNO_3 as internal standard

Substance		Chemical shift p.p.m.	Half-height width Hz
NH_3	neat	$-383 \pm 0{\cdot}5$	22
	H_2O, NaOH	-375 ± 1	110
$MeNH_2$	neat	-378 ± 1	65
	H_2O, NaOH	-370 ± 2	350
$EtNH_2$	neat	-355 ± 1	70
	H_2O, NaOH	-351 ± 2	350
n-$PrNH_2$	neat	-359 ± 1	85
n-$BuNH_2$	neat	-359 ± 2	200
i-$PrNH_2$	neat	-334 ± 1	100
Cyclohexylamine	neat	-337 ± 1	185
t-$BuNH_2$	neat	-319 ± 1	98
	H_2O, NaOH	-316 ± 3	270
Me_2NH	neat	-371 ± 1	98
	H_2O, NaOH	-362 ± 2	400
Me_3N	neat	-365 ± 1	110
	H_2O, NaOH	-362 ± 2	400
Et_2NH	neat	-332 ± 1	180
Et_3N	neat	-327 ± 2	320
n-Bu_2NH	neat	-351 ± 3	450
$CH_2{=}CHCH_2NH_2$	neat	-360 ± 1	100
Benzylamine	neat	-356 ± 2	220
$H_2NCH_2CH_2NH_2$	neat	-363 ± 1	160
$H_2N(CH_2)_4NH_2$	neat	-360 ± 1	235
$MeCH(NH_2)CH_2NH_2$	neat	-354 ± 2	285
$HOCH_2CH_2NH_2$	neat	-364 ± 5	900

gaseous NH_3, have been investigated and discussed by Litchman, Alei and Florin.[136] The shift of liquid ammonia is found to be 15·9 p.p.m. to high frequencies of that for gaseous ammonia. The same authors[137] have recently found small isotope shifts in the ^{15}N resonance of ammonia upon deuterium substitution, $^{15}NH_3$ 0 p.p.m., $^{15}NH_2D$ $-0{\cdot}029 \pm 0{\cdot}002$ p.p.m. and $^{15}NHD_2$ $-0{\cdot}053 \pm 0{\cdot}003$ p.p.m. The effects of solvent interaction and hydrogen-bonding on the ^{15}N chemical shifts of aniline, methylamine, *N*-methylacetamide, trimethylamine and quinoline have been examined by Paolillo and Becker[179] by using heteronuclear double resonance. The results, which were originally referred to internal TMS, are given in Table XX after recalculation to the scale used in Table XVII

TABLE XVIII

^{14}N chemical shifts of some ammonium ions.[45] All shifts are measured in aqueous HCl and referred to nitromethane as internal standard

Ion	Chemical shift p.p.m.	Half-height width Hz
$NH_4^{\oplus}$	$-354{\cdot}5 \pm 0{\cdot}5$	5[a]
$MeNH_3^{\oplus}$	-351 ± 1	30[b]
$Me_2NH_2^{\oplus}$	-348 ± 1	40[c]
$Me_3NH^{\oplus}$	-334 ± 1	30[d]
$Me_4N^{\oplus}$	$-333{\cdot}5 \pm 0{\cdot}5$	6·5
$EtNH_3^{\oplus}$	-336 ± 1	40[b]
$Et_2NH_2^{\oplus}$	-320 ± 1	50[c]
$Et_3NH^{\oplus}$	-314 ± 1	50[d]
$Et_4N^{\oplus}$	$-311 \pm 0{\cdot}5$	10
t-$BuNH_3^{\oplus}$	-314 ± 1	60
$(NH_3CH_2CH_2NH_3)^{2\oplus}$	-342 ± 2	90
$HONH_3^{\oplus}$	-293 ± 5	500
$NH_3^{\oplus}SO_2^{\ominus}$	-285 ± 2	60

[a] A quintet. [b] A quartet. [c] A triplet. [d] A doublet.

TABLE XIX

Nitrogen chemical shifts of some aromatic amines

Substance	Solvent	Chemical shift p.p.m.	Reference
Aniline	neat	-319 ± 3[a]	45
		-324 ± 3[b]	129
N-Methylaniline	neat	-320 ± 4[a]	45
p-Nitroaniline	acetone	-306[c]	168
p-Bromoaniline	acetone	-320[c]	168
p-Iodoaniline	acetone	-317[c]	168
p-Toluidine	acetone, $CDCl_3$	-323[c]	168
Anilinium ion	CF_3COOH	-330[c]	168
2-Aminopyridine (NH_2)	acetone	-315 ± 4[a]	45
3-Aminopyridine (NH_2)	acetone	-326 ± 4[a]	45
4-Aminopyridine (NH_2)	acetone	-317 ± 4[a]	45

[a] Measured from nitromethane as internal reference; ^{14}N data.

[b] Data for ^{15}N, measured from external 8·57M HNO_3, and recalculated approximately to the nitromethane scale.

[c] Double-resonance ^{15}N data; referred to TMS, recalculated to the nitromethane scale by setting the shift for aniline at − 320 p.p.m. from nitromethane.

TABLE XX

Solvent effects on some ^{15}N chemical shifts[179]

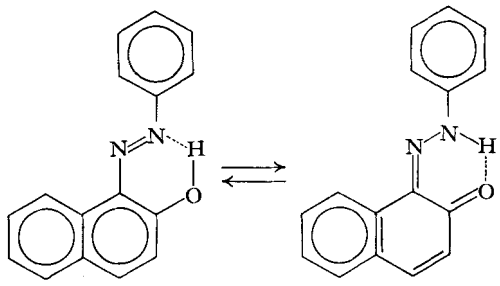
Substance	Solvent	Chemical shift (p.p.m.)
^{15}N-Aniline	C_6D_{12}	−327·2
	CCl_4	−325·0
	dioxane	−326·6
	DMF	−323·0
	pyridine	−322·0
	DMSO	−319·5
$Me^{15}NH_2$	gaseous	−383·4
	neat	(−378·0) (assumed, ref. 45)
	C_6D_{12}	−376·5
	CCl_4	−374·2
	DMF	−376·3
	DMSO	−374·3
$^{15}NMe_3$	C_6D_{12}	−365·8
	$CDCl_3$	−362·3
	CD_3OD	−361·5
^{15}N-Quinoline	C_6D_{12}	−60·6
	$CDCl_3$	−71·1
	CD_3OD	−83·4
$Me^{15}NHCOMe$	CCl_4 0·1M	−276·1
	CCl_4 0·25M	−274·8
	DMSO 0·25M	−274·6
	neat	−268·3

by setting the shift of neat methylamine at −378·0 p.p.m. from nitromethane. There seems to be a contribution to the solvent shifts from hydrogen bonding, but other less well defined solvent effects must also play an important role.

I. Miscellaneous nitrogen chemical shifts

Tautomerism in a series of 1-phenylaza-2-hydroxynaphthalenes has been investigated[71] by ^{14}N NMR data obtained from the corresponding proton spectra in a double resonance experiment. The chemical shifts have been interpreted in favour of a weighted mean average of the shifts of the hydroxyazo and hydrazone tautomers (**6**). The shifts of derivatives substituted at the phenyl ring have been compared with those of two reference substances, azobenzene (+129 ± 6 p.p.m. from $NO_3^{\ominus}$) and 10-(4-methoxyphenylaza)-9-phenanthrol (−176 ± 7 p.p.m.).

Tautomeric equilibria of hydroxypyridine,[44] hydroxyquinoline,[65] hydroxy- and mercapto- benzthiazole[67] systems have also been investi-



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gated by means of ^{14}N chemical shifts. A detailed discussion of these may be found in a previous review.[189]

Some nitrogen chemical shifts for the nitrilium ions (Table XXI) have been measured by Olah and Kiovsky[91] using the INDOR method. The

TABLE XXI

Nitrogen chemical shifts of some nitrilium ions

Substance	Chemical shift, p.p.m. Referred to $NH_4^{\oplus}$	Recalculated to $NO_3^{\ominus}$
$(HC{\equiv}{}^{15}NH)^{\oplus}$	119·4	−235·1
$(MeC{\equiv}{}^{15}NH)^{\oplus}$	115·6	−238·9
$(MeC{\equiv}{}^{14}NMe)^{\oplus}$	107	−247·5

resonance of the ions is remarkably shifted to lower frequencies with respect to the parent cyanides. There is also a small but definite effect on the shift of methyl substitution. Similar shifts have been observed for pyridine and related compounds[44,48] and for *trans*-azobenzene[129] (Table XXII).

TABLE XXII

Nitrogen chemical shifts of trans-azobenzene and some related compounds

Substance	^{15}N Chemical shift (p.p.m.) Recalculated to $NO_3^{\ominus}$
trans-Azobenzene	+127
Conjugate acid of *trans*-azobenzene	−23
Azoxybenzene	−55 −59

VI. SOME EXAMPLES OF NITROGEN CHEMICAL SHIFTS IN INORGANIC MOLECULES

^{14}N chemical shift and line-width differences, dependent upon type of bond formation, have been used as a means of studying inorganic complexes. The donor-acceptor interaction between nitrobenzene, pentafluoronitrobenzene pyridine and some substituted pyridines on the one hand and some boron compounds on the other have been studied by means of ^{14}N NMR spectroscopy.[111,112] In the case of the nitrobenzenes the ^{14}N shifts do not show any simple correlation with the donor properties, although the line-widths reflect the acceptor properties of some boron halides. This has been interpreted in favour of the formation of a bond between one oxygen atom of the nitro group in the nitrobenzenes and the boron atom of the boron halides.[112] In the pyridine-borane complexes the ^{14}N signal shows a low-frequency shift which is unexpectedly smaller than in the pyridine hydrochlorides.[112] This could signify that the paramagnetic contribution to the nitrogen screening tensor, σ_N^{para} is greater in the former than in the latter case.

A. Some diamagnetic metal complexes

The effect on the ^{14}N chemical shift, of bonding to a diamagnetic metal ion, has been studied for ammonia,[23,109,123] nitrite ion,[109] isocyanide ion,[228] cyanide ion,[100,109,123] nitrate ion,[24] ethylene diamine,[123] dipyridyl,[123] some amino acids,[123] nitric oxide,[109] thiocyanate,[97] isocyanate,[226] cyanate[226] and fulminate ions.[121] A range of chemical shifts in excess of 700 p.p.m. has been reported. The chemical shift differences have been discussed in terms of changes in σ_N^{para} upon complex formation.[109] The low-frequency shift observed for the complexes of ammonia and the nitrite ion are found to be essentially independent of the lowest energy electronic absorption maxima. This is thought to arise from the constraint placed upon the ligand's non-bonding pair of electrons when a metal-nitrogen bond is formed. Effectively the pair of electrons are localised between the metal and nitrogen atoms and therefore make a smaller contribution to σ_N^{para} which is correspondingly decreased resulting in a shift to lower frequencies. The ^{14}N shift for the cyanide complexes is to high frequency of the signal given by the cyanide ion. By comparing complexes with the same symmetry the shift is found to depend upon the wavelength of the transitions to the lower-lying excited electronic states of the complexes. This is accounted for in terms of metal-carbon bonding and subsequent *d* electron delocalisation into the π molecular orbital set of the ligand. Electronic transitions can occur between the resulting orbitals which lead to an increase in σ_H^{para} and a consequent high-frequency ^{14}N shift.

In some tris complexes of Co(III) with amino acids the ^{14}N signal for the *trans* isomer occurs significantly to low frequency of that shown by the *cis* isomer.[123] The reduction in symmetry from C_3 to C_1 in going from the *cis* to *trans* isomer could account for this in terms of changes in the composition of the molecular orbitals of the complex.[123] However, a more quantitative account is desirable.

In thiocyanate complexes both low- and high-frequency ^{14}N shifts have been observed and attributed to the formation of metal-nitrogen and metal-sulphur bonds respectively.

The small high-frequency shifts observed in some metal fulminate complexes supports the formulation of M–CNO bonding rather than the formation of a metal-nitrogen bond.[121] A comparison of the positions of the ^{14}N signals from molecules not containing metal-ligand bonds demonstrates the differences in electronic environment of the ^{14}N nucleus in –CNO, –OCN and –NCO compounds.[121,226] With respect to nitrate ion, the ^{14}N shifts are respectively ~ -170 p.p.m., ~ -210 p.p.m. and -350 p.p.m. to low frequency (Section V E). Following the trend found by Kent and Wagner[51,181] for some linear triatomic molecules and ions, this order suggests an increasing π-electron density on the nitrogen atom. In the case of some metal nitrates the ^{14}N resonance position of the nitrate group is the same as in ammonium nitrate supporting the formulation of ionic structures.[24] The ^{14}N peak for $Cu(NO_3)_2$ has a large low-frequency concentration-dependent shift which is consistent with its paramagnetic environment.[24,229]

Nitric oxide has a thermally accessible paramagnetic state which raises difficulties in comparing its ^{14}N shifts with those of diamagnetic ligands. However, it seems likely that both electronic constraint (low frequency) and electronic delocalisation (high frequency) effects operate in complexes of nitric oxide.[108]

^{13}C NMR data on some metal carbonyl complexes indicate that these two effects largely cancel each other out such that the ^{13}C resonance signals of free and complexed CO occur close together.[109] Since the metal-ligand bonding in metal carbonyls and nitrosyls is very similar it is anticipated that the ^{14}N shift between free and complexed $NO^{\oplus}$ will be small. The large low-frequency shifts > -600 p.p.m. observed for the ^{14}N signals of some metalnitrosyl complexes, compared to the signal from $NO^{\oplus}$, have been taken to indicate the absence of formal $NO^{\oplus}$ in these complexes.[121]

B. Some paramagnetic metal complexes

In a paramagnetic environment large chemical shifts and broad NMR lines are expected.[229] The shifts may be to either high or low frequency.

In general the shifts may arise either from the presence of electron-spin density at the nucleus concerned (contact shifts) or from anisotropy in the electronic g tensor (pseudo-contact shifts).[229] The line-width arises from the rapidly fluctuating local magnetic fields produced by the unpaired electrons. Since many ^{14}N resonance signals are quadrupole broadened it is not anticipated that ^{14}N nuclei will be as useful in studying paramagnetic species as is the case for spin-half nuclei. However, in some kinetically inert paramagnetic metal hexacyanides the ^{14}N line-width appears to be predominantly dependent upon quadrupolar rather than rapid electron-spin relaxation.[100, 102, 230] Under these conditions it follows from equation (15) that

$$\frac{3}{8}\left(1+\frac{\epsilon^2}{3}\right)\left(\frac{eq\,eQ}{\hbar}\right)^2\tau_Q > a_N^2\,\tau_e \qquad (28)$$

where a_N is the hyperfine interaction constant and τ_e is the correlation time for the contact interaction. Possible exceptions are $K_3Cr(CN)_6$ and $K_4Mn(CN)_6$ where the two terms are probably of similar magnitudes. In the metal hexacyanides the ^{14}N shifts are attributed to the contact interaction process.[100, 102] A series of strong crystal field complexes of Cr(III) and some other metal ions with the d^5 configuration have been studied by ^{14}N NMR spectroscopy.[117] With the exception of the hexacyanide, the contact interaction contribution to the ^{14}N shift, is reported to be negligible. In an attempt to attribute the ^{14}N shifts to the pseudo-contact process the ESR data of some complexes of d^5 metal ions have been analysed. However, the magnitude of the pseudo-contact contribution required to account for the ^{14}N shift is found to be too large for a ready explanation on the basis of a contribution arising solely from the metal's electrons. An additional term is required in the pseudo-contact shift expression to account for the contribution from the ligand's electrons.[231]

The observed high-frequency ^{14}N shifts for a series of Co(II) and Ni(II) complexes with aliphatic and aromatic bases have been interpreted in favour of contact shifts arising from the delocalisation of positive electron-spin density from the metal to the nitrogen atom.[104, 110, 116, 232]

Ion-association between the diamagnetic tetrabutyl ammonium and phosphonium cations on the one hand and the paramagnetic anions, $[(C_6H_5)_3PCoI_3]^{\ominus}$, $[(C_6H_5)_3PNiI_3]^{\ominus}$ and $[Fe(CN)_6]^{3\ominus}$ on the other has been studied by means of ^{14}N, ^{1}H and ^{31}P NMR spectroscopy.[113, 122, 126, 233] The proton spectra of the cations have been interpreted on the basis of a pseudo-contact interaction between the unpaired electrons on the metal and the tetrabutyl ammonium protons.[233]

However, it has been argued that the high-frequency shifts reported for the ^{14}N and ^{31}P signals favour the direct transfer of positive spin density from the metal to the nitrogen and phosphorus atoms of the cation rather than a pseudo-contact interaction.[113,122] The direct spin transfer mechanism predicts that all of the protons in the cation will experience a low-frequency shift irrespective of which paramagnetic anion is present in solution. The fact that the proton shifts in the tetrabutylammonium cation are in the opposite sense in the presence of $[(C_6H_5)_3PCoI_3]^{\ominus}$ and $[(C_6H_5)_3PNiI_3]^{\ominus}$ invalidates the direct spin transfer mechanism and supports the pseudo-contact interaction.[233] Recent ^{14}N data has been interpreted in favour of the pseudo-contact model with an additional small contact interaction between the anion and cation.[126] This is thought to arise from a weak covalent interaction between the anion and cation in the ion pair.

The kinetics of electron transfer between the paramagnetic ferricyanide and diamagnetic ferrocyanide ions has been followed by means of ^{14}N NMR studies.[101] The ^{14}N signals from both the diamagnetic and paramagnetic species are of comparable width and the changes in their shapes resulting from electron exchange are the same as those of a simple collapsing doublet.

^{14}N NMR has been used in kinetic studies of ammonia exchange between nickel ammine complexes and ammonia both in aqueous and anhydrous ammonia solutions.[103] This system has also been studied in aqueous ammonia by means of proton NMR data, showing that the ^{14}N and proton results give similar exchange rates.[234] Hence, it is concluded that neutral ammonia is being exchanged homogeneously with the $Ni(NH_3)_6^{2\oplus}$ ion and that the individual protons exchange at a much slower rate. A similar conclusion is reached from the ^{14}N and proton data on the liquid ammonia solutions of $Ni(NH_3)_6^{2\oplus}$.[106,235,236] Some of the kinetic data obtained from proton studies do not agree with that provided by the ^{14}N results,[106] however, more recent proton measurements confirm the predictions made from the ^{14}N data.[235,236]

Ligand exchange studies involving ethylenediamine,[108] thiocyanate,[105,237] acetonitrile[238] and pyridine[239] with Cu(II), Ni(II) and Co(II), Mn(II) and Co(II) respectively have also been performed with ^{14}N NMR spectroscopy. By means of the expressions derived by Swift and Connick,[229] to describe the broadening of the NMR lines of nuclei in dilute solutions of paramagnetic ions in the presence of chemical exchange, the kinetic parameters concerning this exchange are obtained. ^{14}N nuclear relaxation measurements, as a function of temperature, for acetonitrile solutions of Mn(II) perchlorate have been reported.[238] The kinetic parameters for the exchange of acetonitrile from the first co-

ordination sphere of Mn(II) are a first-order rate constant $K_1 = (1{\cdot}2 \pm 0{\cdot}3) \times 10^7$ sec^{-1} at 25°C, $\Delta H^{\ddagger} = 7{\cdot}25 \pm 0{\cdot}25$ kcal/mol and $\Delta S^{\ddagger} = -1{\cdot}8 \pm 0{\cdot}8$ e.u. In the case of $Copy_4Cl_2$ the mean lifetime of pyridine attached to the Co(II) ion is $(1{\cdot}5 \pm 0{\cdot}2) \times 10^{-7}$ at 25°C, with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the exchange being $13{\cdot}2 \pm 0{\cdot}5$ kcal/mol and 17 ± 2 e.u. respectively.[239] The equilibrium constant K, where

$$K = \frac{[Copy_2Cl_2][py]^2}{[Copy_4Cl_2]} \tag{29}$$

has been determined from ^{14}N chemical shift data to be $2{\cdot}3 \pm 1{\cdot}2$ M^2 at 38°C. The corresponding values of ΔH and ΔS for the equilibrium are $13{\cdot}0 \pm 0{\cdot}9$ kcal/mol and $43{\cdot}4 \pm 2{\cdot}2$ e.u., respectively.[239]

In the case of aqueous cobalt(II) thiocyanate solutions the use of both ^{14}N and ^{17}O chemical shift data, allow the numbers of $NCS^{\ominus}$ and H_2O species in the first coordination shell of Co(II) to be uniquely determined.[237]Over a concentration range of 0·0 to 7·98 M in NaNCS the complex species found are $[Co(H_2O)_6]^{2\oplus}$, $[Co(NCS)(H_2O)_5]^{\oplus}$, $[Co(NCS)_2(H_2O)_2]$ $[Co(NCS)_3(H_2O)]^{\ominus}$ and $[Co(NCS)_4]^{2\ominus}$. The change from six- to four- coordination has been previously found to occur at the neutral point in going from cationic to anionic species in aqueous solutions of Cobalt(II) chloride.[238]

The exchange of $NCS^{\ominus}$ between $[Co(NCS)_2(H_2O)]$ or $[Co(NCS)_3(H_2O)]^{\ominus}$ and bulk solution is slow and the kinetic data requires the presence of a bimolecular term dependent upon $[NCS^{\ominus}]$. The rate of exchange of $NCS^{\ominus}$ with $[Co(NCS)_4]^{2\ominus}$ is too rapid to provide a meaningful rate constant. In the case of $[Co(NCS)(H_2O)_5]^{\oplus}$ the overall low concentration of $NCS^{\ominus}$ makes measurements very difficult and reliable kinetic parameters are not available. It is significant that experiments using highly enriched ^{15}NCS do not provide better results.[237]

In the tetrahedral thiocyanate species the fraction of unpaired 2*s* electron on the nitrogen atom is 0·022, which may be compared with a value of 0·023 for four planar nitrogen atoms in bis-(ethylenediamine) Cu(II). The larger degree of π bonding in the tetrahedral Co(II) species might be expected to produce a larger amount of unpaired 2*s* spin density on the nitrogen atom than in the square planar Cu(II) complex. The reduction in 2*s* spin density could imply either that the π bonding contributes a negative factor to the 2*s* spin density or that some of the thiocyanate ions are bonded to cobalt through sulphur. More experiments are required to decide between these two possibilities.

The temperature dependence of the Knight shift of the sodium-ammonia system has been studied by means of ^{14}N and ^{23}Na NMR experiments and kinetic data have been derived.[38] The observed spin

densities are not accounted for on the basis of the species $Na.(NH_3)_6$. In order to obtain more accurate values of the spin density it appears to be necessary to determine the amount of orbital expansion occurring due to the dielectric medium.[38]

C. Solid state studies

Using potassium azide, Forman reported the first ^{14}N quadrupole coupling constants in solids to be determined by ^{14}N NMR[240] (Section III). The ^{14}N spectrum for an arbitrary orientation of the single crystal specimen consists of eight lines. These may be separated into two groups of four lines each with the intensity of one group corresponding to the equivalent end nitrogen atoms, being twice that of the other. By rotating the crystal until each group consists of only two lines the relative orientations of the molecular and crystallographic axes are found. In this way Forman[240] has shown unambiguously that the azide groups lie along [110] axes and are not bent. The interpretation of X-ray diffraction data has not unambiguously supported this structure.

The single crystal ^{14}N spectra of uranyl nitrate hexahydrate and rubidium uranyl nitrate have been reported.[114] From the ^{14}N data the orientation of the nitrate groups with respect to the crystallographic axes has been determined. In the case of uranyl nitrate hexahydrate the results have been used to decide between conflicting crystal structures. It has also been shown that the previously reported two crystal "habits" of rubidium uranyl nitrate are not different habits but different crystal structures. The ^{14}N data obtained from powdered samples of the anhydrous nitrates of Zn(II), Cd(II) and Hg(II) show that the nitrate species in the zinc and mercury compounds are bidentate whilst in the case of cadmium these are most probably ionic.[114]

^{14}N data have been reported for the mononitrides TbN,[241] TmN,[241] ThN[242] and UN[119] which exist in sodium chloride type of lattice structures. Recently ^{15}N data have been obtained for UN.[243] The ^{14}N NMR data have been interpreted in terms of Knight shifts and linewidths. These are independent of temperature and applied magnetic field in the spectra of the diamagnetic nitrides, but depend upon both of these experimental variables in the case of paramagnetic UN.

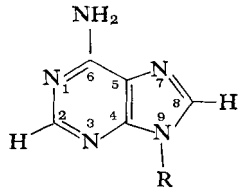
On account of the low sensitivity and saturation effects it may frequently not be possible to observe the pure ^{14}N NQR spectrum of a sample. However, by means of dispersion mode operation the ^{14}N NMR spectrum is usually available.[240] Consequently ^{14}N NMR is potentially a more powerful tool than NQR in studying phase transitions, crystal structure, symmetry and other solid state data which reflect changes in nuclear quadrupole interactions. The only requirement is that sufficiently

large and well-defined single crystals of the material be available for NMR investigations.

The range of chemical information available from ^{14}N NMR studies on metal compounds is encouraging and demonstrates that, in spite of its quadrupole moment and rather low sensitivity, the ^{14}N nucleus is worthy of serious consideration as an NMR probe.

D. ^{15}N data on metal compounds

So far little work on metal compounds using ^{15}N NMR has been reported. Evidence has been presented from ^{15}N data,[135] on labelled ATP, that $Mg^{2\oplus}$ does not complex with the nitrogen atoms of ATP whereas $Zn^{2\oplus}$ interacts with both the 6-amino nitrogen and the nitrogen in position 7 (**7**).



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The low-field 6-amino nitrogen shift produced by $Zn^{2\oplus}$ is the same as that observed for the amino group in glycine when it is complexed with $Mg^{2\oplus}$.

As mentioned previously (Sections VI B and VI C), ^{15}N data are available for some metal compounds which have already been studied by means of ^{14}N NMR.[237,243] In general it does not appear that the ^{15}N results on metal compounds, so far reported, provide a more detailed account of structure and reactivity than that available from ^{14}N data. An exception to this lies in the case of molecules which contain a number of different nitrogen environments. An example being that of metal binding to biologically interesting molecules. It is anticipated that this will prove to be an attractive field for ^{15}N NMR investigations in the near future.

VII. SPIN-SPIN COUPLING IN NITROGEN NMR

Spin-spin coupling involving nitrogen nuclei is much more readily observed for the ^{15}N isotope than for ^{14}N. Since ^{15}N nuclei possess a spin of 1/2 and no quadrupole moment, these give NMR spectral patterns similar to those arising from ^{1}H and ^{19}F interactions. Whilst a great deal of work in nitrogen NMR investigations has been devoted to the obser-

vation and interpretation of ^{15}N spin-spin interactions the study of ^{14}N coupling constants has been limited to those instances in which the quadrupole relaxation is slow (Section IV). The data obtained prior to 1968 have been discussed in an earlier review[189], hence only the recent work will be considered here.

Since the gyromagnetic ratios of ^{14}N and ^{15}N have opposite signs and different magnitudes (Section I), the corresponding coupling constants also differ in the same manner. A convenient way of introducing uniformity is to define a quantity called the reduced coupling constant, K(A–B) between nuclei A and B,

$$K(\text{A–B}) = \frac{2\pi}{\hbar\gamma_A\gamma_B} J(\text{A–B}) \tag{30}$$

where J(A–B) is the coupling constant and γ is the gyromagnetic ratio with the proper sign. One may calculate ^{14}N coupling constants using ^{15}N data, and vice versa, from equation (31).

$$J(^{14}\text{N–X}) = -0{\cdot}7129J(^{15}\text{N–X}) \tag{31}$$

Such procedures have been used in a study[5] of ^{14}N quadrupole relaxation where the required ^{14}N couplings were not experimentally accessible and were obtained from the corresponding ^{15}N data.

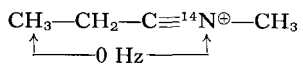
Nitrogen coupling constants are often designated with symbols which denote the number of intervening bonds between the nuclei in question, e.g., one-bond coupling, ^1J(N–H), ^1J(N–C), two-bond coupling, ^2J(N–H), etc.

Theoretical calculations of coupling constants[244] may be greatly improved, by using finite perturbation theory as suggested by Pople, McIver and Ostlund.[245] This theory may be readily extended to consider coupling constants involving nitrogen nuclei.

A. Nitrogen-14 coupling

The direct ^{14}N–H coupling was recently observed in the ^{14}N spectra of the pyridinium and related ions,[48] the value of ^1J(N–H) is 68 ± 1 Hz.

A number of ^{14}N coupling constants have been determined for nitrilium ions (**8** to **11**).[222] It is interesting that the two-bond couplings are larger than the three-bond couplings in these ions, contrary to the relative magnitudes of the coupling constants in alkyl isocyanides[61, 62, 64] and alkylammonium ions.[40, 41, 64, 79, 88]



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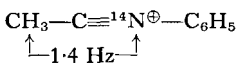

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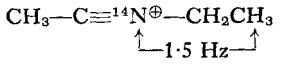

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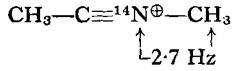

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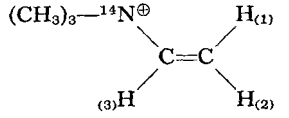
The signs and magnitudes of ^{14}N–H coupling constants in partially deuterated ammonium bromide[68] have been investigated by a variety of double-resonance methods including INDOR and spin tickling (**12**).

$NH_4^{\oplus}$, $NH_3D^{\oplus}$, $NH_2D_2^{\oplus}$, $NHD_3^{\oplus}$ $\quad J(^{14}N\text{–}H) = +52{\cdot}8$ Hz; $J(^{14}N\text{–}D) = +8{\cdot}1$ Hz; $K(N\text{–}H) = +60{\cdot}8 \times 10^{20}$ cm^{-3}; $K(N\text{–}D) = +61 \times 10^{20}$ cm^{-3}

12

No significant isotope effect on the coupling is found. Similar methods have been used for the ^{14}N coupling constants in trimethylvinyl ammonium bromide.[70] All three N–H couplings in the vinyl group are found to be positive (**13**).

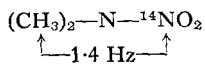


$J(^{14}N\text{–}H_1) = +2{\cdot}54$ Hz
$J(^{14}N\text{–}H_2) = +5{\cdot}59$ Hz
$J(^{14}N\text{–}H_3) = +3{\cdot}54$ Hz

13

Direct ^{14}N resonance measurement for the alkylammonium ions $MeNH_3^{\oplus}$, $Me_2NH_2^{\oplus}$, $Me_3NH^{\oplus}$, $EtNH_3^{\oplus}$, $Et_2NH_2^{\oplus}$ and $Et_3NH^{\oplus}$ have provided approximate values for the ^{14}N–H coupling constants of 50 ± 1 Hz. The proton and ^{14}N spectra of $NH_4^{\oplus}$ in ammonium sulphate dissolved in H_2SO_4 have been used as models for heteronuclear tickling experiments which have produced experimental coupling data in agreement with theoretical estimates.[75] The ^{14}N–H coupling in this sample is 53·0 Hz.

Detectable ^{14}N couplings are shown to exist in aliphatic nitramines[73,94] between the α-CH protons in the alkyl substituents and the nitrogen nucleus in the nitro group (**14** and **15**). In only two cases is it possible to



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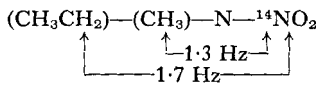

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measure the coupling constants from the proton spectra.[94] However, the coupling has been found, by double resonance methods in the other cases.[73] On the basis of chemical shift measurements the nitrogen nucleus involved is shown to be of the NO_2 group rather than of the

N–R group (**16** to **18**). The coupling becomes more pronounced if the proton spectra are measured at higher temperatures (Section IV). A very interesting study of the angular dependence of the three-bond ^{14}N–H coupling constant[95] has been carried out by analysis of the proton resonance spectra of 3,3-dimethylbutyl isocyanide and allyl isocyanide at various temperatures (**19** and **20**). The variation of the apparent N–H

$CH_3—O—{}^{14}NO_2$ (−2·75 Hz) **16**

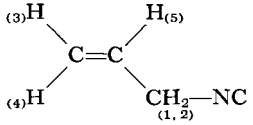
$CH_3—CH_2—O—{}^{14}NO_2$ (−2·75 Hz) **17**

$CH_3—C({}^{14}NO_2)_3$ (−1·8 Hz) **18**

$(CH_3)_3C—CH_2—CH_2—{}^{14}N{\equiv}C$

^3J(N–H)*trans* = 6·9 Hz ^3J(N–H)*gauche* = 0·7 Hz
^3J(N–H) = 1·275 → 1·694 Hz (− 12°C → +93°C)

19



^3J[N–$H_{(5)}$]*trans* = 4·9 Hz
^3J[N–$H_{(5)}$]*gauche* = 0·2 Hz

^2J[N–$H_{(1,2)}$] = − 1·97 → − 2·03 Hz (− 35°C → +62°C)
^3J[N–$H_{(5)}$] = 2·67 → 2·18 Hz (− 35°C → +62°C)

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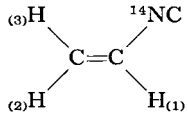


	C_2H_5OH	CCl_4	$(CH_3)_2SO$
^2J[N–$H_{(1)}$]	2·31 Hz	2·25 Hz	2·33 Hz
^3J[N–$H_{(2)}$]	6·28 Hz	6·19 Hz	6·31 Hz
^3J[N–$H_{(3)}$]	3·20 Hz	3·04 Hz	3·22 Hz

21

coupling with temperature has been used in the calculation of the coupling in single rotamers. Additionally, the proton spectrum of vinyl isocyanide yields the values of the ^{14}N–H coupling constants as shown in **21**. The data from this work and that on the angular dependence of ^{14}N coupling in ammonium ions[93] have been used in setting up an approximate relationship between $^3J(^{14}N–H)$ and the dihedral angle ϕ (Fig. 2). There appears to be a minimum value of the coupling constant at about 90° and two maxima at 0° and 180°.

Simple alkyl isocyanides have been the most thoroughly investigated group of molecules from the point of view of ^{14}N coupling to both ^1H and ^{13}C.[61, 62, 64, 96] The results are given in Table XXIII. The ^{14}N–H coupling constants in isonitriles and substituted ammonium ions are similar in both sign and magnitude. A discussion of these may be found in an earlier review.[189] In the case of methyl isocyanide the reduced

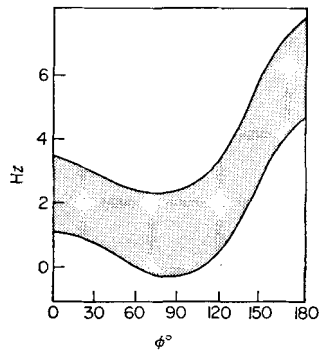


FIG. 2. Relationship between $^3J(^{14}N–H)$ and the dihedral angle ϕ for some vinyl isocyanides.

TABLE XXIII

^{14}N coupling constants in alkyl isocyanides in Hz

Molecule	^1J(N–C)	^1J(C–N)	^2J(C–N)	^2J(N–H)	^3J(N–H)
CH_3NC	$6{\cdot}5 \pm 0{\cdot}3$[a]	$+7{\cdot}0 \pm 1$[b]	..	$-2{\cdot}3 \pm 0{\cdot}1$[b]	..
CH_3CH_2NC	$5{\cdot}2 \pm 0{\cdot}3$[a]	$7{\cdot}3 \pm 0{\cdot}3$[a]	<1[a]	$-1{\cdot}9$[b]	$+2{\cdot}5$[b]
$(CH_3)_3CNC$	$5{\cdot}1 \pm 0{\cdot}3$[a]	$6{\cdot}7 \pm 0{\cdot}3$[a]	<1[a]	..	$+2{\cdot}0$[b]
CH_3CN	..	$+12{\cdot}5$[c]	..	..	..

[a] Ref. 96. [b] Ref. 62 and 64. [c] Ref. 31.

coupling constant for the coupling between singly bonded carbon and nitrogen nuclei is positive in agreement with theoretical predictions.[64] INDO molecular orbital calculations predict negative values of $J(N{\equiv}C)$ for isocyanide bonds and positive values for cyanides. Preliminary data from proton-decoupled ^{13}C spectra of some isocyanides appear to support this prediction.[96]

The ^{14}N spectrum of HNCO shows a doublet arising from ^{14}N–H coupling with $^1J(^{14}N–H) = 69 \pm 5$ Hz.

B. Nitrogen–15 coupling

Much more data is available on ^{15}N couplings than those involving ^{14}N. Most of the values of ^{15}N coupling constants have been obtained from proton spectra of ^{15}N-enriched molecules.

The ^{15}N couplings in hydrogen cyanide[162] and its protonated form[91] and other nitrilium ions[91] have recently been reported (22). The values

$HC^{15}N$	$^2J(^{15}N\text{–}H) = 8{\cdot}7 \pm 0{\cdot}1$ Hz
$(HCNH)^{\oplus}$	$^1J(^{15}N\text{–}H) = 134$ Hz
	$^2J(^{15}N\text{–}H) = 19{\cdot}0$ Hz
$(CH_3CNH)^{\oplus}$	$^1J(^{15}N\text{–}H) = 136$ Hz
	$^3J(^{15}N\text{–}H) = 2{\cdot}8$ Hz

22

of the $^1J(^{15}N\text{–}H)$ coupling constant for the nitrilium and methylnitrilium ions are in rather good agreement with the postulated relationship between the coupling constant and the *s*-character of the NH bond:[130]

$$2s = 0{\cdot}43J(^{15}N\text{–}H) - 6 \qquad (32)$$

giving 52 and 53% *s*-character, respectively.

Configurational assignments of the ^{15}N coupling constants have been made for several groups of molecules with restricted rotation around partial double bonds.[160, 161, 171, 172] In some *N*-nitrosamines,[160] where an equilibrium may exist (**23**), the *trans* $^{15}N\text{–}N\text{–}C\text{–}H$ coupling constants are found to be larger than the *cis* constants, where *trans* and *cis* denote the position of the group R relative to the oxygen atom, Table XXIV.

TABLE XXIV

$^{15}N\text{–}N\text{–}C\text{–}H$ coupling in N-nitrosamines, in Hz, taken from ref. 160

R_1, R_2	J_{cis}	J_{trans}
$PhCH_2$	0·5	2·1
Me	0·8	2·2
$PhCH_2$	0	2·4
Et	0·8	2·5
$PhCH_2$	0	3·1
Me_2CH	0	2·4
$PhCH_2$	0	..
Me_3C	..	..
$PhCH_2$	0	2·4
$PhCH_2$	0	2·4
PhMeCH	0	3·0
PhMeCH	0	3·0
Ph	..	..
Me	0·8	..

The same situation exists in *N*-nitrosohydrazines[161] (**24**) (Table XXV), in *N*-nitrosohydroxylamines[171] (**25**) (Table XXVI), as well as in alkyl nitrites (**26**)[172] (Table XXVII).

TABLE XXV

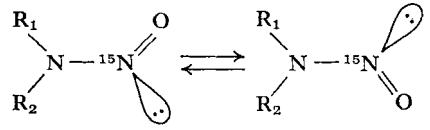
^{15}N–N–C–H coupling in N-nitrosohydrazines, in Hz, taken from ref. 161

R_1	R_2	R_3	J_{cis}	J_{trans}
$PhCH_2$	H	H	..	2·2
Me	$PhCH_2$	H	..	2·2
$PhCH_2$	Me	H	..	2·2
$PhCH_2$	Me	Me	0	2·2
PhMeCH	Me	Me	0	1·9

TABLE XXVI

^{15}N–N–C–H coupling in N-nitrosohydroxylamines, in Hz, taken from ref. 171

R_1	R_2	J_{cis}	J_{trans}
Me	Me	0·7	2·0
Me	$PhCH_2$	0·7	2·2
$PhCH_2$	$PhCH_2$	0	2·0
$PhCH_2$	Me	0	2·0
Et	$PhCH_2$	..	2·1
PhMeCH	Me	..	1·6
$PhCH_2$	H	..	2·6



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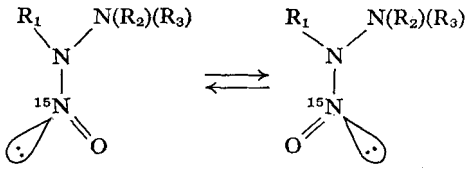

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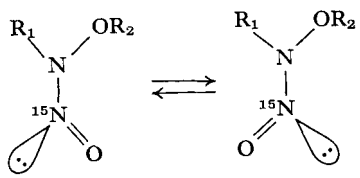

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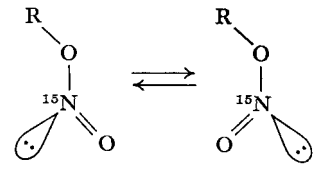

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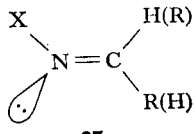
TABLE XXVII

^{15}N–O–C–H coupling in alkyl nitrites, in Hz, taken from ref. 172

R	J_{cis}	J_{trans}
$PhCH_2$	1·7	2·4
$PhCH_2CH_2$	1·8	2·3
PhMeCH	1·9	2·4
PhEtCH	2·1	2·1
$Me_3CCH_2CH_2$	1·7	2·4

It seems from the data in Tables XXIV to XXVII that there is an effect on the hydrogen atom arising from the proximity of the lone pair electrons, which results in an increase of the corresponding ^{15}N–H coupling constants. This has also been suggested by some ^{15}N-coupling-constant studies of oximes and heterocyclic ring molecules[5,156,163,167] where both the sign and magnitude of the coupling constants have been determined. The absolute value of $^2J(^{15}N–H)$ in (**27**) is largest for the hydrogen atom which is *cis* to the lone-pair electrons;[156,167] see also **28** to **34**.

The signs of the reduced coupling constants are opposite to those quoted above. Protonation of the nitrogen lone pair leads to a formal



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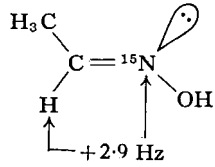

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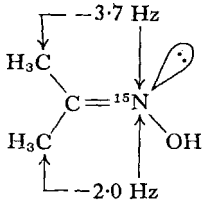

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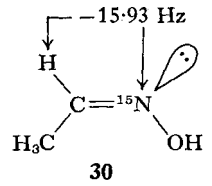

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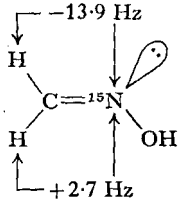

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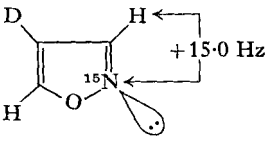

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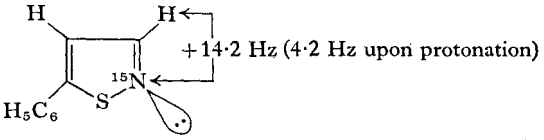

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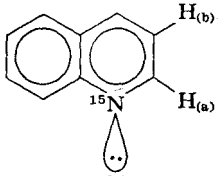

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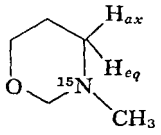
positive charge at the nitrogen atom and results in changes in the reduced coupling constant:

^1K(N–H) — positivation
^2K(N–H) — negativation
^3K(N–H) — positivation

Stereospecificity of ^{15}N coupling constants has been found in some 1,3-oxazines[164] and oxaziridines[178] (**35** to **37**) where the orientation of the



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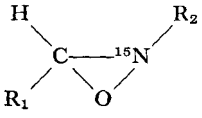
^2J(N–H_{ax}) = 0 Hz
^2J(N–H_{eq}) = 1·5 Hz
^2J(N–CH_3) = 1·1 Hz



^2J(^{15}N–C–H) = O Hz

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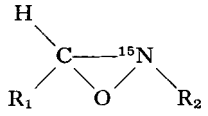


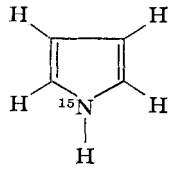
$^2J(^{15}N\text{–}CH) = 4{\cdot}8$ to $5{\cdot}4$ Hz

37

lone-pair electrons appears to have an important effect on the magnitude of the coupling.

The angular dependence of the $^3J(^{15}N\text{–}H)$ coupling constants in amino acids[176] appears to be in good agreement with the relationship found for ^{14}N coupling.[93, 95] The values of $^3J(^{15}N\text{–}H)$ are 1·8 and 5·1 Hz for dihedral angles of 60° and 120°, respectively.

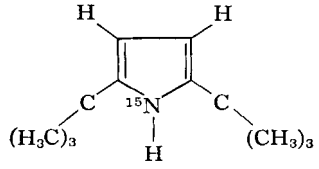
The ^{15}N–H coupling constants in pyrrole (**38**)[170] and 2,5-di-*t*-butylpyrrole (**39**)[175] have recently been measured.



$|^1J(^{15}N\text{–}H)| = 96{\cdot}56$ Hz
$|^2J(^{15}N\text{–}H)| = 4{\cdot}36$ Hz
$|^3J(^{15}N\text{–}H)| = 5{\cdot}35$ Hz

38

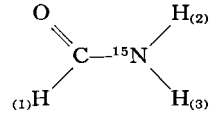
38



$^1J(^{15}N\text{–}H) = -91{\cdot}5$ Hz
$^3J(^{15}N\text{–}H) = -5{\cdot}2$ Hz

39

39



$^2J[^{15}N\text{–}H_{(1)}] = -14{\cdot}147$ Hz
$^1J[^{15}N\text{–}H_{(2)}] = -86{\cdot}93$ Hz
$^1J[^{15}N\text{–}H_{(3)}] = -91{\cdot}30$ Hz

40

The spin-tickling technique has been used for the determination of the signs of the coupling constants in some ^{15}N-substituted formamides (**40**).[169]

The $^1J(^{15}N\text{–}H)$ coupling constants in aniline derivatives[166, 168, 173] have been investigated from the point of view of stereochemical changes at the nitrogen atom. An almost linear correlation has been reported

between the constants and the Hammett σ-factors.[168] More recent data[173] show appreciable differences in the values of the constants for $CDCl_3$ solutions relative to those previously reported[168] (Table XXVIII).

TABLE XXVIII

Absolute values of $^1J(^{15}N–H)$ in some aniline derivatives, in Hz (±0·2 Hz), taken from refs. 168 and 173

Substituted aniline	DMSO	$CDCl_3$	Acetone	CF_3COOH	Reference
4-NO_2	89·4	86·4	..	..	173
	..	78·7	88·9	..	168
2,3,6-Br_3	..	..	87·8	..	168
3,5-Me_2, 4-NO_2	87·0	83·2	..	..	173
2,4-Br_2	..	..	86·0	..	168
3-Br	85·3	80·5	..	..	173
3-Cl	85·1	80·9	..	..	173
3-I	84·4	80·4	..	..	173
4-I	84·0	79·7	..	..	173
	..	78·5	84·1	..	168
4-Br	84·0	79·6	..	..	173
	..	..	83·6	..	168
4-Cl	83·7	78·9	..	..	173
3-NO_2	..	..	83·0	..	168
3-MeO	83·0	79·4	..	..	173
H	82·6	78·6	..	..	173
	..	78·0	81·9	..	168
3-Me	82·0	78·2	..	..	173
3,5-Me_2	82·1	77·5	..	..	173
4-F	81·6	77·8	..	..	173
4-Me	81·4	76·5	..	..	173
	..	76·9	79·6	..	168
4-MeO	79·4	75·6	..	..	173
Anilinium ion	..	..	..	75·0	168

The effect of silicon, germanium and tin atoms on the ^{15}NH coupling in corresponding *N*-substituted anilines[166] is contrary to the expected increase in the coupling from possible π-orbital interaction. The values of ^1J(N–H) are lower than for aniline (Table XXIX).

No isotope effect on the ^{15}N coupling constant in liquid NH_3, NH_2D, NHD_2 and ND_3 has been found.[137] The $^{15}N–H$ and $^{15}N–D$ coupling constants are 61·8 ± 0·5 and 9·45 ± 0·2 Hz in all cases. Appreciable solvent effects on the $^{15}N–H$ coupling constant in aniline and trimethylamine have been reported[179] (Table XXX).

TABLE XXIX

^{15}N–H coupling in trimethylsilyl, trimethylgermyl and trimethylstannyl anilines $(CH_3)_3M^{15}NHPh$, in Hz, taken from ref. 166

M	$^1J(^{15}N–H)$	$^3J(^{15}N–M–CH)$
Si	76·0	1·1
Ge	71·1	1·1
Sn	73·8	..
$(Me_3M)_2{}^{15}NH$	66·5	..

TABLE XXX

Solvent effects on ^{15}NH coupling, in Hz, taken from ref. 179

	Solvent	$^1J(^{15}N–H)$
^{15}N-Aniline	cyclohexane	78·0
	CCl_4	78·0
	$CDCl_3$	78·0
	dioxane	80·6
	pyridine	81·4
	acetone	82·1
	DMF	82·3
	DMSO	82·3
$^{15}NMe_3$		$^2J(^{15}N–CH)$
	cyclohexane	0·85
	$CDCl_3$	0·80
	CD_3OD	0·60

The coupling observed in the ^{15}N NMR spectrum of the sodium salt of dinitromethane[140] has been used as an argument for the equivalence of the NO_2 groups in the anion (**41**).

The observed coupling constant, J_{obs}, for 1-phenylaza-2-naphthol is assumed to result from averaging between two sites involving internal proton migration with conservation of the spin system (Section VI). For one site $J_{NH} = 0$, the naphthol form, and for the other $^1J(^{15}N–H)$ has been calculated to be 88 Hz by adjusting to a linear relationship between ln K, where K is the tautomeric equilibrium constant, and $1/T$. The value of K being calculated for various temperatures from equation 33.

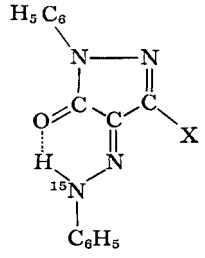
$$K = \frac{J(^{15}N–H) - J_{obs}}{J_{obs}} \tag{33}$$

At room temperature, $74 \pm 5\%$ of the hydrazone form is found, in good agreement with the results of ^{14}N chemical shift measurements.[71] The same type of tautomerism has been examined by means of the proton spectra of some ^{15}N-labelled 2-pyrazolin-5-one dyes.[174]

$[H\text{–}C\text{–}(^{15}NO_2)_2]^{\ominus}Na^{\oplus}$ in DMF solution

$\uparrow$—6 Hz—$\uparrow$

41



$^1J(^{15}N\text{–}H) = 96 \pm 1$ Hz

42

The value of the coupling constant suggests that the above structure is the only significant one in chloroform solutions.

The $^{15}N\text{–}C\text{–}^1H$ coupling in amino acids is reported to increase with pH[177] (Table XXXI).

TABLE XXXI

$^{15}N\text{–}C\text{–}^1H$ coupling in amino acids, in Hz, taken from ref. 177

Substance	pH	$^2J(^{15}N\text{–}H)$
Glycine	6·33	$0{\cdot}5 \pm 0{\cdot}1$
	13·68	$1{\cdot}5 \pm 0{\cdot}1$
DL-Alanine	6·37	$< 0{\cdot}5$
	13·64	$2{\cdot}2 \pm 0{\cdot}1$
DL-Phenylalanine	5·6	$< 0{\cdot}5$
	12·22	$2{\cdot}2 \pm 0{\cdot}3$

Recently, the ^{15}N coupling constants and their signs[246] for $(CH_3)_2P\,^{15}NH_2$ have been reported (Table XXXII). The signs were determined by several double-resonance techniques. The ^{15}NH coupling constants in some aminophosphines, aminoarsines and sulphenamides have been

TABLE XXXII

^{15}N coupling in $(CF_3)_2PNH_2$, from ref. 246

	J (Hz)	K (10^{20} cm^{-3})
^{31}P–^{15}N	+52·60	−106·75
^{15}N–^{1}H	−85·64	+70·36
^{15}N–P–C–^{19}F	−1·53	+1·34

used in a determination of the nature of the bonding in these molecules.[247] Equation 32 has been applied in the calculation of the *s*-character of the NH bonds (Table XXXIII).

TABLE XXXIII

^{15}N coupling in aminophosphines, aminoarsines and sulphenamides taken from ref. 247

Substance	$^{1}J(^{15}N–H)$ Hz	% 2*s* character in NH bond
$(CF_3)_2PNH_2$	85·6	30·8
$PF_3(NH_2)_2$	87·5	31·6
$(CF_3CH_3P)_2NH$	78·9	27·9
$(CF_3)_2AsNH_2$	73·4	25·6
$(CF_3CF_3As)_2NH$	79·0	28·0
CF_3SNH_2	80·6	28·7
$(CF_3S)_2NH$	99·1	36·6

As can be seen by the annual increase in the number of references quoted in the bibliography, nitrogen NMR is finding new applications all the time. It has been our aim to cover some of the more recent of these applications to a reasonable depth in this review.

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Nuclear Magnetic Resonance Spectroscopy in Liquids containing Compounds of Aluminium and Gallium

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I. INTRODUCTION

THE PERIOD since the beginning of 1967 has seen a tremendous upsurge of interest in the nuclear magnetic resonance spectroscopy of compounds and complexes of aluminium and, to a lesser extent, of gallium. The present time, when multinuclear spectrometers are becoming increasingly available, is particularly opportune to review progress made in the field and one hopes, to stimulate further advances.

As in other fields the nucleus which has been used most often is the proton and the techniques adopted will be familiar to the majority of readers. Much of the work reported is, however, somewhat qualitative and relatively little attention has been given to assessing the significance of the magnitudes of chemical shifts or coupling constants of any of the compounds studied, the only exceptions being found in the section dealing with β-diketonate complexes and in that dealing with donor complexes of MX_3 compounds.

The group IIIa chemist is doubly fortunate in that the metals upon which his subject is based also possess nuclei with magnetic moments. The part played in boron chemistry by ^{11}B NMR is already well known and it has been increasingly realised that the aluminium and gallium nuclei may also give us further information, not available in any other way.

These nuclei differ from the proton in possessing a nuclear quadrupole moment which results in their relaxation processes being dominated by nuclear quadrupole relaxation. A torque is exerted on the nucleus by electric field gradients which originate in asymmetries in the molecule. As the molecule rotates randomly due to the brownian motion in the sample, the fourier component of the torque at the NMR frequency of the nucleus causes energy exchange between nuclei and lattice so giving rise to spin-lattice relaxation, T_1. Since the fourier component arises from random motion it also, effectively, has random phase and this leads to loss of phase coherence between nuclei or in other words to spin-spin relaxation, T_2. The two relaxation times are equal and are given by:—[1]

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40} \cdot \frac{2I+3}{I^2(2I-1)} \left(\frac{eQ}{\hbar}\right)^2 \left(\frac{d^2v}{dz^2}\right)^2 \tau_c \qquad (1)$$

Where I is the nuclear spin quantum number ($I \nless 1$), Q is the nuclear quadrupole moment, d^2v/dz^2 is the maximum electric field gradient at

the nucleus and τ_c is the correlation time for molecular brownian motion.

The arrangements of substituents normally encountered in aluminium and gallium chemistry are (a) octahedral in the solvated ions $M^{3\oplus}$, (b) tetrahedral in the ions $MX_4^{\ominus}$, (c) near tetrahedral in the dimers Al_2X_6 and Al_2R_6 and in the adducts $B \rightarrow AlX_3$ and (d) trigonal in the monomers MR_3 where these exist.

The arrangements (a) to (c) all possess cubic symmetry about the metal atom, particularly where the ligands are identical, so that the field gradients at the metal nucleus should be small or zero, the relaxation times should be long and the resonance lines narrow. If the ligands are not identical then the electron densities in the bonds will not be equal and the field gradient and line widths may be increased.

The trigonal molecule (d), however, does possess an appreciable field gradient with its maximum direction along the C_3 axis of the molecule. Monomer line widths are correspondingly expected to be larger than those of species (a) to (c). Compare for instance the ^{11}B line widths of $BF_4^{\ominus}$ ($\sim$0·8 Hz) and of $B(OMe)_3$ ($\sim$20 Hz).

There are suggestions in the literature that the symmetry of a molecule as a whole affects the field gradient at an atom. Field gradients, however, vary in magnitude as the inverse cube of the distance from a charge and the gradients near atomic nuclei consequently originate from charge density variations quite near to the nucleus.[241] For this reason the major factors which affect the gradients are the disposition of the bonds around the nucleus and the electron density associated with each bond near the nucleus. An illustration of this point may be found in Ogg and Ray's ^{14}N results for the alkylammonium ions:[2]

ion	$NMe_4^{\oplus}$	$NH_4^{\oplus}$	$PhCH_2NMe_3^{\oplus}$	$PhNH_3^{\oplus}$
^{14}N line width (Hz)	7	7	12	100

The correlation time τ_c also has considerable influence on relaxation times. For a spherical molecule the Debye relation gives

$$\tau_c \propto \eta a^3 \qquad (2)$$

where η is the bulk viscosity and a is the radius of the molecule. Thus the sample viscosity should always be considered in any detailed discussion of relative line widths though the dependence of line width upon viscosity seldom seems to be so simple as suggested by (2).

Increasing molecular size, a, leads to increased line widths though here the Debye relation affords only an approximation since real molecules may depart markedly from spherical. The effect of molecular size upon

the ^{27}Al line widths of aluminium alkyls and their adducts has been discussed in detail and is considered in the appropriate sections.

It is also to be expected that exchange processes will affect line widths in the same way as they do for nuclei with $I=\frac{1}{2}$ though in addition exchange modulation of the field gradient direction in the molecule might modify the observed effects, effectively reducing τ_c if exchange were fast enough. The effects of exchange on the resonances of these nuclei have, however, received virtually no attention.

Since most readers will not be familiar with these nuclei their properties are summarised in Table I, which contains the data of practical importance to the NMR spectroscopist. In addition to the raw data the

TABLE I

Nucleus	^{27}Al	^{69}Ga	^{71}Ga	^{1}H
Isotopic abundance %	100	60·2	39·8	99·98
Relative sensitivity at constant field for equal numbers of nuclei	0·206	0·069	0·142	1·0
NMR frequency at 14 092 gauss MHz	15·63	14·42	18·30	60·00
I, multiples of h	5/2	3/2	3/2	1/2
$Q \times e \times 10^{-24}$ cm^2	0·149	0·19	0·12	—
$(2I+3)/I^2(2I-1) = F(I)$	0·32	1·33	1·33	—
$Q^2F(I)/0{\cdot}0071$ (relative width)	1·0	6·7	2·75	—
Relative peak height (3)	33·3	1·0	3·3	—

value is given of $(2I+3)/I^2(2I-1)$ [from equation (1)] which is designated $F(I)$ and of $Q^2F(I)$ which term gives the relative (hypothetical) line widths expected for nuclei in identical environments. In addition a term is calculated which gives the relative peak heights after allowing for relative width differences, i.e. gives a measure of the true, hypothetical sensitivities. This term is obtained from:

$$\text{relative peak height} = \text{relative abundance} \times \text{sensitivity}/Q^2F(I) \quad (3)$$

The values of $F(I)$ illustrate that, far from being unfavourable, a large value of I leads to narrower lines so that of the three naturally abundant isotopes shown in the Table, ^{27}Al would be expected to have the narrowest lines. This coupled with its large abundance and larger sensitivity leads one to expect ^{27}Al to be the most favourable nucleus to examine, and indeed it has received most attention of the three. Of

the two gallium isotopes, the least abundant, ^{71}Ga, has the higher sensitivity and lower quadrupole moment and this, coupled with the fact that both isotopes have the same spin quantum number, leads us to conclude that it would be better to study this nucleus rather than the more abundant ^{69}Ga. Both have, however, received attention, though as will be seen later the ^{71}Ga produces the better resolved spectra.

Because ^{27}Al has a quadrupole moment it has been long assumed that its lines would be very much broader than those obtained with spin $\frac{1}{2}$ nuclei and that it would be best observed in the derivative mode. Because high resolution spectrometers tended to be for proton or fluorine spectrometry only, wide line machines with their low-grade magnets were used for ^{27}Al and consequently broad lines *were* observed, even for the most symmetrical species. It is now realised, however, that under favourable circumstances absorption mode lines as narrow as 3 Hz can be obtained, that in many cases derivative working is not appropriate and that much information can be lost if one does not use a reasonably high resolution magnet. An example taken from the author's own work, and to be discussed in detail later, is the second ^{27}Al line in aqueous aluminium sulphate which is immediately apparent in a high-resolution magnet when working in the absorption mode.

It has also in the past been normal to use fairly low magnetic fields when observing ^{27}Al. This was not counted a disadvantage since chemical shifts with the heavier elements are relatively large and the need for high field-resolution was not felt to be so great as with the proton. However, small line separations do occur in ^{27}Al spectra and because these lines are quadrupole broadened high fields are needed to resolve them. That the high field machines do give further information can again be demonstrated by reference to the work with aluminium sulphate solutions where it has now been shown that in the presence of concentrated sulphuric acid and at 21·1 kilogauss the second line splits into two components. Only a single line has previously been observed at 13·5 kilogauss. There is every reason to believe that other closely overlapping ^{27}Al resonances will be found in other systems.[3]

In addition, since these metal nuclei are inherently less sensitive than the proton they benefit proportionately to an even greater extent from the sensitivity enhancement obtained at higher fields. The application of super-conducting magnet techniques should particularly benefit this area of NMR spectroscopy.

A consequence of the relatively short relaxation times of the three metal nuclei is that spin coupling is not normally observed, the only known instances of well-defined coupling being seen in molecules of type $AlX_4^{\ominus}$, in $Me_3N \cdot Al(BH_4)_3$ and in some adducts Ph_3PAlR_3. It follows

that all the information obtained with these nuclei comes from chemical shift measurements, though quantitative line area measurements are also sometimes important. Information ought also to come from line-width measurements but, to date, the interpretation of such data is probably ambiguous and it will be shown, its significance may often be obscured by exchange.

The work reviewed in this article falls naturally under a series of headings with little overlap. We deal with:

(a) Solutions of ionic salts, the solvation complexes formed therein and their hydrolysis.
(b) The dimer self-adducts of compounds such as the tri-alkyls and tri-halides.
(c) The complexes formed by these compounds with donor molecules such as ethers and amines; borohydride adducts.
(d) The chelate complexes, particularly of the β diketonates.
(e) Aluminium borohydride.

We conclude with tables of aluminium and gallium chemical shifts and line widths.

II. IONIC COMPLEXES OF ALUMINIUM AND GALLIUM

The last few years have been marked by the discovery and characterisation by NMR of a considerable number of complexes of aluminium and to a lesser extent of gallium. Solvation complexes are reported with water, dimethylformamide, *N*-methyl acetamide, ammonia, dimethyl sulphoxide, and acetonitrile, and some mixed complexes are also reported containing either one of the above components or acetone or tetrahydrofuran together with water. The solvation number for water on aluminium ion $Al^{3\oplus}$ now seems to be established as integrally six. Replacement of solvation water has been observed to occur by sulphate ion, phosphoric acid and dihydrogen phosphate ions, and by fluoride ion. Perchlorate ion probably also forms a complex with $Al^{3\oplus}$ in acetonitrile and possibly in aqueous acetone solution. Hydrolysis to form a dimeric ion has also been observed.

All the possible tetrahalo aluminate ions, except those involving fluoride, have been observed in non-aqueous media while it has been confirmed that the tetrahalogallates exist in aqueous gallium halide solutions to which a halo acid has been added, and it has been found that these probably form mixed halo-aquo complexes at reduced acidity. The total number of aluminium complexes detected must now be about sixty, many have been "seen" for the first time using NMR. Proton and

aluminium spectroscopy have been the most fruitful sources of results but ^{14}N, ^{17}O, ^{19}F and ^{31}P NMR have also been used where appropriate. Considerable results have also been obtained for the gallium ion using mainly proton and gallium spectroscopy, but this field is not so well developed as is that of aluminium.

A. Aqueous systems

1. *Solvation number*

A considerable effort has been spent on determining hydration numbers, n, for the cations. This is of importance since there is some disagreement among chemists as to whether these ions form stoichiometric solvation complexes with water or whether their interaction with water is much less definite.

Early isotopic work using ^{18}O had indicated that n was about six and that the rate of oxygen exchange was slower than about $0{\cdot}02$ sec^{-1}.[4] ^{17}O NMR was an obvious alternative technique to try and a preliminary study[5] showed that though the ^{17}O resonances of bulk and bound water overlapped, the addition of a paramagnetic ion ($Co^{2\oplus}$) would separate the signals and a comparison of line areas could be made which was consistent with $n=6$ for both aluminium and gallium. This was followed up by workers using more highly enriched ^{17}O and values of n near six were reported for $Al^{3\oplus}$,[6] and for $Ga^{3\oplus}$ [7] [and also for $Be^{2\oplus}$ ($n\sim4$)[6]]. The values obtained are summarised in Table II. The molal shift method also gave values of n for $Al^{3\oplus}$ near to six. This method relies on the fact that adding $Al^{3\oplus}$ to water containing paramagnetic $Dy^{3\oplus}$ alters the contact shift of the water oxygen since some of the water is strongly complexed by the aluminium and can no longer interact with the $Dy^{3\oplus}$.[8]

The rate of exchange of the water oxygen has also been measured by variable temperature ^{17}O NMR, assuming hexahydration and a curve-fitting procedure was adopted.[9] The results are summarised in Table II and the entropy changes for exchange suggest that exchange on aluminium occurs via a five coordinate species (SNI) whereas gallium can form a seven coordinate species and exchange via an SN2 mechanism. A correlation time for rotation of $Al(H_2O)_6^{3\oplus}$ was calculated;

$$\tau_c = 6{\cdot}67 \times 10^{-11} \text{ sec}$$

These results strictly apply to the oxygen part of the hydration water only and give no information as to the behaviour or number of the protons in the system. These are expected to exchange rapidly with the bulk water because of the hydrolysis reaction, which results in the loss of a proton from the aquo ion, and indeed the room temperature proton spectrum of aluminium salt solutions comprises only a singlet. A number

TABLE II

Solvation numbers n and kinetic data for exchange of solvent (oxygen and hydrogen separately in the case of aquo complexes) on solvates of water, acetonitrile, dimethyl sulphoxide and ammonia

Ion	Solvent	Method	n	ΔH^* kcal mol^{-1}	ΔS^* e.u.	k (sec^{-1}) and temperature		Ref.
$Al^{3\oplus}$	H_2O	^{17}O NMR + $Co^{2\oplus}$	$5{\cdot}92 \pm 0{\cdot}09$	—	—	—	4 determinations	6
	H_2O	^{17}O molal shift	$5{\cdot}94 \pm 0{\cdot}43$	—	—	—	5 determinations	8
	H_2O	$^{17}O + Co^{2\oplus}$	assumed 6	27	28	0·13 at 25°	oxygen exchange	9
	H_2O	^1H relaxation	—	—	—	$\sim 10^{-5}$ at 25°	hydrogen exchange	11
	H_2O	^1H relaxation	—	—	acid dissociation	$1{\cdot}1 \times 10^5$ at 30° 9×10^8 at 30°	both hydrogen exchange two processes	12
	H_2O	^1H areas	$6{\cdot}0 \pm 0{\cdot}05$	24	—	—	hydrogen exchange at −50°	18
	H_2O	^1H areas and line shapes	$6{\cdot}1 \pm 0{\cdot}1$	4·9	—	$1{\cdot}8 \times 10^{-4}$ at −29·5°	oxygen exchange	20
				20·9	—	$2{\cdot}2 \times 10^5$ at −29·5°	hydrogen exchange	
	H_2O	^1H areas	$6{\cdot}01 \pm 0{\cdot}02$	—	—	—	nitrate salt at low temperatures	21
	H_2O + acetone	^1H areas	$5{\cdot}90 \pm 0{\cdot}14$	—	—	—		23

	H_2O+ solvent	^1H areas	5·7–6·3	—	—	—	DMSO and DMF form mixed solvates. Acetone, tetramethyl urea and dioxan do not solvate in presence of H_2O	25
	H_2O+ DMSO	^1H areas	6	—	—	—	mixed solvates form	30
	H_2O+ DMSO	^1H areas	$5·92 \pm 0·09$	8·4 to 10·8	−5 to −20	35 ± 6 at 7°	water protons	29
			total H_2O+ DMSO	20 to 10·6	+8 to −21	0·6 to 3·8 at 25°	DMSO part $n = 2·8$ to 0·6 DMSO per Al	
	H_2O	^1H and ^{27}Al areas	$5·97 \pm 0·05$	—	—	—	part hydrolysed solutions	43
	MeCN	^1H and ^{27}Al areas	6·2 (6·0)	—	—	—	$ClO_4^{\ominus}$ can displace MeCN	65 66
	NH_3liq	^{14}N areas	$6·03 \pm 0·45$	—	—	—		84
$Ga^{3\oplus}$	H_2O	^{17}O NMR+ $Co^{2\oplus}$	$5·89 \pm 0·2$		—	—		7
	H_2O	^{17}O NMR+ $Dy^{3\oplus}$	$6·28 \pm 0·26$	—	—	—	modal shift method	3
	H_2O	^{17}O NMR+ $Co^{2\oplus}$	assumed 6	6·3	−22	$1·8 \times 10^3$ at 25°		9
	H_2O+ acetone	^1H areas	$5·93 \pm 0·14$	—	—	—	independent of anion	23
	H_2O+ acetone	^1H areas	6 and lower	—	—	—	$Cl^{\ominus}$ reduces hydration	26, 27, 33

of indirect studies of the system using the proton resonance have nevertheless been reported. Addition of aluminium nitrate to nitric acid decreases the acid dissociation as measured by ^1H NMR and this can be accounted for on the basis of a common ion effect and the assumption that the water hydrating the aluminium is not available to the acid.[10] Proton relaxation studies lead to a reliable value of the proton exchange rate, $\tau_H \approx 10^{-5}$ sec.[11] More recent and extensive pulsed NMR studies at various solution acidities have, however, detected two proton exchange processes, one involving the acid dissociation of $Al(H_2O)_6^{3\oplus}$ and a much faster one ($k_{30} = 9 \times 10^8$ sec^{-1}) which appears to involve $Al(H_2O)_6^{3\oplus}$, $Al(H_2O)_5OH^{2\oplus}$ and two or more water molecules.[12]

Early relaxation work[13] was used to determine a hydration number in combination with viscosity data and the large value of $n = 16$ was obtained. This was regarded as including all the water molecules which might rotate with the ion though this now seems a doubtful conclusion in view of the short rotational correlation time derived above.[9] Relaxation measurements are now to be regarded as measures of the exchange reactions present rather than relating to the motions of integral water molecules.

An attempt has been made to determine the number of protons in the hydration complex, using an empirical method based on line width changes which are observed in the proton signal of manganous salt solutions when a salt with a hydrated cation is added.[14] The results demonstrate that aluminium and gallium are equally hydrated but have received some criticism.[15,16] The variation of the proton shift with temperature in aluminium nitrate solutions has also been used in an attempt to obtain hydration numbers. The straight lines obtained between 0° and 100° at different concentrations of salt all intersect at a common point at $-210°$ and $-6{\cdot}38$ p.p.m. from ethane gas. This is taken to indicate the position at which the chemical shifts of bulk water (which moves downfield as temperature decreases) and of bound water (whose shift is assumed temperature independent) coincide and a value of $n = 13{\cdot}4$ is calculated. It is suggested that this high number is obtained either because of interaction with water in the secondary hydration sphere of the aluminium or because of interaction with the nitrate ion.[17] However, a value of the shift of bound water from bulk water at $-50°$ is now known from the work to be discussed in the following paragraphs. This allows an estimate to be made of the shift of bound water from ethane gas. It is considerably lower field than assumed by Malinowski and Knapp; perhaps at $-8{\cdot}9$ p.p.m. and insertion of this value into their calculations gives $n \approx 6$. It seems that the very long extrapolation from near 0° to $-210°$ may not be valid.[17a]

Our knowledge of hydration of these ions was transformed in 1967 when Fratiello and Schuster announced[18] the observation of two proton lines for bulk and bound water in concentrated aqueous aluminium chloride at the remarkably low temperature of $-50°$ (Fig. 1). This discovery has initiated a considerable amount of work in this area. The

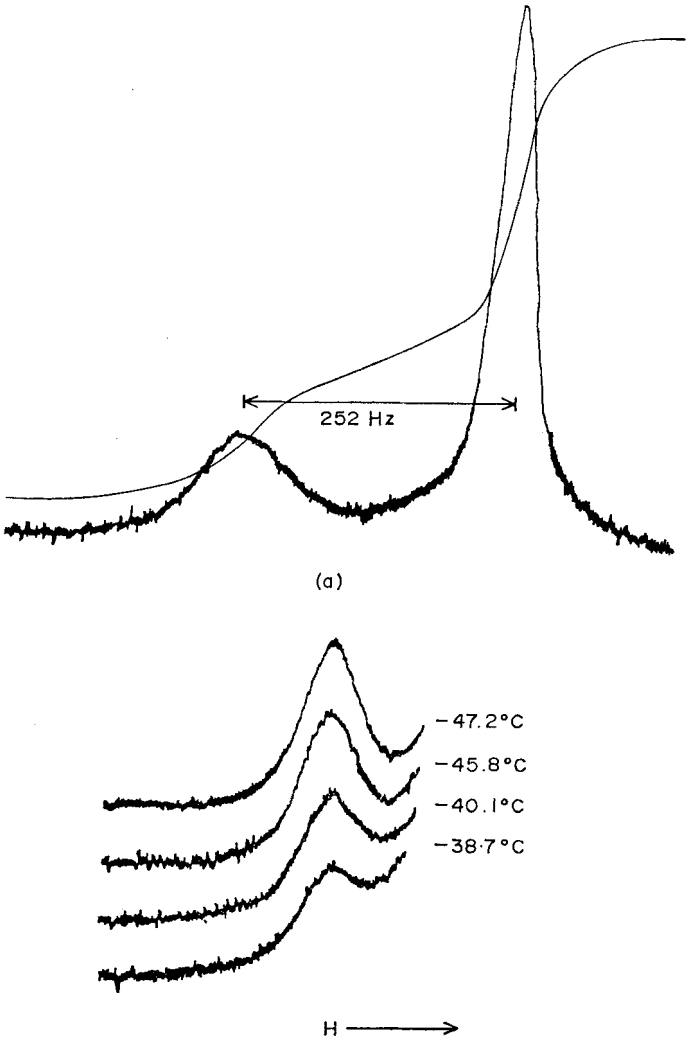


FIG. 1. Proton resonance signals of cooled aqueous aluminium chloride solutions. The low field peak arises from protons in $Al(H_2O)_6^{3\oplus}$. (From Schuster and Fratiello.[18])

bound water is 4·2 p.p.m. to low field of the bulk and the peak areas integrated to show that 6·0 to 6·1 molecules of water were bound to each $Al^{3\oplus}$ agreeing well with the previous ^{17}O determinations. The change in line widths with temperature allowed a rough value of ΔH^* to be obtained for proton exchange. This is shown in Table II. Similar observations were announced shortly afterwards by Takahashi[19] who has subsequently reported[20] detailed variable temperature studies, also based on line width changes, which enabled both the hydrolytic proton exchange and whole water molecule exchange rates to be measured. The proton exchange rate is accelerated by the addition of acid.

The freezing point is also highly depressed in aqueous aluminium nitrate, and proton spectroscopy again gave the value $n = 6{\cdot}01 \pm 0{\cdot}2$,[21] a value which it was pointed out precludes the formation of intimate ion pairs with the nitrate ion which had previously been suggested on the basis of IR evidence; this, however, is in line with current interpretations of the IR results.[22]

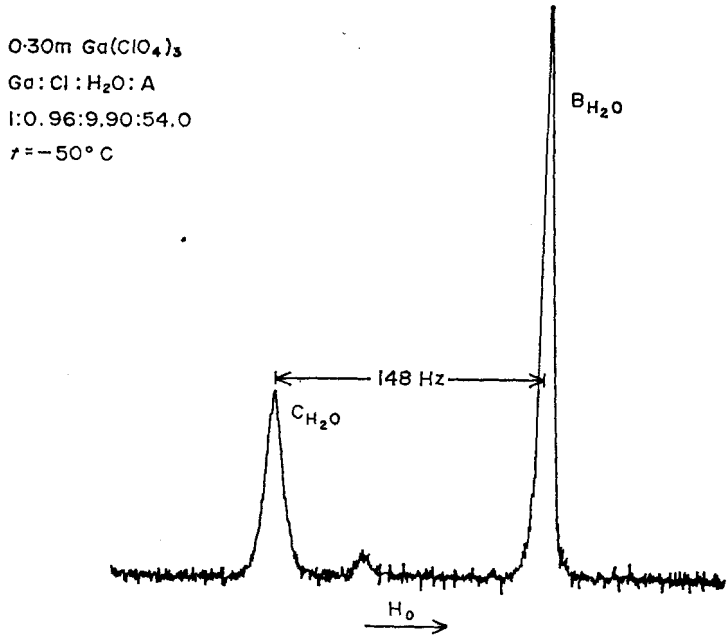


FIG. 2a. The water proton magnetic resonance (PMR) spectrum of a $Ga(ClO_4)_3$ solution in a water-acetone mixture containing a 1:1 mole ratio of HCl to $Ga(ClO_4)_3$. The spectrum was recorded at $-50°$ on a Varian A-60 NMR spectrometer. The signals arising from bulk water (B_{H_2O}) and water molecules in the $Ga^{3\oplus}$ solvation shell (C_{H_2O}) are labelled in the diagram as are the mole ratios of all species. (From Fratiello *et al.* [26, 27])

Fratiello has subsequently published more detailed results giving n as about 6 for both aluminium and gallium in aqueous and mixed aqueous solutions.[23 to 25] The value of n is independent of anion ($Cl^{\ominus}$, $ClO_4^{\ominus}$) though line width changes were observed to occur with changes in composition or concentration which may indicate specific ion effects. More extensive studies of gallium halides in acetone-water solution have, however, shown that as the acetone concentration is increased the hydration number of the gallium is reduced and at the highest acetone concentrations two bound water resonances were seen. It is postulated that a series of chloro-aquo complexes is formed leading eventually to the well-known $GaCl_4^{\ominus}$ ion.[26, 27] (See Fig. 2.) This work confirms conclusions reached previously on the basis of ^{71}Ga spectroscopy.[28]

The non-aqueous components of the many solvent mixtures studied during this work can be placed into three categories; (a) those such as dimethyl formamide and dimethyl sulphoxide which interact strongly

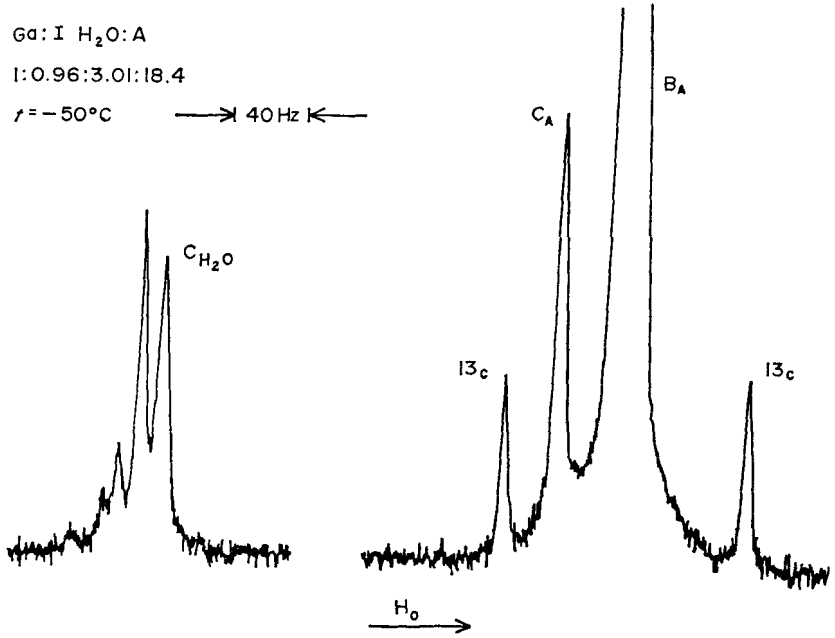


Fig. 2b. The water PMR spectrum of a GaI_3 solution in a water-acetone mixture. The $I^{\ominus}$ to $Ga^{3\oplus}$ mole ratio was reduced to 1:1 by addition of $AgClO_4$. The spectrum was recorded on a Varian A-60 NMR spectrometer. The signals arising from bulk water (B_{H_2O}) and water molecules in the $Ga^{3\oplus}$ solvation shell (C_{H_2O}) and bulk and complexed acetone (B_A and C_A) are labelled in the diagram, as are the mole ratios of all species. (From Fratiello *et al.* [26, 27])

with the ions even in the presence of water, (b) those such as acetone and tetrahydrofuran which do not solvate the ions in the presence of a large proportion of water but which will coordinate with the ion where the water present is insufficient to fill all the vacant coordination sites and (c) solvents such as tetramethylurea, dioxan, dimethyl sulphone, dimethyl sulphate and tetramethylene sulphone which do not appear to displace water from the ion at all.

The interactions of dimethyl sulphoxide with aluminium ions in aqueous solution has been studied in detail elsewhere.[29,30] The total solvation number is always near six and both acid catalysed and protolysis controlled water proton exchange were detected.

Proton shifts observed in aqueous dioxan solutions suggest that despite Fratiello's results dioxan may undertake some solvation in aqueous aluminium perchlorate under certain circumstances, though it is not clear whether anion or cation solvation is involved.[31]

The gallium solutions have been studied in addition by four groups of workers using gallium spectroscopy. The first study of interest to chemists was essentially a determination of the relative magnetic moments of ^{69}Ga and ^{71}Ga but included the observation that the gallium line widths observed in solutions of gallium trichloride in hydrochloric acid depended markedly upon the amount of acid present. The line due to ^{71}Ga was narrower than that due to ^{69}Ga.[32] The effect of varying the acidity of these solutions has subsequently been studied using the ^{71}Ga resonance. It was found that in strongly acid solution a narrow line was obtained due to the ion $GaCl_4^{\ominus}$. When the acidity of the solution was reduced this line broadened and moved, indicating the presence of exchange between mixed chloro-aquo ions, while at the same time a second and stationary peak due to $Ga(H_2O)_6^{3\oplus}$ appeared which became the dominant species at low acidities.[28] The bromide and iodide systems showed similar behaviour and fast exchange was seen in a mixed system. The chloride system has subsequently been studied without added acid in aqueous acetone solution where the exchange reactions may be slower.[33] The isotope ^{69}Ga was chosen for these measurements and is an unfortunate choice since it gives much broader lines than ^{71}Ga. The spectra given by the two isotopes are compared in Fig. 3. Table I indicates that the ^{69}Ga lines should be about 2·5 times wider than the ^{71}Ga lines but in fact factors of between four and eight times are observed, suggesting that either exchange broadening or overlap of lines is occurring in the ^{69}Ga spectra. The spectra are interpreted as indicating exchange between chloro ions and the hexaquo ion though this is not compatible with the previous ^{71}Ga work which excludes the hexaquo ion from the exchange processes; however, the different solvent media may

explain these differences. The ions $GaCl_4^{\ominus}$ and $GaBr_4^{\ominus}$ have been observed elsewhere using ^{71}Ga spectroscopy[34] and their chemical shift measurements differ by 10 to 20 p.p.m. from those of previous workers. This difference may merely reflect the breadth of the resonances (the width of the narrowest line is about 10 p.p.m. at 12 MHz) or may be due to unsuspected specific interactions in these solutions.

N-methyl acetamide strongly solvates the aluminium ion in aqueous solution,[35 to 37] as does hexamethyl phosphortriamide (HMPT). In this

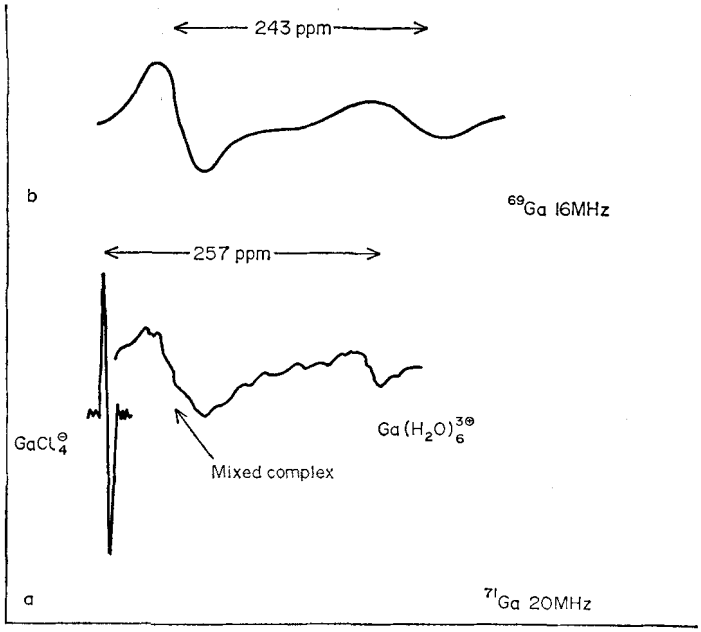


FIG. 3. ^{69}Ga and ^{71}Ga spectra of gallium chloride solutions. (a) ^{71}Ga spectra of two solutions of $GaCl_3$ containing HCl. (From Akitt *et al.*[28]) (b) ^{69}Ga spectrum of a solution of $GaCl_3$ in aqueous acetone. (From Fratiello *et al.*[33])

latter case two ^{31}P and two ^{1}H signals were observed at $-30°$ in a solution containing 5% HMPT and which show that on average 0·55 molecules of HMPT and 5·4 molecules of water solvate the ion; a total solvation number of 5·95.[38] Phosphate complexes are also discussed in ref. 293.

The results of the determinations of solvation numbers of aluminium and gallium are recorded in detail in Table II. These are invariably near six though the determination is difficult to make accurately especially where there is a slight overlap of peaks and the contention that there exists a molecular complex of exact stoichiometry six has been challenged for this reason. It is suggested that for instance hydrolysis could affect

the results fractionally. It is believed that all the authors of the above papers were aware of this possibility and ensured adequate acidity of

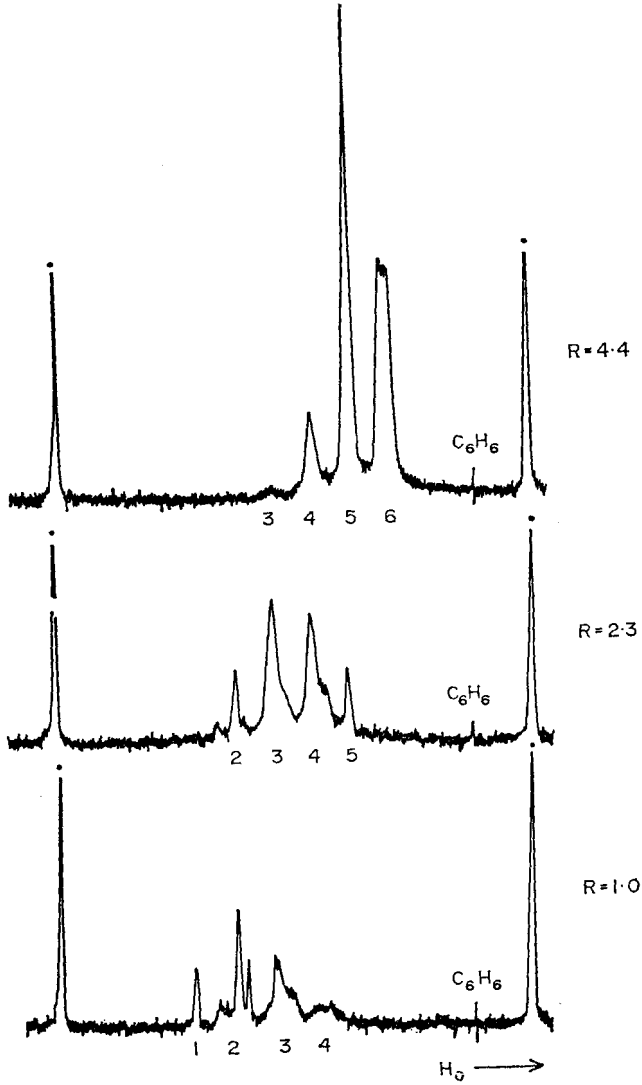


FIG. 4. ^1H resonances of the NMR spectra from dilute solutions of $Al(ClO_4)_3$ and water in acetonitrile. (R denotes the $H_2O:Al^{3\oplus}$ molecular ratio in these solutions. The numerals show our tentative assignment of the H_2O resonances in terms of the number of water molecules in each aquated $Al^{3\oplus}$ species. · denotes reference frequency markers; C_6H_6 the resonance from a small amount of benzene in the CH_3CN solvent.) (From Supran and Sheppard.[39a])

their solutions. The effect of hydrolysis will in any case be discussed shortly where it will be shown that combined ^{27}Al and ^{1}H measurements still give $n=6$. The average of all the results of Table II is $5{\cdot}97 \pm 0{\cdot}05$, very near to six.

That the hydration number of six must indeed be integral has been demonstrated for $Al^{3\oplus}$ by the work of Supran and Sheppard.[39a] Room temperature proton spectra obtained in aqueous acetonitrile solutions of aluminium perchlorate exhibit a number of low field water resonances which can be assigned to the series of solvates $Al(MeCN)_n(H_2O)_{6-n}^{3\oplus}$ on the basis of their intensity dependence upon water concentration (Fig. 4). Exchange must be slow. The line assigned to the symmetrical ion $Al(H_2O)_6^{3\oplus}$ is broad and flat topped and sharpens if the ^{27}Al is double irradiated. The symmetrical hexaquo ion would be expected to have a low rate of aluminium quadrupole relaxation and to be the one most likely to show aluminium-proton spin coupling in the absence of proton exchange. This experiment therefore indicates the existence of chemical bonding between oxygen and aluminium so that a stoichiometric complex must be formed, with n integrally six. Several ^{27}Al resonances were also detected in these solutions. This work confirms Raman results which also indicate the existence of Al–O covalent bonding.[39b, 39c]

It is of interest to note here that the ESR of $Ti^{3\oplus}$ in aqueous tertiary butanol shows hyperfine splitting due to eight protons on four water molecules and that in this ion also, covalent bonding must exist between oxygen and the metal ion.[40]

2. *Hydrolysis in aluminium salt solutions*

The hydrolysis of the $Al_{aq}^{3\oplus}$ ion has been of interest since the end of last century. A considerable body of data has been gathered which is agreed that the monomeric hydrolysis

$$Al(H_2O)_6^{3\oplus} \rightleftharpoons Al(H_2O)_5OH^{2\oplus} + H^{\oplus} \qquad (4)$$

takes place but disagrees on the nature of the subsequent steps in hydrolysis, one school favouring the formation of polymers such as $Al_8(OH)_{20}^{4\oplus}$, the other the formation of dimers, $Al_2(OH)_2^{4\oplus}$. The effects of reaction (4) on proton exchange rates have already been reviewed.[11 to 13] It has been found also that hydrolysis affects the line width of the ^{27}Al resonance of $Al(H_2O)_6^{3\oplus}$. The line is narrow in the presence of excess acid but broadens considerably as the acidity is reduced, the line width depending upon $1/[H^{\oplus}]$ in accordance with (4). In order to account for the line widths observed it was found necessary to suggest that the hydrolysed ion is associated with an $Al(H_2O)_6^{3\oplus}$ ion.[41] It was subsequently shown, using a more sensitive spectrometer, that the line broadening is accompanied by a loss in the line area, a second aluminium species

being formed which gave a much broader, and therefore weaker, resonance to low field.[42] The results can be accounted for by the formation of a dimer ion $Al_2(OH)_2(H_2O)_n^{4\oplus}$ which has been observed to constitute up to 30% of the total aluminium in solutions obtained by prolonged boiling of hydrogen chloride from aluminium chloride solutions. The variation of dimer content with acid content suggests further loss of protons to give $Al_2(OH)_n(H_2O)_m^{(6-n)\oplus}$;[43] a conclusion recently reached on the basis of e.m.f. measurements.[43a] Further hydrolysis with NaOH or Na_2CO_3 at 80° leads to the appearance of a narrow ^{27}Al resonance 60 p.p.m. to low field due to the polymeric cation.

$Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7\oplus}$ which contains a highly regular AlO_4 tetrahedron at its centre. The dimer and polymer are long lived with a lifetime of about 2 sec but when the proton spectra of hydrolysed solutions are examined at low temperatures only the protons on $Al(H_2O)_6^{3\oplus}$ are seen

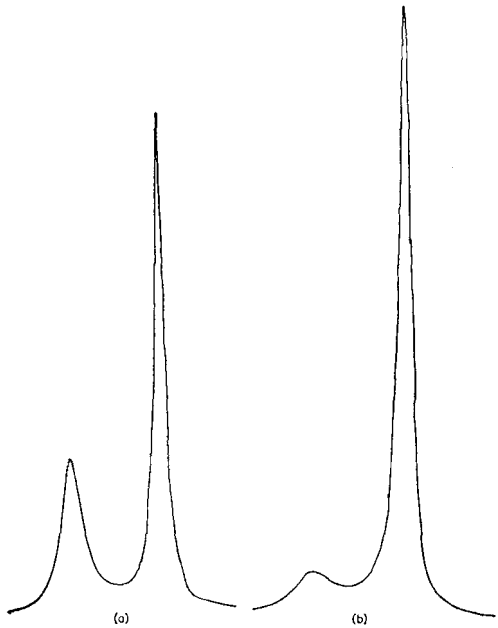


FIG. 5. Proton resonance signals of cooled aqueous aluminium chloride solutions: (a) non-hydrolysed, (b) containing dimer ion. (From Akitt *et al.*[43])

as a separate low field resonance (Fig. 5), the polymer protons being involved in very fast exchange. This is presumably the same fast process observed by Grunwald.[12] Hydration numbers were determined for the non-hydrolysed ion at different acidities by using ^1H assays of bound protons and ^{27}Al assays of $Al(H_2O)_6^{3\oplus}$ and it was found that n was in-

variably near six whatever the proportion of hydrolysis. The formation of polymers can equally well be followed using low-temperature proton NMR and it is of interest to observe that the ready availability of pure $AlCl_3 \cdot 6H_2O$ in the U.S.A. probably prevented the American workers from making this observation.

It was also observed that as the dimer concentration increased the proton exchange rate on $Al(H_2O)_6^{3\oplus}$ increased. This may be related to the availability of rapidly exchanging protons in these solutions, a similar effect having been seen upon the addition of calcium nitrate.[44]

Sweitzer and Stephens have recently published proton results which appear to indicate that the hydration number of aluminium in aqueous solutions containing calcium or sodium halide is appreciably less than six and they conclude that complexes involving chloride must be formed. It is significant that their method of preparation of the samples involved passing nitrogen through the warmed solutions; conditions which we believe will lead to the loss of hydrogen halide and the production of dimer ion, particularly in solutions rich in halide. Their results may not, as might at first appear, be at variance with the work reviewed above. Their results for gallium presumably do include contributions both from dimerisation and from halo complexes.[45a, 45b]

Since the chemistry of the aqueous gallium system is so like that of the aqueous aluminium system one would expect that gallium resonance studies at different acidities might well also reveal information about complexing and hydrolysis in these systems and preliminary results have indeed shown that the ^{71}Ga line width and line area of $Ga(H_2O)_6^{3\oplus}$ in aqueous gallium sulphate solution are sensitive to hydrolysis.[46]

As a postscript one must note that determination of n for $Al^{3\oplus}$ is now proposed as a teaching experiment.[47]

^{27}Al relaxation studies have recently been made but ignoring pH effects.[292]

3. *Complexes with sulphate, fluoride, hydroxide and orthophosphates*

Observation of the ^{27}Al resonance in a solution of aluminium sulphate placed in a high-resolution magnet quickly reveals the presence of a second weak line 3·3 p.p.m. to high field of the major one arising from $Al(H_2O)_6^{3\oplus}$.[41, 48, 48a] The weak line, which is absent in nitrate or chloride solutions, can be intensified by the addition of sulphuric acid and was attributed to the ion $Al(H_2O)_5(HSO_4)^{2\oplus}$.[41] Further work[49] using a spectrometer with a higher magnetic field has led us to believe that this is a sulphate complex $Al(H_2O)_5(SO_4)^{\oplus}$ and has also revealed the presence of a third peak in these solutions which appears at high sulphuric acid concentrations and is thought to arise from complexes with sulphuric acid (Fig. 6). The equilibria in these solutions are far more complex than was

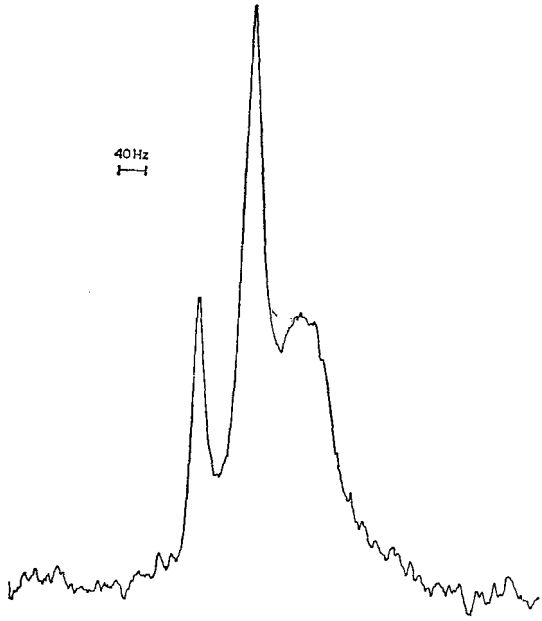


FIG. 6. ^{27}Al resonance at 23·45 MHz of aluminium sulphate solutions in the presence of excess sulphuric acid. (From Akitt *et al.*[49])

originally thought and dimer $Al_2(OH)_2^{4\oplus}$ is also present in aluminium sulphate solutions and remains until a considerable quantity of sulphuric acid has been added.

Interaction of $Al^{3\oplus}$ with fluoride is well known and the equilibrium constants for the series of reactions

$$AlF_n^{(3-n)\oplus} + F^{\ominus} \rightleftharpoons AlF_{n+1}^{(2-n)\oplus}$$

has been determined potentiometrically.[50]

^{19}F NMR provides a convenient means of studying these ions and Connick and Poulsen were able to detect lines due to the ions $AlF^{2\oplus}$ and $AlF_2^{\oplus}$ in solutions containing an aluminium salt and sodium fluoride. The fluorine chemical shifts of the complex ions were sensitive to the concentration of sodium salt, both resonances moving to high field as the sodium concentration increased.[51,52]

The topic was then neglected for eight years but has recently received considerable attention from several groups of workers who have applied variable temperature techniques to the problem. Yamazuki and Takeuchi, in a paper in Japanese, report the observation at low temperatures of a third low field peak in solutions similar to those studied by Connick and Poulsen and which probably arises from AlF_3 and perhaps from higher

fluorides and free fluoride ion.[53] This line has also been observed in solutions in which ammonium fluoride replaced the sodium fluoride of previous workers. It was found that much higher fluoride concentrations could be attained with the ammonium salt and that the third line could thus be intensified. Comparison with Brossett's constants suggested that the third peak was due to AlF_3, $AlF_4^{\ominus}$ and free fluoride ion. Ammonium fluoride has the opposite effect to sodium fluoride on the fluorine chemical shifts, increasing concentrations shifting all the resonances low field.[54] This may be a hydrogen bonding effect similar to that suggested by Gillespie *et al.* for the $BF_4^{\ominus}$ ion.[55]

During the course of the most recently reported studies of this system it was found that the salt $AlF_3 \cdot 9H_2O$ is very soluble in water. Solutions were made up using this and aluminium nitrate so that the proportions of aluminium and fluoride could be adjusted; these solutions thus contained a minimum of superfluous ions. Spectra were run at reduced temperatures and four ^{19}F lines were observed corresponding to $AlF^{2\oplus}$, $AlF_2^{\oplus}$, AlF_3 and $AlF_4^{\ominus}$, the latter being particularly obvious in $AlF_3 \cdot 9H_2O$ solution to which had been added 0·01 M Co^{II} which produces a contact shift in the anion but not in the cations or neutral AlF_3 (Fig. 7). Low-temperature proton NMR was also carried out and led to the detection of the water molecules bound to the aluminium in all the ions present. Only a single line was observed for bound water and its area was consistent with the formation of the octahedral complexes $(H_2O)_5AlF^{2\oplus}$, $(H_2O)_4AlF_2^{\oplus}$ and $(H_2O)_3AlF_3$. The solution composition and temperature affects the relative ^{19}F shifts between $AlF^{2\oplus}$ and both $AlF_2^{\oplus}$ and AlF_3 and hydration and hydrogen bond effects are discussed as possible causes. The equilibrium quotients derived differ from those of Brossett and it is suggested that the fluoride ion is not involved in the equilibria.[56] A single broad ^{27}Al resonance about 500 Hz wide for the fluoride species is seen by both these and the previous workers, with a chemical shift of about 2 p.p.m. down field from the sharp $Al(H_2O)_6^{3\oplus}$ line. The latter was used to estimate the amount of aluminium not complexed by fluoride.[54,56] This line had been reported previously in O'Reilly's pioneering ^{27}Al paper where it was observed in the derivative mode, though the shift obtained was greater, presumably due to difficulties in measuring the shift between closely overlapping derivative curves.[57]

Complexes formed between gallium and fluoride have also recently been reported, using silver fluoride as the fluoride ion source.[58] Ga^{III} was added to silver fluoride solutions and the line due to fluoride was observed to decrease in intensity while a second, initially broad, line appeared which both narrowed and shifted as further gallium was added. The formation of species analogous to the aluminium system is

postulated with exchange among them but not involving free fluoride. The contribution of gallium quadrupole relaxation to the ^{19}F line width via gallium–fluorine spin coupling is discussed. However, a calculation based on the large width of the ^{27}Al line of aluminium fluoride complexes suggests that one should expect that the ^{69}Ga and ^{71}Ga relaxation times

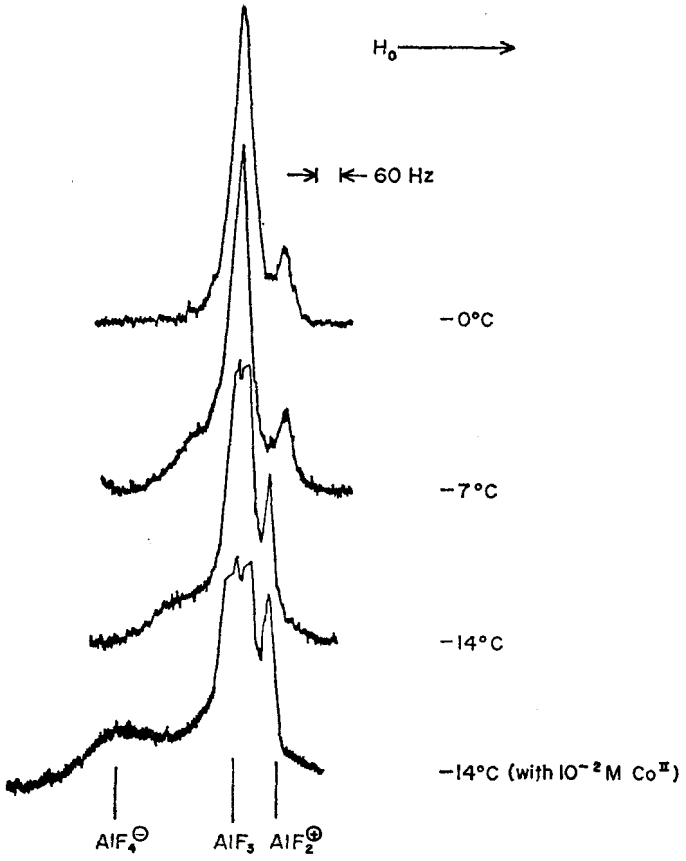


FIG. 7. Temperature dependence of the ^{19}F NMR spectra of a 0·997M solution of $AlF_3 \cdot 9H_2O$ in water. The magnetic field increases from left to right. (From Matwiyoff and Wageman.[56])

might be of the order of only 280 μsec so that the fluorine spin multiplet would be fully collapsed, producing very little effect on the fluorine line width; unless of course ^1J(F–Ga) was very large.

This topic seems to be by no means fully worked out and the interesting questions of the source of the medium effects observed on both ^{19}F

shifts and the exchange behaviour of the ions deserves further attention. It is also of interest to note in passing, the recently observed and similar behaviour of the beryllium fluorides.[59]

A single ^{27}Al resonance is seen in highly alkaline solutions of aluminium salts and is 80 p.p.m. low field of the resonance due to $Al(H_2O)_6^{3\oplus}$. The line is narrow and has been attributed to the tetrahedral species $Al(OH)_4^{\ominus}$.[57] More recent work, however, based upon sodium and proton NMR[60] and upon infrared spectroscopy[61] claims that this species is in fact not present but that these solutions of aluminates contain hydrated $AlO_2^{\ominus}$ ions and perhaps a square planar or polymeric form of $Al(OH)_4^{\ominus}$. These claims are refuted in a paper based on Raman, IR, and ^{23}Na and ^{27}Al NMR spectroscopy. Vibrational spectroscopy supports the presence of tetrahedral $Al(OH)_4^{\ominus}$ whose Raman frequency is found to be sensitive to deuterium substitution. The ^{27}Al line width increases with concentration and may be broadened on account of the presence of dimeric species $(HO)_3AlOAl(OH)_3$ or perhaps merely due to the high viscosities of these solutions. A ^{23}Na down field shift was observed with increasing concentration.[62] Further evidence that the ionic species involved is probably a tetrahedral negatively charged ion can be found in the Table of ^{27}Al chemical shifts, at the end of this review, where it will be observed that the resonance in these alkaline solutions falls very close to other $AlX_4^{\ominus}$ species and is well separated from the resonances due to octahedral oxygen coordinated species.

A number of complexes of phosphoric acid species with aluminium have been detected using low temperature ^{31}P NMR together with ^{27}Al NMR which was used to determine the amount of uncomplexed $Al(H_2O)_6^{3\oplus}$ present. Three ^{31}P lines were observed due to the complexes at 15·7, 12·3 and 7·6 p.p.m. upfield of uncomplexed acid and were probably due to complexes of stoichiometry $Al \cdot H_3PO_4^{3\oplus}$ (15·7 p.p.m.), $Al \cdot H_2PO_4^{2\oplus}$ and $Al(H_2PO_4)^{\oplus}$ (12·3 p.p.m.) and to a complex with a polymeric form of the acid (7·6 p.p.m.). The stoichiometry of this latter complex corresponds to $Al(H_3PO_4)_3$ though the line can be resolved into several components which may indicate that a range of polymeric acids is formed at high acid concentrations.[63] Two complexes were formed with aluminium dimer and addition of fluoride ion results in the formation of at least eight fluorophosphato complexes, which were detected by ^{19}F NMR.

B. Non-aqueous solvents and the non-aqueous components of some mixed aquo complexes

Haraguchi and Fujiwara have reported the ^{27}Al shifts of an extensive series of complexes of the types AlL_6, AlL_4, $(Donor)AlX_3$ and Al_2R_6.[64]

Complex spectra were obtained when aluminium halides were dissolved in aceto-, acrylo- or benzo- nitrile. In general, two lines were seen, one due to $AlX_4^{\ominus}$ and one due to $Al(nitrile)_6^{3\oplus}$, though in the case of Al_2Br_6 in benzonitrile only $AlBr_4^{\ominus}$ was observed, while a third line due to the dimer Al_2Cl_6 was visible when the chloride was dissolved in the same solvent. It is thought likely that excess halide may exist in all solutions. The systems are in equilibrium and the $AlX_4^{\ominus}$ concentration can be increased by adding halide ion. Similar results were obtained for the iodide in ethyl isocyanate solution but the chloride gave only the dimer and the bromide gave only $AlBr_4^{\ominus}$. Hon has also studied aluminium chloride dissolved in acetonitrile using proton absorption mode and ^{27}Al derivative NMR. Two ^{27}Al resonances were seen and their intensities supported the equilibrium

$$4AlCl_3 + 6MeCN \rightleftharpoons Al(MeCN)_6^{3\oplus} + 3AlCl_4^{\ominus}$$

the intensity of the proton resonances of free and complexed nitrile giving a solvation number of 6·2 for the cation. Addition of lithium chloride converted all the aluminium to $AlCl_4^{\ominus}$, there being no suggestion that any $AlCl_6^{3\ominus}$ is formed;[65] no mixed ion species were observed. More recent proton data support this work and also provide the kinetic parameters for exchange.[66] In acetonitrile solutions of aluminium perchlorate the line due to bound acetonitrile was observed to have fine structure and the presence of several species involving intimate ion pairs with perchlorate ion are suggested. The average solvation number of the aluminium was only $2{\cdot}9 \pm 0{\cdot}3$. Exchange of solvation acetonitrile is slower in perchlorate solutions but the rate is increased if chloride is present, the latter anion catalysing the exchange, a phenomenon that has also been observed in dimethyl formamide solutions. In acetonitrile the exchange presumably involved the equilibrium proposed by Hon.[65]

Absorption mode ^{27}Al spectra have shown that the ion $AlCl_4^{\ominus}$ is present in solutions of aluminium trihalides in phosphoryl chloride. The reaction probably involves a number of equilibria and is of interest since no exchange was thought to take place in the absence of free halide in these solutions. In the case of the chloride and iodide solutions a resonance assigned to $Al(POCl_3)_6^{3\oplus}$ was also observed.[67]

Mixed tetrahalo aluminate ions have been prepared by dissolving aluminium trihalides and tetrapropyl ammonium halides of differing halogens in methylene chloride or bromide.[68] The addition of the alkyl ammonium salt reduced exchange rates so that different ^{27}Al lines could be observed for the different mixed ions, the solvent acting as an additional source of halide ions. Thus all the ions $(AlX_nX'_{4-n})^{\ominus}$ and $(AlX_2X'X'')^{\ominus}$ were observed in solutions of suitable composition with

X, X′ and X″ any of Cl, Br or I. The spectra were observed in the absorption mode using a high-resolution magnet and a line width of 15·1 Hz obtained for $AlCl_4^{\ominus}$ should be compared with the results obtained by previous workers (Fig. 8). The line widths ΔW of the mixed

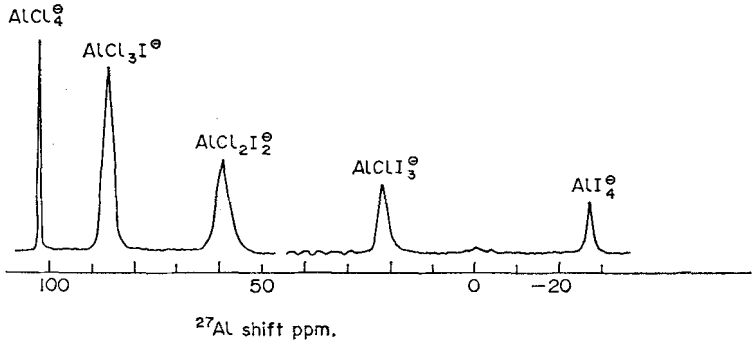


FIG. 8. ^{27}Al spectrum of the series of ions $(AlCl_nI_{4-n})^{\ominus}$. (From Kidd and Truax.[68])

ions were larger than those of the more symmetrical $AlX_4^{\ominus}$ ions though the line width of the latter increased with ionic mass.

ion	$AlCl_4^{\ominus}$	$AlCl_3I^{\ominus}$	$AlCl_2I_2^{\ominus}$	$AlClI_3^{\ominus}$	$AlI_4^{\ominus}$
ΔW Hz	15·1	42·0	57·6	46·0	23·9

Attainment of equilibrium is rapid in these solutions indicating the presence of fairly fast halide exchange and consequent exchange of aluminium among all possible environments. Thus some ^{27}Al exchange line broadening would be expected. This suggests that the above results may be indicative of exchange processes rather than of differences in electric field gradients at aluminium. The spectrum of Fig. 8 could arise if exchange was fastest among the iodo anions. Certainly the figures by no means represent the ultimate resolution, lines 8 Hz wide having been observed in the author's laboratory for both $AlCl_4^{\ominus}$ and $AlBr_4^{\ominus}$ in acetonitrile solution,[69] which could imply merely that exchange is slower in this solvent than in methylene chloride. The ^{27}Al shifts in the series $AlCl_nI_{4-n}^{\ominus}$ are not a linear function of n so that the contribution of each halogen depends on the nature of the other substituents. The $AlI_4^{\ominus}$ ion, contrary to expectations based on electronegativity or covalency considerations, is the most highly shielded ion and this is rationalised on the basis of the nephelauxetic or cloud expanding effect of the iodide ion which reduces the value of $\langle 1/r^3 \rangle$ in the Ramsey equation for paramagnetic shielding.[68] This suggestion is of interest also for the $BX_4^{\ominus}$

and $GaX_4^{\ominus}$ series which show exactly the same trends of metal shift with nature of halide. Similar conclusions were reached by Malinowski[70] based upon the above workers' results and who showed that the ^{27}Al shifts are pairwise additive in terms of pairs of halide ions. Thus $AlI_4^{\ominus}$ involves six pairwise interactions of four iodine atoms and its ^{27}Al shift is given by $6\eta_{I.I}$ where $\eta_{I.I}$ is the pairwise parameter for a pair of iodide atoms.

The tetraalkylaluminate ions have also received some attention although, since they contain protons, proton spectroscopy has been the favoured tool for their study. Alkyl group exchange is slow on $LiAlMe_4$ in ether solution unless trimethylaluminium is also present, when exchange probably involves the formation of solvent-separated ion pairs; the lithium in contrast exchanges rapidly. The proton spectra show no evidence of ^1H–^{27}Al coupling in contrast to $LiBMe_4$ solutions where the coupling is well resolved and this was attributed to a rapid exchange reaction between solvent-separated and intimate ion pairs, which causes ^{27}Al relaxation.[71] ^1H–^{27}Al coupling is, however, seen for solutions of $LiAlMe_4$ in 1,2-dimethoxyethane (DME) which strongly complexes with lithium and where wholly solvent separated ion pairs are obtained, the value of the coupling being 6·34 Hz.[72] A more detailed analysis of the proton line shapes obtained over a range of temperatures in each of the solvent ethers, THF or DME for both lithium and sodium salts confirms that the coupling is 6·3 Hz in the solvent-separated ion pair. It also proved possible, by including ^{27}Al line width data, to calculate the value of the coupling in the intimate ion pairs and this was given as 7·1 Hz for $LiAlMe_4$ and 9·1 Hz for $NaAlMe_4$. Both types of ion pair exist in THF and the equilibrium constants of ion pair formation were obtained for both salts.[73, 291] No ^1H–^{27}Al coupling is seen in ether solutions of $LiAlEt_4$ and ^7Li shift data show that dissociation into LiEt and Al_2Et_6 does not occur.[74] ^1H NMR titrimetric studies have also been carried out to discover whether complexing of sodium by arene rings occurs in the system $NaAlBu_4^{\oplus}$ benzene or toluene in cyclohexane solution; the results were negative.[75] The salt has been used as a probe of several ion-solvent interactions.[75a, 75b] The perfluoro arene compounds $LiAl(C_6F_5)_2Br_2$ and $LiAl(C_6F_5)_3Br$ have been reported.[76] A solution of $Mg[AlMe_4]_2$ or $[MgAlMe_5]_2$ in trimethylaluminium undergoes methyl exchange at room temperature but at $-60°$ lines arising from three components can be observed.[77]

The aluminium(III) and gallium(III) ions form strong solvation complexes with dimethyl formamide (DMF) and six sharp proton signals, three each due to bound and bulk solvent, can be observed in pure and in aqueous DMF solutions of aluminium trichloride at 60 MHz and up

to 40°.[78, 79] The formyl proton is shifted down field by the largest amount and the formyl-methyl coupling constant is increased. This implies greater double bonding and therefore *O*-coordinated solvent. The formyl shift correlates with $z/(0{\cdot}2+r)^2$ where r is the ionic radius. Variable temperature experiments were carried out to obtain enthalpy values for exchange of solvent, the results of this and subsequent investigations being included in Table III. A solvation number of about six was estimated for each ion, and the exchange rate was determined by migration

TABLE III

Solvation number n and kinetic data in dimethyl formamide and dimethyl sulphoxide solution

Ion	Solvent	n	ΔH^* kcal mol^{-1}	ΔS^* e.u.	k (sec^{-1}) and temperature	Ref.
$Al^{3\oplus}$	DMF	6	18		4·89 at 23·5° ($AlCl_3$) 31·8 at 49°	80
	DMF	5·7	16·6		41·9 at 41° ($AlCl_3$) 1·9, 2·2 at 41° ($AlBr_3$, AlI_3)	81
	DMF	6	17·7	1·2	6 to 11 at 50° ($Al(ClO_4)_3$)	82, 83
	DMSO	5·90 ± 0·2	20	3·7	0·29 at 40°	85
$Ga^{3\oplus}$	DMF	6	21		5·3 at 23·5° ($GaCl_3$)	80
		6	14·6	−8·3	1·7 at 25°	34

of DMF into the solvation sphere.[80] The enthalpy for exchange may depend upon the nature of the halide used, the exchange rate being particularly rapid for the chloride. The formyl proton shift also depends upon the nature of the halide.[81]

Separate bulk and bound DMF signals were also seen by Movius and Matwiyoff in solutions of aluminium perchlorate at 100 MHz and at up to 90° giving the solvation number as 6·0 ± 0·3 independent of temperature. The figure obtained for enthalpy of exchange is similar to Fratiello's result but the rate is less and depends on aluminium concentration. The ^{27}Al resonance is narrow and occurs near that of $Al(H_2O)_6^{3\oplus}$ thus confirming octahedral *O*-coordination.[82] These authors have also confirmed that the DMF shifts are affected by halide in the form of lithium halide or aluminium trihalide, the formyl proton exhibiting the largest effect, a maximum observed shift of 33 Hz to low

field being seen in aluminium trichloride solution. This is interpreted as being due to the electric field of halide ion complexed in the second solvation sphere and a formyl proton-halide ion distance of 2·3 to 2·7 Å is calculated.[83]

Similar results are obtained below 40° for DMF complexed to gallium, the solvation number being six also. A much lower enthalpy of exchange was obtained than that found by previous workers. As in the case of water exchange the entropy is negative for the gallium system.[34] The ^{71}Ga resonance is narrow and is 26 p.p.m. to high field of $Ga(H_2O)_6^{3\oplus}$ confirming octahedral *O*-coordination. Mixed complexes with DMF and acetylacetone were also characterised; aqueous DMF is also discussed.[24]

Coordination of $Al^{3\oplus}$ by *N*-methyl acetamide[35–37] and *N*-methyl formamide[78] in aqueous solution has already been discussed and also probably involves *O*-coordination.

The $Al^{3\oplus}$ ion is also solvated by six molecules of ammonia in liquid ammonia solutions of aluminium tri-iodide; the determination was made using ^{14}N NMR. Cupric ion was added to broaden the resonance of bulk ammonia beyond the limits of detection and the amount of bound ammonia found by comparison with the ^{14}N resonances of standard solutions. It was found that $n = 6{\cdot}03 \pm 0{\cdot}45$.[84]

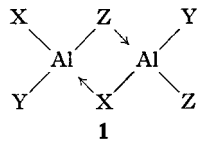
Coordination by dimethyl sulphoxide (DMSO) has also been studied. The solvation number in this case was determined by comparing the areas of the bound solvent peak with that of a ^{13}C satellite of the bulk solvent and is six.[85] Exchange is slow at 40°: $k_{40} = 0{\cdot}29$ sec^{-1} but the lines broaden as the temperature is raised giving $\Delta H^* = 20 \pm 1$ kcal mol^{-1}, $\Delta S^* = 3{\cdot}7 \pm 2{\cdot}5$ e.u. at 40°. DMSO will also coordinate in the presence of water and mixed complexes are formed.[24, 25, 29, 30] Small quantities of water do not affect the determination of the solvation number of DMSO but as the water content of the solutions increases the mixed complexes form almost statistically, the exception being $Al(DMSO)_6^{3\oplus}$ which tends to lose one DMSO molecule easily due presumably to steric crowding.[30] Thus water preferentially solvates aluminium when its mole fraction in the solvent is greater than 0·8. DMSO exchange occurs in this region by replacement by water, which is replaced in turn by DMSO. Below 0·75 mole fraction of water, however, DMSO exchange occurs directly. The total coordination number is near six at all solution compositions and the DMSO chemical shift is dependent upon the number coordinated to the aluminium.[29]

^{71}Ga NMR has also been used to detect gallium ions in non-aqueous media. The gallous ion $Ga^{\oplus}$ has been observed in melts and benzene solutions of the dihalides and is found at very high fields presumably due to the lack of paramagnetic screening of the spherical ion. The

ions $GaCl_4^{\ominus}$ and $GaBr_4^{\ominus}$ were also detected in these solutions. The ion $GaH_4^{\ominus}$ was observed as a weak, broad resonance in ether solution and no evidence was seen of coupling between gallium and hydrogen.[28]

III. TRISUBSTITUTED ALUMINIUM AND GALLIUM COMPOUNDS

This section deals with compounds of the general formula $[MXYZ]_n$ where M is the metal and the substituents XYZ may be alkyl alkoxy, halide, siloxy, germyloxy or various nitrogen bonded groups. Dimer aggregates are usually formed ($n=2$) but in a few specific cases $n=4$ (e.g. $[Al(OR)_3]_4$) or $n=3$ (e.g. $[AlMe_2(N_3)]_3$) or $n=1$ (e.g. $Al(NPr^i_2)_3$). The dimers have the structure (**1**) and can be regarded as mutual adducts, there being many similarities between them and the adducts discussed in the following section. The bridging groups are usually



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identical but under suitable conditions mixed bridges appear to be formed. In the case of trialkyl compounds with small alkyl substituents weak alkyl bridges are formed and these compounds exhibit rapid exchange of bridge and terminal groups. Consequently their spectra are usually examined at low temperatures, or over a range of temperatures, so that kinetic data can be obtained.

Almost all the work has been done using proton spectroscopy. The ^{27}Al resonances of the dimers are broad lines and have so far given very little information except for one case where Reilly has observed two lines in a solution of a cobalt-aluminium halide catalyst. The relevance of the ^{27}Al results to exchange and dissociation in the alkylalanes* is discussed.

The work involving the alkyl and halide compounds has obvious relevance to the field of olefinic polymerisation catalysis, though much of the literature cited here avoids mentioning this aspect of the work. Very

* The term alane (or gallane) has been used to denote compounds in which part or *all* of the hydrogen in the parent alane, AlH_3 (or gallane, GaH_3) has been substituted by alkyl groups or by halide. If less than three substituents are named then the remaining substituents are hydrogen. The term is also occasionally used generically.

little NMR work dealing with the catalyst systems has appeared in the polymer journals, at least as far as the author has been able to ascertain from a short search based on Professor Ivin's recent review[86] though the discovery of soluble catalysts based on titanium dicyclopentadienyls is obviously much more amenable to investigation by NMR and a few papers have already appeared dealing with these systems.*

We deal first here with the organo alanes, then the halides and alkyl halides, the oxy compounds and finally the nitrogen bridged molecules. Most of the work deals with aluminium compounds but references to a few gallium compounds will be found throughout the section.

An overall background to the work described in this and in the next section is contained in a very recent review by Mole[87] describing the redistribution reactions of these compounds and which is recommended to the reader.

A. The trialkyl and alkyl-aryl compounds

Physical measurements[87a, 87b] indicate that trimethyl alane is a methyl bridged dimer but the proton spectrum at room temperature comprises only a singlet so that, if the dimer formulation is correct, then the terminal and bridge methyl groups must be rapidly exchanging. This was confirmed to be the case by experiments using low-temperature spectroscopy when it was found that two lines in the intensity ratio 1:2 could be observed in cyclopentane solutions at $-75°$.[88 to 90] The lines were separated by 1·13 p.p.m. the bridging methyls appearing at low field. The existence of terminal-bridge exchange was also demonstrated at room temperature using mixtures of trimethyl alane and tri-isobutyl alane. The methyl resonance moved to low field as the proportion of iso-butyl alane was increased indicating that the methyl ligands were becoming increasingly displaced from the terminal positions but not from the bridging positions.[91] A rigorous analysis of the A_3B_2 spectrum of triethyl alane has confirmed that it also is alkyl bridged,[92, 93] and this was further demonstrated by low-temperature spectra obtained in toluene.[94] A variable temperature study of tri-methyl-, tri-ethyl-, tri-n-propyl- and tri-n-butyl-alanes has detected the formation of alkyl bridged dimers in each case, the shifts of the α protons of the higher members of the series being about 0·6 p.p.m. (bridge) and 0·75 p.p.m. (terminal) further down field of the corresponding methyl resonances in trimethyl alane. The kinetic parameters of activation for exchange of alkyl groups in the latter were:

* The author is indebted to Dr. Caunt of I.C.I. who kindly supplied a list of relevant papers.

$\Delta H^* = 15{\cdot}6$ kcal mol^{-1}, $\Delta F^* = 11{\cdot}0$ kcal mol^{-1} and $\Delta S^* = 20$ e.u.

The ^1H spectra are shown in Fig. 9. Since the dissociation energy of the dimer in the vapour phase is about 20 kcal mol^{-1} it was suggested that exchange occurred *via* breaking a single bridge bond and reforming the bond to another methyl.[95]

Mixtures of trimethyl alane with other trialkyl alanes, Al_2R_6 where R = Me, Et, Pr^n or Bu^i, have been examined at a range of temperatures and with different proportions of the components. Thus, for example,

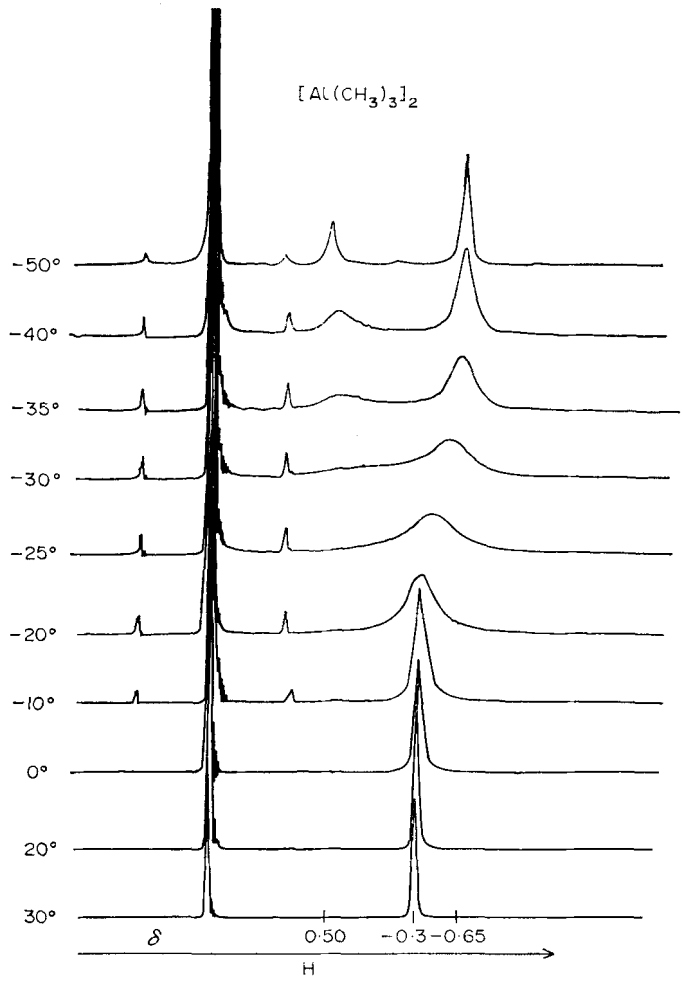


FIG. 9. ^1H spectra of Al_2Me_6 in cyclopentane over a range of temperatures. (From Romey *et al.*[95])

low-temperature spectroscopy shows in a mixture of trimethyl- with triethyl- alane that where the former predominates there are no bridging ethyl groups, whereas if the methyl compound is the minor constituent all the methyl groups bridge and some mixed bridges are formed also. The equilibria were discussed in terms of the room temperature shifts and relative bridge bonding factors were calculated $Me > Et > Pr^n > Bu^i$ in the ratios $1 : \frac{1}{6} : \frac{1}{7} : \frac{1}{17}$ the bulky group being the weakest bridging group.[96]

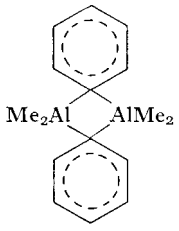
Tri-methyl and tri-ethyl gallane on the other hand appear, from molecular weight measurements in benzene or cyclopentane, to be entirely monomeric and a methyl singlet is invariably observed even at the lowest temperatures.[97]

Williams and Brown have studied the exchange in trimethyl alane solutions both alone and with trimethyl gallane[98] or with lithium tetramethylaluminate.[99] In the latter case it is found that the rate of alkyl exchange depends upon the concentration ratio of the two components and it is suggested that exchange is controlled by the rate of formation of solvent separated ion pairs. The alkyl exchange rate on alane alone was found to be different in toluene and cyclopentane and it was proposed that exchange proceeded *via* dissociation of the dimer Al_2Me_6 into monomers and was solvent dependent because these were solvent caged.[98,99] Jeffrey and Mole have, however, recently re-examined these systems and claim that the dissociation of dimer is the rate determining step and that the rate of dissociation is very much greater in benzene than in cyclopentane.[100] This is a somewhat controversial paper, the differences with previous workers being ascribed to 10° differences in temperature measurements even though it is recognised that the work was done carefully in each case. It is emphasised by Mole that a $\pm 1°$ range of temperature stability is equivalent to a $\pm 15\%$ change in rate in these systems. It is interesting to speculate whether such differences may exist throughout the NMR literature or whether in this case some undetected special factor may have affected the results. The exchange rate is slowed in the presence of donor solvents such as pyridine.[101]

The idea that exchange is initiated by dissociation into monomers is apparently not consistent with the known dissociation energies.[95] Lockhart, in her recently published review, has, however, suggested that the dissociation energy in solution should be lower than that found in the vapour phase and has estimated a value of only 15·5 kcal mol^{-1}. This is very similar in magnitude to the measured enthalpies of exchange in these systems.[102] Data is also reported for $[(F_3CCO)_2CH]_3Al$.[103]

Mole has also given attention to a number of alanes containing alkynyl

or aryl substituents with available π electrons which might assist in making them good bridging groups. Thus, for instance, only one methyl signal is seen at low temperatures in solutions of dimethyl-phenyl-alane and it is concluded that the phenyl must bridge. It is argued, using as a guide the X-ray structure of tri-phenyl alane where the phenyl plane is at 90° to the line connecting the aluminium atoms, that the phenyl group does not form a three-centre bond but rather undergoes partial sp^3 hybridisation at the bridging carbon[104] (**2**). It would be interesting to know whether the phenyl protons show a high field shift in this compound due to a reduction in ring current. If trimethyl alane is added a mixed bridged compound is formed (**3**).



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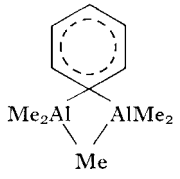

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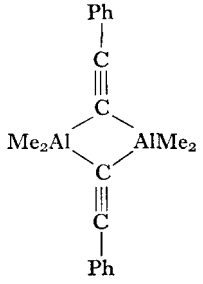

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Similarly *para*-tolyl-dimethyl-alane dimer contains aryl bridges only, but mixed bridges are formed if trimethyl alane is added.[105] The aryl bridge is thus stronger than the methyl bridge.

Dimethyl phenylethynyl alane has ethynyl bridges with the bridging centre thought, from IR evidence, to be a terminal acetylenic carbon (**4**). Mixed ethynyl-aryl and possibly ethynyl-methyl bridges can also be formed since the mixed bridges seem to be favoured energetically.[105] The phenylethynyl ligand is an exceptionally strong bridging group, so much so that it will cause dimethyl-phenylethynyl-gallane and -indane to form dimers which will nevertheless disproportionate in the presence of THF.[106] Methyl group exchange occurs in mixtures of (**4**) and trimethyl alane and the kinetic data indicates that a monomer $AlMe_3$ molecule attacks a dimer $[Me_2(PhC{:}C)Al]_2$; the rate of exchange is given by $1/\tau = k[Me_6Al_2]^{1/2}[Me_4(PhC{:}C)_2Al_2]$.[107] The dimethyl alkynyl derivatives have also been prepared. They undergo a number of reactions: oxygen can be inserted between ethyl substituents and aluminium to give the di-ethoxy derivative and a number of unsaturated

organic derivatives can be formed by reaction among the alkyl and alkynyl ligands. For example $CH_2:CMeOH:CHMeEt$ is formed when the alkynyl ligand is propyne. Demarne and Cadiot suggest that reaction occurs *via* brief association of monomers but these compounds presumably may be all alkynyl bridged dimers, the ligands in the dimer being suitably placed for a chain lengthening reaction.[108] These compounds can be prepared by reacting alanes with acetylenes.[109,110] For instance dimethyl alane will react with phenyl acetylene to give a number of aluminium alkyls, it being possible to observe the loss of acetylenic hydrogen as reaction proceeds. Several products are obtained: $PhC{:}CAlMe_2$, $PhC{:}CAlMeH$, MeH, $PhCH:CHAlMe_2$ and $PhCH_2CH(AlMe_2)_2$.[111]

The cyclopropyl ligand has also been found to be a strongly bridging group, the resonances of terminal and bridge ligands of tricyclopropyl aluminium being well distinguished at temperatures up to near 70°. Exchange is only seen above 70° and the bridge is probably stabilised by π interactions with the metal.[112] It has been inferred that the vinyl group will form bridges in alkyl alkene gallanes.[112a]

The rates of reaction of trimethyl gallane and trimethyl indane with dimethyl cadmium or dimethyl zinc have been measured at various temperatures. The gallium compound is the most reactive, the rate of $group^{II} \leftrightarrow group^{III}$ exchange being intermediate between the rates of $group^{III} \leftrightarrow group^{III}$ and $group^{II} \leftrightarrow group^{II}$ exchange reactions. All reactions are first order in each component.[113]

A number of miscellaneous papers concerning organo alanes have been published. The interaction of trimethyl alane and vinyl chloride, which will react to give cuprene and isobutane has been investigated using NMR. No shift changes are observed on mixing the two components and reaction must proceed *via* a transitory complex.[114] On the other hand the ethylenic proton chemical shifts in the series $(Bu)_2Al(CH_2)_nCH:CH_2$ where $n=3$ to 6 may indicate some π interaction with the metal atom.[115] Allyl alanes have also been prepared and where the aluminium is attached to a carbon β to a double bond the aluminium can exchange intramolecularly with a corresponding double bond shift.[116]

$$Ph_2C{=}CH\cdot C(AlR_2)HMe \rightleftharpoons Ph_2C(AlR)_2CH{=}CHMe$$

Analysis of the AA'BB' spectrum of the $-CH_2-CH_2-$ part of the *neo*hexyl ligand in tri*neo*hexyl alane, $(Me_3CCH_2CH_2)_3Al$, shows that the ligand is configurationally stable up to 150°.[117]

Cyclopentadienyl aluminium compounds have also been examined using proton spectroscopy. The C_5H_5 signal is invariably a singlet in

various solvents down to $-90°$ and a sigma bonded whizzing ring is proposed to account for this.[118]

Three aluminium resonance studies have been reported of trialkyl alanes, AlR_3 where R = Et, Pr^n, Bu^i, Bu^n, Hex^n.[119 to 121] At low viscosities (η) the ^{27}Al line widths of a series of solutions of different trialkyls is proportional to a molar volume term, a^3 where the magnitude of a is taken as $2{\cdot}2 + 1{\cdot}3n$, and n is the number of carbon atoms in the alkyl chain. A single broadened ^{27}Al line is seen in a mixture of alanes.[119] The line width varies with temperature and estimates were made of activation energies from both this and from the temperature variation of viscosity. The two values were similar in some cases but different in others.[120] More recently these results have been criticised by Petrakis who measured the ^{27}Al line widths of trimethyl, tri-n-propyl, tri-n-butyl and tri *iso*butyl alanes at infinite dilution in many solvents and over a range of temperatures. The activation energy obtained from NMR measurements has a range of values which brackets the value derived from viscosity measurements. The quotient, (^{27}Al line width)/($\eta \times$ molecular volume), is remarkably constant for solvents such as benzene, cyclopentane or iso-pentane, but deviates markedly for other solvents such as decane or cyclohexane and it is felt that the microviscosity at the solute molecules would be a better measure for the motion within these systems. It is concluded that a detailed re-examination of line width data is needed and that present models for these systems are far too crude.[121] See also a recent review.[297]

The above ^{27}Al work was carried out in parallel with the proton work already reported for these systems though, to date, no attempt seems to have been made to correlate the two sets of results; this we now intend to do.

All the alkyl alanes whose ^{27}Al spectra have been measured have been shown to form alkyl bridged dimers. They all have broad ^{27}Al lines whose widths vary from a minimum of about 500 Hz for pure trimethyl alane up to a maximum of about 50 000 Hz for pure tri-n-butyl alane (reduced to $\sim$4000 Hz in dilute solutions), and these values contrast remarkably with the ^{27}Al line widths obtained for the dimeric halides: aluminium trichloride has a line width of 300 Hz in toluene and 120 Hz in diethyl ether, the tribromide line width is 200 Hz in ether and the tri-iodide has a line width of only 660 Hz in toluene. The geometry around aluminium is similar in both the halides and in the alkyls and is near tetrahedral so that electric field gradients should not be large and relatively narrow lines would be expected. The halides are also the more massive molecules, the iodine atom for instance possessing a mass equivalent to a C_9H_{19} alkyl group, though despite the greater inertia of

Al_2I_6 its ^{27}Al line is almost seventy times narrower than that of pure tri-n-butyl alane. Viscosity differences between solvents will of course play a part but can hardly account for such a gross difference as this.

Proton spectroscopy has, however, amply demonstrated that rapid exchange of alkyl groups occurs at room temperature on the dimeric alkyl alanes and that the mechanism probably involves dissociation into monomeric units, AlR_3. The effectiveness of the alkyl groups as bridging units falls off as the alkyl chain length increases[96] and therefore one would expect the degree of dissociation to also increase with alkyl chain size.[87a] It seems significant that this parallels the observed increase in aluminium line widths with size of substituent. Of course, exchange of halide also occurs on the halide dimers but the degree of dissociation is very much smaller.[87]

We therefore consider the effect of the equilibrium

$$Al_2R_6 \rightleftharpoons 2AlR_3 \tag{1}$$

upon the observed line widths. We know that the quadrupole coupling constants of the monomers are almost certainly at least an order of magnitude larger than those of the dimers.[122,123] If we call the resulting quadrupole relaxation times T_{2M} and T_{2D} respectively then we can write for the case of fast exchange according to (1)

$$\frac{1}{T_{2\,OBS}} = \frac{P_M}{T_{2M}} + \frac{P_D}{T_{2D}}; \qquad \frac{1}{T_{2M}} \gg \frac{1}{T_{2D}} \tag{2}$$

where P_M and P_D are the proportions of monomer and dimer. Thus $1/T_{2\,OBS}$, and therefore line width, will increase markedly as P_M increases.

Pitzer and Gutowsky's polymerisation ratios[87a] indicate that in approximately 3% solution in benzene Al_2Me_6 is less than 0·3% dissociated, Al_2Et_6 is about 5% dissociated, $Al_2Pr^n_6$ is about 11% dissociated and $Al_2Pr^i_6$ is about 94% dissociated. Unfortunately the ^{27}Al line widths of only three of these compounds have been measured and these have not all been measured under sufficiently similar conditions to make a calculation of line widths according to (2) meaningful, though the line widths follow the degree of dissociation closely, as is demonstrated below.

Alane	Al_2Me_6 pure	Al_2Et_6 10% in hexane	$Al_2Pr^n_6$ 10% in hexane	$Al_2Bu^n_6$ 10% in hexane
Line width (Hz)	500	1100	2800	3900

If this view of the origin of line broadening in the alanes is correct then the ethynyl di-alkyl dimers and tricyclopropyl alane should possess quite narrow ^{27}Al lines because of the strong bridging capabilities of the ethynyl and cyclopropyl groups.

The line widths will of course always be viscosity dependent because the relaxation times of both components will be viscosity dependent. The changes in temperature dependence of line widths relative to viscosity noted by Petrakis possibly reflect changes in the position of the equilibrium (1). The molecular sizes will also affect the line widths but since the monomers are smaller units than the dimers the effect of increasing alkyl substituent size will be to some extent offset by the increasing degree of dissociation.

Further evidence in favour of this hypothesis comes from a consideration of the ^{27}Al chemical shifts of the alkyl alanes:

Alane	Al_2Me_6	Al_2Et_6	$Al_2Bu^i_6$
Shift, p.p.m. from $Al(H_2O)^{3\oplus}_6$	157	171	220

Such large changes in chemical shift with ligand size occurring for a group of chemically very similar ligands can be easily understood if the proportion of monomer were to increase along the series and the chemical shift observed were the exchange average of that of the monomer and dimer.

A calculation made assuming that triisobutyl alane is all monomer and trimethyl alane is all dimer and that ^{27}Al shift depends only on whether the molecules are associated or not gives the shift of triethyl alane as 167 p.p.m. based on Gutowsky's figures for dissociation. The triisobutyl alane, however, would be expected not to be fully dissociated[96] and the chemical shift calculated if the degree of dissociation were known would be nearer still to the observed one.

If the rate of exchange were slowed there would presumably be some tendency for the line to broaden further and to approach the "collapsed" state obtained for intermediate rates of exchange between chemically shifted species. That this mechanism may also contribute to the observed line widths is supported by Mole's observation that the rate of dissociation of trialkyl aluminium dimer is greater in toluene than in cyclohexane. The ^{27}Al line width of Al_2Et_6 at infinite dilution in these solvents when divided by solvent viscosity is marginally smaller in toluene (2·85) than in cyclopentane (3·29).[121]

B. Halo-alkyl alanes and some Ziegler catalysts

Since the halides are better bridging units than the alkyl groups these compounds form halo-bridged dimers. A detailed study of the series

$Me_nAl_2Cl_{6-n}$, using low-temperature proton NMR, shows, however, that when n is large, dialkyl bridges may also occur. Thus when $n=5$ singlet signals are seen due to two sorts of terminal methyl and one sort of bridge methyl, and this is interpreted as showing that only dimethyl bridges occur and not mixed bridges. The compounds $Me_2Al\mu\text{-}Cl_2AlMeCl$ and $MeClAl\mu\text{-}Cl_2AlMeCl$ were also examined.[124, 124a, 124b] A more recent study has confirmed that mixed halide-methyl bridges are only formed to a modest extent. The positions of equilibria vary widely for systems consisting of mixtures with two types of bridging group:

$$Me_2Al\mu\text{-}X_2AlMe_2 + Me_2Al\mu\text{-}Y_2AlMe_2 \rightleftharpoons Me_2Al\mu\text{-}X\mu\text{-}YAlMe_2$$

where X = Cl and Y = Me, Br or PhC≡C; X = Br and Y = Ph, PhC≡C or Pr^iO or X = PhC≡C and Y = Pr^iO. The order of bridging capability is

$$Pr^iO > Cl > Br > PhC{:}C > Ph > Me$$

and the mixed bridges X = Me and Y = Pr^iO or Br do not appear to form.[125] The mixed halide bridged compound which Mole found to be unstable has been observed mass spectrometrically.[126]

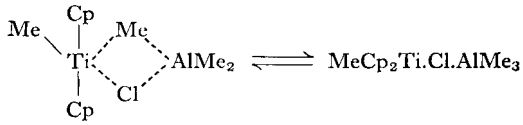
The ethyl-halo dimer compounds, like the methyl-halo system, may also show no evidence for the formation of a mixed halo-ethyl bridge, the only compounds easily observed at $-20°$ in a mixture of Et_6Al_2 and $Et_4Al_2Cl_2$ being the two starting materials, which do nevertheless undergo ethyl exchange.[127] Spectra are also reported elsewhere for $Al_2Me_4Cl_2$, $Al_2Me_2Cl_4$ and $Al_2Et_4Cl_2$.[88, 92, 93] The lack of mixed halo-alkyl bridge formation contrasts with that in the mixed alkyl compounds where mixed bridges appear to be preferred.

A few studies are reported of Ziegler-type catalyst systems using both ^1H and ^{27}Al spectroscopy. Adding titanium trichloride to triethyl alane or to $(AlClEt_2)_2$ has no effect on either ^{27}Al line width or shift, ^{27}Al NMR proving of little assistance in this particular case.[128] It has, however, proved possible to obtain information on systems based on cobaltous chloride. Solutions of Al_2Cl_6 and $CoCl_2$ in benzene are active as stereoregular diene polymerisation catalysts and give rise to two ^{27}Al resonances, one due to the aluminium chloride and one some 316 p.p.m. upfield and due to a complex. The spectral shifts and line widths are altered if $LiAlCl_4$, or thiophene or butadiene (of which the latter two form charge transfer complexes) are added. The results are accounted for by the formation of the complex $Co(AlCl_4)_2$ which exhibits a very large high field ^{27}Al shift (the highest so far recorded) because of a pseudo contact shift arising from the anisotropic g factor of $Co^{2\oplus}$. The addition of unsaturated molecules leads to formation of an organometallic

complex which broadens the aluminium resonance beyond the limits of detection and reduces the intensity of the observed signals. A mixture of Al_2I_6 and Al_2Cl_6 in toluene was observed to give an exchange averaged line.[129]

Proton spectroscopy has been used to examine the soluble catalysts based on titanium dicyclopentadienyls. If $Ti(C_5H_5)_2Cl_2$ is mixed with $Al_2Me_4Cl_2$ then methyl groups migrate from aluminium to titanium and a system similar to $Ti(C_5H_5)_2ClMe \cdot Al_2Me_2Cl_4$ is obtained.[130] The mixture consisting of $(C_5H_5)_2TiCl_2$ with $Al_2Me_4Cl_2$ gives rise to two methyl resonances one due to methyl groups attached to aluminium and one to titanium, the position of the latter indicating the presence of the complex $(C_5H_5)_2MeTi \cdot \mu\text{-}Cl \cdot AlMe_2Cl$ with a single chlorine bridge. Addition of phenyl acetylene perturbs only the signal intensity of the methyl attached to titanium and this result is consistent with the titanium-alkyl bond being the catalytically active site.[131] The proton NMR of $Cl_2AlCH_2AlCl_2$ has been reported.[132]

When $Ti(C_5H_5)_2ClMe$ is mixed with excess trimethyl alane three methyl proton resonances are observed, one from the methyl attached to titanium, one from the methyl attached to aluminium and a third whose intensity decreases reversibly if the temperature is lowered. It is suggested that this behaviour indicates an equilibrium between two different complexes, an octahedral, active form which is present at high temperatures and a tetrahedral, inactive, low-temperature form (**5**).[133]



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On the other hand no compounds containing aluminium and titanium were discovered in a tetrahydrofuran solution of trimethyl alane and titanium tetrachloride, the products of reaction being $Al_2Me_4Cl_2$, titanium trichloride and methane; some $TiCl_2Me$ may also be formed.[124]

Methyl exchange on dimethyl mercury is catalysed by aluminium trichloride or by $Al_2Me_2Cl_4$.[134] Proton data is reported for $MeHGa\mu\text{-}Cl_2GaCl_2$.[135]

Some studies have also been made on fluoro alanes. Diethyl fluoro alane is an unusually viscous liquid and is a tetramer in benzene. Proton and fluorine NMR support the structure as being based on an $[AlF]_4$ ring. The ethyl groups are all equivalent down to $-60°$ and the ^{19}F

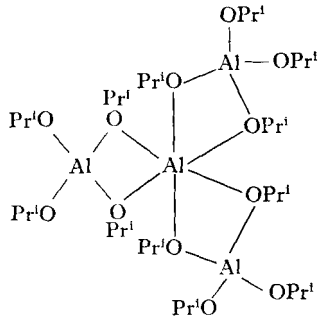
resonance remains a singlet at all temperatures.[136] The dimethyl analogue exhibits a 1:2:1 triplet methyl resonance, $^3J(H-F)=4{\cdot}65$ Hz, showing that all the methyls are coupled equally to two fluorine atoms which therefore must be coordinatively bivalent.[137] Data are also given for dimethyl and diethyl fluoro gallanes which, in contrast to the alanes, are trimeric. These have since been studied in more detail in several solvents and the complex A_3B_2 spectra given by the ethyl groups fully analysed. The proton shifts are very solvent dependent. The axial and equatorial ethyl groups are equivalent and it is suggested that the compound exists as a rapidly flexing ring.[138] Preliminary results are also reported for a few series of fluoro alanes including AlX_nF_{3-n}, where X = halide, OPr^i or Et and $n=1$ or 2 and which support the presence of fluoride bridged oligomer chains of variable length.[139]

Similar results have been obtained for the dimethyl gallium hydroxide tetramer which has a singlet methyl signal and must therefore be flexing in solution.[140]

C. Alkoxy, phenoxy, siloxy and germyloxy compounds, and some N–O and N-bridged dimers

Aluminium 2,2,2-trichloroethoxide is a dimer in benzene or methylene chloride but is a strong Lewis acid and adducts are formed in pyridine or dioxane.[141]

Aluminium isopropoxide has, however, a much more complicated structure. It can be prepared as a tetramer which exhibits three methyl doublet resonances in the ratio 1:1:2. This is consistent with the structure (**6**) where the $OCHMe_2$ groups bridging to the central aluminium atom are expected to be sterically hindered and so give two doublets from non-equivalent methyl groups, the remaining intense doublet arising from the six terminal OPr^i groups.[142]



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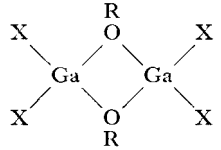
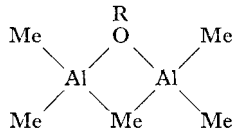
The hexacyclic trimer is formed on heating and its spectrum is temperature dependent there being intramolecular exchange of bridging and terminal groups. Aluminium isopropoxide can also be prepared containing both tetramer and trimer, the latter being separated by extraction with pyridine.[143] Mixed alkoxy-hydrido alanes have been prepared[144] and alcoholysis of aluminium trialkyl compounds has given the series of products $[Me_2AlOR]_2$. There are no methyl bridges since the alkoxy group forms an excellent bridging unit. Reaction to give $MeAl(OR)_2$ species is not important.[145] The reaction of trialkyl aluminium with the products of alcoholysis above has been followed by proton spectroscopy. The alkyl groups exchange in preference to the alkoxy group and the order of reactivity decreases in the order RO = $Et_2O > Pr^iO > BuO$. The methoxy compounds react anomalously slowly since they are trimeric and not dimeric.[146] The mixed alkoxide $Al_2(OPr^i)_2(OBu^i)_2$ may have an asymmetric structure and mixed bridges.[146a] Alkoxy gallium dihalides have been prepared by alcoholysis of organogallium dihalides. They are soluble and are dimeric in solution and vapour state; proton spectroscopy supporting an alkoxy bridged structure (**7**).[147] $Ga_2(Bu^tO)_6$ is an alkoxy bridged dimer.[146a]



R = Me, Et, Pr^n or Bu^n

7

Mixed aluminium alkoxy-alkyl bridged complexes (or hemialkoxides) may be prepared from a mixture containing excess trialkyl. Thus 1 mole of $Me_4Al_2(OCPh_2Me)_2$ and 2 moles of trimethylalane gives rise to two methyl signals, one from Al_2Me_6 and one from (**8**). The mixed bridged compound is preferred, its formation constant from the initial reactants being 625. The alane (**8**) exhibits intramolecular exchange and



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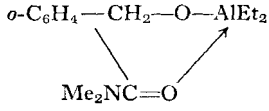
a separate methyl signal is only seen at $-65°$ though no intermolecular exchange was seen up to $+35°$.[148] These compounds have also been prepared by reaction of the trialkyls with ketones or aldehydes and

NMR data is given at $-30°$ for $Me_2Al\mu$-$Me\mu$-$(OR)AlMe_2$ for R = Bu^t, $CPhMe_2$, CPh_2Me, C_7H_{13}, CHPhMe and N=CMePh. The dimer with R = Bu^t undergoes intermolecular exchange, the mechanism involved being an opening of only one Al–Me bridge bond since no exchange occurs with trimethylgallium. The other compounds exhibit intramolecular exchange the rate increasing with the number of phenyl substituents in R.[149] Bridging tertiary butoxy groups have been observed previously.[150]

A mixture containing a trialkyl alane AlR_3 and an *N*-phenyl amide, R'CONHPh actively catalyses acetaldehyde polymerisation and has been shown using NMR to contain the dialkyl alkoxide R_2AlOCR'=NPh. A singlet signal is seen for the alkyl groups but this does not preclude a dimer structure as the authors suggest.[151]

Acid anhydrides or lactones will react with diethyl dimethylamido alane Et_2AlNMe_2 by inserting into the Al–N bond to give diethyl alkoxy alanes with an amide substituent in the alkoxy chain. NMR has shown that in one of these compounds (**9**), the amide oxygen donates



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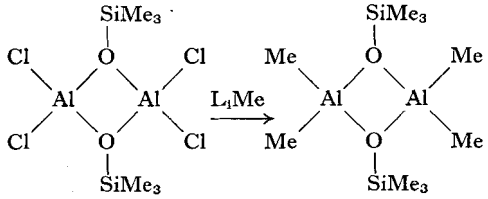
to aluminium thus forming a seven membered ring in which the CH_2 protons give rise to an AB quartet.[151a]

The substance of empirical formula Me_2AlOPh is initially dimeric when dissolved in toluene and exhibits a single methyl peak; over several hours a second methyl peak appears 0·2 p.p.m. to high field of the original one and molecular weight measurements and NMR determinations of the equilibrium ratios of dimer and trimer suggest this is probably a trimer.[152]

The structures of tribenzyloxyaluminium and the 4-chlorobenzyloxy derivatives in solution have been examined in detail using proton spectroscopy, associated with molecular weight determinations. The degree of association rises with concentration and in the most concentrated solutions the spectra are consistent with a tetrameric structure similar to that of the isopropoxide. A trimer is formed at lower concentrations. The benzyl CH_2O protons of the bridging groups are non-equivalent and give rise to AB quartets. Such non-equivalence could not exist in a dimer or trimer structure; for instance the protons of the bridge molecules in $[(Cl_3CCH_2O)_3Al]_2$ give rise to a singlet.[153, 154]

As might be anticipated the alkoxy bridges in these molecules can be functionally replaced by siloxy or germyloxy bridging units. The rings of (**10a**) and (**10b**) for instance are very strong and cannot be split by



10a **10b**

donor molecules. The shifts of the methyl groups may be indicative of silicon to carbon p–π bonding in these molecules.[155] The values of $^2J(^1H–^{29}Si)$ and $^1J(^1H–^{13}C)$ in the dimer $[(Me_3SiO)_3Al]_2$ are different for the terminal and bridge sites and this may also indicate a changed degree of p–π bonding in the bridging groups.[156] Spectra of the oxygen-bridged dimers $[\mu\text{-}Me_3SiOAlXY]_2$ are also reported for XY pairs ClH, Cl_2 or Me_2,[157] and for $[Me_3SiOGaMe_2]_2$[158] and NMR has been used to help determine the structures of $[\mu\text{-}Me_3GeOMMe_2]_2$ where M = Al or Ga. The shifts of the siloxy and germyloxy bridged compounds are compared and discussed in terms of their bonding.[159, 160]

Some dimers containing substituents which form bidentate nitrogen-oxygen bridges have also been described. The compounds $[R_2Al(O(CH_2)_nNR'_2]$ have been prepared, for $n = 2$, 3 or 9 and $R' = Me$ or H, and their NMR spectra have been examined. Only one sort of metal alkyl group could be detected at temperatures down to $-80°$ so that the $O(CH_2)_nNR'_2$ ligands probably form the bridges. These could be either normal oxygen bridges or nitrogen donor-type bridges as shown in (**11**), though NMR could not differentiate between these two

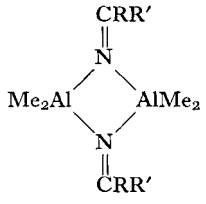
11

possibilities. IR results showed however that (**11**) was probably the correct formulation for all except the 3-amino-propoxide which is oxygen-bridged.[161, 162] Dialkyl 2-amino ethoxide aluminium monomer molecules will form adducts with aluminium trialkyls and redistribution of alkyl groups and exchange occurs in the adduct, though exchange is slow at room temperature.[163] The dialkylamido dimers with nitrogen instead

of oxygen formally bonded to the aluminium and with the oxygen donating to the neighbouring metal atom have also been described and seem to differ from the previously described dimers (**11**) in that the alkyl protons α to aluminium are shifted slightly to lower field.[164]

An isocyanate can be inserted between aluminium and nitrogen in Et_2AlNMe_2 to give a series of compounds $Et_2AlN(R)CONMe_2$ which are amides with non-equivalent *N*-methyl groups. The compounds in this case are believed to be monomeric.[165] $[Me_2C{=}NOAlMe_2]_2$ and $[Me_2C{=}NOGaMe_2]_2$ are both dimeric.[166]

A number of compounds containing pure nitrogen bridges have been prepared, principally by two research groups. Wade and co-workers have heated nitrile adducts of aluminium trialkyls to give compounds of type (**12**).



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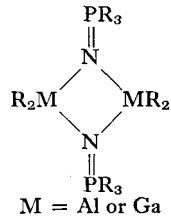
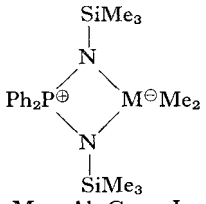


M = Al or Ga

13

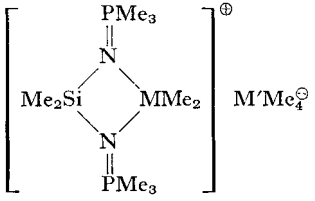
If R and R′ are dissimilar then *cis-trans* isomerism is possible and both forms are detected for the RR′ pairs Me H and Ph Me, but only the *trans* form for example for RR′ pairs Me_2; Et Me; Bu^t Me; Ph H or Me_2N H.[167 to 169] The halides, $(R_2C{:}NAlCl_2)_2$ and $(R_2C{:}NAlBr_2)_n$ (where *n* is probably 2) and the monomer $(R_2C{:}N)_3Al$ have also been prepared though the monohalides could not be obtained. The proton resonance of $(Bu^t_2C{:}N)_3Al$ is a singlet so that the butyl groups are equivalent, supporting a linear $C{=}N{\rightarrow}Al$ bond with some donation from nitrogen.[170] Some ethyl aluminium analogues were also prepared and data are given for the gallium dimers $(PhCH{:}NGaEt_2)_2$ and $(Bu^tCH{:}NGaEt_2)_2$.[171] Schmidbaur, who describes these compounds as compounds with small inorganic rings, has prepared a large series of similar compounds but with the nitrogen bonded to pentavalent phosphorus (**13**). The alkyl groups R are usually ethyl or methyl but three phenyl groups are attached to the phosphorus in one case. Adducts with trimethyl-alane or -gallane are also described.[172] If $Me_3GeN{:}PR_3$ is used as starting material then an adduct is formed whereas the tin analogue leads again to dimer compounds of type (**13**) since the Sn–N bond is more labile to electrophylic reagents.[173] The silicon methyls of (**14**),

which can also be regarded as a monomeric self adduct, give a singlet so that the rings must be symmetrical.



M = Al, Ga or In

14



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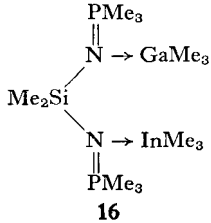
Long-range coupling is seen between phosphorus and silicon methyl, ^4J(P–N–Si–C–H) is 0·4 Hz for M = Ga and 0·5 Hz for M = In.[174] The compounds (**15**), where M and M′ = Al or Ga, have also been prepared. Two M-methyl signals are seen for the aluminium containing compound and these are further split in the presence of $AlMe_4^{\ominus}$. The PMe_3 groups give rise to an $[A_9X_2]$ spectrum. One of the precursors of these compounds (**16**) shows metal alkyl group exchange which may occur



16

possibly *via* ring closure to give a compound such as (**15**) and $MMe_4^{\ominus}$.[175] Dimethyl azo aluminium is reported and is a six-membered ring trimer.[176] $[(Pr^i)_2N]_3Al$ shows no non-equivalence of the isopropyl methyl groups and is a monomer, probably for steric reasons.[177]

The nitrogen bridge is strong and it has been shown that the presence of such a bridging group is conducive to the formation of mixed bridges.[126] Thus a mixture of diethyl chloro alane and dimethyl-dimethylamide alane exhibits two quartets at 25°. Heating to 100° allows reaction to proceed and a third ethyl quartet develops at the expense of the other two. Prolonged heating leads to the entire conversion of the mixture to the mixed bridged dimer $Et_2Al\mu\text{-}Cl\mu\text{-}(NMe_2)AlEt_2$. Mixed bridges with one methylamide component were also made containing Br, I, OEt or SMe as the other component and the diethylamide-bromide and ethoxide-bromide mixed bridges are also reported.[126]

Equally, if trimethyl alane and diphenylamine are reacted the nitrogen bridged dimer $(Ph_2NAlMe_2)_2$ is obtained. After reaction with excess trimethyl alane, three proton peaks are observed, one being due to a mixed bridged dimer $Me_2Al\mu\text{-}Me\mu\text{-}(Ph_2N)AlMe_2$.[178]

Variable temperature spectra are reported in benzene for the trimers $(Me_2GaPMe_2)_3(Me_2MPR_2)_3$ and $(Me_2NAsMe_2)_3$ where M = Al or Ga and R = Me or Et. Slight line broadening is seen at low temperatures which may indicate the presence of an inverting ring.[179] The trimers $(MeNHGaH_2)_3$, however, exhibit three methyl doublets which probably arise from isomers (a) with all methyls equatorial and (b) one axial and two equatorial. $(MeNHGaMe_2)_3$ gives a similar *N*-methyl signal although the gallium methyl region was too complex to interpret. $(Me_2NGaMe_2)_2$ on the other hand forms the usual four-membered ring which is less sterically crowded and gives singlet methyl signals.[180]

IV. ADDUCTS OF SUBSTITUTED ALANES AND GALLANES

The compounds considered in this section have some similarities to the dimers which we have just discussed since the dimers may be regarded as self adducts with a donor and acceptor centre in each half molecule. The division between the two sections is thus to some extent artificial.

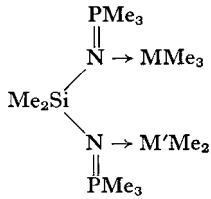
The study of these compounds is of importance both from the point of view of understanding the donor-acceptor interaction and also industrially since the addition of a donor to a Ziegler catalyst system can markedly alter both the rate and stereospecificity of a catalytic reaction. The work has been divided into three parts: (A) exchange reactions involving the substituents on the metal, (B) determinations relating to adduct strengths and donor/acceptor exchange (the question of whether five coordinate adducts exist in solution is considered under this heading), (C) adducts of aluminium borohydride. References 163, 167 to 175 also contain data on adducts.

A. Alkyl exchange reactions

Mole has studied the exchange of alkyl groups between various substituted alane-base complexes in solutions containing excess base. Exchange may occur with or without dissociation of base. Exchange of methyl groups between trimethyl alane and triphenyl alane is fast in a hydrocarbon solvent but becomes slow in an excess of base so that if dimethyl phenyl alane is dissolved in ether three methyl resonances are seen, indicating disproportionation into $Me_3Al\cdot B$, $Me_2PhAl\cdot B$ and $MePh_2Al\cdot B$ where B represents the ether molecule. $Me_2PhAl\cdot B$ was

slightly preferred over the other disproportionation products. An excess of ether of at least two equivalents with respect to alane is required to fully retard the rate of alkyl exchange and it is suggested that the adducts dissociate.[181] If the base is in a large excess in solutions containing pyridine the reaction is bimolecular and occurs without loss of base from the complexes. If, however, the concentration of pyridine is small the rate of exchange becomes faster and dependent upon base concentration so that dissociation probably occurs prior to exchange.[182] Mixtures of trimethyl alane and a dimethyl halo alane, Me_2AlX where X = Br, Cl or Ph, undergo exchange in solutions containing anisole. In excess of anisole the exchange rate is strongly dependent on the amount of excess anisole present and dissociation occurs prior to exchange, even if the excess of anisole is small. Exchange between the dimethyl halo alane adducts $Me_2AlCl \cdot B$ and $Me_2AlBr \cdot B$ on the other hand is not strongly dependent upon the excess of anisole and probably proceeds directly without loss of base though some dissociative exchange may occur also.[183] This paper[183] contains a useful summary of the exchange mechanisms possible in these systems. Exchange involving other complexed alanes such as $Me_2AlX \cdot B$ has also been discussed, where X may be alkyl or halide and also methyl. Mixtures of any two of the compounds of formula Me_nAlCl_{3-n}, $n = 0$ to 3, in ether give rise to one or two methyl peaks which show that the products exchange slowly. If the stoichiometry of the mixture is Me_2AlCl or $MeAlCl_2$ then the compounds tend to exist as single etherates and not as mixtures.[184] Exchange in mixtures of trimethyl alane and dimethyl ethyl alane etherates in toluene solution increases in rate with concentration but becomes slower if excess ether is present and it is concluded in this case that reaction occurs without dissociation.[185]

Alkyl exchange occurs on the metals of (**17**) probably *via* the formation of a ring compound and $MME_4^{\ominus}$.[175]



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Disproportion has been observed in THF solutions of dimethyl cyclopentadienyl alane, $(C_5H_5)AlMe_2$, using proton spectroscopy.[186]

B. Adduct strengths and base-acid exchange

This topic has recently been reviewed by Satchell and Satchell[187] who consider that in order to determine relative donor bond strengths the equilibrium constant of the series of reactions

$$B + A \underset{}{\overset{K}{\rightleftharpoons}} B \cdot A$$

should be obtained. They consider briefly the role played by NMR in the determination of donor bond strengths and conclude that because of steric effects NMR results will not be reliable. In their conclusions they state that "short cuts to relative acidities are neither direct nor profitable".

Their opinion is based mainly on the NMR of boron compounds where most results are available. Very much less work has been done with aluminium compounds, but the majority of workers seem to be aware of the difficulties inherent in the method and in several cases comparisons have been founded on experiments where bases were allowed to compete for acceptor sites so that results are effectively measures of K and are obtained independently of the absolute magnitudes of the NMR parameters. Indeed the aluminium literature abounds with examples where the absolute NMR parameters are obviously not good measures of donor-acceptor bond strengths and this situation may in part account for the much more cautious approach taken.

It is generally held that in a complex containing groupings of the type $R\text{–}CH_2\text{–}X \rightarrow Al\text{–}CH_2\text{–}R'$ the formation of the dative bond should, for inductive reasons, lead to a high field shift of the protons α to the aluminium of the acceptor and a low field shift of the protons α to X on the base. Such behaviour is often observed (Table IV) and the magnitude of the effect has been correlated particularly in boron chemistry with the strength of the adduct. Such a view, however, ignores the possible electric field shifts introduced by the creation of a polar dative bond and the effect of the new magnetic anisotropies introduced into the adduct and one would expect the shift-bond strength relationships to be much more complex than often hitherto assumed. For instance a weak bond might be less polar and produce a lower electric field effect but a larger anisotropic effect than a strong bond.

Perkampus and Krüger[188] have carried out calculations of the π electron densities in the special case of pyridine-borane adducts and conclude that the α and β pyridine proton adduct shifts arise from:

(a) a reduction in electron density on complexing which gives a downfield shift greatest for the α protons,

(b) a reduction in ring current which gives an equal α and β upfield shift,

(c) a reduction in the paramagnetic effect of the nitrogen lone pairs which could give a 0·7 p.p.m. upfield contribution to the α proton shift and a smaller one to the β-protons.

The overall effect of (a)–(c) is that on complexing the β protons move further downfield than the α protons. These effects will act in addition to those discussed in the preceding paragraph.

Another factor which has a bearing on the observed shifts is the large range of solvents used including Freon 11, cyclohexane, cyclopentane, benzene, toluene and the pure adducts (melt or liquid). The aromatic solvents are particularly liable to produce large solvent effects in adduct resonances due to the different shapes of the free and complexed molecules. Thus if one compares a free ligand shift with that of the ligand in a complex one could expect part of the difference to be accounted for by a solvent shift. Mole has published a table which demonstrates the importance of these solvent effects.[189] The changes

TABLE IV

Chemical shifts of α and ω protons of ether adducts of triphenyl alane in benzene and deuterochloroform. Bracketed figures are for pure ether.

Compound	Solvent	Chemical shifts (δ), p.p.m. αCH_2	ωCH_3	Internal shifts $\alpha-\omega$, p.p.m.
$Et_2O \cdot AlPh_3$	benzene	3·52 (3·23)	0·57 (1·10)	2·95 (2·13)
	$CDCl_3$	4·17 (3·50)	1·20 (1·2)	2·97 (2·30)
$Bu^n_2OAlPh_3$	benzene	3·67 (3·30)	0·56 (0·80)	3·11 (2·50)
	$CDCl_3$	4·23 (3·42)	0·71 (0·92)	3·52 (2·50)

in α proton shift are greatest for the dibutyl ether though subsequent displacement studies showed this to be the weaker donor. The order of changes in internal shifts are different in the two solvents.

Standardisation also poses a problem for these very reactive solutions and many workers have been reluctant to use TMS in case of interfering reactions and also because the resonances of protons on carbon attached to aluminium fall very near to TMS. This has resulted in the use of many different standards both internal and external which make it very difficult to compare different workers' results though trends are easily followed in any one set of results. In view of this and of the

solvent effects it is perhaps not too surprising that the most consistent sets of results, that is those that correlate best with the various measures of adduct dissociation energies, appear to be the internal shifts of ethyl groups, though even these do not always give the same relative orders as the thermochemical results.

The considerable reactivity of these compounds also introduces considerable handling difficulties and for this reason a major effort is required to obtain accurate concentrations and even then one cannot be absolutely certain that contamination by moisture has not affected the result.

It is also now certain that many substituted alane and gallane adducts dissociate in solution and that the shifts observed are not adduct shifts but an average for free and dissociated adduct. Under these circumstances it seems desirable that before any claims are made as to the meaning of shifts which occur upon forming a complex, at least a simple dilution study should be undertaken with the complex or else attempts made to measure the shifts of one component in an excess of the other. Alternatively the degree of dissociation might be measured by other means.

Adducts are considered below in an order determined by the nature of the donor atom, namely oxygen in ethers, sulphur in sulphides, other oxygen donors, nitrogen and phosphorus. A discussion of the possible existence in solution of five coordinate acceptors is given in the nitrogen donor section.

Mole has discussed the factors which we need to know to make meaningful comparisons of dative bond strengths and has studied the displacement of one base by another from triphenyl aluminium. Exchange of base is fast in the presence of excess ether and the various ethers present in mixtures of bases give signals at positions average between those of free and complexed base. Proportions of ethers were varied and the shifts recorded in order to obtain the concentrations of free and complexed ether and thence to calculate equilibrium constants. Thus diethyl ether will displace di-n-butyl ether from tri phenyl alane ($K = 1{\cdot}5$) but is in turn displaced by phenyl cyanide ($K \approx 1$) (Table IV). Triethylamine in contrast exchanges slowly with the triethylamine adduct but exchange is catalysed by added ether presumably *via* displacement of ether from the etherate by the free amine.[189] A similar study has been made of the gallium bromide or chloride complexes of diethyl ether and diethyl sulphide. In this case it is found that gallium trichloride is a stronger acceptor than the bromide and that diethyl sulphide is a stronger ligand than diethyl ether. The shift-composition plots are curved and this indicates that the complexes dissociate. The

estimated formation constants follow the trends in the calorimetrically determined heats of formation. The diethyl ether chemical shifts which occur on complexing tend to be less for gallium chloride adducts though thermochemical evidence suggests that the trichloride forms the strongest complex.[190] The internal shifts in the sulphide were the only data which followed the thermochemical sequence; those seen in diethyl ether did not (Table V).

TABLE V

Changes in α proton shifts and in internal shifts δ_i of ethyl protons of diethyl ether and sulphide complexes of gallium halides

Complex	Changes in* α proton shifts, p.p.m.	Changes in δ_i,† p.p.m.	Formation‡ constants	Donor-acceptor bond dissociation energy, kcal mol^{-1}
Et_2OGaCl_3	1·54	0·59	24	50·7
Et_2OGaBr_3	1·91	0·65	18	47·4
Et_2SGaCl_3	1·11	0·33	55	56·2
Et_2SGaBr_3	1·35	0·24	25	51·8

* The methylene protons move low field on complexing.

† δ_i increases on complexing.

‡ The equilibrium constants for pairs of ethers with one halide show that Et_2SGaX_3 is more stable than Et_2OGaX_3. The sulphides, however, show the smallest chemical shift effects.

The metal alkyl shifts have been measured in Freon solution for a series of adducts of trimethyl gallane and correlate well with dissociation bond strengths for the bases SMe_2, OMe_2, PMe_3 and NMe_3. The internal ethyl shifts measured for the adducts $Et_3Ga \cdot SMe_2$ and $Et_3Ga \cdot NMe_3$ were noted to correlate with the degree of dissociation of the complexes.[191] The internal shifts of the diethyl etherates of triethyl alane and gallane have also been discussed in earlier work.[192]

The reactions of dichloroalane etherate are reported and compounds were prepared with dimethyl-, di-isopropyl-, di-isoamyl- ethers, THF, tetrahydropyran, 1,2-dimethoxyethane and dioxane.[193] Thermochemical data show that THF is a stronger ligand than diethyl ether for aluminium and gallium halides and that the aluminium halides are the better acceptors. Diethyl ether internal shifts appear to parallel these relative strengths but the NMR effect is small and may be fortuitous[194] (Table VI). The adducts $AlHX_2 \cdot 2THF$ and $AlH_2X \cdot 2THF$, where X is a halide,

have been characterised by NMR.[195] The protons of the base in $H_3Al \cdot THF$ and $H_3Al \cdot NMe_3$ are shifted by 0·6 and 0·4 p.p.m. respectively between melt and benzene solution.[196] *p*-Dimethoxy benzene forms 1:1 and 2:1 adducts with $AlMe_3$ and $AlMe_2Cl$; the methoxy resonance of the 1:1 complex is a singlet at 25° and a doublet at −60°, indicating exchange of alane between methoxy oxygens.[197]

A mainly thermochemical study of adducts of diethyl sulphide and the sulphur analogue of tetrahydrofuran conclude that while the NMR shift data do give a guide to relative donor strengths in a closely related series of complexes the thermochemical data is far more reliable.[198]

TABLE VI

Changes in internal ethyl chemical shifts δ_1 of diethyl-ether complexes of aluminium and gallium trihalides

Complex	Increase in δ_1,* p.p.m.	Temperature	Donor-acceptor bond dissociation energy, kcal mol^{-1}
$Et_2O \cdot AlCl_3$	0·68	25°	69·5
$Et_2O \cdot GaCl_3$	0·62	25°	51·0
$Et_2O \cdot GaBr_3$	0·63	25°	47·4
$Et_2O \cdot AlCl_3$	0·72	60°	69·5
$Et_2O \cdot AlBr_3$	0·67	60°	65·8
$Et_2O \cdot GaCl_3$	0·65	60°	51·0

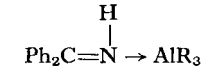
* The increase in δ_1 corresponds to a low field shift of the methylene proton resonance.

Other oxygen donors which have been used to form adducts are amine and phosphine oxides, sulphoxides and esters. The alumoxanes $R_3PO \cdot AlR'_3$ where R, R′ = Et or Me are isosteric with the disiloxanes.[199] The value of ^2J(H–P) is the phosphine part of the adducts Me_3POMMe_3, where M = Al, Ga or In, varies over a small range and it is suggested that this may be related to the acceptor strengths of the metal alkyls, which lie in the order R_3Al (^2J = 13·5 Hz) > R_3Ga (^2J = 13·3 Hz) > R_3In (^2J = 13·25 Hz), though this range of variation in coupling seems rather small for it to be generally reliable. Data are also given for the amine oxide and the sulphoxide adducts,[200] and for adducts of type $Me_3EOM(OSiMe_3)_3$, where E = P or N, M = Al or Ga.[201] Hexamethylphosphortriamide also forms complexes, only the oxygen acting as a

donor centre. The complex is stable and in the presence of excess trimethyl alane and at low temperatures signals are seen for both complex and free alane.[202]

When ethyl acetate is complexed by aluminium bromide the acyl methyl protons move downfield as expected but the ethyl methylene protons move upfield.[203] Epoxide oxygen will donate to $AlEt_3$.[204]

Further evidence that shifts are not related solely to inductive effects is obtained from Wade's observation that the imine resonances of diphenylketimine adducts of alkyl and aryl alanes and trimethyl gallane (**18**) move upfield by up to 1·2 p.p.m. when the complex is formed.



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This is contrary to the expected inductive effect. The phenyl resonances of the imine and the metal alkyl resonances also move slightly upfield. Neither is there any regular progression in the imine shift in the adducts of the metal series BMe_3 (−0·04 p.p.m.) $AlMe_3$ (1·16 p.p.m.) or $GaMe_3$ (0·84 p.p.m.).[205,206] Data are also reported for $Me_3GeN(:PR_3) \rightarrow MMe_3$,[173] for $HN(:PR_3) \rightarrow MMe_3$, where M = Al, Ga or In,[172] and for cyanamide adducts.[169] The methyl groups of dimethyl cyanamide also move upfield on forming adducts with aluminium alkyls.

The internal shift of the metal ethyl groups in aluminium triethyl adducts appears to increase as the donor power of the base increases. The pyridine complex forms a notable exception, however, and the ring current anisotropy of the base may affect the measured shift by about 0·2 p.p.m.[207]

The 4-ethyl pyridine complexes of aluminium trihalides have been studied in some detail in the light of Perkampus and Krüger's results.[188] The absolute α and β shifts do not correlate with the calorimetric bond dissociation energies of the adducts though the changes in internal α-β shifts which occur on complexing do.[208] The results are summarised in Table VII.

Alane and alkyl alanes have been complexed with trimethylamine. The amine signal positions are markedly dependent on sample state and differ by 0·4 p.p.m. between melt and benzene solution.[196] The resonances of the aluminium alkyl groups in the alanes $R_nAlH_{3-n} \cdot NMe_3$, where R = Et or Me and $n = 1$ or 2, show extra splitting and the complexes are shown cryoscopically to be associated in cyclohexane solution. The splitting may arise from dimers which are alkyl bridged.[209] Strong complexes are formed between triethyl alane and nitrogen bases and

exchange proceeds in the presence of excess base. The internal chemical shifts of the triethyl alane are a guide to the electronegativity of the donor.[210] Ether and pyridine adducts were also studied. All the compounds studied were found to undergo ionisation and the THF adduct showed evidence of considerable dissociation.

Complexes have been prepared between all the diethyl halo alanes and trimethylamine. The complexes formed are all 1:1 adducts and the use of the dialkyl halides allows comparison of a non-ionic fluoroalane with the other halides. Proton spectroscopy was used to determine an order of acceptor strengths. The internal ethyl shifts are independent of the concentration of complex in cyclohexane and the α protons of the

TABLE VII

Changes in α proton chemical shifts and in internal chemical shifts δ_1 between α and β protons of 4-ethyl pyridine adducts of aluminium halides

Complex	α proton shifts,* p.p.m.	Decrease in δ_1 on complex formation, p.p.m.	Donor-acceptor bond dissociation energy, kcal mol^{-1}
$4\text{-}EtC_5H_4N \cdot AlCl_3$	8·82	0·54	77·6
$4\text{-}EtC_5H_4N \cdot AlBr_3$	8·89	0·48	75·7
$4\text{-}EtC_5H_4N \cdot AlI_3$	9·07	0·32	64·8

* Moving increasingly to high field from free base.

ethyl groups are shifted upfield on complexing, the iodide showing the largest shift and the fluoride the least, the acceptor properties of the alane decreasing in the same order, a conclusion confirmed by qualitative competition studies. The effect on the amine protons is much smaller (Table VIII). No exchange occurs in the absence of free diethyl halo alane. If one halide is added to the adduct of another, two signals are seen but not corresponding to the signals exhibited by any single adduct. The shifts are probably perturbed by exchange reactions and it was not possible to obtain accurate data, even at low temperatures.[211]

The rates of exchange of a series of amine adducts of trimethyl gallane has been extensively examined by variable temperature spectroscopy. The methyl shifts in mixtures of trimethylamine and trimethylgallane vary linearly with composition so that dissociation cannot be extensive.

The lines remain narrow at all temperatures in the presence of excess base. However, if excess trimethyl gallane is present two lines are seen below 0°. Line-broadening studies showed that the adduct lifetime is independent of concentration whereas in contrast that of the gallane is concentration dependent and exchange *via* a dissociative pathway is suggested.[212]

$$Me_3N \cdot GaMe_3 \rightleftharpoons Me_3N + GaMe_3$$

Similar results were obtained for dimethylamine adducts but for adducts of methylamine and ammonia exchange occurs by nucleophylic displacement and the reactions have lower activation energies. In the

TABLE VIII

Changes in internal ethyl chemical shifts δ_1 of diethyl halo alane complexes of trimethylamine and pyridine

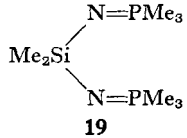
Complex	Increase in δ_1* on complex formation, p.p.m.	Al–N frequencies cm^{-1}
$Et_2AlF \cdot NMe_3$	0·18	—
$Et_2AlCl \cdot NMe_3$	0·19	303
$Et_2AlBr \cdot NMe_3$	0·30	306
$Et_2AlI \cdot NMe_3$	0·39	312
$Et_2AlCl \cdot C_5H_5N$	0·08	302
$Et_2AlBr \cdot C_5H_5N$	0·13	292

* Increase in δ_1 corresponds to a high field shift of methylene protons.

case of dimethyl ether the exchange was too fast to measure and the adduct, like that of diethyl ether, was observed to be considerably dissociated. The different mechanisms are rationalised in terms of steric factors.[213] Nitrogen donors are also discussed in references 188, 189, 191.

A number of systems have been investigated in which bidentate nitrogen or phosphorus donors were used to form the adducts. In the solid phase these contain five coordinate aluminium.[214] The proton spectrum of a solution of, for instance, a tetramethyl hydrazine adduct is a singlet showing that the methyl groups are magnetically equivalent and it was proposed that these complexes remained five coordinate in solution.[215 to 218] However, investigations at different mole ratios of donor and acceptor suggest that in fact the donor is rapidly exchanging its donor centre.[219] This has been confirmed in one case for the bidentate

nitrogen donor (**19**) which forms 1:1 complexes with trimethyl alane or



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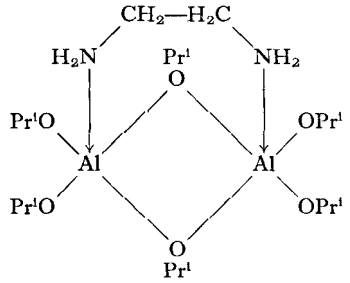
gallane which exhibit a single *P*-methyl doublet at room temperature. On cooling, the doublet splits into two doublets so that the nitrogens must be non-equivalent. Schmidbaur coins the term "oscillatory acceptors" for the acceptor molecules in these complexes;[220] similar results have been obtained for a diether.[197]

Recent work, in which a number of complexes $Me_3MMe_2N(CH_2)_nNMe_2$ and $Me_3MMe_2N(CH_2)_mNMe_2MMe_3$, where M = B, Al, Ga or In, $n = 1$–3 and $m = 2$ or 3, were characterised, supports these conclusions.[221] The methylene protons move to low field on forming the complex in benzene solution while, remarkably, the *N*-methyl protons move slightly upfield. Reference to Table XV, however, shows that the shift change of the *N*-methyl protons is normal for an aromatic solvent and that it is the low-field *N*-methylene shift which is unusual. The anomalous methylene behaviour decreases in the series $NCH_2N > N(CH_2)_2N > N(CH_2)_3N$, and this suggests that the more sterically hindered methylene suffers the least upfield solvent effect.

Ethylene diamine will react with aluminium isopropoxide to give an adduct containing two moles of aluminium per molecule of amine. Exchange of amine with excess amine is rapid at room temperature but two amine NMR signals can be observed at −18°. The adduct appears to contain only one type of isopropyl group although some broadening of the methyl resonance is seen at low temperatures which may indicate the existence of differentiated substituents; the structure may be (**20**) or (**21**).



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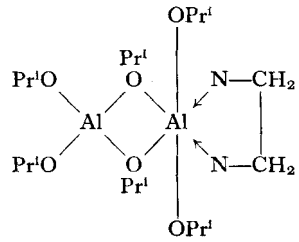

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Addition of isopropanol causes rapid intermolecular exchange of isopropoxy groups. Two moles of alcohol give a 23 Hz low-field shift of amine methylene protons which may be caused by coordination of alcohol at aluminium to give six coordinate metal.[222] The molecule $AlR_2OCH_2CH_2NR'_2$ is thought to form a simple 1:1 nitrogen adduct with aluminium trialkyls.[163]

A number of complexes have recently been reported which were formed from phosphines, phosphites, phosphonates and triethyl alane or dichloro ethyl alane. When complexes are formed with the latter the methylene protons α to aluminium move upfield and the internal chemical shifts of the ethyl groups may be related to donor bond strengths. The absolute and internal shifts do not correlate well. The complexes, particularly those of trimethyl phosphine, rapidly exchange donor molecules even at $-80°$ and the measured shifts are very concentration dependent. The donor ^{31}P resonances move downfield on complexing (the table in reference 223 is correct). NMR also provides evidence that in trimethyl phosphite adducts it is the phosphorus and not the oxygen which donates, since the methyl shift is almost completely unaffected by complexing.[223, 224]

Aluminium-Phosphorus spin coupling is observed in the adducts X_3AlPR_3 where X = Cl, Br; R = Me or Et. $^1J(Al–P) = 263$ Hz (X = Cl) or 248 Hz (X = Brl, R = Me) and the aluminium resonance appears at 99 to 110 p.p.m. low field of $Al(H_2O)_6^{3\oplus}$. Excess phosphine causes exchange and the ^{27}Al resonance moves upfield to +57·4 p.p.m.[224a]

Pyrolysis of $Me_2PHAlEt_3$ yields $(Et_2AlPMe_2)_3$ which has a P–Me quartet which is the X part of an $[AX_6]_3$ spin system.

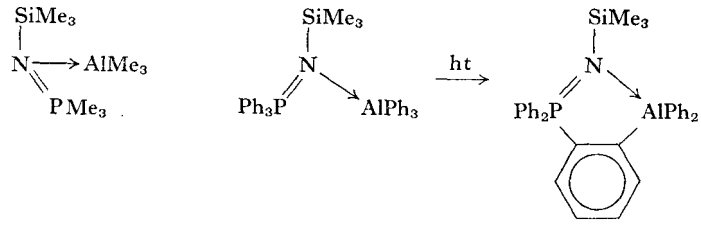
Gallane adducts have been made with triphenyl- and trimethylphosphine. NMR was used to study the equilibrium:

$$Me_3N + Me_3PGaH_3 \underset{}{\overset{K}{\rightleftharpoons}} Me_3NGaH_3 + Me_3P$$

and a value of $K = 2{\cdot}94$ obtained. The two donors thus have similar donor strengths towards gallane, a conclusion also reached from IR measurements. Exchange of donor is rapid in the presence of excess donor.[225] The similar adducts with trimethyl gallane have also been recently examined. The activation energy and entropy for the exchange of donor on the complex $Me_3P \cdot GaMe_3$ suggests that exchange probably follows a dissociative pathway similar to that observed for the nitrogen analogue. Exchange rates were measured using curve fitting techniques.[226]

Adducts of alanes and gallanes made from donors containing five coordinate phosphorus and three coordinate nitrogen atoms are reported by Schmidbaur and Wolfsberger, based on the ligand $Me_3Si \cdot N{:}PR_3$

where R = Me, Et or Ph;[227 to 229] in this case the nitrogen is the donor (**22**). The resonances due to silicon methyl protons and to protons α to phosphorus move downfield on complexing, the protons on phosphorus always being most sensitive to the changes occurring on complexing and alanes always having a greater effect than gallanes, the latter therefore being the poorer acceptors. Heating the phenyl derivative (**23**) gives the internal or self adduct (**24**). The change is accompanied by an



22 **23** **24**

upfield silicon methyl shift which presumably arises from steric changes since it is virtually the same for both the aluminium and gallium compounds.[229] Data are also recorded for the adducts of the metal halides which show perturbation of the phosphorus methyl shifts in the order $AlI_3 > AlBr_3 > AlCl_3 > GaCl_3 > InBr_3 > InCl_3$. These shifts are possibly a fairly good indication of relative acceptor strengths because of the presence of the double bond.[230] Benzene may interact with aluminium tribromide.[231]

Three papers have also been published on the ^{27}Al NMR of adducts of aluminium compounds. The ^{27}Al resonances of nitrogen, oxygen and sulphur adducts of triethylalane are chemically shifted from free triethylalane. The shift depends on the donor atom and moves downfield in the order N > O > S. The line widths of the adducts in solution and extrapolated to infinite dilution are greater than that of the free alane, the measured line widths of mixtures of alane and base increase with addition of base until a maximum is reached at equimolar composition. It is suggested that the increase in line width may occur because the symmetry at the aluminium is less perfectly tetrahedral in the adduct than in the alkyl dimer or it may be related to the increased molecular volume of the adduct.[232, 233] The line widths observed in the presence of mixtures of donors were used to estimate relative donor strengths.[232]

A ^{71}Ga result has also been reported for the adduct formed between gallium trichloride and diethyl ether but the line is very broad.[28] Subsequently much narrower lines were observed for nitrogen adducts of gallium trihalides.[234] The etherate is now known to be highly dis-

sociated[190] whereas the nitrogen adducts are dissociated to only a small extent,[191] though exchange of base occurs in both cases. It is therefore not unreasonable to propose that the large line widths observed both for the gallium and the aluminium adducts arise because of the dissociation and exchange in these systems. The situation is similar to that already discussed for the dimeric alkyl alanes except that three metal environments are possible in these systems; namely (a) in the tetrahedral adduct, (b) in the case of dissociative exchange in the form of monomer trialkyl alane, with its short relaxation time, and (c) in the case of a bimolecular mechanism of exchange in the form of a five-coordinate species which will also have a short relaxation time. The ^{27}Al chemical shifts of the adducts are well removed from that of free Et_6Al_2 and exchange at the correct rate could lead to further line broadening from this cause also and explain why the adduct lines were broader than that of the free alane. The possibility of ionisation reactions of these adducts introduces a further metal environment which might also contribute to line widths. Large donor molecules give rise to the broadest ^{27}Al lines and this may be simply a Debye effect or it may also be due to increased dissociation related to steric strain in such adducts.[233] Where donor—Al spin coupling is observed there is no dissociation and the ^{27}Al lines are [224a] narrow.

The sodium fluoride adducts of trialkyl alanes have also been examined using ^{27}Al line width studies. The 2:1 adducts $Al_2R_6 \cdot NaF$ have a single ^{27}Al line although they do not undergo exchange if mixed, two ^{27}Al resonances being seen in a mixture of $Al_2Et_6 \cdot NaF$ and $Al_2 \cdot Bu^n_6 \cdot NaF$. Neither does alkyl exchange occur in a mixture of triethyl alane and $Al_2Pr^n_6 \cdot NaF$, two ^{27}Al lines again being seen. The equivalence of the aluminium atoms in the complex is consistent with a linear Al–F–Al bond.[235]

C. Adducts of aluminium borohydride

Aluminium borohydride will also form adducts with a number of donors, that formed with trimethylamine having been extensively studied. The ^{11}B spectra of the series of adducts $H_nAl(BH_4)_{3-n}NMe_3$ are quintets very similar in appearance to that obtained from aluminium borohydride itself. Very rapid intramolecular bridge-terminal proton exchange must therefore also occur in the BH_4 groups of the adduct.[236] 1:1 Adducts can be formed with a variety of donors: NMe_3, NEt_3, PMe_3, $AsMe_3$, Me_2O, Et_2O and Me_2S. In the case of amine or phosphine donors, reaction with excess base leads to the formation of adducts of alane and borane. The hydride proton spectrum of the 1:1 adduct $Al(BH_4)_3 \cdot NMe_3$ is highly complex consisting of a 1:1:2:2:3:3:3:3:2:

2:1:1 multiplet. This is interpreted as arising from spin-spin coupling to boron, $^1J(B–H) = 88$ Hz and to aluminium $^2J(Al–H) = 44$ Hz.[237] This adduct has been examined more recently using in addition ^{27}Al and ^{11}B NMR. The proton spectrum is confirmed (Fig. 10) and a multiplet due to coupling to twelve protons is seen in the ^{27}Al spectrum. A mixture of the adduct and free aluminium borohydride exhibits two ^{27}Al

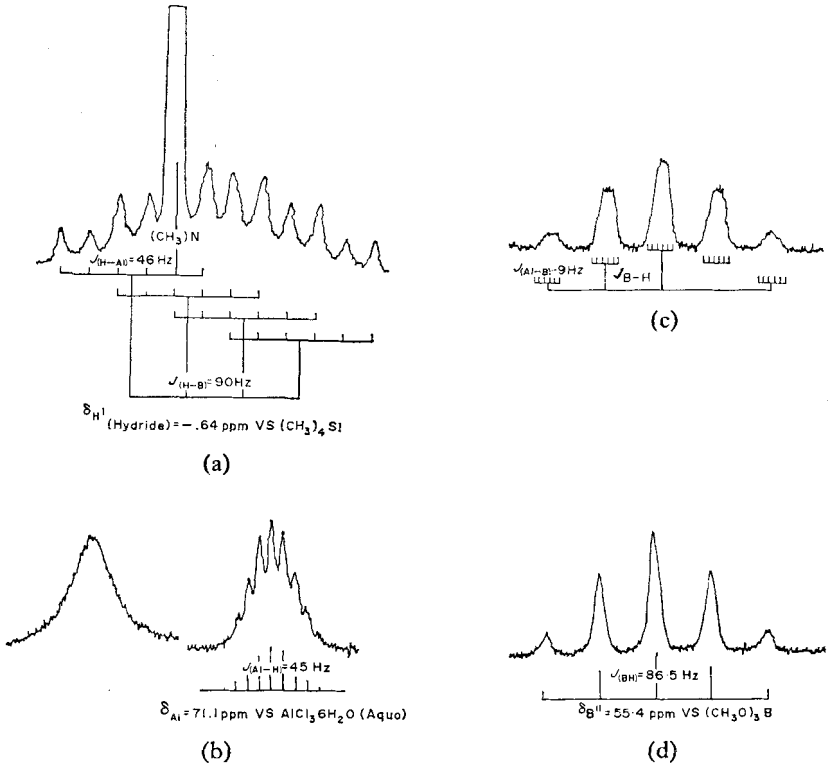


FIG. 10. (a) Proton magnetic resonance spectrum of $(CH_3)_3NAl(BH_4)_3$ in benzene at 60 MHz. (b) ^{27}Al NMR (8·5-MHz) spectra of $Al(BH_4)_3$ and $(CH_3)_3NAl(BH_4)_3$ in benzene. (c) ^{11}B NMR spectrum of $(CH_3)_3NAl(BH_4)_3$ in benzene at 15·1 MHz. (d) ^{11}B NMR spectrum of $(CH_3)_3NAl(BH_4)_3$ in benzene at 15·1 MHz with ^{27}Al decoupling. (From Lauterbur *et al.*[238])

peaks so that the adduct is not appreciably dissociated and is not undergoing base exchange.[238] The stereochemistry around the aluminium in the borohydride adduct at room temperature is near tetrahedral[239,240] so that the field gradient at the aluminium nucleus would be expected to be small. This can occur even where one of the ligands around the

metal is different from the other three provided all the ligands give rise to similar electron densities near the nucleus since the field gradients originate almost entirely in the bonding electrons in close proximity to the nucleus.[241] The symmetry of the molecule as a whole is irrelevant in determining the field gradients at a particular atom. In consequence the ^{27}Al relaxation time is long, the spectrum of Fig. 10 suggesting a value of about 0·02 sec corresponding to a line width of about 18 Hz which may be estimated from Fig. 10 after allowing for 9 Hz coupling to boron. This is in marked contrast to the line widths observed for the dissociated adducts[232 to 234] and lends support to the suggestion that the broad lines arise from dissociation and exchange. Whether a hypothetical undissociated adduct would have a line as narrow as 18 Hz cannot be determined. The detailed symmetry around the aluminium in the borohydride adduct is complex and is only tetrahedral on average[240] so that the narrow ^{27}Al line may well arise partly because of a rapid fluctuation in direction of field gradient.

Adducts with trimethyl arsine and dimethyl sulphide show only coupling to boron in the hydride proton spectrum while those with trimethyl phosphine and diethyl or dimethyl ether have a broad structureless proton line.[237] These differences may be caused either by dissociation which seems the most likely explanation in the first case or by the existence of field gradients at aluminium which would cause partial collapse of the aluminium coupling in the second case. Thus the narrow lines of the trimethylamine adduct may arise fortuitously because this particular base provides just the right electron density near the nucleus. Coupling to phosphorus has, however, been recently observed in the author's laboratory between Al and P in $Me_3P \cdot Al(BH_4)_3$, $^1J(Al\text{–}P) \approx 270$ Hz, ^{27}Al line width ≈ 70 Hz.[237a]

The donor methyl resonances of the trimethylamine adduct and also of the trimethylphosphine adduct have also been studied over a range of temperatures. The resonance position is temperature dependent and tends to split into a doublet at higher temperatures. It is suggested that some 1:2 adduct is formed at high temperatures according to:[242]

$$2Al(BH_4)_3 \cdot L \rightleftharpoons Al(BH_4)_3 \cdot 2L + Al(BH_4)_3$$

The trimethylamine adduct of $Et_2Al(BH_4)$ shows no evidence of coupling between aluminium and hydride protons.[243]

The preparation of anionic borohydride species from lithium salts is reported. If lithium borohydride is used then $Al(BH_4)_4^{\ominus}$ may be formed. The proton resonance of the compound consists of a broad signal which at $-50°$ becomes a sharp quartet superimposed on a broad signal while at the same time the boron signal appears to be an over-

lapping series of quintets. The anion must therefore undergo exchange with the reactants. If the anion were stable one might expect to see sharply defined coupling to aluminium as in the trimethylamine adduct.[244]

Aluminium borohydride reacts with six molecules of ammonia in liquid ammonia solution. The ^{11}B spectrum of the compounds consists of a quintet with $J(B–H)=80$ Hz and a triplet with $J(B–H)=110$ Hz both in the region expected for tetrahedral boron and the resonances are assigned to the ions $BH_4^{\ominus}$ and $BH_2\cdot(NH_3)_2^{\oplus}$ respectively. A separate proton resonance was observed for the bound ammonia. The structure of the complex may be $AlH_2(NH_3)_4^{\oplus}\cdot BH_2(NH_3)_2^{\oplus}\cdot 2BH_4^{\ominus}$.[245]

D. Tables of shifts in complexes

A proportion of the data from the papers discussed above is collected here, and serves to illustrate some of the points made in the text. The data have been chosen selectively in the sense that each Table contains data for a series of related complexes so that any trends with composition

TABLE IX

Changes in chemical shifts of methylamine protons due to complex formation with alanes and a few gallanes

Complex	Change in shift p.p.m.* due to forming complex	Solvent	Ref.
H_3AlNMe_3	−0·2	ext H_2O std, benzene	196
	0·4	ext H_2O std, melt	
H_3GaNMe_3	−0·13	benzene	229
$H_2MeAlNMe_3$	0·38	C_6H_{12} solvent and std	209
$H_2EtAlNMe_3$	0·40	C_6H_{12} solvent and std	209
HMe_2AlNMe_3	0·31	C_6H_{12} solvent and std	209
HEt_2AlNMe_3	0·30	C_6H_{12} solvent and std	209
Me_2AlNMe_3	−0·32	int TMS std, benzene	220
Me_3GaNMe_3	0·21	int C_5H_{10} std, freon 11	212
Et_3AlNMe_3	−0·2	int TMS std, benzene	224
FEt_2AlNMe_3	0·29	C_6H_{12} solvent and std	211
$ClEt_2AlNMe_3$	0·43	C_6H_{12} solvent and std	211
$BrEt_2AlNMe_3$	0·47	C_6H_{12} solvent and std	211
IEt_2AlNMe_3	0·49	C_6H_{12} solvent and std	211
$(BH_4)Et_2AlNMe_3$	0·02	C_6H_{12} std, neat	243
$(BH_4)AlNMe_3$	0·35	benzene solvent and std	237

* The minus sign denotes an upfield shift of NMe_3 protons contrary to the expected direction.

may be detected. Data for isolated types of complex have been omitted. The data are presented so as to emphasise the change which occurs in resonance position between free and complexed substance and data are given both for the donor protons in series of complexes with several acceptors (Tables IX to XII) and for acceptor protons in other series with different donors (Tables XII to XIV).

The symbol δ_i indicates an internal shift in an ethyl group. For metal

TABLE X

Changes in chemical shifts of protons in dimethyl cyanamide and diphenylketimine due to complex formation with alanes and gallanes

Complex	Shift change, p.p.m.	Solvent	Ref.
D = Me_2NCN			
Me_3AlD	−0·5	benzene + TMS	169
Et_3AlD	−0·2	benzene + TMS	169
D = $Ph_2C{=}NH$			
Me_3AlD	−1·16	benzene d_6 + TMS std	205, 206
Me_3GaD	−0·04	benzene d_6 + TMS std	
Et_3AlD	−0·36	benzene d_6 + TMS std	205, 206
Et_3GaD	−0·93	benzene d_6 + TMS std	
Ph_3AlD	−0·41	toluene d_8 + TMS std	205, 206
Ph_3GaD	−0·54	toluene d_8 + TMS std	

* All shifts are upfield on complexing contrary to expectation.

TABLE XI

Changes in chemical shifts of protons in the nitrogen donor (D) $Me_3P{:}N{\cdot}SiMe_3$ due to complex formation with alanes and gallanes

Complex	Shift change, p.p.m.		Solvent	Ref.
	P Methyl	Si Methyl		
Me_3AlD	0·38	0·33	CCl_4 + TMS (int std)	228
Me_3GaD	0·29	0·26	CCl_4 + TMS (int std)	228
Et_3AlD	0·37	0·36	CCl_4 + TMS (int std)	228
Cl_3AlD	0·69	0·62	CH_2Cl_2 + ext TMS std	230
Cl_3GaD	0·71	0·62	CH_2Cl_2 + ext TMS std	230
Br_3AlD	0·81	0·72	CH_2Cl_2 + ext TMS std	230
I_3AlD	0·92	0·83	CH_2Cl_2 + ext TMS std	230

ethyl resonances the methylene protons move upfield and away from the methyl protons on forming a complex and the shift is given a negative sign. For donor ethyl resonances the methylene protons move downfield and away from the methyl resonance on forming a complex and the shift is given a positive sign. A negative sign here means that an upfield methylene shift occurs on complexing.

Some shift changes for α protons are also recorded. Those on metal atoms usually move upfield and have a negative sign, those on donor atoms usually move downfield and have a positive sign.

The nature of the solvent and standard and the method of standardisation are also given.

TABLE XII

Changes in chemical shifts of α protons and in internal shifts δ_i of protons in ethyl groups of diethyl ether or diethylsulphide, due to complex formation with alanes and gallanes

Complex	Change in shift of α* protons, p.p.m.	Change in δ_i, p.p.m.	Solvent	Ref.
Et_3AlOEt_2	—	−0·25	neat, ext. std	192
		0·39	toluene (solvent+std)	207
	0·83	0·37	neat+ext TMS	210
Et_3GaOEt_2	—	−0·38	neat, ext std	192
Cl_3AlOEt_2	—	0·68	$-\Delta H$ = 69·5. neat+2% TMS (int)	194
Cl_3GaOEt_2	—	0·61	$-\Delta H$ = 51·0. neat+2% TMS (int)	194
	1·54	0·59	$-\Delta H$ = 50·7. neat, ext std	190
Br_3GaOEt_2	1·91	0·65	$-\Delta H$ = 47·4. neat, ext std	190
	—	0·63	neat+2% TMS (int)	194
$(BH_4)_3AlOEt_2$	0·49	0·63	benzene (solvent and std)	237
Cl_3AlSEt_2	0·53	0·27	$-\Delta H$ = 58·9. neat+2% TMS (int)	198
Cl_3GaSEt_2	0·62	0·34	$-\Delta H$ = 56·0. neat+2% TMS (int)	198
	1·11	0·33	$-\Delta H$ = 56·2. neat, ext std	190
Br_3AlSEt_2	0·56	0·26	neat+2% TMS (int)	198
Br_3GaSEt_2	0·57	0·27	neat+2% TMS (int)	198
	1·35	0·24	neat, ext std	190

* α protons move downfield on complexing.

TABLE XIII

Change in chemical shifts of methyl protons of trimethyl-alane and -gallane due to complex formation with bases

Complex	Change in methyl* proton shift, p.p.m.	Solvent (all standards internal)	Ref.
$Ph_2C:NHAlMe_3$	−0·09	benzene d_6 + TMS	205
$Ph_2C:NHGaMe_3$	−0·24	benzene d_6 + TMS	206
$Me_2NCNAlMe_3$	0·0	benzene + TMS	169
Et_3NAlMe_3	−0·21	toluene (solvent + std)	207
Me_3NGaMe_3	−0·66	freon 11, C_5H_{10} std	191
	−0·66	freon 11, C_5H_{10} std	212
H_3NGaMe_3	−0·61	freon 11, C_5H_{10} std	191
$H_2MeNGaMe_3$	−0·58	freon 11, C_5H_{10} std	191
HMe_2NGaMe_3	−0·72	freon 11, C_5H_{10} std	141
$C_5H_5NAlMe_3$	−0·10	toluene (solvent + std)	207
$Me_3P:N(SiMe_3)AlMe_3$	−0·72	CCl_4 + TMS	228
$Me_3P:N(SiMe_3)GaMe_3$	−0·61	CCl_4 + TMS	228
$Et_3P:N(SiMe_3)AlMe_3$	−0·71	CCl_4 + TMS	228
$Et_3P:N(SiMe_3)GaMe_3$	−0·61	CCl_4 + TMS	228
Et_2OAlMe_3	−0·21	toluene (solvent + std)	207
Dioxane $AlMe_3$	−0·25	toluene (solvent + std)	207
THF·$AlMe_3$	−0·19	toluene (solvent + std)	207
$PhOMeAlMe_3$	−0·19	toluene (solvent + std)	207
Ph_2OAlMe_3	0·0	toluene (solvent + std)	207
Me_2OGaMe_3	−0·47	freon 11, C_5H_{10} std	191
	−0·55	freon 11, C_5H_{10} std	212
Me_2SGaMe_3	−0·4	freon 11, C_5H_{10} std	191

Comments on Tables IX to XIV

Perhaps the most striking feature of the Tables is the small value of the shifts which occur upon complexing. The maximum observed α CH shift for compounds which have been internally standardised is 0·72 p.p.m. for two methyl alanes and a gallane in Table XIII. These are, however, exceptional and most values fall in the range 0 to 0·4 p.p.m., and this in itself suggests that meaningful correlations with bond strengths may be hard to find.

Much larger downfield shifts are observed for α donor protons of externally standardised samples of halo alanes, Table XI[230] and Table XII.[190 to 210] The effect increases in the sequence Cl < Br < I and this order probably reflects increases in diamagnetic susceptibilities along the series. Internal ethyl shifts in these samples are, however, comparable with the results obtained in internally standardised samples.

TABLE XIV

Changes in chemical shifts of methylene protons and in internal shifts δ_l of ethyl groups of triethyl alane and -gallane due to complex formation

Complex	Changes in methylene* proton shifts, p.p.m.	Changes in δ_l, p.p.m.	Solvent (standard internal except where noted)	Ref.
$Ph_2C:NHAlEt_3$	−0·4	−0·44	benzene d_6 + TMS	205
$Ph_2C:NHGaEt_3$	−0·2	−0·35	benzene d_6 + TMS	206
$Me_2NCNAlEt_3$	−0·3	−0·45	benzene + TMS	169
Et_3NAlEt_3	−0·19	−0·47	log K_b = 10·74. toluene (solvent + std)	207
	+0·58	−0·45	neat + ext TMS	210
Me_3NAlEt_3	−0·4	−0·52	benzene + TMS	224
Me_3NGaEt_3	—	−0·37	ΔH = 17. freon 11, C_5H_{10} std	191
$H_2NMeGaEt_3$	—	−0·41	freon 11, C_5H_{10} std	191
H_3NGaEt_3	—	−0·41	freon 11, C_5H_{10} std	191
pyridine $AlEt_3$	−0·65	−0·32	neat, ext TMS	210
	+0·02	−0·25	log K_b = 5·17. toluene (solvent + std)	207
$Me_3P:N(SiMe_3)AlEt_3$	—	−0·44	CCl_4 + TMS	228
Me_3PAlEt_3	~0	−0·36	benzene + TMS	224
Me_3PGaEt_3	—	−0·34	freon 11, C_5H_{10} std	191
Et_2OAlEt_3	−0·2	−0·43	log K_b = −0·27. toluene (solvent + std)	207
	−0·75	−0·43	neat, ext TMS	210
Et_2OGaEt_3	—	−0·31	neat	192
		−0·08	neat	192
$Bu^n_3OAlEt_3$	−0·15	−0·41	log K_b = −2·32. toluene (solvent + std)	207
$PhMeOAlEt_3$	−0·19	−0·36	log K_b = −6·40. toluene (solvent + std)	207
Ph_2OAlEt_3	−0·07	−0·14	log K_b = −9·79. toluene (solvent + std)	207
$THF \cdot AlEt_3$	−0·20	−0·43	toluene (solvent + std)	207
	~ −0·63	−0·31 to −0·47	(dissociation) neat + ext TMS	210
dioxane $AlEt_3$	−0·28	−0·43	toluene (solvent + std)	207
Me_2OGaEt_3	−0·47	−0·27	freon 11, C_5H_{10} std	191
Me_2SGaEt_3	−0·4	−0·23	freon 11, C_5H_{10} std	191

The only other protons which show a large change on complexing are the ketimine NH protons, all of which move strongly upfield contrary to expectation, the weaker gallane acceptors having a larger effect than alanes. This behaviour could arise if as suggested by Perkampus and Krüger the paramagnetic effect of the nitrogen lone pair were removed on complexing. The weaker gallium acceptors would then give rise to the larger shifts since their inductive effect, which gives a low-field contribution, is less than that of the alanes. Both effects would be expected to be particularly large for NH protons. Part of the shift may also be an aromatic solvent effect—see Table XV.

Samples can also be classified by the type of solvent in which measurements were carried out, namely aromatic or non-aromatic. In a few cases the neat adduct was used and these are classified with the latter. An inspection of the Tables shows that the aromatic solvents seem to be associated with particularly small or unusual values of complexing shifts of α protons. This is obvious in Table IX where, with one exception, methylamine protons are observed to move to high field on complexing in benzene solution but low field in the melt, cyclohexane or freon 11. The effect is also observed in Table XIII where the metal methyl protons move about 0·6 to 0·7 p.p.m. upfield on complexing in the non-aromatic solvents, but only 0·1 to 0·3 p.p.m. in the aromatic solvents. The figures are grouped together in Table XV which shows strikingly that in general metal α alkyl protons shift further upfield in non-aromatic solvents and that *N*-methyl α protons shift downfield in non-aromatic solvents, but upfield in aromatics. This suggests strongly that α proton shifts may be more a function of solvent than of any other parameter.

The internal shifts of Tables XII and XIV, however, do not appear to be affected by solvent and as suggested in the literature are perhaps the only reliable parameter to use in making NMR comparisons of adducts, though the effect is remarkably small. The triethyl alane adducts whose dissociation constants K_b are noted in Table XIV have δ_i values which vary from $-0{\cdot}47$ p.p.m. ($\log K_b = 10{\cdot}74$) to $-0{\cdot}14$ p.p.m. ($\log K_b = -9{\cdot}79$), a change of 0·33 p.p.m. for a change of twenty orders of magnitude of K_b. Similarly the two triethyl gallane adducts for which ΔH values are noted have shifts δ_i of $-0{\cdot}37$ p.p.m. ($-\Delta H = 17$) and $-0{\cdot}23$ p.p.m. ($-\Delta H = 6$), again a very small change accompanying a large change in bond energy and one that could easily be obscured by the other effects described above.

In Table XII on the other hand we see that series of oxo and thio ether complexes of the metal halides exhibit respectively different ether ethyl internal shifts even though the energies of the donor bonds are

TABLE XV

Acceptor and donor α proton complexation shifts in aromatic and non-aromatic solvents.

All samples except two internally standardised. Data rearranged from Tables IX and XIII. Protons giving rise to data are underlined.

Aromatic solvents		Non-aromatic solvents	
Complex	α proton shift charge, p.p.m.	Complex	α proton shift charge, p.p.m.
$Ph_2C{:}NH{\cdot}AlMe_3$	−0·09	$Me_3N{\cdot}GaMe_3$	−0·66
$Ph_2C{:}NH{\cdot}GaMe_3$	−0·24	$HMe_2N{\cdot}GaMe_3$	−0·72
$Et_3N{\cdot}AlMe_3$	−0·21	$H_2MeN{\cdot}GaMe_3$	−0·58
		$H_3N{\cdot}GaMe_3$	−0·61
$C_5H_5N{\cdot}AlMe_3$	−0·10		
		$Me_3P{:}N(SiMe_3)AlMe_3$	−0·72
		$Me_3P{:}N(SiMe_3)GaMe_3$	−0·61
$Et_2O{\cdot}AlMe_3$	−0·21	$Me_2O{\cdot}GaMe_3$	−0·47
$Dioxane{\cdot}AlMe_3$	−0·25		−0·55
$THF{\cdot}AlMe_3$	−0·19	$Me_2S{\cdot}GaMe_3$	−0·4
$PhMeO{\cdot}AlMe_3$	−0·19		
$Ph_2O{\cdot}AlMe_3$	0·0		
$H_3Ga{\cdot}NMe_3$	−0·13	$H_2MeAl{\cdot}NMe_3$	+0·38
$Me_3Al{\cdot}NMe_3$	−0·32	$HMe_2Al{\cdot}NMe_3$	+0·31
$Et_3Al{\cdot}NMe_3$	−0·20	$Me_3Ga{\cdot}NMe_3$	+0·21
$H_3Al{\cdot}NMe_3$(ext std)	−0·2	$ClEt_2{\cdot}AlNMe_3$	+0·43
		$IEt_2Al{\cdot}NMe_3$	+0·49
		$H_3Al{\cdot}NMe_3$ (ext std)	+0·4
$Me_3Al{\cdot}Me_2NCH_2$*	+0·63		
NMe_2	−0·18		
$Me_3Ga{\cdot}Me_2N{-}CH_2$	+0·63		
NMe_2	−0·07		
$Me_3Al{\cdot}Me_2N \quad NMe_2AlMe_3$	−0·09		
CH_2	+1·26		
$Me_3GaMe_2N \quad NMe_2GaMe_3$	−0·12		
CH_2	+0·76		
$Me_3AlMe_2N \quad NMe_2AlMe_3$	−0·35		
$CH_2{-}CH_2$	+0·2		
$Me_3GaMe_2N \quad NMe_2GaMe_3$	−0·26		
$CH_2{-}CH_2$	+0·09		

* This and following results taken from reference 221.

very similar. The internal shift seems rather to be a function of the donor atom and is 0·24 to 0·34 p.p.m. for thio ether adducts of the halides and 0·59 to 0·68 p.p.m. for their weaker oxo ether adducts. It is tempting to suggest that the shifts arise from a through space electric field effect due to the polar metal-halogen bond and that the effect is less in the thio ether adducts because the halogen-proton distances are greater. As might be expected the triethyl alane and gallane complexes of diethyl ether exhibit small shifts since they lack the polar bonds of the halides though there seems to be uncertainty about the sign.

Thus the figures collected here seem to suggest that only very small NMR changes occur in these molecules due to complex formation, that only the internal ethyl shifts have any hope of providing reliable means of comparing adduct strengths and that even these may be related more to changes in through space effects involving solvent and molecule shape changes than to inductive effects. The remarks of Satchell and Satchell indeed seem fully applicable to the alane and gallane adducts also. It is thus imperative that NMR adduct strength studies in this field should be restricted to ligand displacement studies.

Finally it is interesting to note that the only large adduct shifts observed occur for the bridge groups of the trialkyl alane dimers.[95,141] For example, the bridge protons of Al_2Me_6 are 1·15 p.p.m. to low field of the terminal protons.

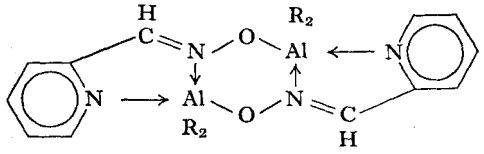
E. Miscellaneous studies of adducts

Worrall and co-workers have given considerable attention to 4-alkyl pyridine adducts of aluminium halides. The α hydrogens of the pyridine in the molten adducts are broadened in the sequence Cl < Br < I and the presence of hydrogen bonding to the halogen and concomitant exchange broadening is suggested. Variable temperature studies in solution and melt showed, however, that the broadening is also dependent on the nature of the alkyl substituent in the pyridine, no broadening being seen in 4-methyl pyridine. Broadening occurs at high temperatures in the melt but only at low temperatures in solution. In the case of melts of adducts of 4-ethyl- and 4-n-propyl- pyridine with aluminium iodide the broad α resonance resolves into a doublet on cooling but in solution the doublet tends to appear on heating. Some association was found in solution.[246 to 248]

Compounds which may contain aluminium-aluminium covalent bonds are reported and a number of structures proposed on the basis of NMR evidence. A prismatic structure is suggested for $Al_4B(NMe_2)_3Me_6$[249] while $Al_3Me_3(NMe_2)_2$ may contain a chain of aluminium atoms.[250] On the other hand $Al_2BN_3Me_{10}H_2$ is believed to contain an AlNAlNBN ring.[298]

The proton-fluorine coupling constant in the trimethylfluorosilane moiety increases by 30% when the adduct $Me_3SiFAlEt_3$ is formed and this suggests that the fluorine is approaching *sp* hybridisation and that the Si–F–Al bond must approach linearity[251] (cf. reference 235 above).

Evidence is presented that the aluminium in (**25**) may be five coordinate when R = Me.[252]



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No stable donor-acceptor complex is formed between alkyl halides and chloroalkylalanes.[253]

The complex $SbEt_5 \cdot 2AlEt_3$ can be prepared.[254]

The proton spectra of trivinyl and tripropenyl gallium adducts of methylamine have been analysed. The propenyl compounds were prepared from the mercury alkyls and reaction proceeds with retention of configuration.[255]

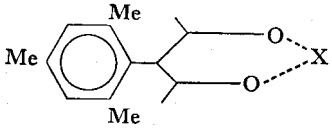
V. ALUMINIUM AND GALLIUM CHELATE COMPLEXES

A. Chemical shifts in acetylacetonate complexes

The source of the chemical shifts of the protons in the chelate ring of acetylacetonate metal complexes has long aroused interest. Complexes of very many substituted acetylacetonate ligands with a large range of metals have been measured, so much so that the subject really deserves a review on its own. Here we are limited to the two metals aluminium and gallium though fortunately the former has figured largely in the work in this field. At the time of writing the subject has reached an interesting stage when considerable modification of previously held ideas may be taking place.

Early theories of the shifts in these compounds were based on two concepts. There was reason to suppose that electron delocalisation took place in the chelate ring and that because of the benzenoid nature of the ring it might sustain a ring current.[256] In addition comparison of *cis* and *trans* hexacoordinate complexes with two chelate and two monodentate ligands showed that the ring protons possessed different shifts and it was suggested that this arose from an electric field effect. Most workers now seem agreed that the ring current in these molecules is small, if it exists at all,[257] and a recent paper using ligands prepared

specially to test this point has confirmed that there is no effect due to ring currents.[258] Thus no real shift differences were observed for protons above the plane of the chelate ring in (**26**) or (**27**) when X = H or when X = a metal.



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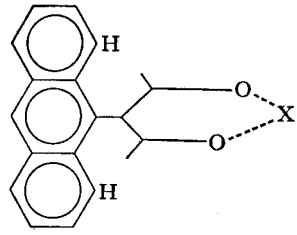

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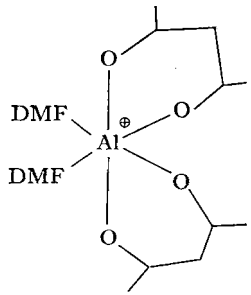
Considerable effort has gone into measuring both proton and ^{13}C shifts in the ligands of these complexes and it is found that the ^{1}H and ^{13}C shifts and also $^{1}J(^{13}C–^{1}H)$ and the relevant IR stretching frequencies are all correlated, the results being interpreted in terms of the electrical asymmetry of the complexes. The shifts observed are, however, not particularly large ranging over about 1 p.p.m. for the γ protons and some of the variation is due to solvent effects.[259 to 261] The solvent effects have been discussed in detail elsewhere and are of similar magnitude to the shifts reported above. The measured shifts agree well with shifts calculated from solvent anisotropies and the results suggest that solvents which can form donor complexes approach along the C_3 axis of the acetylacetonate complex.[262] These results throw some doubt upon the existence of an electric field effect.

An electric field effect would be most easily detected if the shifts were compared of an isomeric pair of *cis-trans* complexes. When this is done it is found that the acetylacetone γ protons of *cis* and *trans*



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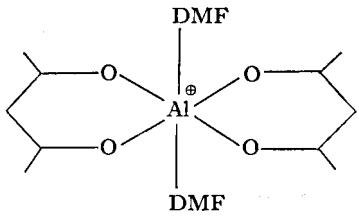

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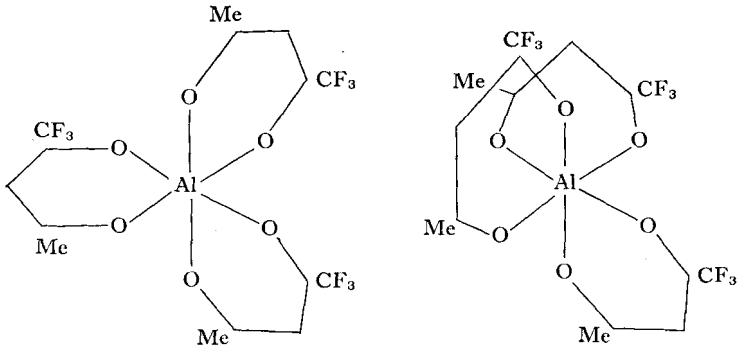
$(MeCOO)_2Si(acac)_2$ are separated by only 0·04 p.p.m., while those of *cis* and *trans* $(DMF)_2Al(acac)_2^{\oplus}$ have identical shifts. The different dipole moments of (**28**) and (**29**) thus do not appear to be correlated with any NMR effect.[263] Further developments in the field will be awaited with interest though it seems that too much reliance has been placed in the past on a single mechanism to describe the chemical shifts in what are very complex molecules.

B. Rearrangements and stereochemistry of acetylacetonate complexes

If an unsymmetrical ligand is used to make tris-complexes it becomes possible to prepare complexes with *cis* or *trans* configuration (**30**). The



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cis form is symmetrical and gives rise to singlet methyl or trifluoromethyl resonances while the *trans* form has no symmetry elements and may give rise to up to three resonances for each group. Thus the tris-benzoylacetoacetonate of aluminium is all *trans*[264] while the tris-trifluoroacetylacetonate has both *cis* and *trans* stereochemistry in solution.[265]

The multiplicity of the resonances of the *trans* complex and the different chemical shift of the *cis* complex makes it possible to follow rearrangement reactions of the ligands in these complexes. Thus the proton resonances of tris-trifluoroacetylacetonato aluminium coalesce at 103° and those of the gallium complex coalesce at 61·5°. The rate constants are 34 sec^{-1} and 38 sec^{-1} respectively at these temperatures. Complete dissociation of ligand does not occur since excess added ligand exhibits separate resonances, and rearrangement must be intramolecular (Fig. 11). If acetylacetone is added to the tris-trifluoroacetylacetonato aluminium complex the fluorinated ligand is displaced to give a mixed

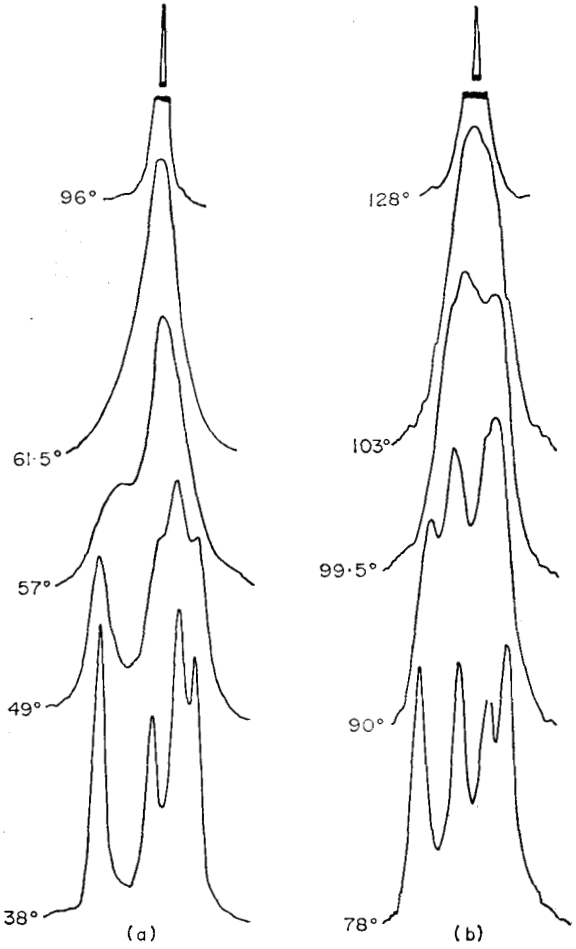


FIG. 11. Fluorine resonance spectra of (a) $Ga(tfac)_3$ and (b) $Al(tfac)_3$ at several temperatures near the coalescence region. (From Fay *et al*[266].)

complex. As the temperature is raised the lines due to $(tfac)_2(acac)Al$ coalesce first at 87° and those due to $A(tfac)_3$ remain resolved up to 103°. At higher temperatures four singlets are observed arising from each of the three complexes $(tfac)_n(acac)_{3-n}Al$ where $n=1$, 2 or 3 and to free trifluoroacetylacetone. Rearrangement is again intramolecular.[266, 267]

The dialkyl acetoacetonates of aluminium contain a bidentate chelate ring and give rise to a single ring methyl resonance.[268]

Mixed complexes have been made using symmetrical β diketonate

ligands which can be written $Al(BB)_2(AA)$ and $Al(AA)_2(BB)$. The terminal groups of the ligands AA in the latter give rise to different resonances which can be made to coalesce at high temperatures where the complex undergoes optical inversion. The method thus permits estimation of the rate of racemisation without prior resolution of the optical

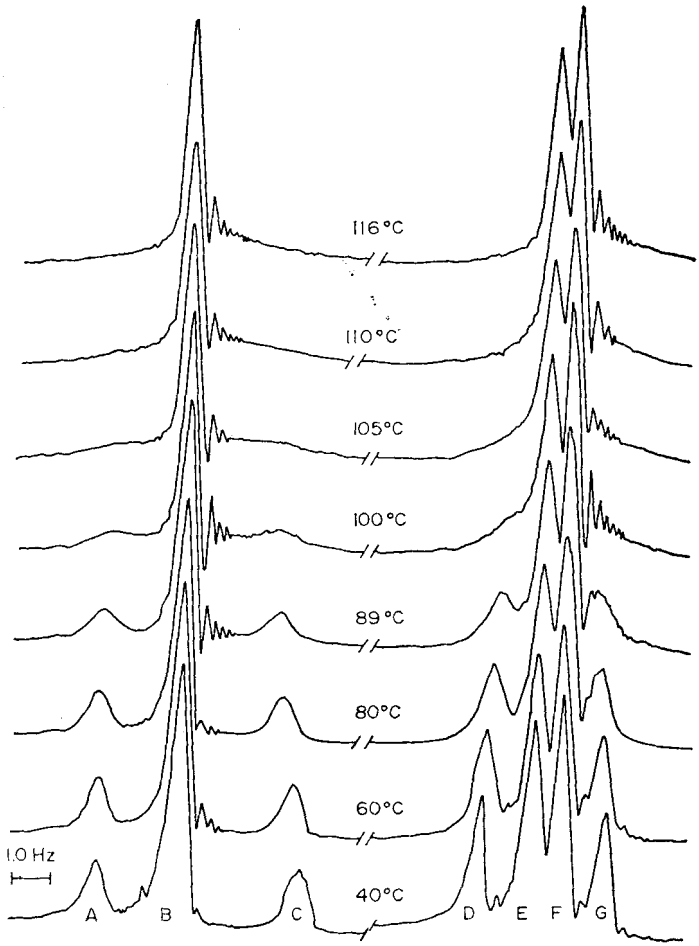


FIG. 12. The NMR spectra of the *t*-butyl (right) and methyl (left) regions of a mixture of $Al(acac)_3$, $Al(acac)_2(thd)$, $Al(acac)(thd)_2$, and $Al(thd)_3$, in chlorobenzene solution at various temperatures. Initial solution was 0·030M in $Al(acac)_3$ and 0·015M in $Al(thd)_3$. The peaks are assigned as follows: A and C, acac in $Al(acac)_2(thd)$; B, acac in both $Al(acac)(thd)_2$ and $Al(acac)_3$; D and G, thd in $Al(acac)(thd)_2$; E, thd in $Al(thd)_3$; and F, thd in $Al(acac)_2(thd)$. (From Fortman and Sievers.[269])

isomers. Coalescence temperatures and rate constants at the coalescence temperature are, $Al(acac)_2(thd)$, 105°, 12·6 sec^{-1}, $Al(acac)(thd)_2$ 105°, 8·5 sec^{-1}, $Al(hfac)(thd)_2$, −8°, 6·9 sec^{-1} and $Al(hfac)(acac)_2$ −18°, 5·3 sec^{-1} (thd = $Bu^tCOCHCOBu^{t\ominus}$); the variable temperature spectra are shown in Fig. 12. Rearrangement is again intramolecular. Mixed ligands are preferred where one of the ligands is $CF_3COCHCOCF_3^{\ominus}$ (hfac).[269] Studies have also been made of mixed ligand complexes of gallium with acetylacetone and $PhCOCHCOPh^{\ominus}$(bzbz) or hfac. The acac-bzbz mixture arranges itself nearly statistically among the metal atoms whereas in the mixture containing hfac the mixed species are again preferred, the equilibrium constants for their formation being some four hundred times higher than for the statistical case. The difference between the two systems is ascribed to enthalpy differences between the complexes which are slight in the first case and large in the second.[270] Variable temperature spectroscopy was used to show that rearrangement of ligands occurs in the mixed complexes $Ga(acac)_2(hfac)$ and $Ga(acac)_2(bzbz)$, the rate being slower in the latter by a factor of 10^4.[271]

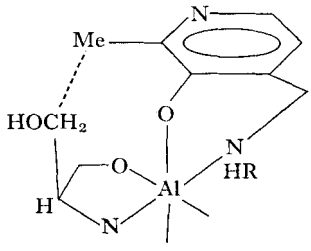
A solution of $Al(acac)_3$ and $Al(DMF)_6^{3\oplus}$ in dimethylformamide exhibits resonances due both to the above two complexes and to the mixed complexes $Al(acac)_2(DMF)_2^{\oplus}$ and $Al(acac)(DMF)_4^{2\oplus}$, the former existing as *cis* and *trans* isomers which give separate proton resonances below −17°. The rate of exchange of solvent on this complex is about twice the rate of *cis-trans* isomerisation and it is suggested that the isomerisation occurs via dissociation of the amide.[272]

The reactions of aluminium acetylacetonates with nitrogen dioxide has also been examined using NMR spectroscopy.[273]

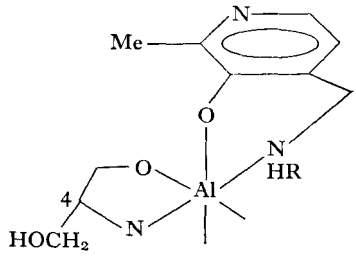
C. Other chelate complexes

An extensive study has been made of the transamination reaction involving alanine in the presence of pyridoxal and zinc or aluminium ions. The formation of the various intermediates and their metal complexes was followed by NMR. The presence of the metal increases aldimine formation below pD 13. Exchange between free and coordinated aldimine is fast with zinc on the NMR time scale but slow with aluminium.[274, 275] Isomeric structures of the bispyridoxylidene serinato complex of aluminium (**31**) have been detected using proton spectroscopy. Some of the isomers are sterically crowded (**31a**)[276] resulting in different methyl shifts for the two forms.

Complexes with 2-methylquinolin-8-ol have also been discussed. These were thought not to exist but in chloroform in the presence of diethylamine a hydroxy bis complex is formed $[Al(OH)L_2]_n$ while in

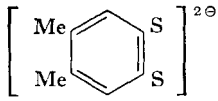


31a



31b

dimethyl sulphoxide a 1 : 1 adduct of the solvent and AlL_3 is obtained.[277, 278] The NMR of complexes of aluminium with EDTA,[279] of $Al(MeNNNMe)_3$,[280] and of gallium with the ligands $S{\cdot}CH{:}CH{\cdot}S^{2\ominus}$ and (**32**)[281] has also been discussed.



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VI. ALUMINIUM BOROHYDRIDES

The literature of the metal borohydrides has recently been reviewed.[282] Two NMR studies of aluminium borohydride have been reported. Ogg and Ray[283] found that the proton spectrum consisted of a broad structureless resonance which became a well-resolved quartet if the ^{27}Al was double irradiated or a less broad line suggestive of a partly collapsed spin multiplet if the ^{11}B was double irradiated. The ^{11}B spectrum was a quintet, the four protons of each borohydride group are thus equivalent. Subsequent work with the trimethylamine adduct suggests that all protons are also probably equally coupled to the aluminium. This is at variance with the known bridged structure of the molecule,[284, 285] and could only arise if there was very rapid intramolecular exchange of the protons in such a way that they remained continuously bonded to both boron and aluminium, the observed coupling being the average of those for the bridge and terminal positions. The fact that the proton to aluminium bonding appeared to remain intact during the exchange led Ogg and Ray to propose a quantum mechanical tunnelling mechanism for the exchange, though such a mechanism is not essential and exchange *via* Al–H–BH_3 structures would give the same effects.[286] Heating was thought to lead to a reversible association of two molecules and the

formation of diborane, though this has subsequently been disputed by Maybury and Ahnell,[287] who have observed in detail the considerable changes which occur in the proton spectrum on heating (Fig. 13). Two processes appear to occur: heating leads to a reversible change of the broad line to a well-resolved quartet. The spectral changes also depend on the concentration of aluminium borohydride and it is suggested that intermolecular borohydride exchange must occur at the higher temperatures.

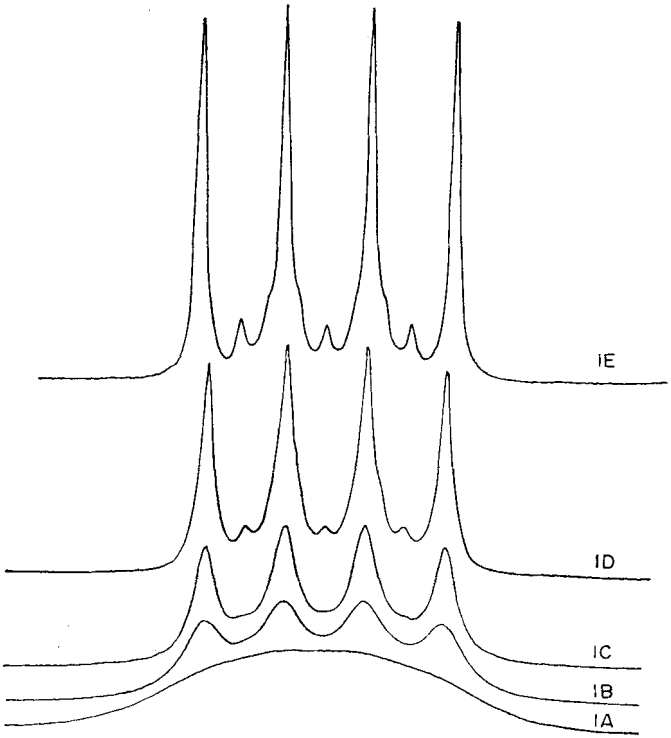


FIG. 13a. Nuclear magnetic resonance spectra of $Al(BH_4)_3$ heated at 80° for: (A) 0 min (room-temperature spectrum), (B) 25 min, (C) 45 min, (D) 70 min, (E) 110 min. (From Maybury and Ahnell.[287])

If the sample is held at 80° the change becomes irreversible. It is tentatively suggested that this is due to conversion of the normal prismatic (trigonal) form to an octahedral form. An octahedral type of structure would, however, also be consistent with the hydrogen bridge arrangement even in the low-temperature structure of the trimethylamine adduct.[240] The field gradient at aluminium in the octahedral form will be

relatively small and the effects of spin coupling to the aluminium might be observed, though the distortion of the octahedron by the steric requirements of bridging might well result in loss of structure. The trigonal form on the other hand will possess a larger field gradient (it is essentially a more highly distorted octahedron) and the effect of coupling to

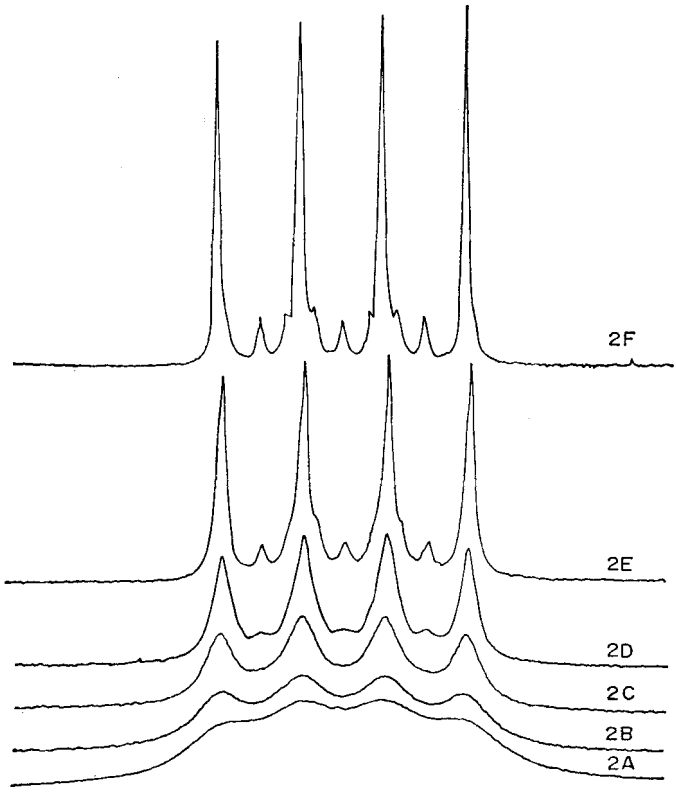
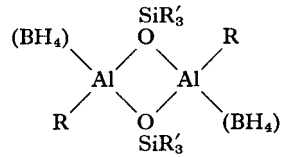


FIG. 13b. Nuclear magnetic resonance spectra of $Al(BH_4)_3$ with temperature probe at: (A) 40°, (B) 50°, (C) 60°, (D) 70°, (E) 80°, (F) 90°. (From Maybury and Ahnell.[287])

aluminium might be completely lost, leaving only the quartet due to ^{11}B coupling. Exchange effects could of course invalidate this picture. A next step which might help to resolve this problem is to obtain the ^{27}Al resonance of the high-temperature form.

The compound Et_2AlBH_4 also exhibits aluminium to hydride proton coupling.[243] Siloxane bridged dimers of aluminium borohydrides have

also been prepared (**33**). The ^{11}B spectrum when $R = BH_4$ is a quintet



$R = BH_4$, H or Cl

33

and a quintet is also seen at 90° when R = H. On cooling, however, the structure is lost and the line is broad at −40° and it is suggested that this is due to exchange involving the aluminium hydride hydrogen.[288]

VII. TABLES OF CHEMICAL SHIFTS AND LINE WIDTHS OF THE ALUMINIUM AND GALLIUM RESONANCES

The metal chemical shifts are reported with respect to the ions $M(H_2O)_6^{3\oplus}$ whose shifts appear to be virtually independent of concentration.[48] Where shifts have been reported relative to another standard a suitable adjustment has been made based upon the figures given in these Tables. The standard is usually external but as the shifts are large and the lines are relatively broad no attempt appears to have been made to make corrections for susceptibility differences between sample and standard. The accuracy of the shift measurement depends upon line width and varies from about 0·2 p.p.m. for the narrowest lines up to ± 10 or more p.p.m. for the broadest lines, which indeed span the whole range over which resonances are observed. The solvent in which the measurement was made is also given.

Compounds are listed in the order of increasing low-field shifts, i.e. the highest field resonance is placed first. Where conflicting values of shifts have been obtained all the values are listed together. The sign − indicates high field of standard, and + low field and is the convention used in this series.* The opposite convention is found in most of the literature. Values of spin-spin coupling constants are also noted where these have been measured.

The line widths quoted in general must be regarded as typical values only. Some of the smaller values are almost certainly overestimated due to field inhomogeneities and modulation broadening if the spectrum was obtained in the derivative mode. The factors affecting line width in these solutions are complex and variations have been observed for instance due to pH changes in aqueous $M(H_2O)_6^{3\oplus}$ and we have suggested

* See p. xii.

TABLE XVI

^{27}Al chemical shifts and line widths [$Al(H_2O)_6^{3\oplus}$ standard]

Compound	Solvent	Chemical shift, p.p.m.	Line width and coupling constants if observed (Hz)	Ref.
$Co(AlCl_4)_2$	benzene	−225	contact shifts	129
$Co(AlBr_4)_2$	benzene	−144	contact shifts	129
$Al(PhCN)_6^{3\oplus}$	AlI_3 in PhCN	−46	100	64
	$AlCl_3$ in PhCN	−32	155	
$Al(MeCN)_6^{3\oplus}$	MeCN	−34	73	64
	MeCN	< −14		65
$Al(CH_2{=}CHCN)_6^{3\oplus}$	CH_2:CHCN	−33	83	64
$AlI_4^{\ominus}$	various including MeCN.	−28	58	64
	CH_2Cl_2	−27	23·9	68
Al_2I_6	benzene	−23	800	64
	toluene	−11	660	129
$Al(POCl_3)_6^{3\oplus}$	$POCl_3$	−21·2 to −22·4	55 to 77	67
Phosphoric acid complexes	H_2O/H_3PO_4	−7·7	100	63
$Al(H_2O)_4(SO_4H)_2^{\oplus}$	H_2O/H_2SO_4	−6·8	80	49
$Al(H_2O)_5(SO_4)^{\oplus}$	H_2O/H_2SO_4	−3·3	5 upwards	48
$Al(DMF)_6^{3\oplus}$	DMF	−1·7	39	82
$Al(H_2O)_6^{3\oplus}$ standard	H_2O	0	3 upwards	48
$Al(acac)_3$	benzene	~0	93	64
	benzene	+2·5	120	77
$Al(C_2O_4)_3^{3\ominus}$	water	~0	125	64
$[Al(OPr^i)_3]_{3\text{ or }4}$	n hexane	~0	90	64
$Al(EtOH)_6^{3\oplus *}$	EtOH	~0	70	64
$Al(Pr^nOH)_6^{3\oplus *}$	Pr^nOH	~0	70	64
$AlF_n(H_2O)_{6-n}^{(3-n)\oplus}$	H_2O	+2	550	54, 56
		+15		57
$Al_2(OH)_2(H_2O)_n^{4\oplus}$	H_2O	+3	450	42, 43
$Al_2(OBu^t)_6$		+7	100	57
$AlI_3Br^{\ominus}$	CH_2Cl_2	+8 est	—	68
$Al_2I_6 + Al_2Cl_6$	toluene	+18	singlet	129
$Al(EtNCS)_6^{3\oplus}$	EtNCS	+20	58	64
$AlI_3Cl^{\ominus}$	CH_2Cl_2	+21·7	46	68
$Al(OOCCH_2)_3N$	H_2O	+24	180	289
$AlI_2Br_2^{\ominus}$	CH_2Cl_2	+37 est	—	68
Al_2I_6	Et_2O	+39	90	57
probably $Et_2O{\cdot}AlJ_3$[296]	Et_2O	+40	81	64
	EtNCS	+36	83	64
$AlI_2BrCl^{\ominus}$	CH_2Cl_2	+47·7	—	68
$Et_2O{\cdot}AlBr_3$		+47	210	64
$Et_2O{\cdot}AlCl_3$		+50	160	64
$AlI_2Cl_2^{\ominus}$	CH_2Cl_2	+39·4	57	68
$AlIBr_3^{\ominus}$	CH_2Cl_2	+60·6	—	68
$Al_{13}(OH)_{24}(H_2O)_{12}O_4^{7\oplus}$	H_2O, central Al only	+62·5	~50	43
$AlIBr_2Cl^{\ominus}$	CH_2Cl_2	+69·3	—	68
$Al(BH_4)_3{\cdot}PMe_3$	toluene	+63·2	J(Al-P) = 265Hz	237a
$Me_3N{\cdot}Al(BH_4)_3$	benzene	+71·1	small 9 < width < 20 J(Al–H) = 45 Hz J(Al–B) ≈ 9 Hz	244
Al_2Br_6	benzene	+75	510	64
$PhCOCl{\cdot}AlCl_3$	PhCOCl	+77	2000	64
$AlIBrCl_2^{\ominus}$	CH_2Cl_2	+79	—	68
$AlBr_4^{\ominus}$	CH_2Cl_2	+80	—	68
	MeCN	+80	35	64

TABLE XVI—*continued*

Compound	Solvent	Chemical shift, p.p.m.	Line width and coupling constants if observed	Ref.
$Al(OH)_4^{\ominus}$	H_2O/KOH	+80	90	57
		+80	60 to 100	64
		+80	23	62
$Co(AlI_4)_2$	benzene	+81	—	129
$Al_2Cl_4Bu^i_2$	pure liquid	+86	4000	57
$AlICl_3^{\ominus}$	CH_2Cl_2	+86·2	42	68
$AlBr_3Cl^{\ominus}$	CH_2Cl_2	+87·2	—	68
$Al_2(OMe)_2Cl_4$	pure liquid	+90	broad	57
$Al_2Me_3Cl_3$		+93	broad	57
$AlBr_2Cl_2^{\ominus}$		+93 est	—	68
Al_2Br_6	Et_2O	+95	104	64
	Et_2O	+96	100	57
	Br_2	+101	300	57
$Al(BH_4)_3$	benzene	+97·4	est 180	244
$MeCO{\cdot}AlCl_4$	MeCOCl	+97	166	64
$AlBr_3PEt_3$	CH_2Cl_2	+99	^1J(Al–P) = 240 Hz	224a
$AlBrCl_3^{\ominus}$	CH_2Cl_2	+99 est	—	68
Al_2Cl_6	toluene	+91	300	57, 129
	Et_2O	+105, +101	110, 126	43a, 57, 64
	EtNCS	+105	100	64
$AlBr_3PMe_3$	CH_2Cl_2	+100·8	^1J(Al–P) = 248 Hz	224a
$AlCl_4^{\ominus}$	$POCl_3$	+101·3 to +102·5	10 to 30	67
	various inc. MeCN	+102 to +108	30 to 33	64
	CH_2Cl_2	+102·4	15·1	68
	MeCN	+110	—	65
$AlH_4^{\ominus}$	Et_2O	+100	420	64
	Et_2O	+103	70 J(Al–H) = 110 Hz	67
$AlCl_3{\cdot}PMe_3$	CH_2Cl_2	+108·2	^1J(Al–P) = 263 Hz	224
$MeAl(BH_4)_2$	neat	+141	—	237a
Al_2Me_6	pure	+156	450	57
Thiophene·$AlEt_3$	C_6H_{12}	+154	1050	228
Al_2Et_6	C_6H_{12}	+142, +174	960, 1000	128, 228
		+171, < +150	1700, 2750	57, 64
$[AlH(Bu^i)_2]_n$		+162	10 000	57
quinoline·$AlEt_3$	C_6H_{12}	+164 est	~2500	228
$Et_3N{\cdot}AlEt_3$	C_6H_{12}	+165	1100	228
$Py{\cdot}AlEt_3$	C_6H_{12}	+167	1440	228
Pyrolidine·$AlEt_3$	C_6H_{12}	+176	1220	228
$THF{\cdot}AlEt_3$	C_6H_{12}	~ +176	1280	228
anisole·$AlEt_3$	C_6H_{12}	~ +176	2100	228
$Et_2O{\cdot}AlEt_3$	C_6H_{12}	+178	1160	228
	C_6H_{12}	+204	2100	228
$MePhS{\cdot}AlEt_3$	C_6H_{12}	+204	2200	228
$Al_2Bu^i_6$-$AlBu^i_3$	C_6H_{12}	+220	6000	57
$Et_2S{\cdot}AlEt_3$	C_6H_{12}	+221	1890	228
Coupling Constants determined from Proton Spectra				
$AlMe_4^{\ominus}$	dimethoxyethane	J(Al–H) = 6·3 Hz	24	72, 73
$LiAlMe_4$	Et_2O	J(Al–H) = 7·1 Hz	182	73
ion pair	THF		35	
$NaAlMe_4$	Et_2O	J(Al–H) = 9·1 Hz	102	73
ion pair	THF		63	

* ^{1}H NMR shows these to be $AlL_4^{3\oplus}$ complexes.[294 295] ^{27}Al shift is low field of standard.[289]

a number of situations where exchange between different metal environments may also affect line widths. In addition the line widths are reduced by temperature increases and are increased if the sample viscosity increases. Molecular size also makes a contribution to line width and metal atoms in larger molecules should have broader lines. In view of all these factors it is not surprising that ranges of line width are reported for many of the compounds listed.

The line width data are also complicated by the fact that the peak to peak line width of a derivative spectrum is only $1/\sqrt{3}$ of the half-height line width of the corresponding absorption curve. In general all broad lines and all early spectra have been obtained in the derivative mode and only recently have line widths of the narrower lines been obtained in the absorption mode. Fortunately all the comparisons made in the text are based upon spectra obtained all in the same way so that it has been decided to report line widths as published. The factors described above probably in any case introduce the major variations.

^{27}Al chemical shifts have now been measured for a sufficient number

TABLE XVII

Table of gallium chemical shifts and line widths. [$Ga(H_2O)_6^{3\oplus}$ standard]

No.	Compound	Solvent	Chemical shift, p.p.m.	Line width, Hz	Ref.
1	$Ga^{\oplus}$ in Ga_2Cl_4	benzene	−685	150	28
		melt	−493	150	28
2	$Ga^{\oplus}$ in Ga_2Br_4	benzene	−652	150	28
		melt	−413	broad	28
3	$GaI_4^{\ominus}$	H_2O/HI	−450	100	28
			−479	est 540 (^{69}Ga)	33
4	$Ga(DMF)_6^{3\oplus}$	DMF	−25	120	34
5	$Ga(H_2O)_6^{3\oplus}$	H_2O	0 standard	300	28
				200	34
				est 1300 (^{69}Ga)	33
6	$GaBr_4^{\ominus}$	H_2O/HBr	+69	100	28
			+64	80	34
		Ga_2Br_4 melt	+127	broad	28
7	$Et_2O \cdot GaCl_3$	pure liquid	+137	very broad	28
8	$Ga(OH)_4^{\ominus}$	H_2O/NaOH	+192	600	28
9	$GaCl_4^{\ominus}$	Ga_2Cl_4 melt	+197	300	28
		Ga_2Cl_4 in benzene	+223	300	28
		H_2O/HCl	+257	100	28
			+239	90	34
			+243	est 870 (^{69}Ga)	33
10	$GaH_4^{\ominus}$	Et_2O	+682	broad	28

of compounds to enable some general conclusions to be reached about the possible relationships between chemical shift and chemical structure. Haraguchi has indeed already made such a study[64] and is responsible for twenty-four of the sets of figures in Table XVI. The Table can be divided into three distinct regions. At the highest fields we have the octahedrally solvated ions from $Al(PhCN)_6^{3\oplus}$ at -46 p.p.m. down to $Al(EtNCS)_6^{3\oplus}$ at $+20$ p.p.m. The only non-octahedral species found in this region are the anions $AlI_4^{\ominus}$ and $AlI_3Br^{\ominus}$ and solutions of the triiodide in aromatic solvents. The symmetrical ions and species all possess narrow lines never broader than 100 Hz except for the acetylacetonate and oxalate complexes which may be slightly distorted from octahedral symmetry. It is of interest to speculate whether conditions might not be found where many of these species might have lines as narrow as that of the $Al(H_2O)_6^{3\oplus}$ ion in dilute acidic solution, namely 3 Hz. Other species which are found in this region and which probably also contain octahedrally bonded aluminium are the fluorides $AlF_n(H_2O)_{6-n}^{(3-n)\oplus}$ which have broadened lines because of loss of regular octahedral symmetry; the dimer ion $Al(OH)_2(H_2O)_n^{4\oplus}$ which probably has four water molecules bonded to each of two hydroxy bridged aluminium ions while the line seen for aluminium isopropoxide may possibly arise only from the octahedrally bound aluminium in the tetramer and a second line due to the tetrahedral aluminium may await discovery.

Immediately adjacent to the high field region is a region which contains the tetrahedral anions and other tetrahedral species all carrying electronegative halide or oxygen substituents and extends from $AlI_3Cl^{\ominus}$ at $+21{\cdot}7$ p.p.m. to $AlCl_4^{\ominus}$ at about $+110$ p.p.m. Adducts of the halides, the adduct $Me_3N \cdot Al(BH_4)_3$, the dimeric halides, a halo alkyl dimer and a halo alkoxy dimer all come within this region and with the exception of the latter two all, even the dimers, have quite narrow lines emphasising that it is the symmetry around the metal which determines the field gradient rather than that of the molecule as a whole. The position of the aluminium resonance in aqueous alkali and which is generally attributed to the anion $Al(OH)_4^{\ominus}$ is certainly not in a position which encourages acceptance of the recent suggestion that it may be an octahedral species.

To low field of $AlCl_4^{\ominus}$ there is a gap of almost 50 p.p.m. where no resonances have so far been reported and below this gap we find the alkyl alanes and their adducts covering the range from $+156$ p.p.m. (Al_2Me_6) down to $+221$ p.p.m. for the adduct $Et_2S \cdot AlEt_3$. The aluminium in many of these molecules remains in a tetrahedral environment so that the shifts observed must be some function of the substituents rather than of the stereochemistry. The alkyl group substituents

appear to result in a large paramagnetic screening of the aluminium nucleus, just as is observed with the monomeric boron alkyls. For example, trimethyl alane is found 74 p.p.m. low field of $Al(OH)_4^{\ominus}$ and trimethyl borane is 85 p.p.m. low field of $B(OH)_4^{\ominus}$. The formation of adducts produces a further low-field shift which appears to depend upon the nature of the donor atom rather than upon the strength of the complex. The line widths of these molecules are very much broader than those of the tetrahedral species found to higher field. The possible effects of dissociation and exchange on their line widths has been discussed above.

One calculation has been made of a chemical shift of aluminium in $AlH_4^{\ominus}$.[57] The result obtained was of the correct order of magnitude.

The gallium chemical shifts appear to follow the same trends as do the corresponding aluminium compounds though there are individual differences for instance, the aluminium shifts of $Al(OH)_4^{\ominus}$ and $AlBr_4^{\ominus}$ are the same whereas the corresponding gallate ions are separated by 130 p.p.m. The ion $GaH_4^{\ominus}$ is well low field of standard, its shift being some sixteen times that of $AlH_4^{\ominus}$ and $GaI_4^{\ominus}$ is seven times higher field of standard than $AlI_4^{\ominus}$ though on the basis of the calculations of Jameson and Gutowski a factor nearer to two would be expected.[290] More extensive data are, however, required before aluminium and gallium shifts can be fruitfully compared in detail.

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The Application of Fourier Transformation to High Resolution Nuclear Magnetic Resonance Spectroscopy

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Notation

E = Excitation applied to linear system
$\mathscr{F}$ = Functional operator for Fourier transformation
$\mathscr{H}$ = Hamiltonian operator
$\hat{I}$ = Spin operator
i = $\sqrt{-1}$
$\mathbf{M}$ = Total magnetisation vector
$\mathbf{M}^-$ = Magnetisation (in the rotating frame) just prior to initiation of a pulse
$\mathbf{M}^+$ = Magnetisation (in the rotating frame) just after a pulse
M'_{xyz} = Total magnetisation vector in x, y, z plane in rotating frame
$M(t)$ = Magnetisation as a function of time
$M(\tau)$ = Magnetisation after a unit impulse
$M(\omega)$ = Magnetisation as a function of frequency
N = Number of data points
R = Response of a system to an excitation
T = Acquisition time (sec)
T_d = Delay between pulse sequences (sec)
T_p = Delay between pulses (sec)
T_1 = Spin-lattice (longitudinal) relaxation time (sec)
$T_{1\rho}$ = Spin-lattice relaxation time in the rotating frame (sec)
T_2 = Spin-spin (transverse) relaxation time (sec)
T_2^s = Component of T_2^* from incoherent effects. See equation 63 (sec)
T'_2 = Component of T_2^* from field inhomogeneities. See equation 63 (sec)
T_2^* = Effective transverse relaxation time. See equation 63 (sec)
Y = Transfer function of a system

γ = Magnetogyric ratio
Δ = Sweep or spectral width (Hz)
δ = Pulse width (sec)
$\delta(x)$ = Impulse function of x
η = Frequency (Hz)
μ = Magnetic mount of nucleus
τ = Time; measured after an event or interval between pulses in a sequence (sec)
χ_0 = Total nuclear susceptibility
χ' = Real/out of phase component of nuclear susceptibility
χ'' = Imaginary/in phase component of nuclear susceptibility
ω = Angular frequency (radians/sec)
ω_c = Frequency of RF centre band/carrier (radians/sec)

ω_i = Difference in frequency of free induction decay of spin i from ω_c (radians/sec)
ω_o = Resonance frequency of spin i (radians/sec)

I. INTRODUCTION

THE FIRST suggestion that the technique of Fourier transformation might be useful in *high* resolution NMR was made by Ernst in 1966.[1] Exciting prospects of sensitivity enhancements an order of magnitude greater than those offered by conventional frequency scanned spectra were indicated. Indeed, this has been borne out by subsequent investigations. The present availability of commercial Fourier transform spectrometers will give chemists of all persuasions access to data which were, for practical purposes, previously unobtainable.

In the light of these developments it was thought timely to review the progress to date so that chemists without special knowledge of NMR may assess the scope of the new techniques. There have been three relevant reviews to date.[2 to 4]

Although we shall restrict our attention to high resolution NMR, ground familiar to the chemist, Fourier transform NMR (FTNMR), leads one into an area previously explored extensively only by physicists, the time domain. In this strange land one studies the time development of the magnetisation after an event such as a pulse of radiofrequency energy. All resonances of interest are excited simultaneously (wide band excitation) and the manner in which the nuclear magnetic system responds contains *at least* as much information as that obtainable from the normal scanned spectrum observed in the frequency domain.

The mathematical process of Fourier transformation relates the time and frequency domains. In the mathematical sense[5] the variables time and frequency are just a particular case of a general relationship,

$$f(x) = \int_{-\infty}^{\infty} f(y)\, e^{-ixy}\, dy \tag{1}$$

where $f(x)$ is said to be the Fourier transform of $f(y)$. The inverse transformation,

$$f(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x)\, e^{ixy}\, dx \tag{2}$$

also holds.

In our particular case equation (1) takes the form,

$$M(\omega) = \int_{-\infty}^{\infty} M(\tau)\, e^{-i\omega\tau}\, d\tau \tag{3}$$

where the magnetisation is expressed as a function of angular frequency $M(\omega)$ corresponding to the ideal steady-state frequency swept spectrum (i.e. infinitesimal departure from equilibrium) and $M(\tau)$ the magnetisation as a function of the time after an "event". The practical realisation of equation (3) is considered in Section II, there the limitation imposed by restriction of the experiment to a finite acquisition time T, and the requirement to sample the data at discrete intervals are considered. The magnetisation at any point in time after the "event" is a property of the whole spin system. In the frequency domain the magnetisation at a given point corresponds only to the particular frequency. Thus if we stop a frequency swept spectrum half-way through we lose half the information. Stopping the experiment half-way in the time domain merely reduces the quality of the information. A hologram (interference picture produced by laser light) is an exact analogue in that reducing the size of the image by a factor of two leaves the same picture but increases the fuzziness.

Spectra in the time domain are intelligible to the eye only in simple cases. The magnetisation of a spin system consisting of a single magnetic species will decay exponentially with time. A complex system, such as that represented by a normal high resolution sample, requires a digital computer to perform the transformation before the information is recognisable to the eye. The practical requirements are detailed in Sections IV, V and VI. This inadequacy of the visual sense is in contrast to that of hearing. The total sound produced by an orchestra is a complex signal in the time domain but the ear is able to select a particular instrument (frequency). Figure 1 shows the data as recorded in the time domain, the so-called free induction decay together with the transformed spectrum in the frequency domain.

The advent of the computer has enabled developments in Fourier transformation which are not restricted to NMR.

Michelson in the 1920s searched for years without success for a practical method to transform interferograms. The modern realisation of this idea is embodied in the far infra red interferometer (IRFT). In common with FTNMR wide band excitation is employed, again with its accompanying improvement in sensitivity, to produce an interferogram as output. The amplitude of the light reaching the detector is a function of a path length difference which, on Fourier transformation, produces a spectrum in the frequency domain, i.e. a "normal" far infra red spectrum. If the inverse transformation into the time domain is made [equation (2)], then we have the time decay appropriate to the lifetime of the excited vibrational state which is of course short (10^{-12} sec) compared to the NMR lifetimes (~ 10 sec). It is clearly not feasible

at the moment to study the IR analogue of the NMR experiment. One requires to observe the decay of the oscillatory electric dipole on a 10^{-12} sec time scale! The merits of IRFT spectroscopy are reviewed elsewhere.[6]

In the usual experiment where the quest is for improved sensitivity, radiofrequency pulses short enough to excite all the required resonances is applied, that is excitation is applied over a wide band of frequencies.

In an alternative method, excitation of the spin system is by random noise introduced by noise modulation of the radiofrequency signal. The

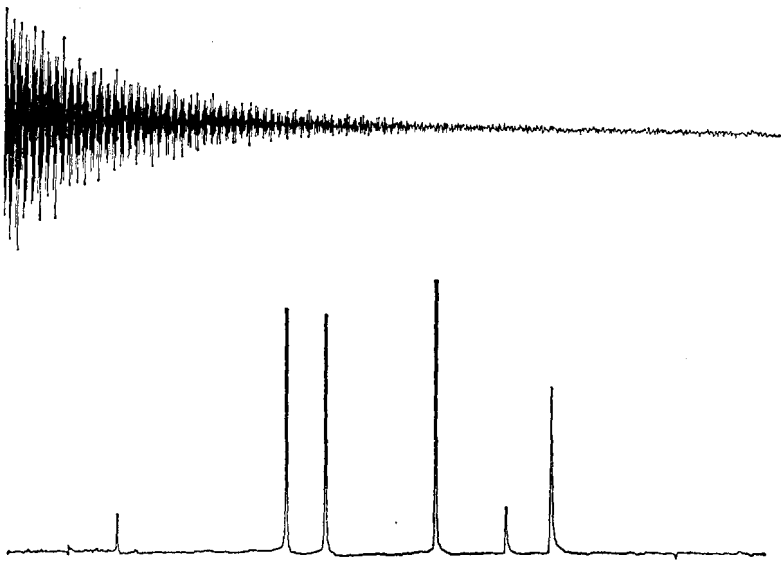


FIG. 1. This illustrates (a) the free induction decay of undecane and (b) its transformation into the frequency domain.

method has been called *stochastic resonance.*[7] The output noise differs from the input in that it is modified by the frequency response of the spin system. The precise relation between the two waveforms is the *cross-correlation function.* An "incident" at the input at a given time t_0 has a consequence in the output at times after t_0. Cross correlation produces the time domain picture, Fourier transformation of which produces the frequency spectrum.

Again this type of technique is not specific to NMR. The effect of wide band noise on any system may be studied in a similar way. For some general applications and discussions of correlation techniques see reference 8. The problem might be circuit analysis and the system could for

instance be a resistor, an LC circuit, a servo system, an amplifier, etc. The experiment is performed to advantage in the time domain and subsequent processing, including Fourier transformation, converts it into the more intelligible frequency domain.

In many situations it is not possible to cross-correlate since no suitable reference signal is available. This situation applies in radioastronomy when one wishes to examine the weak signals from distant stars.

In this situation a signal may be examined for periodicities by comparing with a time development of itself. This is the *auto-correlation function*, whose Fourier transform is the power spectrum. Clearly there is less information here and what is missing is phase information. In the NMR situation there is always some kind of coherent stimulus so the phase information may be obtained.

The characteristic of spectra in the time domain is the ability to obtain information on the complete spin system in a time $\leqslant T_1$. The method consequently lends itself to the time averaging of many runs and an improvement in sensitivity of a factor of ten over normal methods for the same total observation time may be expected. This of course means that a given sensitivity may be achieved 100 times faster.

Thus the spectra of insensitive nuclei such as ^{13}C may be studied to greater advantage. Even for sensitive nuclei such as ^{1}H and ^{19}F there are obvious advantages in the study of nuclei which are low in number by reason of high dilution and/or high molecular weight.

The improvement in time scale may also be used to study for instance:

(a) decaying magnetisations of individual lines to yield individual values for T_1 and T_2 which may be helpful in assignment and also produce exciting information on molecular motion,
(b) chemical kinetics on a time scale faster than that previously possible,
(c) chemically induced nuclear polarisations,
(d) transient population (Overhauser) effects.

II. THE TWO DOMAINS

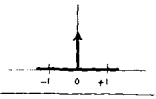
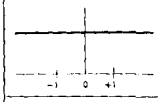
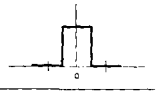
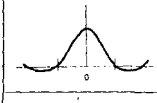
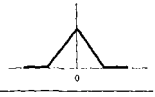
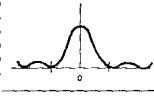
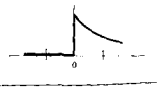
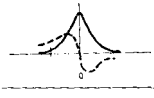
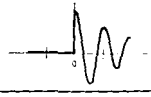
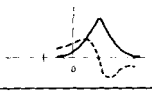
In the introduction we stated that the Fourier transformation enabled us to change from one domain to another. Applications of this freedom to transfer from one domain, where data have been obtained, into another where the results become intelligible are numerous in physics and engineering.[5,8,9] We do not propose to detail these applications or to prove any mathematical relationships used, but simply to refer the reader to suitable texts, e.g. reference 5.

A. Mathematics

Certain mathematical functions and concepts occur very frequently when dealing with applications of the Fourier transformation. These concepts will be stated in a general form now so they may be referred to later when required in a specific form.

Table I illustrates some functions that will be used extensively in this review along with their Fourier transforms. It is designed to give the reader a "feel" for what is the behaviour in the second domain of a function encountered in the first domain.

TABLE I

X Domain			*S* Domain		
Function	Symbol		Symbol	Function	
Impulse	$\delta(x)$		$S = 1$	Unity	
Pulse	$\Pi(x)$		$\frac{\sin \pi S}{\pi S}$	sinc S	
Triangle	$\Delta(x)$		$\left(\frac{\sin \pi S}{\pi S}\right)^2$	sinc^2 S	
Decay	$e^{-\lvert x\rvert} H(x)$		$\frac{1 - i2\pi S}{1 + (2\pi S)^2}$	Lorentzian + dispersive	
Offset Decay	$e^{-\lvert x\rvert} \cos x^{-1} H(x)$		$\frac{1-i2\pi(S-1)}{1+[2\pi(S-1)]^2}$	Offset Lorentzian + dispersive	

The most important concept is that of convolution. Convolution is a moving average and describes the result action of a linear system on an input, e.g. the effect of an electrical filter on a signal. It is defined mathematically thus

$$f_0(x) = \int_{-\infty}^{\infty} h(\tau) f_i(x-\tau)\, d\tau = h(x) * f_i(x) \qquad (4)$$

where $h(\tau)$ is the function which represents the systems perturbation (weighting function), $f_i(x)$ the input signal and $f_0(x)$ the resultant. Each point of the output function is the weighted mean of the input function around that point. The weighting function is then moved using τ as a

running variable and the process repeated.[5] In NMR the convolution integral can describe the effect of a pulse on a nuclear system and effects of analogue filtering on an NMR signal.[10] One useful property of the Fourier transform is that if input and weighting functions are both transformed into a second domain then convolution becomes the easier process of multiplication in the later domain.

$$h(x) * f_i(x) = \mathscr{F}^{-1}[h(s) \times f_i(s)] \tag{5}$$

This is useful in NMR terms as it can simplify data handling, see Section X G.

As mentioned in the introduction, two similar and important ideas are those of cross-correlation and auto-correlation which are used to find hidden periodicities, they are defined thus:

$$R_{hf}(\tau) = \frac{1}{T}\int_0^T h(x)f(x-\tau)\,dx \tag{6}$$

$$R_{hh}(\tau) = \frac{1}{T}\int_0^T h(x)h(x-\tau)\,dx \tag{7}$$

If transformation into a second domain is carried out then correlation becomes complex conjugate multiplication. Correlation techniques are used in stochastic NMR to extract the response of a spin system (e.g. R_{hf}) when both the input and output contain random noise, see Section III C 3.[7,11]

B. The advantages of the time domain

In the previous section we have shown that it is possible, by use of a Fourier transformation, to change from the one domain into another domain and vice versa. We must now ask the question, "What are the advantages to be gained from being able to translate from one domain to the other?" The advantages are that in the time domain greater sensitivity can be obtained from NMR experiments than in the more conventional frequency domain. Any method of improving the sensitivity of a spectroscopic technique, especially if it is as insensitive as NMR, is to be seriously considered.

NMR is an insensitive spectroscopic technique mainly on account of two factors. Firstly, because the energy difference between the ground and excited states studied is very small, the Boltzmann distribution allows very little difference in population. In effect, only a very small number of molecules present can be studied, (1 in 10^6). Since the typical time for relaxation of a nucleus from the excited state to the ground state is in order of a second, this severely limits the power which may be

applied without equilibrating the populations and hence losing the signal.[12] The sensitivity can be increased by various methods; for example, changing the Boltzmann distribution by the use of higher magnetic fields or Overhauser effects, and by instrumental improvements, e.g. use of larger samples and better electronic design. A further way is by radically changing the technique which is used to acquire data. The factors governing the sensitivity of the NMR experiment and methods of improving them have recently been very well reviewed by Ernst.[10]

The normal method of obtaining an NMR spectrum is to slowly sweep the frequency through the range required while observing the changes in magnetisation. The rate at which data may be obtained by this technique is limited by the rate at which the frequency can be swept;[13] this is determined by the relaxation times of the system under consideration. The major inefficiency in the technique lies in the fact that only one frequency may be analysed at a time. A way of overcoming this limitation in an attempt to increase the sensitivity of an NMR spectrometer would be to use multiple transmitters and multiple receivers. Each channel would be gathering information and hence the information gathering rate of the system would be increased with a consequent increase in sensitivity per unit of time. The limit to this approach would be realised when there was one channel per line width of the observed spectrum. After this point, the addition of further channels would just cause duplication of the available information and no further gain in sensitivity would be achieved. At this limit there would be required N channels, where N is the total width of the spectrum divided by the line width of the individual lines present. The increase in sensitivity obtained this way is proportional to the square root of the number of channels used. For protons, this factor is about 100 and for other nuclei, where the spectral widths are larger, the potential improvement is considerably better. As anyone who has handled an NMR spectrometer with only one transmitter and receiver will be well aware, this method of improving the sensitivity would be rather impractical.

If instead of the continuously varying frequency a short pulse of a single frequency is applied to the system a different situation results. Now all the spins are excited simultaneously and when the pulse is switched off they all relax simultaneously. We now have a situation in which it is possible to gather information about all the spins simultaneously, as opposed to one at a time, as in the previous experiment. We are now, however, working in the time domain. As we have shown by the use of a Fourier transformation, the data obtained this way may be transformed into the more familiar frequency domain, where we can

understand it. Put another way, working in the time domain corresponds to the optimum multi-channel experiment as information is gathered about all the frequencies present simultaneously, hence increasing the sensitivity compared with the conventional system. The effect of a pulse of high power in the time domain is a sinc x distribution of frequencies in the frequency domain see Table I. A second way of operating in the time domain would be to provide simultaneously all the frequencies required to excite all the spins; this may be done by noise modulating the carrier frequency. This is the basis of stochastic resonance which will be discussed in more detail later. This technique also gains sensitivity by working in the time domain.

A more detailed comparison of the gains in sensitivity between conventional pulsed, multi-pulsed, and stochastic experiments, will be given in Section IX.

III. THE NMR EXPERIMENT

A. The general experiment

The NMR experiment is concerned with deriving information of chemical interest from a study of the interaction of nuclei with a magnet field.[14] Nuclei available for study by NMR must have a nuclear spin, and their interactions with a magnetic field are described by the Hamiltonian operator given in equation (8).

$$\hat{\mathscr{H}} = -\mu \cdot H \tag{8}$$

Now the magnetic moment is given by

$$\mu = \gamma \hbar I_z \tag{9}$$

so that if the field H_0 is applied along the z direction the Hamiltonian operator becomes

$$\hat{\mathscr{H}} = -\gamma \hbar I_z H \tag{10}$$

Solution of the appropriate Schrodinger equation gives the well-known Larmor equation

$$\omega_0 = \gamma H_0 \tag{11}$$

which describes the resonance behaviour of nuclei in the magnetic field.

NMR spectrometers function by studying the changes in the magnetisation (M) of the nuclei as the Larmor resonance condition is approached. These changes in magnetisation induce a voltage in an observing coil which is placed, around the sample, along an axis perpendicular to the basic magnetic field (conventionally the Y-axis).

The magnetisation is defined in terms of the nuclear susceptibility by equation (12).

$$M = \chi H \tag{12}$$

The energy required to excite transitions at resonance is applied in the form of an oscillating RF field along the third axis. This RF field has an amplitude $2H_1$ and a frequency of ω. The oscillating magnetic field may be considered as consisting of two components, these being magnetic fields, rotating about the z-axis with frequency ω. One of these rotates in a clockwise direction, and the other anti-clockwise, but only one of these fields has the correct sense to excite the spins.

We now have a system able to accept energy—in the form of radio frequency quanta. The ability of this system to go on accepting further quanta is governed by the rate at which the system is able to dissipate its excess energy to the surroundings ("lattice"), described by the relaxation time, T_1. In the presence of too strong an excitation, a non-equilibrium population distribution is set up which reduces the total magnetisation, with the result that the spectral line becomes broadened, a phenomenon often observed in NMR and called saturation.

B. Linear systems

A linear system may be defined rigidly in mathematical terms.[15] This simply is a system whose output response is proportional to the input excitation and is independent of the time at which the excitation is applied. Under non-saturating conditions, an assembly of nuclear spins approximates reasonably closely to a linear system for single resonance experiments.[12] A linear, time-independent system S, may be characterized uniquely by the frequency response function (transfer function) $Y(\omega)$; this function measures the amplitude and phase of the response of the system to an excitation whose frequency is ω, and is related to the frequency response $R(\omega)$ when an excitation $E(\omega)$ is applied to the system by equation (13).

$$R(\omega) = E(\omega)Y(\omega) \tag{13}$$

$E(\omega)$ and $R(\omega)$ are very general, however, in the NMR experiment $E(\omega)$ is the RF excitation and $Y(\omega)$ is the magnetisation of the spin system $M(\omega)$. $M(\omega)$ is detected by a phase sensitive detector analysing $R(\omega)$ with reference to $E(\omega)$; this we would normally consider as an NMR spectrum. This is, however, not what is normally obtained from an NMR spectrometer—what is normally obtained is a spectrum whose frequency is swept as a linear function of time. Here ω is a dummy variable the real variable being time.[16] In this mode transient effects such as

signal distortion and transient oscillations ("wiggles") are often observed, especially in cases where long relaxation times cause memory effects. If, however, we sweep the frequency slowly enough such as to be under equilibrium conditions all the time, i.e. what is described as adiabatic slow passage, the spectrum plotted is now truly a function of frequency, i.e. is the transfer function of the system $M(\omega)$. Under these conditions equation (13) may be rewritten as:

$$M(t) = M(\omega) \cdot E(t \cdot \omega) \tag{14}$$

if $\omega = a \cdot t$ and the sweep rate a tends to zero.

The second way to characterise a linear time-independent system is in terms of its response to an impulse $M(\tau)$, an impulse being an excitation of unit intensity lasting for zero time. The response $M(t)$ to an arbitrary excitation $E(t)$ is given by the convolution integral:

$$M(t) = \int_{-\infty}^{\infty} M(\tau) E(t-\tau)\, \mathrm{d}\tau \tag{15}$$

where t is the real time and τ is the time measured from the application of the pulse. For an NMR system $M(t) = 0$ for τ negative. If the excitation applied to a system is sinusoidal it can be represented by the complex equation:

$$E = 2H_1 \, \mathrm{e}^{-\mathrm{i}\omega t} \tag{16}$$

If this excitation is then placed in equations (14) and (15) and $M(t)$ eliminated, the result $M(\omega)$ is shown in equation (17).

$$M(t) = M(\omega) \, \mathrm{e}^{-\mathrm{i}\omega t}$$

$$M(t) = \int_{-\infty}^{\infty} M(\tau) \, \mathrm{e}^{-\mathrm{i}\omega(t-\tau)} \, \mathrm{d}\tau$$

therefore

$$M(\omega) = \int_{-\infty}^{\infty} M(\tau) \, \mathrm{e}^{-\mathrm{i}\omega\tau} \, \mathrm{d}\tau \tag{17}$$

This equation expresses the frequency response of the system (spectrum) in terms of the response of that system to an impulse. It is interesting to note that the spectrum obtained in this way is not a function of time, i.e. will not show transient effects. This aspect will be discussed in more detail later when considering the use of pulse methods to obtain spectra of a very high resolution (see Section X E).

If the form of equation (17) is compared with that of equation (3), the application of the Fourier transformation to NMR may be seen. We have shown that the spectrum we normally obtain, i.e. as a function of frequency, is the Fourier transform of the response of the system

to an impulse; this relationship was first demonstrated by Lowe and Norberg.[17] In pulsed NMR a short RF pulse is applied to the system and this can be approximated to an impulse, providing that the duration of the pulse is short on the time scale of the nuclear spins. Hence, $M(t)$ may be equated to what is normally referred to as the free induction decay.

C. Bloch equations

The most useful and general description of the behaviour of nuclear spins in a magnetic field is the one put forward by Professor Bloch.[18] These equations are phenomenological in origin and describe the behaviour of nuclear spins in a magnetic field in terms of their magnetisation resolved along the coordinates of the laboratory. They are also useful in so much that they may be easily modified to study time-independent effects on the system. We will now consider the solution of these equations under normal conditions, i.e. with the application of a continuous excitation by an RF field which is at equilibrium with the spin system and of low power (to avoid saturation effects). We will then solve the Bloch equations under two different conditions; firstly, when the spin system is subjected to a train of equally spaced pulses of RF energy, and secondly when the spin system is subjected to an RF field which is modulated by random noise. The latter cases are considered because they are cases where the NMR spin system may be studied as a function of time, as opposed to the conventional function of frequency. The advantages of studying the spin system as a function of time have been discussed previously and are mainly connected with efficiency and increase in signal-to-noise ratio. The spectrum as a function of time, as we have already shown, may be related to the spectrum as a function of frequency by use of a Fourier transformation.

1. *Continuous excitation*

The Bloch equations for these conditions are given in equations (18).

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \tag{18A}$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} \tag{18B}$$

$$\frac{dM_z}{dt} = -\frac{(M_0 - M_z)}{T_1} \tag{18C}$$

where T_1 and T_2 describe the relaxation of the spin system to equilibrium after perturbation (assumed to be first order, i.e. the exciting

RF field H_1 is sufficiently low that saturation effects do not take place); *via* the lattice and spin-spin effects respectively. These equations are normally solved by changing into a rotating frame of reference, i.e. a frame of axes which rotate about the laboratory z-axis with a frequency ω.[19] In this frame, the exciting RF field is a stationary field along the x-axis, the counter-rotating component of frequency 2ω in this frame having negligible influence. The Bloch equations now become:

$$\frac{dM'_x}{dt} = (\omega_0 - \omega)M'_y - \frac{M'_x}{T_2} \tag{19A}$$

$$\frac{dM'_y}{dt} = -(\omega_0 - \omega)M'_x + \gamma H_1 M_z - \frac{M'_y}{T_2} \tag{19B}$$

$$\frac{dM'_z}{dt} = -\gamma H_1 M'_y - \frac{(M_z - M_0)}{T_1} \tag{19C}$$

After the exciting field has been present for a long enough time, the spin system settles down to a steady state and the stationary solutions of equation (19) are easily shown to be

$$M'_x = M_0 \frac{\gamma H_1 T_2^2(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{20}$$

$$M'_y = M_0 \frac{\gamma H_1 T_1}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{21}$$

$$M'_z = M_0 \frac{1 + T_2^2(\omega_0 - \omega)^2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{22}$$

These solutions are only for a spin in the rotating frame. The solutions for an oscillating field are almost the same. This is because, as previously mentioned, the oscillating magnetic field may be considered as two fields counter-rotating about the z-axis.

M_x is the component of the total magnetisation which oscillates in phase with H_1, while M_y lags 90° out of phase. Bloch introduced a complex susceptibility $\chi(\omega)$ to describe these phase relationships. The components of the oscillating magnetic field H_1 and the magnetisation M are written as complex numbers and a complex susceptibility is defined as in equation (23).

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \tag{23}$$

The real part of this equation describes the behaviour of M_x, which is normally referred to as the dispersive or u-mode spectrum and the imaginary term describes the M_y or v-mode spectrum. It is normal in NMR spectroscopy to observe the v-mode spectrum. The v-mode

generally produces higher resolution of spectral lines, the visual appearance of the spectrum is more satisfactory and it is possible to define relative intensities of spectral lines by integrating their areas. Experimental separation of M_x and M_y is possible in NMR since the use of coherent sources of excitation enables the response to be phase detected by phase sensitive detection techniques. These detectors are referenced to the correct component of $E(\omega)$ and measure either M_x or M_y. It has been shown that M_x and M_y can be related to each other by the Hilbert transform;[20] this will be discussed in more detail later.

2. *Pulse excitation*

We will now consider a system of isolated spins in a magnetic field along the z-axis subjected to a sequence of rectangular RF pulses along the x-axis. These pulses are of frequency ω_c and amplitude $2H_1$ their period is T and their duration is δ.

The system eventually reaches a stationary state independent of the initial conditions. During the pulse the magnetisation vector is tipped towards the xy plane by rotation about the x-axis. When the radio-frequency is switched off the magnetisation decays to zero processing about the z-axis at frequency ω_0. The main aim of pulse NMR is to gain sensitivity, hence the pulses are fired as rapidly as is consistent with the required resolution in the final spectrum. The consequence of this, particularly in ^{13}C NMR where T_1 and T_2's may both be long, is that the xy magnetisation is not zero when the next pulse is initiated. Under these conditions the spins settle down into a steady state where refocusing effects occur giving rise to a spin echo; this condition has been recently considered by Freeman and Hill.[21] It is their extension of the original ideas of Ernst and Anderson[1] which we will consider.

The motion of the spin magnetisation will again be considered in a frame of reference rotating about the z-axis with frequency ω_c. The applied field H_1 is assumed to be large enough that its magnitude, expressed in frequency units H_1, is large compared to the range of resonance frequencies in the sample. This condition ensures that all nuclei are effectively at resonance so that their effective field about which they precess in the rotating frame is indeed H_1, pointing exactly along the x'-axis.† As the pulse times are very much shorter than T_1 and T_2 relaxation during the pulses will be neglected.

Each pulse rotates the magnetisation about the x-axis by angle α defined thus

$$\alpha = \gamma H_1 \delta \tag{24}$$

†Jones and Sternlicht have considered the situation when this condition is not met[84] but did not, as was done by Freeman and Hill,[21] include the effect of magnet inhomogeneity.

The magnetisation immediately after the pulse ($\mathbf{M}^+$) is then related to the magnetisation before the pulse ($\mathbf{M}^-$) by the rotation operator $R_x(\alpha)$ thus:

$$\mathbf{M}^+ = R_x(\alpha)\mathbf{M}^- \tag{25}$$

Between the pulses the spins precess through angle θ about the z-axis.

$$\theta = 2n\pi + \theta = \omega_0 T_p \tag{26}$$

where

$$\theta = (\omega_0 - \omega)\cdot T = \omega_i \cdot T_p \tag{27}$$

During this period relaxation takes place according to the following operator,

$$\hat{S}(T_p, T_1, T_2) = \begin{vmatrix} E_2 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_1 \end{vmatrix} \qquad \begin{aligned} E_1 &= \exp(-T_p/T_1) \\ E_2 &= \exp(-T_p/T_2) \end{aligned}$$

Thus if $\mathbf{M}^*$ is the magnetisation at the end of the precession period

$$\mathbf{M}^* = \mathbf{M}_0(1-E_1) + \mathbf{M} + R_z(\theta)S(T_p, T_1, T_2) \tag{28}$$

$\mathbf{M}_0$ being the magnetisation under equilibrium conditions. For a steady-state solution $\mathbf{M}^* = M^-$ the components and after the pulse are found to be:

$$M_x^- = M_0(1-E_1)E_2 \sin\alpha \sin\theta/D \tag{29}$$

$$M_y^- = M_0(1-E_1)(E_2 \sin\alpha \cos\theta - E_2^2 \sin\alpha)/D \tag{30}$$

$$M_z^- = M_0(1-E_1)[1-E_2\cos\theta - E_2\cos\alpha(\cos\theta - E_2)]/D \tag{31}$$

$$M_x^+ = M_x^- \tag{32}$$

$$M_y^+ = M_0(1-E_1)(1-E_2\cos\theta)\sin\alpha/D \tag{33}$$

$$M_z^+ = M_0(1-E_1)E_2(E_2 - \cos\theta) + (1-E_2\cos\theta 0)\cos\alpha/D \tag{34}$$

where

$$D = (1-E_1\cos\alpha)(1-E_2\cos\theta) - (E_1-\cos\alpha)(E_2-\cos\theta)E_2 \tag{35}$$

The magnetisation along the y'-axis of the rotating frame, i.e. what is measured by a spectrometer using a phase detector referenced to the correct frequency ω_c is given by

$$M_y(t) = M_y^+ \cos(\omega_i t)E_2 + M_x^+ \sin(\omega_i t)E_2 \tag{36}$$

This equation shows that the phase of each signal depends on ω_i, hence

the phase differs from line to line. However, as this phase change depends on T_1 through M_y^+ if T is made much longer than T_1, then the response of each pulse if independent of the preceding pulse and $M_y^+ = \mathbf{M}_0 \sin \alpha$, hence constant phase spectrum results. Under these conditions the optimum sensitivity independent of θ can be obtained when

$$\cos \alpha = E_1 \tag{37}$$

and the values of M_y^+ is given by

$$M_y^+ = \frac{\mathbf{M}_0 \sin \alpha}{1+E_1} \tag{38}$$

In the limit of $T \geqslant T$, α tends to 90°.

This value of α is not the one which gives maximum sensitivity if more realistic conditions are considered. To be more specific, firstly, if a second pulse is initiated before M_y' has decayed to zero, i.e. T becomes in the order of or less than T_2 and, secondly, if the time over which the spectrum is sampled, T, is not equal to the separation of the pulses, T_p. The first condition is often dictated by the fact that sensitivity is the prime concern of the experiment. The second situation occurs as sampling cannot start immediately after the end of the pulse because the spectrometer electronics require time to recover from the effect of the pulse (see Section IV C). Both effects can also perturb the phase and intensities present in a Fourier spectrum. Fourier transformation of equation (36) describes the frequency domain spectrum of the spin system. It consists of two terms, the cosine or real term, and the sine or imaginary term.

$$C(\omega) = \frac{KM_0}{(2T)^{1/2}}\left\{\frac{T_2}{1+(\omega_i T_2)^2}\right. \left[1 - E_2^* \cos\theta - E_2 \cos(\omega_i T) + E_2^* E_2 \cos(\theta + \omega_i T)\right] + \left.\frac{\omega_i T_2^2}{1+(\omega_i T_2)^2}\left[E_2^* \sin\theta + E_2 \sin(\omega_i T) - E_2^* E_2 \sin(\theta+\omega_i T)\right]\right\} \tag{39}$$

where

$$K = \frac{(1-E_1)\sin\alpha}{(1-E_1\cos\alpha)(1-E_2\cos\theta)-(E_1-\cos\alpha)(E_2-\cos\theta)E_2}$$

$$E_2^* = \exp(-T/T_2)$$

The first term of equation (39) represents the absorptive part and the second term, the dispersive part. As we have previously mentioned, if the acquisition time is set long compared to T_2, then the dispersive part can be neglected as both E_2 and E_2^* get very small. Under these condi-

tions there will be no phase anomalies either and K becomes independent of θ. Under these conditions the sine term represents the dispersive signal.

When the transformation is carried out digitally, it is interesting to note that even if T is short compared with T_2 then the dispersive signal does not appear provided T is made equal to the separation of the pulses T_p. This occurs as a result of the frequency of digitisation. A total of N samples are taken of the free induction decay between zero and T sec at a regular rate.

$$\omega = \frac{N\pi}{T} \text{ rads/sec} \tag{40}$$

if $T = T_p$ and therefore $E_2 = E_2^*$ then, using equations (26), (27) and (40),

$$\theta + \omega_i T = \omega_c T - (\omega_c - \omega)T = \omega T = N\pi \tag{41}$$

thus

$$\sin\theta = -\sin(\omega_i T) \tag{42}$$

and

$$\sin(\theta + \omega_i T) = 0 \tag{43}$$

the second term of equation (39) vanishes. However, the intensity of a line is still a function of its offset via the dependence of K on θ. This is one cause of anomalous intensities in Fourier spectra.

In most real spectrometers T_p is longer than T to allow for the recovery of receivers, etc. (see Section IV C) after the pulse. Even slight differences between T and T_p cause $\sin\theta$ and $\sin\omega_i T$ to get out of step, e.g. a difference of 50 microseconds would result in a 90° phase shift across a 5 kHz spectral width.[3] These phase changes can easily be corrected after transformation providing they are not too extreme (see Section VI D).

The effect of magnetic field inhomogeneity must now be considered. This effect may be calculated by imposing a Lorentzian distribution on M_x^+ and M_y^+ in equations (32) and (33). An interesting effect emerges, even though field inhomogeneity causes relaxation with a consequent contribution to the dephasing of the magnetisation vectors in the $x'y'$ plane, a repetitive chain of pulses has the property of refocusing them at the time of the next pulse. This situation was first observed by Hahn in a $90° - \tau - 90°$ sequence.[22] In such a sequence a negative going echo appears at time 2τ. In our situation a third pulse occurs at the centre of this echo, two further echos at 3τ and 4τ are thus generated, etc. A steady state is thus built with the $x'y'$ magnetisation dephased by field inhomogeneity (see Section IX) being effectively refocused prior to each pulse.[21] This refocusing is a direct result of setting up a steady

state repetitive in the order of T_2 where M_x^- and M_y^- are non-zero. The effect has been evaluated in detail by Freeman and Hill[21] and is important as it leads to an increase in total integrated signal and hence improves the sensitivity of Fourier transform NMR in a steady state.

Introduction of field inhomogeneity into the experiment simplifies the problem of choosing the optimum pulse angle for maximum sensitivity. Ernst and Anderson showed that the optimum angle had a complex dependence on θ given by:

$$\cos \alpha_{opt} = \frac{E_1 + E_2(\cos\theta - E_2)/(1 - E_2 \cos\theta)}{1 + E_1E_2(\cos\theta - E_2)/(1 - E_2 \cos\theta)} \tag{44}$$

and is hence dependent on line offset, etc. Allowing for inhomogeneity permits one to integrate over a suitably weighted range of θ values. This results in optimum angle of about $0{\cdot}4\pi$ or 72° for α (when $T_1 = T_2 = 10$ seconds and $T_2^* = 0{\cdot}4$ seconds), which is quite insensitive to the value of T.[21, 23] The realisation that a system of nuclear spins subjected to a regular sequence of pulses settles into a steady state where unless the pulse interval is long compared with T_1, phase and intensity anomalies appear which depend on the offset of the line in question from the carrier [see equation (39)†], is a definite limitation on the technique. Since in nearly all cases sensitivity is the prime reason for using the technique, the pulse interval must be as short as possible and hence a steady state where M_y^- is not zero, will result. A steady state is itself desirable on the grounds of increasing sensitivity as mentioned above. The refocusing thus obtained is able to increase the sensitivity of the experiment by almost as much as the complex multiple DEFT and SEFT refocusing techniques.[21]

Phase and intensity anomalies, produced by the steady state, may be suppressed almost entirely by incoherent effects in the spectrometer which increase the rate of decay of the free induction signal (e.g. noise decoupling), i.e. let $M'_{xy} = 0$ or cause destructive interference when signals are averaged (e.g. instability in field/frequency lock system), i.e. effectively average over θ. Reasons of the latter type probably account for lack of detection of these effects until quite recently.[21, 23] It should be noted that field inhomogeneity does not have any effect in this sense as these effects are refocused. As spectrometers develop and general incoherent effects in their electronics are minimised the anomalies of the "steady state" will become more apparent. It would be a pity if spectrometer performance had to be degraded to average out these phase and intensity problems.

†See section 2.17 of reference 1 for the maximum magnitude of this effect and figure 5 of reference 21 for typical distribution of intensities.

There are two basic remedies to this problem,† either to destroy the $x'y'$ magnetisation just prior to the next pulse or to average steady state signals in such a way as to average out the anomalies. The first possibility may be achieved by multiple pulse techniques of the DEFT type (see Section IX A), where a 180° refocusing pulse is applied. The $x'y'$ magnetisation could also be destroyed by causing instability in the field/frequency lock or by pulsing one of the field gradients. Such techniques should not be applied during signal accumulation otherwise line broadening will result.

The second basic remedy may be achieved by averaging θ which will result if a random delay, of say a few milli-seconds, is introduced into the timing of each pulse. The result of this process is that any line with an offset from the carrier of greater than a few hundred Hertz has essentially a random value of θ [see equation (26)]. The disadvantage of this approach is that a steady state is never obtained with its consequent gain of sensitivity. The most satisfactory solution to the problem seems to be to allow a steady state to build up for a certain number of pulses (e.g. 64) then to introduce a small random change in the pulse interval and so allow a new steady state to build up. Summing the decays set up in these random steady states effectively averages the values of θ, hence minimising phase and intensity anomalies. This is achieved without degrading resolution but still gains the sensitivity advantages of permitting a steady state to exist.[21] There are still, of course, intensity anomalies dependent on nuclei having different T_1 values [see equation (39)] which are not θ dependent. These are thus not removed by the above procedure, but may, however, be removed, at the price of sensitivity, by allowing the magnetisation to attain equilibrium before restricting the next pulse. This situation in the approximate analog of the intensity anomalies occurring in frequency domain spectra recorded at sweep rates too high to satisfy the steady-state condition (see Section VII A).

3. *Stochastic excitation*

As discussed in Section II B, on account of the gain in sensitivity which is achievable, working in the time domain is advantageous in NMR. To achieve this gain all the spins must be excited simultaneously, the use of a pulse of RF energy is one way, the use of noise modulation

†A third possible way of dealing with the steady state by accepting it and using 4 pulse experiments at different frequencies to counteract the phase anomalies inherent in the steady state has recently been proposed and called QRFT.[85] The method, only at its best in conditions when magnet inhomogeneity is the dominant contribution to transfer relaxation gives sensitivities comparable with the conventional Fourier sequence used under comparable conditions but including a random delay.[21]

to give a spread of frequencies is another.[24] The idea of stochastic modulation to give a spread of frequencies has become accepted for some time now in noise decoupling experiments.[25] The idea has recently been extended to obtaining high-resolution spectra by Ernst[7] and Kaiser,[11] see Section VIII.

From the theory of linear systems it is known that a linear time independent system may be described in terms of its response to a stochastic excitation $S(t)$. The noise is white and gaussian and has a frequency independent power spectrum, i.e. the frequency domain equivalent of the time domain impulse mentioned in the previous section. In his treatment, Ernst has allowed for the fact that under conditions of multiple excitation, an NMR system is strictly non-linear, for if the powers are high enough decoupling effects will occur. We will, however, for simplicity, only consider the linear terms.

The response of a system $V(t)$ to stochastic excitation $S(t)$ contains the information required along with the consequence of noise added to the system. The effects of the noise can be removed by the technique of cross-correlation.

$$M_{RS}(t) = \lim_{T\to\infty}(2T)^{-1}\int_{-T}^{T} S(t)R(t+\tau)\,d\tau \tag{45}$$

The resulting cross-correlation function is proportional to the response of the system to an impulse; this in turn is related to the transfer function as shown previously by a Fourier transform.

$$M_{RS}(\omega) = \int_{-\infty}^{\infty} M_{SV}(\tau)\,e^{-12\pi\omega\tau}\,d\tau \tag{46}$$

Stochastic resonance will now be described, as we have done previously for continuous and pulse excitation, by solution of the Bloch equations. These equations are satisfactory provided the powers used are kept below saturation levels, if high powers were to be used the density matrix theory must be used and, unlike pulse saturation, double resonance effects may appear in the final spectrum.[7] The Bloch equations, as given in equation (18), are modified thus to include a stochastic excitation.[7]

$$\frac{dM'_x}{dt} = -\frac{M'_x}{T_2} \tag{47A}$$

$$\frac{dM'_y}{dt} = -\frac{M'_y}{T_2} + \sigma s(t)M'_z \tag{47B}$$

$$\frac{dM'_z}{dt} = -\frac{M'_z - M_0}{T_1} - \sigma s(t)M'_y \tag{47C}$$

The excitation is here assumed to a radio frequency field $H_1(t)$ of frequency ω_0 amplitude modulated by a stochastic process $\sigma S(t)$ is a Gaussian time independent random process with a frequency-independent power spectrum $W(f)=1$ and a zero ensemble average, i.e. $S(t)=0$. For white noise σ is the constant power spectra density of the exciting field. The equations are again in a rotating frame but ω_c is no longer a unique frequency as $H_1(t)$ now has equal power at all ω.

These Bloch equations are solved for M'_y and M'_z (note that M'_x is independent of M'_y, M'_z and the excitation). The solution is obtained by expanding the stochastic parts in terms of powers of σ.

$$\begin{aligned} M'_x(t) &= M'_x(t)+\sigma M'_{x1}(t)+\sigma^2 M'_{x2}(t), \quad \text{etc.} \\ M'_z(t) &= M'_z(t)+\sigma M'_{z1}(t)+\sigma^2 M'_{z2}(t), \quad \text{etc.} \end{aligned} \tag{48}$$

The ensemble average of the magnetisation is made time independent, i.e. $\overline{M}_z(t)=0$, $\overline{M}_z$ is then given by

$$\overline{M}_z = \frac{M_0(1+T_1\sigma^2)^{-1}}{2} \tag{49}$$

It is interesting that saturation now does not depend on the product of T_1 and T_2 as in continuous excitation but only on T_1; this occurs as there is now no average magnetisation in the $x'y'$ plane, hence T_2 is ineffective for relaxation of the ensemble average. The cross-correlation function may be evaluated [see equation (56)] in terms of $\overline{M}_z$, thus

$$M_{sr}(\tau) = \overline{M}_z\, e^{-\tau/T_2}\, U(\tau) \tag{50}$$

where $U(\tau)$ is a unit step function. In practice this function is measured as a simple time average making use of the fact that the ensemble average of $S(t)$ is zero. Fourier transform of equation (50) [see equation (2)] yields

$$M_{sr}(\omega) = \frac{\overline{M}_z T_2}{1+i2\pi\omega T_2} \tag{51}$$

which represents a complex Lorentzian line with a width of half-height of $1/\pi T_2$. This line width is independent of power of the excitation, i.e. saturation does not cause line broadening. From equations (49 and 50) it follows that the maximum signal height occurs when $\sigma=\sqrt{(2/T_1)}$.

In practice the calculation is carried out in a slightly different form. Use is made of the fact that cross-correlation of two functions in one domain followed by Fourier transformation into another domain is equivalent to Fourier transforming both functions into the second domain followed by their complex multiplication in the second domain. Both the response and the excitation sequence are Fourier transformed into the frequency domain and their transforms multiplied to obtain

the final spectrum. Phase corrections are carried out by producing new series which are weighted means of the original sine and cosine series as in pulse Fourier spectroscopy. A more simple alternative approach is to calculate the autocorrelation function of the output; this dispenses with the knowledge of the input but only the magnitude spectrum is obtainable.

One major difference in spectra obtained by stochastic excitation compared with either pulse or continuous excitation is that both sensitivity and resolution may be optimised separately. With stochastic excitation, as with pulse excitation the resolution is given by the reciprocal of the acquisition time, but extending the acquisition time with stochastic resonance does not diminish the information available per unit time (i.e. sensitivity), as is the case with pulse work where an exponential decay of the signal is taking place during T. The sensitivity is purely a function of the amplitude of the excitation and the spin lattice relaxation time of the sample. The maximum achievable sensitivity is the same as for a conventional spectrum, being a stationary technique no transient effects, e.g. sweep broadening, will be observed.

IV. THE REQUIREMENTS FOR A PULSE HIGH-RESOLUTION NMR SPECTROMETER

In this section we will discuss the essential requirements for a spectrometer operating in a pulsed mode and producing high-resolution NMR spectra. First, assuming a conventional spectrometer, we shall discuss what additions are required and what changes in the specifications of

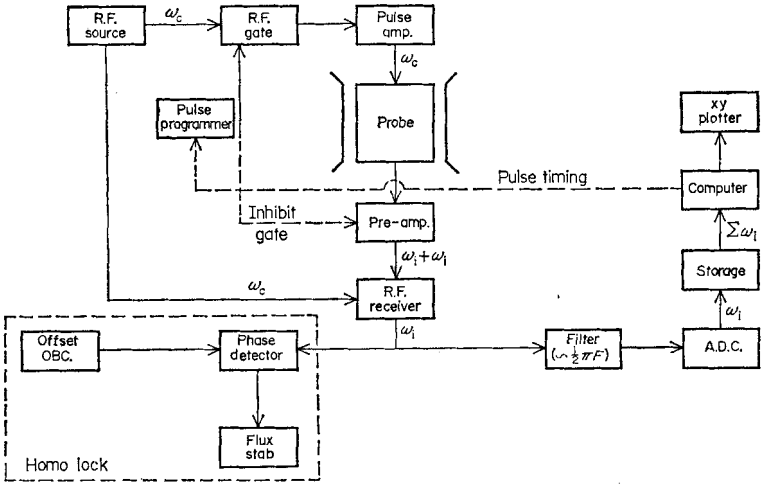


FIG. 2. Block diagram of a typical Fourier transform spectrometer.

existing components are necessary in order for the spectrometer to produce the correct output. The second section will discuss the digitisation of the data into a form acceptable for storage in a computer memory. Finally, we will discuss the computer requirements to transform the incoming data into a frequency domain spectrum and plot it out on to a recorder (usually the recorder of the basic NMR spectrometer). An overall block diagram is given in Fig. 2.

A. The transmitter

The basic radiofrequency of the spectrometer is generated in the normal manner, usually from a crystal controlled oscillator. It is then fed *via* an RF switch or gate which is controlled by the pulse programmer (see later) to a pulse amplifier which amplifies the signal and applies it to the transmitter coil in the probe of the spectrometer. In Section III C 2, it was assumed that the effective field of the pulse was H_1 and not the vector sum of H_1 and $(1/\gamma)(\omega_c - \omega_i)$, in other words, H_1 is a strong field. This can be expressed as:

$$\gamma H_1 \geqslant 2\pi\Delta \tag{52}$$

or $$\delta_{90^\circ} \leqslant \tfrac{1}{4}\Delta$$

However, for most Fourier experiments this requirement may be reduced to:

$$\gamma H_1 = 2\pi\Delta \tag{53}$$

or $$\delta_{90^\circ} = \tfrac{1}{4}\Delta$$

with errors of about 2% in intensity in the final spectrum.[3] As H_1 is progressively decreased not all the resonances are able to experience the same effective RF field. The importance of the term $(1/\gamma)(\omega_c - \omega_i)$ in the vector sum increases. This produces two effects: firstly, the effective field moves away from the x'-axis and secondly has a magnitude greater than H_1. The low level of intensity distortion observed arises from the complementary nature of these two effects.† The use of pulses of power appropriate to equation (43) can lead also to phase distortion which, if not too extensive, may be corrected after transformation. However, if multipulse sequences are used (see later), strong pulses are essential otherwise the required refocusing effects will not be obtained. For a proton Fourier transform spectrometer, working at 23 kgauss (100 MHz), a radio frequency level of about 0·23 gauss (1 kHz in frequency units) is acceptable and this requires only a very modest power amplifier. For typical probes, used in NMR spectrometers, this requires a peak power in the order of tens of watts. If the spectrometer were operating at a

†See reference 84 for a detailed consideration of the consequences of low pulse power.

higher magnetic field, e.g. using a super-conducting magnet, or working on the heavier nuclei, which have a wider chemical shift range, then the power in the pulses would have to be proportionally larger.

B. The probe

The RF pulses obtained as above are now fed into the probe of the spectrometer. The probe is basically of the same design as used in conventional spectrometers. So far only cross coil probes have been used, at least in commercial spectrometers, although the use of single-coil probes has certain advantages, one of these being in the amount of magnetic field which may be generated for a given power applied to the coil (reference 4, section 3.2). The time constant of the transmitter and receiver coil circuits must be sufficiently short so as not to cause distortion of the pulsed signals.

C. The receiver

The free induction decay signals excited by the pulse now enter the pre-amplifier and then the main receiver of the spectrometer as a band of radio frequencies spread about the basic carrier frequency ω_c. The intermediate frequency section of most NMR spectrometers is usually quite adequate to pass this band of signals without distortion. The signals are heterodyned (i.e. the basic RF carrier is subtracted using a phase detector), leaving a band of audio frequencies.

During the presence of the pulse the NMR receiver is subjected to a signal many orders of magnitude larger than that to which it is normally accustomed. The receiver used for Fourier transform work will remain "saturated" for some finite period after each pulse. This period is normally reduced by the choice of suitable RF circuitry to minimise the effect of the pulse or quite often by a gate in the pre-amplifier section, such that the receiver is switched off when the transmitter is switched on. The start of data acquisition must be delayed until the receiver has recovered. It is important that the recovery time should be kept to a minimum. If any residual signal arising directly from the pulse is added into the data ("pulse break-through") this on transformation produces sinc ω function resulting in a broad line centred at zero frequency (ω_c). The differing effects of pulse break-through on absorption and power spectra are dealt with in section VI E. It is possible to discriminate against "break-through" by appropriate adjustment of the reference phase in the receiver whilst observing the transient decay. Such an adjustment is at best tedious and made unnecessary by good receiver design and use of sufficient "dead time". The effect of finite dead time on the phase homogeneity in the transformed frequency spectra as considered earlier (see Section III C 3); these recovery times are about 10 μsec. In

the free induction decay all the frequencies are present at the same time, hence a higher demand is put on the linearity of the receiver when it is used in conventional NMR. Two strong signals will produce combination frequencies, the amplitudes of which are a function of the non-linearity of the receiver. For this reason it is best to avoid samples containing strong lines particularly solvent lines. The signal is then fed through a low pass filter with a band width of approximately the sweep width being studied, and on to the digitisation device. During digitisation frequencies higher than Δ are converted (folded) down into signals in the frequency range being studied, i.e. they contribute to the noise (see later). It is therefore very important to filter out these high-frequency components before the digitisation process. However, over-filtration must be avoided at all costs, as this causes perturbations in the relative intensities of the lines in the spectrum and introduces phase shifts which are strongly dependent on frequency. The perfect filter would pass all frequencies from 0 to Δ Hz with no attenuation or time delay and reject all higher frequencies: no such filter exists. Even if it did, such a filtering process would affect the final spectrum (see Section V C). Typical simple RC filters fall off such that the power is halved as the frequency is doubled, i.e. 6 dB/octave. Multi-pole or active filters can achieve better results, e.g. 12 dB/octave and are advantageous in minimising fold-over problems.

D. The pulse programmer

The pulse programmer is the part of the spectrometer which controls the timing at the RF pulses. It generates the voltages which both switch the transmitter on and off, and start and stop the data acquisition. It must be capable of doing so with great accuracy on the micro-second time scale. The timing signals are obtained from a stable oscillator running in the MHz region. It is often convenient, but not essential, to use the same computer which performs the transformations as the pulse programmer. Use of the computer has the advantage of putting the timing of the experiment under software control making it easy to operate and very flexible, but it does make the system dependent on the presence of a computer all the time. With multi-nuclear spectrometers working on a master crystal (frequency synthesiser) system a suitable harmonic of the master crystal can be used as the clock frequency hence carrying over the stability of such a system into pulse timing. If a homonuclear lock system is used there is an additional requirement. In order to maintain the locking condition, the pulse must be initiated at a constant point on the cycle of the lock reference frequency, to keep a constant phase for the control signal.

E. Field frequency lock

During normal Fourier experiments a large number of free induction decays are averaged before transformation into the final spectrum. In order for the signals to add up coherently, precise control of the field-to-frequency ratio is required.[26,27] Control is required *all* the time, as even during the acquisition of the free induction decay, when the transmitter is switched off, the carrier frequency is required for the heterodyning process in the receiver.

As in conventional NMR both internal and external lock systems may be used. An internal lock may be either of the homo- or hetero-nuclear type. Internal locking gives better stability than external as it operates on a signal originating from the actual sample under investigation and not from a second sample some distance away. In the pulse experiment a further type of locking is possible, which uses the signal from a strong line as a "carrier" for the spectrum. The strong signal is later subtracted but provides a computer with a means of allowing for changes in the field/frequency ratio; the latter technique has been called Fourier difference spectroscopy.[28]

1. *Heteronuclear lock*

The easiest technique for maintaining an internal lock during pulse NMR experiments is by means of a heteronuclear lock. Here the field/frequency ratio is maintained in the normal manner using a signal obtained for a nuclear species present in the sample but not under investigation, i.e. deuterium is especially easy if deuterated solvents are used. The advantage is that the lock can be maintained in a continuous mode independent of the type of pulse experiment being performed. This is especially useful with experiments requiring the observing transmitter to be switched off for long periods of time, e.g. T_1 measurements (see Section X B). The disadvantage of the technique lies in the sophistication of the basic spectrometer electronics required to maintain the locking and observing frequencies coherent over long periods of time. The lack of what may be a large homonuclear signal also eases dynamic range and linearity problems in the spectrometer.

2. *Homonuclear lock*

Instrumentally the simplest solution is to use a homonuclear lock. Now the error signal required to maintain the field/frequency lock is extracted directly from the free induction decay itself. The signal from the locking resonance is extracted from the decay by means of a phase sensitive detector referenced to a suitable audio frequency.[29] The reference frequency must be stable and synchronised with the pulse gate to

maintain a constant dispersive phase output. Unlike continuous wave spectroscopy, the line used for locking purposes does not appear as a "beat" in the spectrum, but as a normal line since it is being excited along with all other lines and does not receive special excitation. This eases the choice of suitable resonances as the region adjacent to the locking line is not obscured. Although relaxation effects cause the error signal to decay between pulses very stable locks can be maintained. Automatic y gradient shimming may be carried out on say 1% TMS for protons or a noise decoupled solvent line for ^{13}C.

3. *Fourier difference spectroscopy*

Ernst has recently developed a technique called "Fourier difference spectroscopy"[28] where the need for any form of conventional field/frequency control is eliminated hence simplifying the basic spectrometer requirements. The sample has to be provided with a reference line considerably stronger than the sample lines. The sample is subjected to a pulse chain just as in normal Fourier spectroscopy. The resulting signals are now detected with a linear (diode) detector instead of the normal phase sensitive detector; use of a linear detector produces envelope of the signal (see Fig. 3C). The difference frequencies between the sample and reference responses are extracted by means of a low pass filter (see Fig. 3D), this difference being digitised and averaged in the normal way. The signal originating from the reference signal is then eliminated by subtraction of a suitable function, typically a Legendre polynomial of the 4th to 6th order (see Fig. 3F). The remaining signal is then Fourier transformed into the frequency domain to produce the required spectrum.

The reference compound used in this technique must have a strong single line, situated outside the spectral range of interest, as Fourier difference spectroscopy cannot distinguish positive and negative difference frequencies. As the reference line can easily be 10 to 100 times the intensity of the sample lines, complications from spinning and ^{13}C sidebands of the reference are to be expected. Suitable compounds have been suggested such as trifluoroacetic acid for ^{1}H, and carbon disulphide for ^{13}C. The compounds are best put in a central capillary to minimise spinning sidebands. The use of a capillary also enables a longer T_2 to be obtained which is useful, as a signal from the reference must be present at the detector throughout the period of accumulation.

Fourier difference spectra have been shown to be insensitive to homogeneous modulation of the local magnetic field but modulation which is inhomogeneous over the sample volume does produce effects, e.g. spinning sidebands appear. This insensitivity could be used to

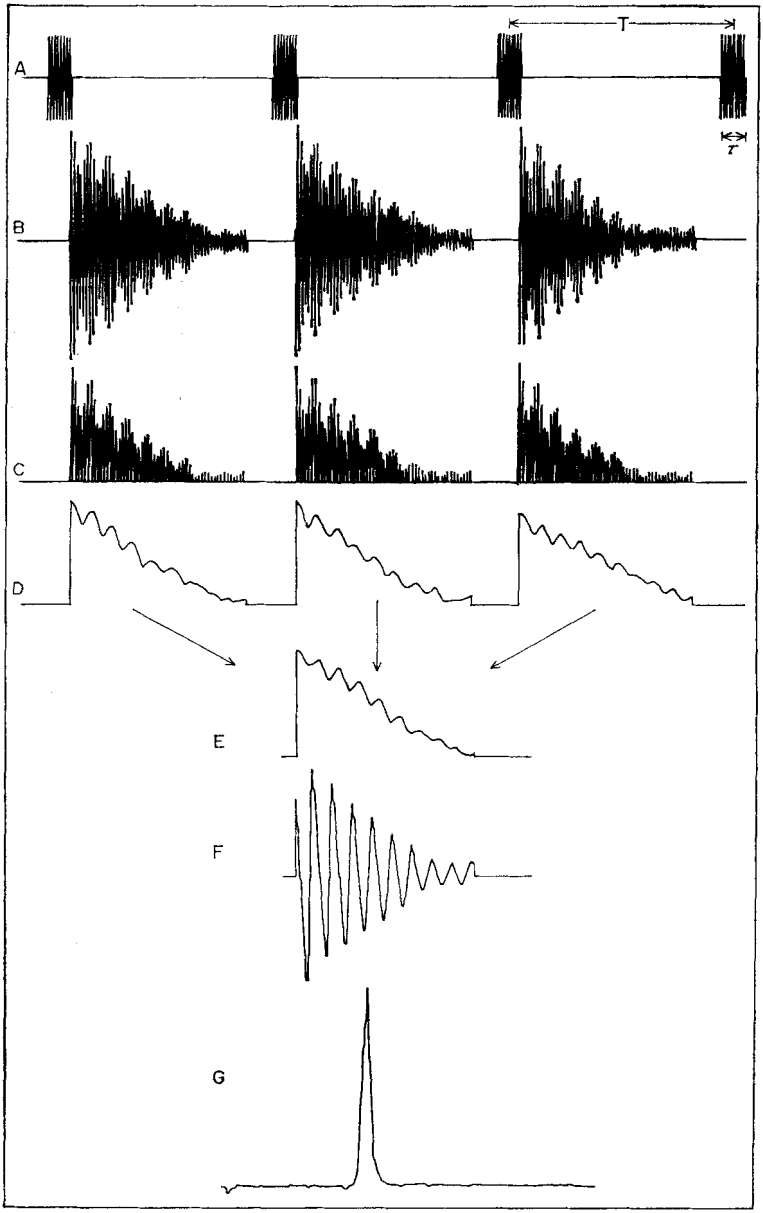


FIG. 3. Schematic representation of the principles of Fourier difference spectroscopy. A. The exciting sequence. B. Response of sample and reference. C. Signal after diode detector. D. Low-frequency component of C. E. Ensemble average of D. F. Signal with reference response eliminated. G. Fourier transform of F. (From Ernst.[28])

simplify magnet power supply design as line frequency ripple is eliminated. Ernst has suggested a novel consequence of this insensitivity for, if the magnetic field were stochastically modulated, proton "noise decoupling" could be achieved with a coherent proton irradiating field without affecting a ^{13}C "difference" spectrum.

The property of this technique, that no field/frequency lock need be set up and its general simplification in basic spectrometer requirements, enables one to envisage a completely automatic NMR spectrometer functioning on these lines.

V. DIGITISATION

All Fourier transform experiments require storage of the complete free induction decay prior to transformation and most involve time averaging of many decays. Since in most cases transformation is *via* a digital computer and the averaging of decays is in a computer or "computer type" store, digitisation is a fundamental step. The conversion from an analogue to a digital signal is performed by a device called an analogue to digital converter or ADC. In this section we will discuss this conversion and the fundamental effects it has on the final spectrum. We wish to represent the free induction decay in digital form as a series of samples taken at constant intervals in time. How frequently and how many of these samples must we take to accurately represent the original signal?

A. Rate of digitisation; fold-over; number of data points

The spectrum we wish to represent consists of a mixture of frequencies from zero Hz (the carrier frequency ω_c) to Δ Hz ($\omega_c - \omega_0$). Figure 4a shows a sine wave, digitised at a rate of twice its frequency (2Δ), a rate at which it is defined. Figure 4b shows the same wave form digitised at a rate of less than 2Δ, say f samples/sec, the data now partially define this wave form but also define a second wave form of lower frequency of $(\Delta - f)$ Hz. This illustrates a basic theorem of sampling theory; that is, to define a frequency Δ Hz it must be sampled at a rate of at least 2Δ samples per second. If digitisation is at a rate less than 2Δ the wave form will be "aliased" or folded back as a frequency of $(\Delta - f)$ Hz. To accurately digitise a free induction decay it is necessary to sample at a rate of at least twice the highest frequency present, that is at twice the spectral width. This is the pulse equivalent of sweep width in continuous wave spectroscopy as the spectrum runs from zero to the spectral width. Sampling at 2Δ samples/sec is the most efficient way of representing the signal, sampling at a slower rate will cause ambiguity arising from fold-

back; sampling faster uses more data points than is necessary. The accuracy of timing of the digitisation is the factor which controls the accuracy of the frequency measured in a Fourier transform spectrum. It must be noted that any noise of frequency higher than Δ Hz, will be folded back and cause unnecessary noise in the spectrum, hence the input should be filtered to remove frequencies higher than Δ Hz before digitisation in order to minimise this problem. As the use of very sharp filters can itself cause problems "over-digitisation" is sometimes used to minimise noise fold-over problems.

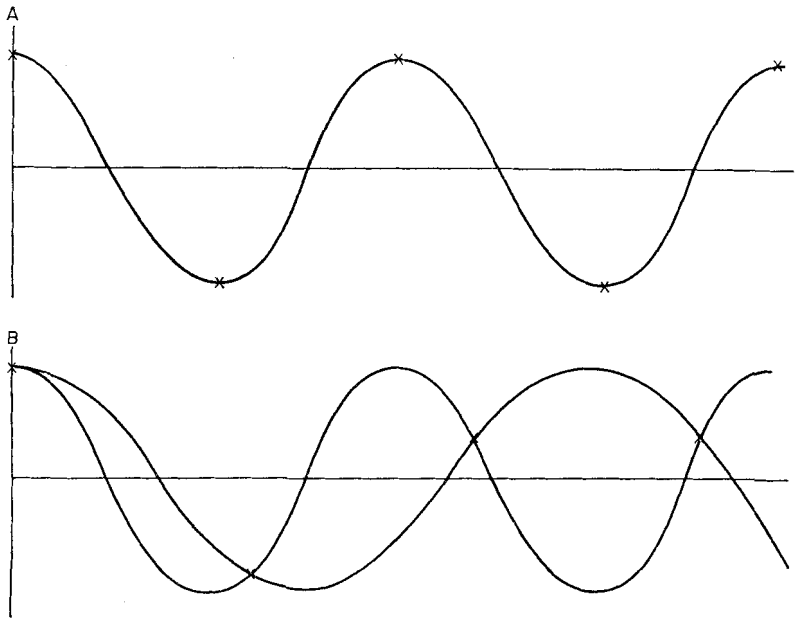


FIG. 4. Effects of rate of digitisation. A. Frequency digitised at 2Δ. B. Frequency digitised at $< 2\Delta$ with consequent alaised frequency.

The digitisation rates needed in practice for Fourier spectroscopy depend on the field used and the nucleus being studied. For ^{1}H at a field of 23 kgauss with a chemical shift range of 10 p.p.m. sampling rates are in the order of 2000 samples/sec. ^{13}C at the same field requires rates in the order of 10 000 samples per second. Nuclei with larger chemical shift ranges and spectrometers operating at higher fields require consequently higher rates of digitisation.

Having evaluated the rate of digitisation necessary to represent the free induction decay we must ask how many points are necessary. To answer this question we must first decide the resolution required in the

final spectrum. As we will see later, if the spectrum is sampled for time T sec, the resulting resolution is $1/T$ Hz. Thus, the number of data points, N_1, needed is given by:

$$N = 2\Delta T \tag{54}$$

In practice N is normally limited by the size of the store available. Δ is the required spectral width and hence T is then determined by the above equation, e.g. if 4000 data points are used then to obtain a spectral width of 1000 Hz an acquisition time of 2 sec is required giving a resolution of 0·5 Hz. During the transformation the N time data points are changed to $N/2$ v-mode and $N/2$ u-mode points. As both these modes contain complementary information[2, 20] (being interconvertible via a Hilbert transform) the resulting frequency domain spectrum has $N/2$ points with a resolution of 0·5 Hz. The larger the number of points the better defined the spectrum produced but the longer the acquisition time required. The longer the acquisition time, since the signal decays exponentially, the lower the signal-to-noise ratio becomes. This is an example of the usual conflicting requirements of sensitivity and resolution. Typical values of core store are in the region of $8k$ points.

B. ADC dynamic range, computer word length

We must now consider the accuracy, in magnitude, with which the samples must be taken. This problem is in two parts, the ADC and computer word lengths, and has been discussed in detail by Ernst.[28] The dynamic range of the ADC must be large enough to allow recovery of a signal buried in the noise whilst accepting the largest signal present without distortion. Ernst has shown that a signal buried in noise may be completely recovered if the quanta of digitisation are smaller, by a factor of about two, than the r.m.s. noise. For most experiments this signal-to-noise ratio is normally less than 100:1 hence ADC with a word length of about 10 bits is adequate. This ratio should not be confused with the final signal-to-noise ratio of the final spectrum for two reasons. Firstly, it is for one pulse only and secondly it is in time domain. The first is obvious since, as more pulses are added, the signal-to-noise ratio can be increased up to the word length of the computer storage. The second is not quite so obvious; the signal-to-noise of the free induction decay is defined by the ratio of the maximum *amplitude* present to the r.m.s. noise. In the time domain spectrum information about any line is contained in every point, therefore, on transformation not only does the signal-to-noise, as defined above, matter but also its distribution along the time axis. For the case of a single narrow Lorentzian line the signal-to-noise in the frequency domain may be up to 100 times that of the time domain.

The word length of the computer limits the final dynamic range of the spectrum. As we have said above, the typical data word length from a single spectrum is about 10 bits, so if four such spectra were added coherently together they would overflow in 12 bit memory, and similarly 1024 for a 20 bit memory. Unlike conventional spectroscopy, overflow cannot be tolerated on any point, since this effects every frequency point in the transformed spectrum. To avoid these problems most computers use a system of weighted averaging, e.g.[4]:

$$\text{New value} = \text{old value} + \frac{\text{new sample} - \text{old value}}{\text{number of samples}} \tag{55}$$

The procedure works until the difference added becomes less than one bit of the computer word when no further gains are made. The computer word length is now limiting the maximum obtainable signal-to-noise. For most NMR purposes word lengths of about 16 bits are suitable. If larger dynamic ranges are required either double precision must be used, or a computer with longer word length utilised. The arithmetic operations of the computer are themselves, owing to round off errors, a source of noise and if large dynamic range experiments are performed these must be allowed for. The "digital errors" are usually minimised by carrying out a second averaging process, after transforming into the frequency domain.

C. Some consequences of digitisation

In the previous section we have assumed that the Fourier transformation is carried out as required mathematically, i.e. as an integration from $+\omega$ to $-\infty$; in practice this is not usually the case! The free induction decays are stored as a series of discrete points (sampled at N/T samples/sec) and as the transformation is carried out in a digital computer the integration is replaced by summing over a finite series of N points.

$$M_n(\omega) = \frac{\sqrt{(2T)}}{N} \sum_{t=0}^{N-1} M(\tau)\, e\, \frac{-2\omega int}{N} \tag{56}$$

where $M_n(\omega)$ is the coefficient of the nth point of the frequency domain transform, and $\sqrt{(2T)}/N$ is a normalising constant. As

$$e^{-ix} = \cos x - i \sin x \tag{57}$$

the transform appears as the complex sum of a series of sine and cosine terms.

The first and most obvious results of the digital approach is that the resulting frequency spectrum is discontinuous about $1/T$. A second

complication arises from the sampling taking place for only T and not ∞ seconds. We have in effect, in the time domain, multiplied the transient by a window or pulse function of unit amplitude running from 0 to T seconds. ($\Pi(t/T)=1$, if $0=t<T$ and 1 if $0>t\geqslant T$). As shown in Section II multiplication in one domain is convolution in the co-domain. Since we have multiplied $M(\tau)$ by the window function, $\Pi(t/T)$ in the time domain, the resulting frequency domain spectrum will be the convolution of the transform of $M(\tau)$ and $\Pi(t/T)$. The transformation of $\Pi(t/T)$ is sinc $\pi T\omega$; see Table I; this function is a maximum at $T=0$ and is zero at $\omega=1/T$, hence the resulting lines broadened to slightly less than $1/T$ and oscillation appear in the wings with frequency $1/T$. If the spectrum is sampled only at $1/T$, as is normal, then the oscillations do not appear since sinc $\pi T\omega$ is zero at $1/T$ (see Section III C 3).

VI. COMPUTATION

A. Weighting functions

Before performing the transformation it is normal to use the computer to carry out certain data processing functions to improve the final spectrum. Initially the computer determines the average value of the data points and subtracts this value from all of them. This in effect removes any DC component present which does not contain any useful information and will transform into a large spike at origin of frequency spectrum (see Table I). Secondly the transient signal is weighted for either sensitivity or resolution and finally, if necessary, an apodising function is applied to minimise the effects of discontinuities at time T.

Ernst has shown that, to obtain maximum signal-to-noise in a conventional spectrum, an analogue filter, whose band pass matches that of the spectral lines, should be added to the circuit.[10] This means the signal in the frequency domains is convoluted with a function identical in shape to that of a single line. In the time domain this becomes multiplication by the Fourier transform of a single line. The Fourier transform of a Lorentzian line is a simple exponential (see Table I). Thus multiplying the free induction decay by an exponential e^{kt}, where k is negative and approximately $-(1/T_2^*)$, optimises the signal-to-noise with respect to line width; likewise resolution can be enhanced at the expense of signal-to-noise if k is positive. Freeman and Hill have recently pointed out that under conditions where refocusing takes place, M_y is non-zero where the next pulse is initiated, a simple exponential is no longer the correct function to apply and a procedure of weighting by the local signal to noise should be adopted.[21]

B. Apodising functions

As shown in the previous section, the resultant resolution in a Fourier experiment is limited to $1/T$ hence on grounds of resolution, T should be as long as possible. However, after a time of, say, $3T_2$, when the value of M_y the detected signal has fallen to about 1/20th of its original value only noise is probably being recorded then. On the grounds of sensitivity alone the next pulse should be initiated as doing so would limit the final resolution and the number of plotted points. Under these conditions data acquisition should be terminated at time T after N_T samples have been stored and then zeros placed in the remaining $(N-N_T)$ data locations to create an apparently longer signal without adding to the signal's noise content. The resolution is still limited by sampling effects to $1/T$, but the final plotted spectrum contains $N/2$ points instead of $N_T/2$, if the remaining points had not been set to zero and transformed also. This interpolation in the *time domain*, however, improves the spectral appearance and *definition*. We now have points in the frequency spectrum more frequent than $1/T$, hence the lobes of the sinc function, introduced by sampling over the finite time, will appear in the spectrum; these lobes may be reduced by applying an apodising function. Such a function multiplies the transient in the region just before the discontinuity at T by a function which goes to zero much slower than the square window usually a triangular function. Since a triangular function transforms a $\text{sinc}^2 x$ the side lobes are attenuated more rapidly. The choice of N is normally limited to multiples of $2K$ (see following section) and the appropriate apodising function applied automatically.

C. The fast Fourier transform

The Fourier transformation itself is usually calculated using a programme based on the Cooley Tuckey algorithm[30] as modified by Bergland.[31] The fast Fourier transform algorithm has been discussed in detail by Cochran *et al.*[32] The technique involves calculation of the coefficients $M_n(\omega)$ using a sequence of progressively larger weighted sums of data and involves sorting of data points. As the algorithm involves considerable pairwise sorting, it works most efficiently when the number of data points is a power of 2. The calculation is performed "in place", the original data being overwritten as locations originally used to store raw data are used to hold intermediate values during iteration and then the final coefficients. The "in place" nature of the calculation has the disadvantage that a copy of the time domain spectrum must first be made if further data handling or data addition is required. The need for these manipulations sometimes only becomes apparent after

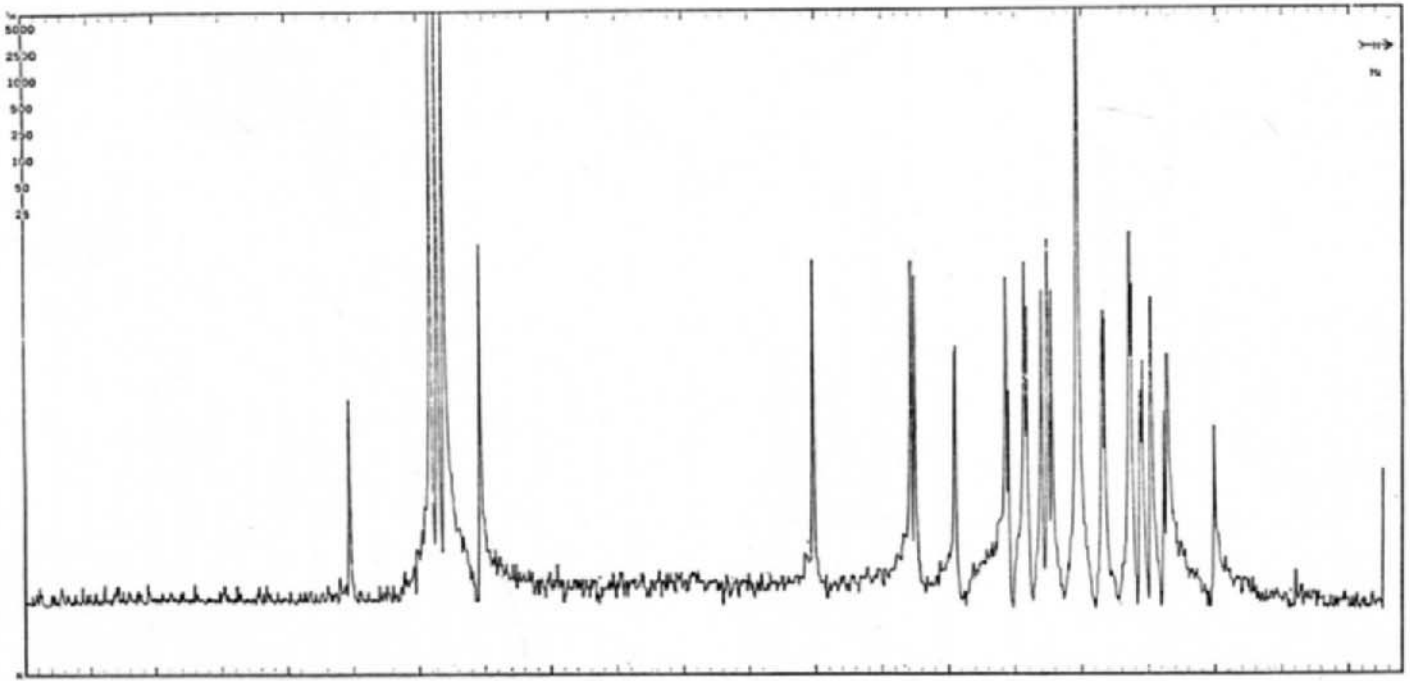
the frequency spectrum has been studied. But the great advantage of "in place" calculations is that N data points may be transformed in only a little over N words of core, hence making the maximum use of the core available. The fast Fourier transform is quicker (hence its name!) than the direct evaluation of $M_n(\omega)$ using simple summing and multiplication. The time saving arises when the number of calculations necessary is considered. The direct method requires N^2 multiplications per N points compared with $2N \log_2 N$ for the fast algorithm. If $N=4k$ points then the time saving is in the order of 175 and rapidly increases as N increases. The time taken for a $4K$ transform is about 10 sec with a typical modern computer.

D. Phase correction routines

Following transformation the spectrum is formed of two series of terms, ideally the cosine series representing the pure absorption mode as already indicated. In reality, however, each series will be a mixture of modes and it is therefore necessary to make two new series which are weighted means of the original series thus in effect changing the phase of the spectrum.

$$A_n(\omega) = KC_n(\omega) + (1-K^2)^{1/2} S_n(\omega) \tag{58}$$

The mixing of modes is the result of many factors in the experiment, mainly errors incurred while having to wait for receiver recovery and the effects of filters used to minimise noise prior to digitisation. The setting of the reference phase to the receiver phase detector will also affect the spectrum produced just as it does in conventional spectroscopy. In general it is impossible and unnecessary to set the RF phase before transformation for pure absorption in a Fourier experiment. The phase correction programmes necessary to compensate for the above effects also easily take care of this adjustment at this stage. The weighting factor is itself a function of frequency, in practice it may be quite satisfactorily approximated to a linear function. K may be calculated by the computer either by means of a calibration sample or by an iterative programme maximising the area above the base line, while simultaneously minimising the area below. A second, more common approach, involves interaction *via* an oscilloscope, with a spectroscopist. The spectrum is displayed and the operator adjusts "phase knobs" (usually two in number each of which changes the rate of change of K as a linear function of frequency, one having maximum effect at zero frequency, the other having minimum effect at zero) until the desired phase corrected spectrum is displayed.



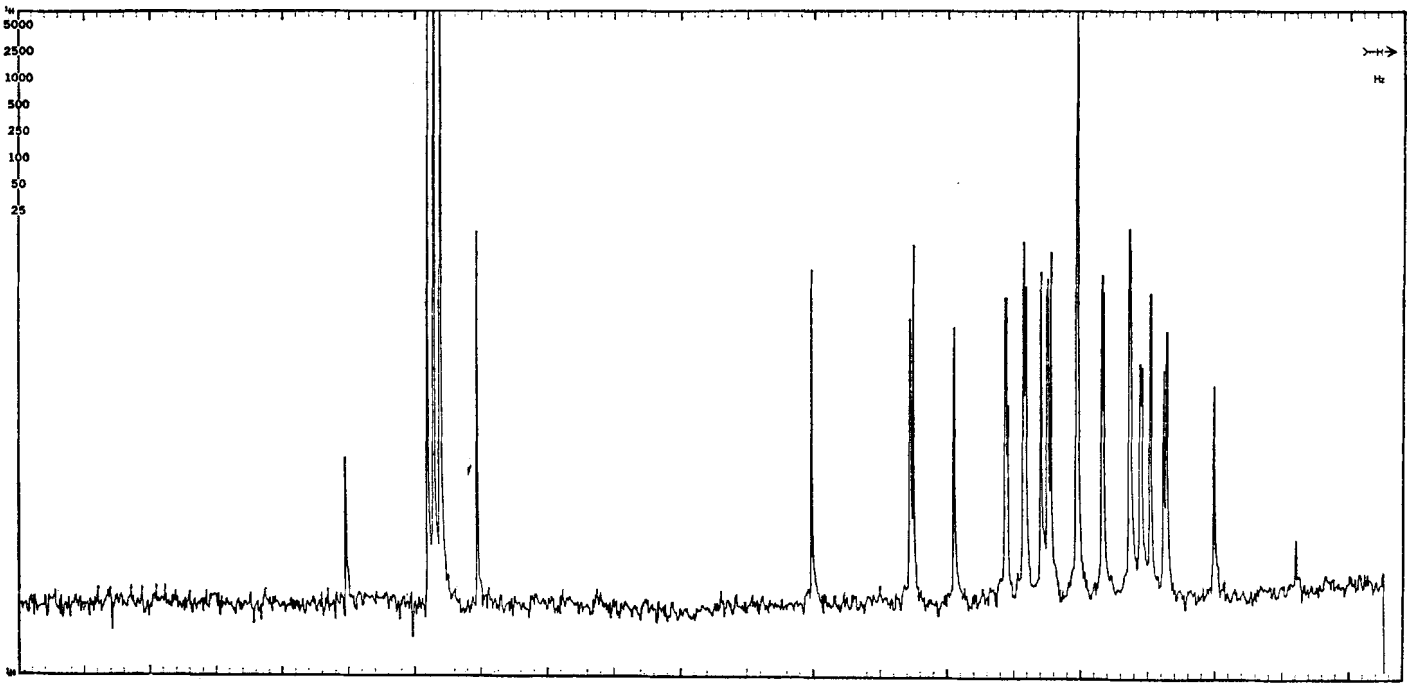


FIG. 5. Comparison of ^{13}C magnitude spectrum $\sqrt{(u^2+v^2)}$ (*top*) and v^2 (*bottom*) modes for cholesterol.

E. The magnitude (absolute value) spectrum

A method of circumventing the phase problem is by the use of the so-called auto or absolute value spectrum.

$$p_n = (u^2+v^2)^{1/2} = (C_n^2+S_n^2)^{1/2} \tag{59}$$

The spectrum so obtained is of the magnitude of the magnetisation in the $x'y'$ plane; all phase information has been lost in the quadratic averaging. This type of spectrum is the type normally presented when Fourier analyses are performed on systems where phase information cannot be obtained owing to the lack of coherent sources, etc. The magnitude spectrum is also produced by analogue devices called spectrum analysers. The use of magnitude spectra has two serious drawbacks as far as NMR is concerned; see Fig. 5. Firstly, the line shape produced has long "tails" extending outwards at the base which are the result of the presence of u-mode components in the spectrum which fall off much slower as a function of frequency offset than the v-mode component. The second, and much more important, limitation is that if lines overlap their signals are not, unlike v-mode, additive, the u-mode components tending to cancel in the region of overlap, see Fig. 5. Thus the frequencies and intensities of lines lying in the "tail" of another line are subject to distortion. This problem is specially acute if a very strong line, e.g. a solvent resonance, is present in the spectrum. Despite their lack of phase content magnitude spectra can show what appears to be phase errors if there is a broad "signal" from pulse break-through present.

VII. PRACTICAL PULSE FOURIER SPECTROSCOPY

A. Choice of pulse width

The selection of these parameters involves a set of factors which are interdependent. Firstly one must decide upon the longest value of T_1 for any resonance to be studied and select the mean RF power appropriately. This situation also appears in CW spectroscopy, where the criterion for setting the RF level to achieve maximum sensitivity will not be satisfied simultaneously for all lines in a spectrum consisting of resonances with differing T_1 values.

Having decided on an appropriate value of T_1 the mean RF power must be set either by changing the pulse width or interval. In general it is preferable to set the pulse interval to be the acquisition time and adjust the pulse width accordingly. This approach uses the minimum pulse width. The acquisition time will be set either as dictated by the spectral width and available data points or by the required resolution (see Section VII C).

A method of determining the optimum pulse width for sensitivity is to

use equation 37 which leads to an angle of $\alpha = \cos^{-1} T/T_1$ where T is fixed as previously.† Equation 37 assumes $T > T_1$ and ignores homogeneity effects and hence will usually lead to too small a value for α. For example if T/T_1 is taken as 0·1 then the angle thus calculated is too small by a factor of 2.[21] Under practical conditions the effects of homogeneity, and noise decoupling, if used are too complex to evaluate. However, as their effects on the optimum value of α are generally smaller in magnitude than those dictated by the various T_1's present in a typical spectrum the above criterion forms a reasonable basis for choice.

The flip angle α is given $\alpha = \gamma H_1 S$. In practice α is most conveniently adjusted by changing the pulse width whilst keeping H_1 constant. Calibration of the pulse angle, for a particular spectrometer, may best be achieved by measuring the 180° pulse, recognised by a minimum free induction decay.

B. Position of RF carrier; fold-over

The positioning of the RF carrier (ω_c) in the pulse experiment is the equivalent of offsetting in conventional spectroscopy and is likewise achieved by changing either ω_c or H_0 depending on the spectrometer design. The position of ω_c determines the zero point of the spectrum, which extends from zero to Δ Hz. In the spectrometer electronics the carrier frequency is subtracted from ω_0 to produce ω_i hence (without the use of multiple phase detectors) frequencies coming from both sides of the carrier are not distinguished. For this reason ω_c is normally chosen so as to be at the extreme edge of the spectrum ($\omega_c >$ all ω_0 or $\omega_c <$ all ω_0). If it is necessary to examine only a portion of the spectrum, e.g. to obtain greater resolution if the number of data channels is the limiting factor, then the carrier must be placed at the zero point required and a filter with a cut off frequency equal to the desired spectral width applied before digitisation. If there are peaks present in the spectrum within the spectral width on the opposite side of the carrier, these will appear in the final spectrum, but usually with different phase. As mentioned in Sections 5 A and C, lines of frequency greater than Δ will be digitally folded back unless these are completely removed by the filter.

C. Spectral width/acquisition time/number of data channels

The choice of acquisition time is governed by the spectral width (Δ) required and the number of data points thus:

$$T = \frac{N}{2\Delta} \tag{60}$$

† Jones and Sternlicht[84] have calculated the penalties in terms of time resulting from non-optimum settings of α, judged by this criterion.

and it in turn limits the resolution obtainable to $1/T$ Hz. If the criterion of the experiment is resolution then, for a given spectral width, T should be set to by several times the longest T_2^*; this will be limited by the available number of channels. If, however, sensitivity is the criterion then a decision must be made as to what resolution is acceptable (or attainable) as this will then define T. Note that the time domain signal decays and hence the longer the acquisition time, the worse the sensitivity of the experiment. Having defined T and Δ, N is fixed. The value of N fixed by these criteria may be less than the total available in the computer. In this case the remaining points are set to zero prior to transformation to enable the frequency domain spectrum to have the maximum number of points. Under these circumstances apodising functions must be applied (see Section VI B). For computational reasons the choice of N is not always completely free, it is usually limited to powers of two, to facilitate the fast Fourier algorithm (see Section VI C). As usual, in practice a compromise between sensitivity and resolution is necessary.

D. Sensitivity/resolution enhancement

The data prior to transformation may be weighted (multiplication in the time domain) so as to enhance either the sensitivity or resolution. The weighting function is usually a simple exponential whose time constant is the resolution required in the final spectrum. A fast decaying exponential decreases the tail of the signal and hence enhances sensitivity and vice versa (see Section VI A).

E. Display and plotting

Following the transformation to a frequency spectrum the data is usually displayed on an oscilloscope. It will typically be a mixture of u and v modes and the phase can be corrected either by pure software or by an interactive approach as outlined in Section VI D. The final plotting of the spectrum depends purely on the type and sophistication of the computer used and may range from a simple stepwise readout to elaborate systems employing digital smoothing, base-line straightening, etc. The computer will normally calibrate the spectra, print out all line intensities and positions and expand any region on request.

F. Integration

Fourier spectra may be integrated after transformation either by analogue or by digital means just as for normal spectra. The resulting integration, if enough data points are used, is in general as accurate as that obtained conventionally under comparable conditions. In a pulse spectrometer all nuclei are excited simultaneously and inter-nuclear

Overhauser effects can take place under favourable circumstances,[33] e.g. with degassed samples, and may thus produce erroneous integratals. Spectra obtained only in magnitude form (see Section VI E) cannot be meaningfully integrated.

G. Common spurious spectral features

Most NMR spectroscopists are familiar with the consequences of instrumental shortcomings on the resultant spectrum when using conventional spectrometers as yet this is probably not the case when spectra are obtained *via* a Fourier transformation. We will now list just a few common examples.

(i) A spike in the output from the spectrometer results after transformation in a line with a sinc ω shape whose width depends on the duration (see Table I) of the spike and whose position depends on the time at which it occurred.

(ii) General RF radiation, normally producing a beat will produce an extra line. If this is incoherent with the spectrometer frequency on the experimental time scale it will average to zero. One common example of this type of effect is computer radiation. The computer usually attendant on a Fourier transform spectrometer will tend to radiate from its arithmetic units frequencies in the MHz region which, unless the spectrometer is very well shielded, will produce lines in the resulting spectrum. Such lines are nearly always "out of phase" and unless they are absolutely phase coherent with the spectrometer's detector reference signal they will tend to average to zero as accumulation continues.

(iii) A spike at "zero offset" is indicative of a DC bias in the free induction decay. See Section VI.

(iv) Any pulse "break through" will, by nature of its sinc x form, result in a "rolling base line" (see Sections IV C and V C).

(v) Extra lines, present when the spectrum contains a strong line, e.g. a protonic solvent in ^{1}H NMR, indicates receiver non-linearity (see Section IV C).

(vi) The presence of one line which is always "out of phase" indicates that line probably has a T_2 much longer than the interval between the phases.

VIII. STOCHASTIC RESONANCE

Ernst[7] and Kaiser[11] have demonstrated that high-resolution NMR spectra, fluorine and proton respectively can be obtained using stochastic excitation. The basic theory of this approach has been dealt with previously in Section III C 3. We will now describe the experimental realisation of the approach.

The basic spectrometer used is a conventional high-resolution instrument. The transmitter frequency is noise modulated and the resulting signals detected in the normal way. The spectrometer output is sampled for a time T sec, the sample digitised and stored. As in pulse spectroscopy the attainable resolution is $1/T$ Hz and usually many samples are coadded before transformation. The spectrometer is field/frequency locked using the response of a line not affected by the noise modulation.

The main difference in approach between Ernst and Kaiser lies in the technique used for generation of the noise and the consequent mathematical technique. Kaiser used pure white noise suitably filtered by analogue means to give the desired band-width. Ernst used a suitably filtered pseudo-random noise sequence obtained from a shift register whose band width is governed by the input frequency to the register. The difference between these two approaches becomes apparent when the addition of a second sequence is considered. The behaviour of the spin system immediately after the start of a sample depends on events immediately beforehand. With pure white noise excitation the same behaviour before the start of sampling can only be guaranteed, hence coherent addition be possible, if the magnetisation is allowed to reach equilibrium. The excitation must be switched off for at least $3T$, between samples and both the excitation and sampling started simultaneously. However, if a pseudo-random sequence, repeating with the same period as the sampling is used, a steady state is produced, samples may be co-added and the excitation need only be transformed once. The excitation and response are Fourier transformed and subjected to complex multiplication to yield a frequency spectrum. Phase corrections, plotting etc. are carried out as outlined in the previous section.

The advantages over pulse excitation lie in two directions. Firstly, stochastic excitation requires less peak power than pulsed excitation. As the frequency range of nuclei to be excited increases, e.g. when dealing with nuclei having a large chemical shift range such as ^{19}F, the power required to produce a 90° pulse greatly increases causing, as this power must be applied in very short periods of time to produce the required bandwidth, instrument problems especially at the probe. With stochastic excitation the power is applied continually hence the peak power is much lower and easier to handle. The second advantage of stochastic resonance lies in its ability to optimise resolution independently of sensitivity. Whereas the achievable sensitivity by stochastic resonance is the same as that by pulse excitation they differ in one experimental aspect, which favours the pulse technique. In pulse work the transmitter and receiver are never working simultaneously, hence leakage is minimised. In stochastic resonance, excitation and detection occur at the

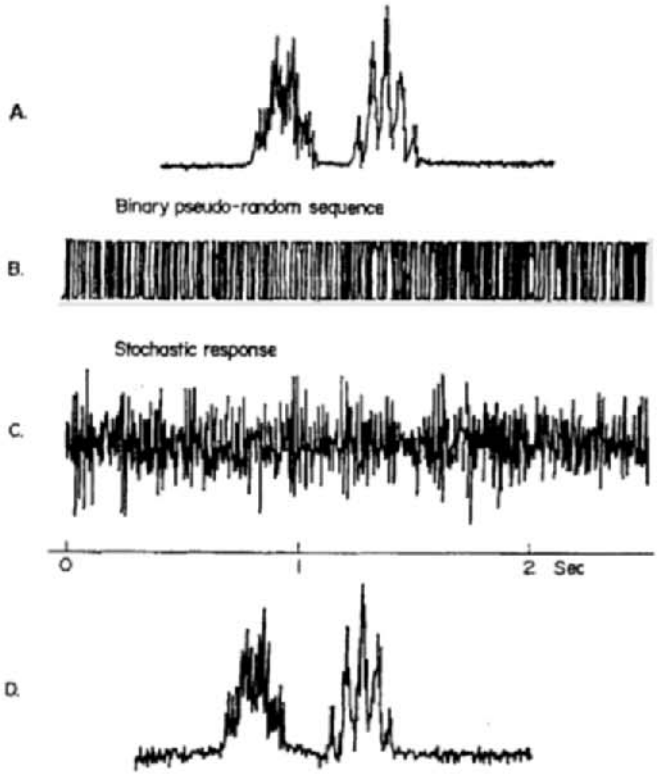


FIG. 6. ^{19}F spectrum of 2,4-difluoro toluene at 56·4 MHz. A. 250 sec conventional scan. B. Exciting noise sequence. C. System response 2·5 sec. D. Spectrum resulting from C. (From Ernst.[7])

same time hence special care must be taken in probe design to avoid exciting energy leaking directly into the receiver. Two other potential limitations with stochastic resonance are the appearance of decoupling effects (deviation from a linear system) if too high a power is used and, unlike pulse spectroscopy, it is not ideally suited to relaxation measurements. T_1 can however be measured by a progressive consideration approach as no line broadening occurs.

IX. COMPARISON OF THE SENSITIVY ACHIEVABLE BY CONTINUOUS WAVE, PULSE AND STOCHASTIC NMR

Ernst has compared the sensitivities achievable by conventional (CW) and pulse Fourier transform spectroscopy[1] and further included sto-

chastic resonance.[7] It was shown that the relative signal-to-noise ratios are given by:

$$\frac{(S/N)_{pulse}}{(S/N)_{cw}} = 0{\cdot}799[\Delta\pi T_2^*]^{1/2} G\left(\frac{T}{T_1}\right) \tag{61}$$

where the line width at half height is $(\pi T_2^*)^{-1}$ and $G(T/T_1)$ is defined from

$$G(x) = \left[\frac{2(1-e^{-x})^2}{x(1-e^{-2x})}\right]^{1/2} \tag{62}$$

To achieve maximum sensitivity in the pulse mode, $G(T/T_1)$ must be unity, a situation which requires that $T \ll T_1$. The dependence of sensitivity on T/T_1 is however slight as long as $T/T_1 \ll 1$. In fact, when $T_1 = T$ the sensitivity has degraded by only a factor of 0·95. This minor degradation relieves the resolution penalty that would be incurred for cases when T_1 is relatively short, e.g. if $T_1 = 1$ sec and $T = T_1$, a resolution of 1 Hz is still obtainable. If T had to be kept less than T_2^* less than T_1, then line broadening would consequently result.

It has been shown that in the stochastic resonance experiment the achievable signal-to-noise ratio is identical to that obtainable by the pulse method.[7] However, in this case the sensitivity may be optimised independently of resolution since the response in the time domain of the spin system is continuous, compared to the decaying response in the pulse situation. The degree to which this advantage may be realised in the practical situation is governed by the number of data storage points available. Thus with a given spectral width Δ, and a given number of channels N, the resolution in each experiment is limited to $N/(2\Delta)$ Hz.

The signal-to-noise ratios for each experiment; CW pulse and stochastic depend on the ratio T_2^*/T_1, hence as T_2 cannot exceed T_1, each has a maximum when $T_1 = T_2$. We must consider what happens when T_2^* decreases either inherently, or by the presence of incoherent decoupling radiation and/or by inhomogeneities in the magnetic field. Deviation from the ideal condition when T_2/T_1 is unity, has differing practical effects on the sensitivity obtainable by each technique.

In the CW case a unilateral decrease in T_2 may be advantageous, permitting an increased sweep rate without consequently degrading the resolution, i.e. intermediate passage conditions are applicable. The sensitivity is thus improved over the slow passage situation,[13] a fact which has been used to great advantage in CW ^{13}C spectroscopy, as compared with proton spectroscopy. ^{13}C spectra as normally run, rarely show evidence of ringing (line distortion) although being swept at a relatively fast rate. The explanation lies in short T_1 (hence T_2) values;

such values are now being reported for other than small molecules (see Section X B). Thus CW operators have become accustomed to higher sensitivities than those appropriate to the then accepted norm that both ^{13}C relaxation times are very long. These factors must be borne in mind when comparing the gain in sensitivity achievable by the use of pulse techniques. If typical values for ^{13}C are taken as $\Delta = 5000$ Hz, $T_2^* = 1$ sec, then according to equation (51) the pulse technique is better by a factor of 70. In practice factors between 10 and 20 are achieved indicating the "super efficiency" of CW ^{13}C NMR as now practiced.

In the pulse method a shortened T_2^* also results in a lower sensitivity. In reality, however, this can hardly, if at all, be compensated for as it can in CW work. The lowering in sensitivity now arises because the magnetisation once dephased in the $x'y'$ plane is lost to the spectrometer's detector system. This situation is illustrated in Fig. 7. At the

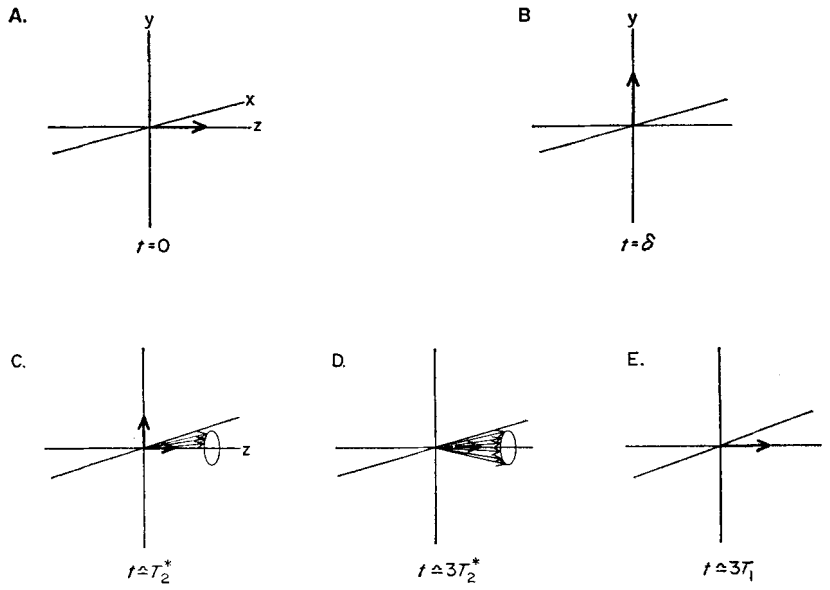


FIG. 7. The behaviour of the magnetisation vector (in the rotating frame) as a function of time after the application of a pulse.

start of a pulse experiment the magnetisation is along the x'-axis, Fig. 7a. The pulse (assumed 90° for simplicity) rotates the magnetisation into the y'-axis, Fig. 7b. While along the y'-axis it generates a detectable signal. After the pulse the magnetisation decays according to T_1, from the $x'y'$ plane back to the z'-axis. At the same time the magnetisation

remaining in the $x'y'$ plane relaxes (decays) from its original position along the y'-axis towards a random (dephased) orientation in the $x'y'$ plane, see Fig. 7c. As the spectrometer detects only the mean signal along the y'-axis it is the second process T_2^* which governs the decay of the observed free induction signal. Thus after, say, $3T_2^*$ only 5% of the original magnetisation is detectable; however, if $T_1 > T_2^*$ a much larger proportion has not yet returned to the z'-axis. If a second pulse is now initiated the signal induced in the spectrometer will be less than from the original pulse by a factor depending on the difference between T_1 and T_2^*. The magnetisation left in the $x'y'$ plane is random and hence it cannot contribute to the detected signal from the second pulse. Maximum signal from the second pulse can thus only be obtained if M_z' is allowed to reach equilibrium, i.e. a delay of about 3 to 5 T_1 must be used between the pulses. As the detectable signal has ceased at about 3 to 5 T_2^* this is inefficient. These limitations also apply in principal to CW spectroscopy but only if a line was to be scanned for a second time within 3 to 5 T_1, a much less likely situation than occurs in pulse work.

The above situation can be improved on if the factors contributing to T_2^* are considered. T_2^* is the total relaxation time of magnetisation in the $x'y'$ plane. It is made up of many terms: T_2 the "real" spin-spin relaxation time (which itself may have many components), T_2' which represents the effects of magnetic field inhomogeneity, and T_2^s representing random effects present in the spectrometer and also, if noise decoupling is used, the random effects transferred from the irradiating nucleus by scalar coupling thus:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'} + \frac{1}{T_2^s} \tag{63}$$

If $T_2 = T_1$ and the effects of T_2' and T_2^s are neglected, as was assumed by Ernst and Anderson, then the timing of the second pulse presents no problems.[1] Hahn showed that the dephasing effects of T_2' could be refocused by a suitable chain of pulses.[22] If the effects of T_2' are refocused at the time of the second pulse, then there is some M_y' magnetisation which can participate in the signal detected after a second pulse. These ideas are the basis of the multipulse approach to improving the sensitivity of pulsed NMR. Waldstein and Wallace[23] and Freeman and Hill[21] have recently pointed out that the refocusing inherent in a $90° - \tau - 90°$ sequence enables some of the losses owing to T_2' effects to be regained, without any further experimental complications.[21] As the dephasing effects of T_2 and T_2^s are not refocusable, if they dominate T_2^* the detec-

ted signal is irretrievably lost on a time scale of T_2^*. If this is shorter than T_1 the sensitivity of the pulse approach inevitably suffers.

A. Multipulse techniques

Multipulse techniques have recently been designed to regain the magnetisation components dephased as a result of field inhomogeneity.

Spin echo Fourier transform (SEFT) NMR[34] uses the Carr-Purcell sequence.[35]

$$90° - \tau - (180° - 2\tau - 180° -)_m - T_d - 90°$$

which produces a series of echoes at times $2n\tau$, the amplitude of which, in the absence of spin diffusion and T_2^s effects, decay as T_2 rather than T_2^*. These echoes, which may be considered as back-to-back free induction decays are averaged and transformed to produce a spectrum in the frequency domain. The time τ is fixed by considerations of resolution and available data store ($\tau = T$). Two other variables are the length of each sequence (determined by T_2), and the delay before the next pulse sequence is initiated (determined by T_1). Optimisation of the latter parameters has been considered for the case when $T_1 = T_2$.[36, 37] Since the echo reaches a maximum half-way through the acquisition time, problems of receiver recovery time are minimised. The SEFT technique gains in sensitivity when good echoes are formed, i.e. T_2 is long and T_2' dominates T_2^*. It is very sensitive to T_2^s [38] effects and is probably of little use under high-resolution conditions when T becomes long.

In driven equilibrium Fourier transform (DEFT)[40] a

$$90° - \tau - 180° - \tau - 90° - T_d - 90° \ldots$$

sequence is used. As before, an initial echo is established at time 2τ but now its magnetisation is restored to the z' direction to enhance the value of M_z' for the next pulse sequence by the application of a further 90° pulse. The two decays per cycle are added and transformed as usual. τ is again defined by considerations of resolution and size of data storage. The optimum delay, before the next sequence is initiated is 4τ if $T_1 = T_2$[35] and increases as T_2 decreases with respect to T_1.[37] This allows the rest of the magnetisation (i.e. that not focused by inhomogeneity) to return to equilibrium along the z' direction.

Waugh[36] has shown that the relative optimum efficiencies of conventional pulsed, SEFT and DEFT are $T/(2T_1)$ to 0·102 to 0·148 respectively. DEFT is the more efficient of the multipulse experiments and its gain over the conventional experiment is greatest when T_1 is long. The calculated advantage for ^{13}C was a factor of 20 with T as 0·4 sec (5000

Hz width represented by $4K$ data points) and T_1 equal to 30 sec. If the more typical value of $T_1 = 3$ sec is used (see Section X B) the apparent advantage is reduced to a factor of 2.

Included in the above analysis is the assumption that $T_1 = T_2$ and that T_2^* is dominated by T_2', the contribution from field inhomogeneities. If $T_2 < T_1$ and if a value of $T_1 = 3$ sec is again adopted, the fractional contribution to T_2^* from T_2' is reduced. Since this is the only contribution that is refocused and, further, if one allows that the intrinsic T_2 may be a good deal less than T_1 and also T_2^* reduced effectively by the normal use of proton noise decoupling T_2^s,[41,42] then the theoretical advantages of refocusing T_2' are minimal.

There are two limitations on the use of multipulse techniques. Firstly, contributions arise in the presence of homonuclear coupling (J modulation,[43,44] see Section X F) which are fortunately absent in ^{13}C spectra but not, of course, in proton spectra. Secondly, successful refocusing requires high-power pulses with very accurate timing of both their intervals and also their widths, the latter being necessary to ensure an exact 180° pulse for all nuclei in the spectral range. The required accuracy of the 180° pulse may be reduced if a Meiboom-Gill modification is introduced.[45]

The instrumental obstacles outlined above may be worth overcoming in the following situations: when T_2^* is in fact dominated by T_2', when nuclei with a large range of T_1 value are present in the same spectrum, when the insensitivity[37] of DEFT intensities to T_1 is advantageous, and finally when the nucleus in question really has a long T_1,† may be ^{15}N?.[46]

X. APPLICATIONS

A. Sensitivity enhancement

1. ^1H

The sensitivity improvement over conventional methods may be taken as a factor of 10 resulting in an improvement of 100 in time scale for a given sensitivity. The preparative chemist may be expected to take full advantage of the technique when limited either by the amount of sample or its solubility; also in the situation when one is looking for one proton in a high molecular weight molecule. In the industrial situation the technique may often be used to improve throughput of samples, and the necessary presence of a computer possibly used to automate the whole process from sample insertion to spectral assignment.

Utilisation of the increased sensitivity means that more importance

† Similar conclusions have recently been reached by Jones.[86]

will have to be placed on the removal of impurities, e.g. residual acetone from tube cleaning. Also the presence of any very strong lines, e.g. from protic solvents should be avoided since their presence creates problems of dynamic range.

As an example of sensitivity we cite cortisone acetate a satisfactory spectrum of which was obtained at 220 MHz from 25 μg dissolved in 8 μl of $CDCl_3$. 9000 transients were accumulated in 1 hour, the spectrum is shown in Fig. 8a.

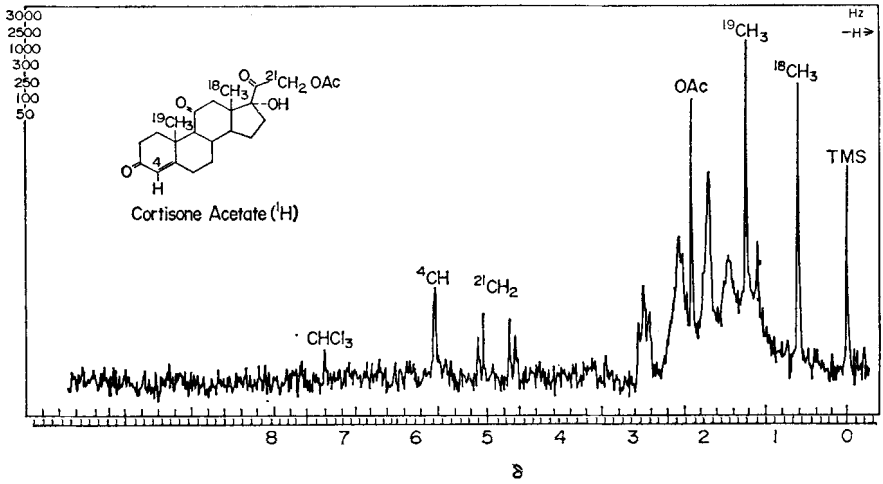


FIG. 8a. Proton Fourier transform spectrum of cortisone acetate 25 μg/8·5 μl $CDCl_3$ at 220 MHz; 9000, 0·4 sec decays. (From Varian Associates.)

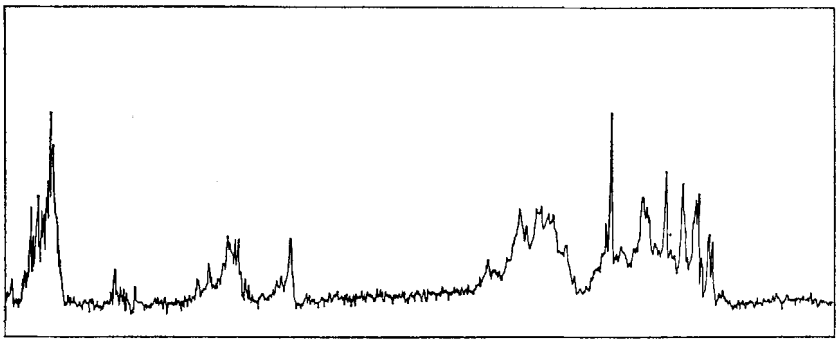


FIG. 8b. ^{13}C Fourier transform spectrum of ribonuclease A, 0·012 M in D_2O; 100 000, 0·4 sec decays. (From Varian Associates.)

2. *^{13}C*

This nucleus has for a long time defied routine observation by the combination of both its low inherent sensitivity and low natural abundance. Although CW techniques had mounted a strong attack using larger samples and proton noise decoupling it remained for Fourier transform spectroscopy to provide a factor of about 10 improvement in sensitivity. This latter fact has really opened up the field and all the studies involving ^{13}C mentioned under subsequent headings are dependent on it.

The realisation that ^{13}C longitudinal relaxation times [see Section X B 3] in most molecules of interest are not too long has been particularly fortuitous. A full discussion of factors influencing the sensitivity appears in Section IX.

One might predict an increase in use of ^{13}C labelling procedures by which, unlike with the radioactive ^{14}C nucleus, one can tell to which part of a molecule the label has gone without complicated chemical degradations.

Increased sensitivity will speed up variable temperature studies such as those of Roberts *et al.*[47] on 1,1-difluorocyclohexane.

A comprehensive review of the applications of ^{13}C NMR has appeared recently.[48]

As one example of the order of sensitivity that has been achieved we cite the case of the enzyme ribonuclease A, $C_{587}H_{909}N_{171}O_{197}S_{12}$ (0·012 M, pH 7) a molecule containing 587 carbon atoms distributed among 124 amino acid residues. A spectrum at 25·1 MHz, the result of 100 000 scans of duration 0·4 sec in a total time of 11 hours, is shown in Fig. 8. The equivalent CW time would be 46 days!

3. *Other nuclei*

The first natural abundance Fourier transform spectra of ^{15}N in $H^{15}NO_3$ have been obtained recently.[49] The nucleus is worse than ^{13}C in that it has a lower intrinsic sensitivity, γ is negative, lower natural abundance and probably longer relaxation times since it is much more commonly found with no attached protons. Application to enriched compounds is quite practical,[50] although the fact that γ is negative means that the sense of the Overhauser enhancement is negative and the peak intensities will hence initially decrease, and go through zero before increasing in the negative sense. A general review of nitrogen NMR has appeared recently.[46]

Results on ^{31}P in ATP have been reported[51] as have measurements involving ^{29}Si,[52] ^{119}Sn,[53, 85] ^{207}Pb[85] and ^{57}Fe[85]. Clearly the extension to many other nuclei may be expected.

B. Measurement of longitudinal relaxation time, T_1

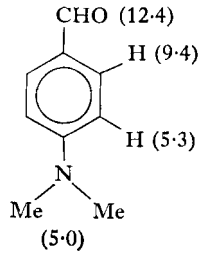
The ability to acquire data for a complete spectrum in a time short compared to T_1 enables T_1 measurements to be made on individual spectral lines in complex spin systems. The first report of such a technique was by Vold *et al.*[54] who measured proton T_1 values simultaneously for acetic acid and water (1:1 mixture in presence of $1{\cdot}5 \times 10^{-3}$ M $FeCl_3$). The paper demonstrated a technique which only has begun to be exploited fully for ^{13}C resonances.

1. $180-\tau-90°$ *sequence*†

A 180° non-selective pulse places the magnetisation of all the spins along the $-z'$ direction. The magnetisations are left to decay according to their individual T_1's for τ sec after which time a non-selective 90° pulse is applied initiating free induction decay along the y'-axis which is recorded. The Fourier transform of this transient produces a spectrum in the frequency domain whose individual line intensities reflect the magnetisations present after the relaxation for τ sec. The intensities, $S(\tau)$, start out negative at low τ values (magnetisation still inverted) and as τ increases pass through zero and approach the equilibrium value (S_∞) according to:

$$S(\tau) = S_\infty(1-2\,e^{-\tau/T_1}) \tag{64}$$

This pulse sequence has, of course, been used for a long time in T_1 measurements but to deal only with relatively simple spin systems whose free induction decays are readily analysable in the time domain. Freeman and Hill[29] provided a *partial* solution in the time domain for the four distinct proton resonances in *para*-dimethylaminobenzaldehyde (**1**);



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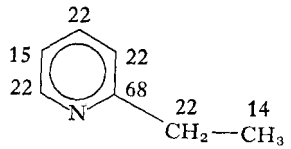
the figures in parentheses are the proton T_1 values.

The method involved four sets of experiments whereby the frequency component for a particular resonance was extracted from the decay signal by narrow band filtering using a suitably referenced phase sensitive detector.

† For analysis of the errors in T_1 measured by this technique resulting from non-ideal pulses see reference 87.

For complete T_1 analysis in complex spin systems, Fourier transformation into the frequency domain is essential. Indeed, it is now apparent that, in a given molecule, there may be a wide range of T_1 values for ^{13}C. In larger molecules some T_1's may be less than 1 sec, see Section X B 3. The fast relaxation of such nuclei would be difficult to observe in the time domain against a much more slowly decaying signal from a nucleus with a longer T_1. This fact, combined with a tendency to first study small molecules, perhaps has conspired to give the misleading impression that T_1 values of ^{13}C resonances are universally "long".

The ability to measure T_1's for ^{13}C does, of course, presuppose suitable sensitivity enhancement and thus a repetitive experiment. Thus a series of $180° - \tau - 90°$ sequences for each value of τ may be required to improve sensitivity. Freeman and Hill[55] used four observations for each τ value in their study of 2-ethylpyridine (**2**). The figures are the



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^{13}C T_1 values found. Between each sequence a time (150 sec), long compared to the longest T_1, was allowed such that the magnetisation was at thermal equilibrium before each sequence. The spectra are shown in Fig. 9. Recently Allerhand and co-workers have embarked on an

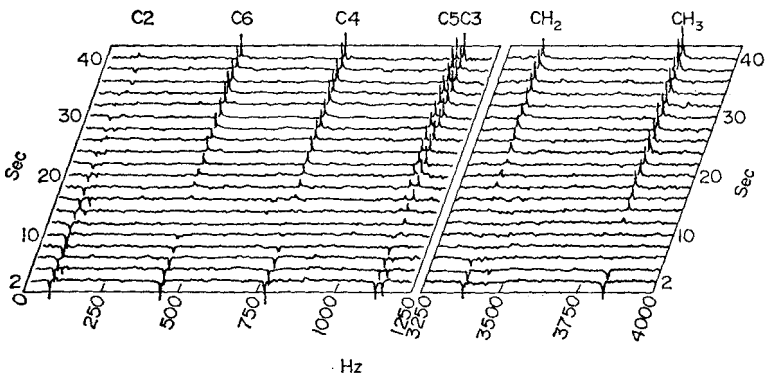


FIG. 9. A montage of carbon −13 spectra illustrating the recovery of the individual lines of 2-ethylpyridine after population inversion by a non-selective 180° pulse. The time axis represents the delay (τ, seconds) between the 180° pulse and the 90° pulse used to excite the free induction signal. Each trace is the Fourier transform of four time-averaged free induction signals. (From Freeman and Hill.[55])

extensive programme to study T_1 values in larger molecules, particularly those of biological importance. The method is as outlined above, a process they aptly name as "Partially Relaxed Fourier Transform Nuclear Magnetic Resonance", (PRFT).

A useful modification of the experiment has been introduced[42] which avoids the passing of the signal through zero intensity with its consequent S/N problems by the use of a $[\ldots T \ldots 180° \ldots \tau \ldots 90°(S_\tau) \ldots T \ldots 90°(S_\infty)]$ sequence, where T is long compared to the longest T_1. The free induction decay S_τ is subtracted from that corresponding to equilibrium, S_∞ so that $S_\infty - S_\tau$ is stored and later transformed. This method also improves the accuracy of $(S_\infty - S_\tau)$ since these are recorded within a time short compared to possible longer term drift in spectrometer operating conditions and is illustrated in Fig. 10.

2. "*Progressive saturation*"

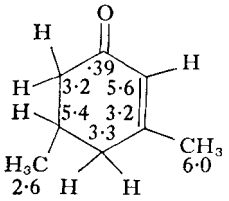
An alternative to the traditional $180° - \tau - 90°$ sequence has been introduced by Freeman and Hill.[42] The response of a spin system to a succession of equally spaced pulses is a dynamic steady state where the effects of the pulses and of relaxation are balanced. The deviation of the observed line intensity from the equilibrium value is an exponential function of the pulse interval, with a time constant of T_1. The intensities are not affected by T_2 as long as there are firstly, no transverse components left immediately before each pulse and secondly no echoes. The latter decay rapidly anyway in ^{13}C NMR when proton noise decoupling is used. Immediately after the pulse all magnetisation must be transverse (90° pulse for all nuclei). The above conditions are easily met in a standard Fourier transform spectrometer.

In practice, then, the spin is subjected to a succession of (90°) pulses and the dependence of the line intensities on the pulse repetition rate gives T_1. Waugh[36] calculates that the use of 90° pulses rather than those of flip angle optimised for sensitivity leads to a reduction of only 18·6% in sensitivity.

The experiment has certain advantages over the $180° - \tau - 90°$ sequence in that one does not have to await thermal equilibrium between pulses. Thus an experiment may be started with a fast repetition rate and the knowledge of T_1's, built up as the experiment proceeds, used to set an appropriate lower limit to the rate.

Although "progressive saturation" allows a much higher data rate than the inversion recovery method, with consequent increase in sensitivity, the latter method suffers in only equalising the spin populations rather than inverting them. The extra convenience of the new method pays off particularly in qualitative applications where observation at

only two pulse rates may be sufficient, for instance, to assign a spectrum. The data from the two methods were compared for 3,5-dimethyl cyclohex-2-ene-1-one (**3**) and found to be identical within experimental error; again the figures are the T_1 values found for each carbon.†



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3. *Results for ^{13}C in larger molecules*

Allerhand and co-workers have made T_1 measurements for ^{13}C in natural abundance in the protein ribonuclease[56] (active and denatured); liquid 1-decanol;[57] cholesteryl chloride, sucrose and adenosine 5′-monophosphate (AMP);[39] stachyose, raffinose and sucrose;[58] aqueous solutions of cobinamide cyanide (0·067 M), cyanocobalamin (vitamin B_{12}) (0·024 M), dicyanocobalamin (0·14 M) and coenzyme B_{12} (0·038 M).[59]

Three principles have been put forward in consideration of ^{13}C longitudinal relaxation times for large and asymmetric molecules.[58]

(a) Relaxation of protonated carbons is overwhelmingly dominated by dipolar interactions with the attached protons, with T_1 given by:[60]

$$\frac{1}{T_1} = N\hbar^2\gamma_C^2\gamma_H^2 T_{CH}^{-6}\tau_{eff} \tag{65}$$

where γ_c and γ_H are the magnetogyric ratios for ^{13}C and ^1H, N is the number of directly attached protons, r_{CH} is the CH distance, and τ_{eff} the effective correlation time for rotational reorientation. The equation is valid under conditions of complete proton decoupling only when $1/\tau_{eff}$ is much larger than the ^1H resonance frequency. In the case of small or very symmetric molecules the equation may not apply as there may be significant contribution to $1/T_1$ from spin-rotation interaction. Longer range dipolar interactions were discounted on the grounds of the inverse sixth power dependence on r_{CH}.

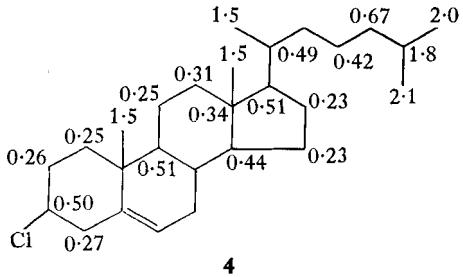
(b) A non-protonated carbon, even if it has a comparable value for τ, will have a relaxation time much longer than a protonated carbon.

(c) Different carbons in the same molecule do not necessarily have the same τ_{eff} since differences may arise from anisotropic motion of the molecule as a whole[61] and/or from the effect of internal reorientation.

† Measurement of T_1's by this technique has been successfully automated. The computer used to do the transform being programmed to optimise the pulse delays.[88]

Utilisation of these principles has added a new tool for spectral assignment in complex molecules to be used in conjunction with the previous methods of empirical shift comparisons, splitting patterns from off centre double resonance studies and internuclear Overhauser enhancements. The individual values of T_1 shed important new light on the nature of the molecular motion.

Consider cholesteryl chloride (**4**), 1 M in CCl_4, where the numbers refer to ^{13}C T_1 values.[39,58] Protonated carbons on the ring backbone



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have the same value for $1/NT_1$, and hence the same value of τ_{eff}. This was taken as indicating that the overall reorientation of the molecule was isotropic with a correlation time of 9×10^{-11} sec so that T_1 values can be taken to distinguish CH from CH_2 situations. The fact that T_1 increases as one goes down the side chain indicates a progressive increase in the rate of internal reorientations leading to reduced values for τ_{eff} and a consequent loss in efficiency of relaxation (increased T_1). A more rigorous development of these ideas has been given.[39]

Increasing motion in an alkyl chain as one moves away from a "fixing" group was noted in liquid 1-decanol with T_1 increasing gradually on moving away from the OH group, implying shorter correlation times and more "segmental" motion. The T_1 values go from 0·65 to 3·1 sec as the correlation time decreases from 36 to 5×10^{-12} sec. It is interesting to note that the ^{13}C chemical shifts do not change in anything like a regular manner.

The PRFT method was used to assign the ^{13}C resonance in stachyose,[58] an oligosaccharide consisting of four sugar moieties—galactopyranose-galactopyranose-glucopyranose-fructopyranose. By conventional techniques it was not possible to distinguish the galactose entities. Two sets of PRFT spectra were all that were required to show two sets of galactose lines distinguished by their relaxation times. The longer times were associated with the freer moving, less efficiently relaxed, terminal galactose.

In sucrose, a two-ring system consisting of glucopyranose-fructofuranose, it was shown that the molecule behaved as a rigid entity reorienting isotropically with correlation times of 7×10^{-11} and 3×10^{-10} sec for 0·5 M and 2 M aqueous solutions respectively.

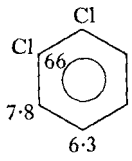
In adenosine 5′-monophosphate, another two-ring system, relaxation studies indicated that the motion of the adenine ring was more restricted than that of the sugar moiety.

The PRFT method has also been applied to the much larger protein molecule of ribonuclease A in both its native and denatured forms,[56] measurements being taken with solutions of concentration as low as 0·017 M. The normal ^{13}C spectrum of denatured protein displays lines uniformly and relatively narrow compared to the native protein where they are generally broader with quite large variations within the spectrum. These indications (T_2) are borne out in the T_1 measurements. In both cases the carbons of the lysine entities have relatively long T_1 values of ~ 300 msec indicative of motion on a time scale of 7×10^{-11} sec more appropriate to a small molecule. However, the backbone situation is very different, giving much shorter T_1 values of ~ 40 msec for the native and ~ 100 msec for the denatured protein. The correlation times are 3×10^{-8} sec and 4×10^{-10} sec respectively, confirming the impression from the line widths that there is much freer segmental motion in the backbone of the denatured protein. It was concluded that the PRFT method provides a powerful technique for studying the reorientation of bipolymers, and proteins in particular, in solution. It augments the previous methods of electron or nuclear spin labels but, unlike them, does not require modification of the biopolymers.

The PRFT method has been applied to great effect in the study of vitamin B_{12} and other corrinoids.[59]

4. *Results for ^{13}C in smaller molecules*

To the data for 2-ethylpyridine (**2**) and 3,5-dimethyl cyclohex-2-ene-1-one (**3**) we shall add *ortho* dichlorobenzene (**5**).[62] We note that



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the relaxation times are longer than for molecules considered in the previous section. In particular the values for the non-protonated carbons,

68 sec in (**2**), 39 and 32 sec in (**3**), and 66 sec in (**5**) are very long. As expected, protonated carbons have shorter T_1's. As in the larger molecules there is an increase in T_1 in going along the ethyl side chain in (**2**).

T_1 values for $^{13}CH_3I$ (13·4), $^{13}CH_3COOCD_3$ (19·2) and $^{13}CS_2$ (48), have been measured in the time domain by standard pulse techniques[41] and their values are added for information (see Table II).

5. *Practical significance of short* T_1

The overall impression is that in the major application of Fourier transform ^{13}C NMR to larger asymmetric molecules the relaxation times are much shorter than previously anticipated. It means also that T_2 is short and thus the contribution to T_2 from field inhomogeneity is not dominant and the need for refocusing methods such as DEFT,[40] SEFT,[34] and other schemes[35] appears to be unnecessary,[39] see Section IX. The non-feasibility of maintaining the echo phase coherence essential for signal averaging under high-resolution conditions (2 Hz line width or less, $T = 500$ msec or more) has been pointed out.[38,39]

C. Measurement of transverse relaxation time, T_2

Recently, Freeman and Hill have considered the above problem.[62] In principle, a technique analogous to the $180° - \tau - 90°$ technique applied for T_1 measurements may be used which involves the Fourier transformation of the free induction decay at some point along a spin echo train. The method is complicated in practice by the presence of homonuclear coupling which produces modulation of the echoes.[43,44] This phenomenon, although useful in some situations (see Section X F), makes extraction of T_2 values difficult and can only be avoided in the present case by using high repetition rates such that $2\pi\delta\tau \ll 1$ where 2τ is the interval between 180° pulses and δ is the largest chemical shift difference. The experiment described below may be considered as the limit of the above situation as $\tau \rightarrow 0$ since the initial 90° pulse along the x'-axis, which puts the magnetisation along the y'-axis, is followed by a continuous RF field, H_1, along the y'-axis. This is applied for a relatively long time, t seconds, during which the transverse magnetisation decays at a rate determined by the spin lattice relaxation time in the rotating frame, $T_{1\rho}$ which is equal to T_2 for many liquids.[64 to 66] The relaxation is longitudinal with respect to the effective field H_1 along the y'-axis. Interruption of the RF field leaves a normal free induction decay, Fourier transformation of which, yields a high-resolution spectrum where each line has decayed to a fraction $\exp(-t/T_{1\rho})$ of its initial intensity.

The application of the method to the measurement of ^{13}C transverse relaxation times was suggested by Redfield and implemented by Free-

man and Hill to the molecule *ortho*-dichlorobenzene. Figure 10 shows both T_1 and T_2 results, the former achieved by the modified $180° - \tau - 90°$ method [see Section X B 1]. The long T_1 for the carbon attached to chlorine (66 sec) is typical for non-protonated carbon in a small molecule [see Section X B 2], but the T_2 value is much less (4·2 sec), a fact caused by the influence of the quadrupolar chlorine nuclei ^{35}Cl and ^{37}Cl. For the other two carbons, $T_1 = T_2$ within experimental error as expected. The fast relaxation of the chlorine nucleus modulates the energy levels of the carbon nucleus by reason of the scalar (J) coupling leading to a shorter T_2 value.[34, 41]

A further contribution to T_2, that from the use of proton noise de-

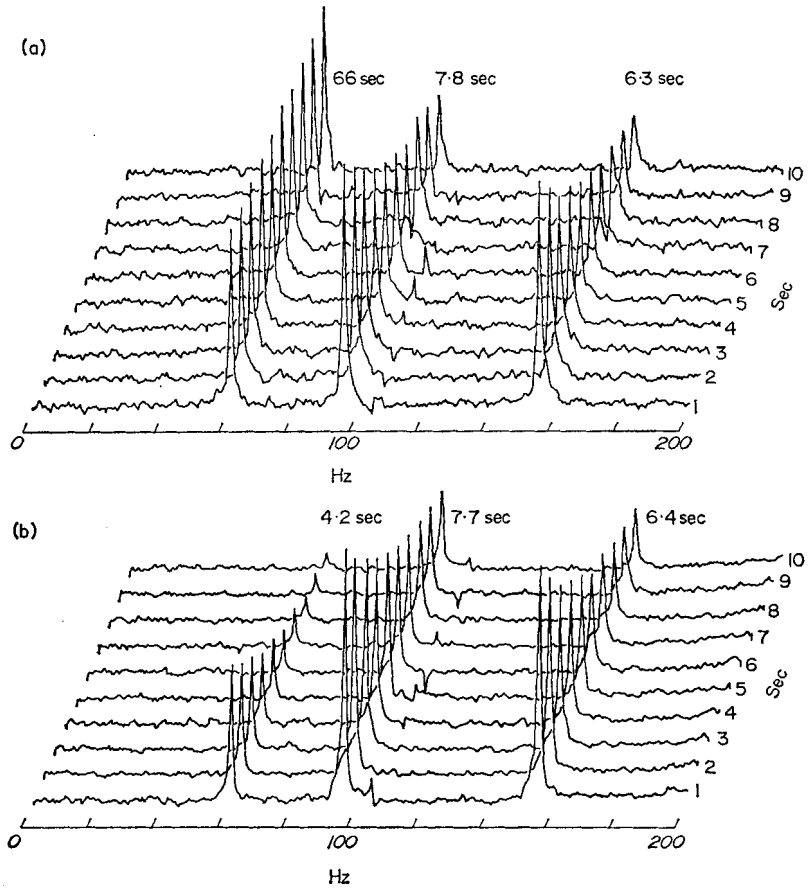

FIG. 10. Spin lattice (a) and spin-spin relaxation (b) of ^{13}C resonance of *ortho*-dichlorobenzene. (From Freeman and Jones.[72])

coupling had to be circumvented in the above experiments since, with the decoupler on, it was found that the $T_{1\rho}$ values were very small. The incoherence introduced to the proton nuclei is transferred by scalar (J) coupling in a manner analogous to the quadrupolar situation above again leading to a shortening of T_2. Hence, coherent proton decoupling which removes this difficulty was used for the t sec whilst the spins were relaxing according to $T_{1\rho}$, in order to obtain the Overhauser enhancement. Immediately afterwards, during the free induction decay the decoupling was made incoherent to remove those residual splittings which are not removed from the spectrum by coherent decoupling.

The dependence of sensitivity in Fourier transform NMR on T_1 and T_2 values has been discussed in detail earlier. Any extra shortening of T_2 by effects such as magnet inhomogeneity, chemical exchange and chemical modulation of coupling constants is potentially harmful. Modulation of the proton-^{13}C coupling constants by chair-chair interconversion in cyclohexane was blamed for the lack of sensitivity in the SEFT spectrum compared to that found in the completely deuterated molecule.[34] Roberts *et al.*,[47] in the CW ^{13}C variable temperature study, of 1,1-difluorocyclohexane found that although one- and two-bond carbon-fluorine couplings appeared to be invariant to conformation, the three-bond coupling was non-zero only when the fluorine was equatorial. It was thus predicted that the sensitivity gain for the C-3 carbon would be reduced.

Recently Shoup and Vander Hart[41] have measured the relaxation times shown in Table II by conventional (time domain) pulse methods.

TABLE II

Relaxation times for 60% enriched compounds at 25°C

	T_{1C} sec	T_{2C} sec	T_{1H} sec
$^{13}CH_3I$	13·4	3·9	10·9
$^{13}CH_3COO\,CD_3$	19·2	6·1	12·5
$^{13}CS_2$	48	38	

The authors suggest that the much reduced values for T_{2C} compared to T_{1C} are caused by the scalar (J) coupling of the ^{13}C nucleus to the relaxing ^{1}H nuclei when the condition $2\pi\tau \geqslant 1/T_{1H}$ holds a mechanism analogous to the shortening of ^{13}C T_2 values by scalar coupling to quadrupolar nuclei. These effects may be "pulsed away" at pulse rates sufficiently high that $(2\tau)^{-1} \geqslant 2\pi J$.

In the presence of proton noise decoupling the effective lifetimes, τH^{-1}, of the proton spin states are reduced. At low RF power levels in the region where the condition $2\pi J \geqslant \tau_H^{-1}$ holds, a shortening of T_{2C} is expected. With power levels sufficiently high that $2\pi J \ll \tau_H^{-1}$ the protons are effectively decoupled and the T_{2C} value should increase to a value corresponding to a situation where there are no scalar contributions.

D. Kinetic studies

The improved time scale of Fourier transform NMR may be used to follow chemical rate processes. The only example to date is the ^{13}C study of the anomeric equilibria of ketoses in water.[67] There have been several proton studies of anomeric equilibria of aldoses in solution which relied on the anomeric proton being relatively isolated to low field. In the ketoses there is no such proton since the anomeric carbon is not protonated consequently ^{13}C NMR is particularly relevant. The molecules studied were D-fructose and 3-*O*-(α-D-glucopyranosyl)-D-fructose (D-turanose).

β-D-Fructose was dissolved in water 3·7 M, pH 5) and a few minutes later (5·8) after 128 scans, a spectrum was observed which was analysed as consisting largely of β-D-fructopyranose (A) and a relatively small amount of β-D-fructofuranose (B). At equilibrium 22 hours later there were four components including the two above, the new ones being α-D-fructofuranose (C) and α-D-fructopyranose (D). Figure 11 shows the species involved and indicates the presence of approximately 40% furanose forms at equilibrium at 36°C.

These results represent another powerful application of NMR in sugar chemistry. The above estimate of 40% furanose forms compares favourably with that found by the optical rotation measurements (32% at 25°C) of Andersen and co-workers.[68,69] The latter measurements were also concerned with the change of optical rotation as a function of time (mutarotation) which is dependent on changes both in ring size (pyranose-furanose) and configuration ($\beta - \alpha$). The former process is generally faster and the NMR evidence that only β forms are significant after the short time period of a few minutes indicates that the assumptions used by Gronlund and Andersen were essentially correct. The NMR spectrum, however, does show a small amount of α-fructopyranose (C) to be present even then. The rotation at equilibrium, however, must have a significant contribution from α forms. The view in Bates,[70] quoting reference 71 stating that the equilibrium mixture of D-fructose does not contain an appreciable amount of β-pyranose form (A) appears to be in error.

The equilibrium proportions for the saccharide turanose are indicated in Fig. 11. The furanose forms are more favoured (total 60%). The α forms are relatively more favoured but this time virtually all is in the furanose form.

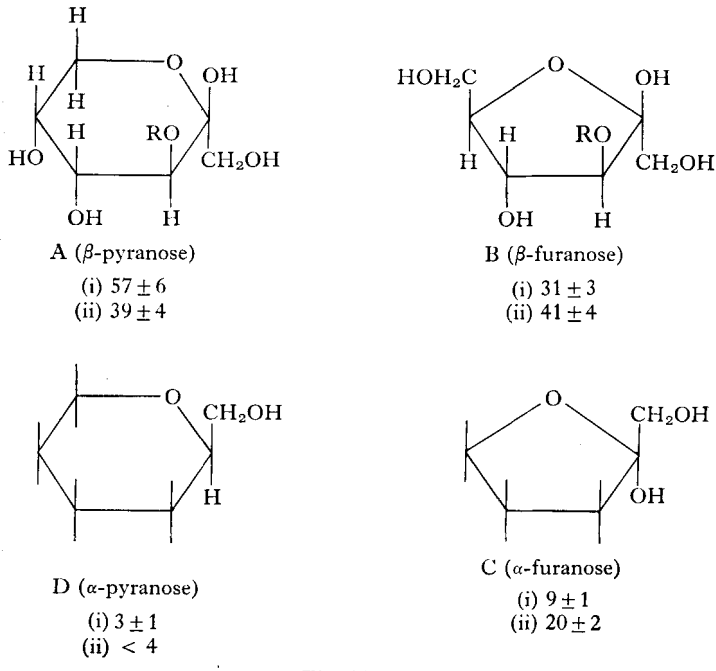

Fig. 11.

FIG. 11. Species present in aqueous solutions of (i) D-fructose (R = H); 3·7 M, ρH5; (ii) D-turanose (R = −D-glucopyranoxide, 1 M, pH 5. The figures refer to equilibrium concentration at 36°C, see reference.

In all the above NMR work no mention was made of the acyclic form, the presence of which is not necessary to assign the spectra, and hence its concentration is probably too low for detection.

One foresees a big future for ^{13}C NMR in this area, giving the chemist a means of monitoring the individual components of a mixture as an alternative to optical rotation, a bulk property data from which it is not possible to directly distinguish the species involved. The application to more general kinetic measurements including studies on chemically induced polarisation is keenly awaited.

E. Studies at very high resolution

It has been pointed out[72] that in the quest for the highest possible resolution, great attention has been paid to magnetic field homogeneity

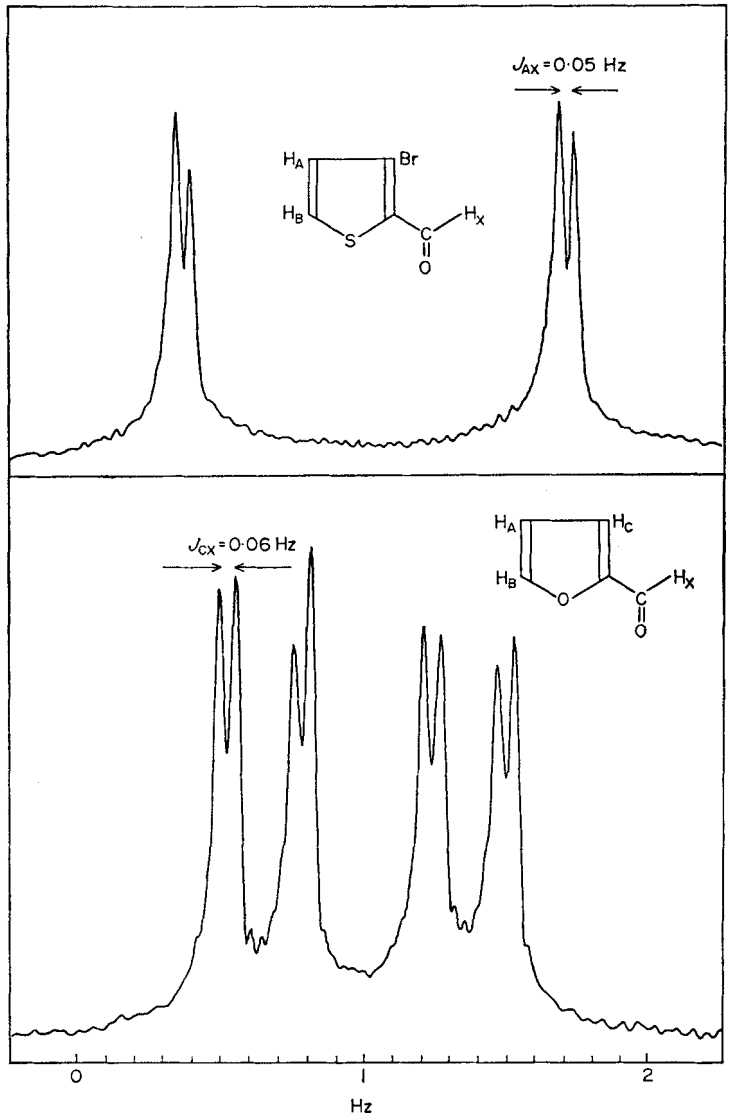

FIG. 12. High-resolution spectra of aldehyde resonance in 3-bromothiophene-2-aldehyde (*top*) and furan-2-aldehyde obtained by Fourier transform. (From Freeman and Jones.[72])

but that the rate of progress has slowed markedly since the advent of sample spinning in 1956.[73] The advent of field/frequency lock procedures[26,27] with the subsequent provision of automatic y gradient control greatly helped the routine achievement of good high resolution spectra.

Freeman and Jones suggest that there is an important line width contribution in conventional NMR from the failure to satisfy the slow passage condition, i.e. that the time taken to sweep through a given spectral line is long compared to T_2^*. The resulting extremely slow sweeps required ($\sim$0·20 Hz/min for lines $\sim$0·05 Hz wide) (corresponding to $T_2^* \sim 6$ sec) show up the instabilities in the field/frequency lock system. Fourier transform NMR largely overcomes these difficulties since the measurements, taking place during the free induction decay, require a relatively short time; thus the requirements on spectrometer stability are relaxed.

The technique was demonstrated by resolving splittings of 0·05 and 0·06 Hz in 3-bromothiophene-2-aldehyde and furan-2-aldehyde respectively. The data were acquired in 32 sec as 512 samples. The band width was limited to 7 Hz and the carrier (at 0 Hz) adjusted to include the region of interest. The fineness of the digitisation was increased from 32 to 256 points/Hz by approximating the decay to zero for 3584 points beyond the 512 sample points. Spectra are shown in Fig. 12 and were obtained in a time (32 sec) that in CW mode would be required for one line.

The coupling constant in 3-bromothiophene-2-aldehyde has also been

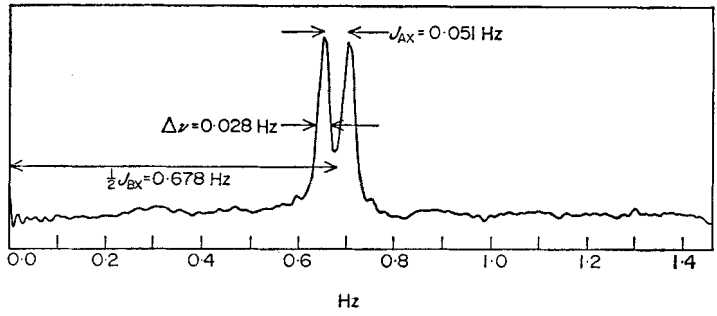

FIG. 13. Partial J-spectrum of 3-bromothiophene-2-aldehyde. Carr-Purcell spin-echo responses of the aldehyde proton were detected selectively at a repetition rate of 2·5 Hz. 150 samples were taken, one at the peak of each echo, and subject to Fourier transformation in a digital computer. Resonance responses appear at $(J_{bx}-J_{ax})/2$ and $(J_{bx}+J_{ax})/2$ with widths that correspond to a spin-spin relaxation time of $11{\cdot}2 \pm 0{\cdot}4$ sec. (From Freeman and Hill.[44])

measured as $0{\cdot}051 \pm 0{\cdot}002$ Hz by a spin echo Fourier transform technique, more detailed discussion of which is reserved for Section X F. Figure 13 shows the splitting and the line width (0·028 Hz).

F. Spin echo Fourier transform spectra

Under this heading we include all experiments which include refocusing of the transverse magnetisation by means of a 180° pulse, and thus nulling the effects of magnet inhomogeneity. The feasibility of utilising these methods for T_2 measurements has been discussed in Section C, and for sensitivity improvement in Section IX.

1. *Studies in liquid crystal solvents*

Vold and Chan have demonstrated[74] the fact that modulated spin echoes are obtained in liquid crystal solvents. They studied methylene chloride to which 17% by weight of poly-α-benzyl-L-glutamate had been added. It was shown that the echoes were invariant to both chemical shift effects and to dipolar and scalar interactions between resonant and non-resonant nuclei. In other words, the echo modulation was determined by interactions between resonant nuclei only. Assuming the pulse rate to be high enough, Fourier transformation of the echo envelope produces a spectrum describable by the "average Hamiltonian",

$$\hat{\mathscr{H}} = \sum_{i<j} D_{ij}\hat{I}_{zi}\hat{I}_{zj} + (A_{ij} - \tfrac{1}{3}D_{ij})\hat{I}_i\hat{I}_j \qquad (66)$$

where A_{ij} and D_{ij} are the scalar and dipolar coupling constants respectively and the sum is over resonant nuclei only.

A dipolar splitting of 78 Hz was measured and it was thought that the simplified spectra obtained would be sufficient incentive to overcome instrumental difficulties.

2. *J spectra*

Freeman and Hill[44] have made a study of spin echoes modulated in the presence of J coupling. In an AX system where both nuclei are resonant the amplitude of the echo will display a modulation at frequency $\frac{1}{2}J_{AX}$ Hz when studied either as a function of τ or if multiple echoes are generated. The modulation is of course superimposed on any damping caused by T_2 spin-spin relaxation. It is only the peaks of the spin echo profiles which are unaffected by chemical shifts and field inhomogeneity. It is at these maxima that the signal must be digitised and, since the echo spacing is 2τ sec, it follows that the highest frequency recoverable is $1/4\tau$ Hz. These points when acquired for T sec produce a complex modulated waveform which, on Fourier transformation, produces a spectrum in the range 0 to $1/4\tau$ Hz.

The spectra obtained may be very complicated and so attention was restricted to situations which were strictly first order. Further, the pulse repetition rate must be low compared to the smallest shift difference,

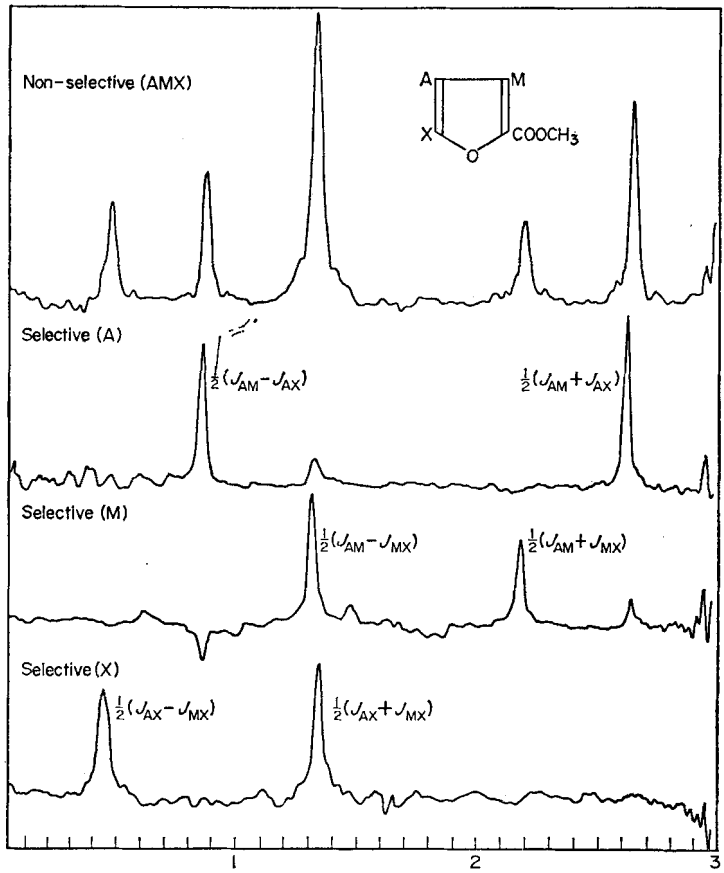

FIG. 14. *J*-spectra of the AMX spin system of methyl furoate. In the top trace the envelope of the spin-echo peaks from all three groups of nuclei was recorded using a detector bandwidth of 60 Hz. Fourier transformation gives the complete *J*-spectrum of six lines, with an accidental degeneracy of the third and fourth lines. This spectrum can be assigned (in terms of sums and differences of spin coupling constants) through the three partial *J*-spectra obtained by tuning the detector to each chemical shift in turn with a restricted bandwidth of 6 Hz. This required ±32 Hz frequency displacements to detect the partial *J*-spectra of A and X (second and fourth traces) resulting in a slight perturbation of these frequency scales because of an incidental instrument effect. (From Freeman and Hill.[44])

the 180° pulse must be accurate, and lastly, other sources of echo modulation such as that observable in liquid crystal solvents must be absent.

With the above conditions applied the spectra were called "J spectra" and displayed lines with Lorentzian shapes separated by frequencies which are sums and differences of coupling constants. In practice the spectra were simplified further by selectively detecting the echo modulation at one particular resonant frequency, these were called "partial J spectra".

In practice special care has to be taken to minimise error in the phase angle of nuclear precession between 180° pulses, a factor aggravated by even a momentary deviation from the correct field/frequency ratio.

The pulse sequence used was essentially that of Carr-Purcell,[35] $90° - \tau - 180° - 2\tau - 180° \ldots$ except that the phase of the 180° pulse was alternated, a method which compensates for inaccuracy in the setting of the 180° pulse.[49]

The method was applied to the resolution of the small splitting of $0{\cdot}051 \pm 0{\cdot}002$ Hz (this method) in the spectrum of 3-bromothiophene-2-aldehyde. Couplings are resolvable by this technique as long as $\frac{1}{2}|J| \geqslant (\pi T_2)^{-1}$, the natural line width of the line. The two coupling constants to the aldehyde proton could be extracted from the time domain without Fourier transformation, the measurement being simplified by selective decoupling.

A transformed partial J spectrum is shown in Fig. 13. The line width at half-height of 0·028 Hz, gave a value of $T_2 = 11{\cdot}2$ sec in good agreement with the previous time domain value (11·5) reported in the same paper.

The partial J spectra of the ring protons in methyl furoate, an AMX system were studied; the spectra are shown in Fig. 14. However, linewidth perturbations and frequency shifts were observed which depended to a greater or lesser extent on the first-order approximation stability of the field/frequency lock, spinning rate, timing of samples and accuracy of pulse lengths.

The extension of these methods to handle complete J spectra of non-first-order spin systems adds theoretical complexity which need not be insurmountable.†

G. Data processing in the time domain

The time domain is particularly advantageous in connection with filtering for optimum sensitivity or resolution. In the frequency domain filtering corresponds to a convolution or "moving average" process. In the time domain the equivalent process is very simple involving multi-

† Vold and Chan[89] have produced a general density matrix formulation of the Carr-Purcell spin echo experiment, and considered it Fourier transform.

plication by an appropriate weighting function,[10,13] which is the frequency response function of the filter.

The method was compared to other methods for resolution enhancement for resolving the small coupling in 3-bromothiophene-2-aldehyde.[75] Resolution enhancement is at the expense of S/N ratio and vice versa.

Freeman and Hill have pointed out that in the repetitive pulse experiment the signal ought to be weighted according to the local S/N ratio to allow proper significance to the intensity of the inherent echo. It is very easy to "construct" an appropriate filter by modifying the computer programme.

Redfield and Gupta[76] applied an impulse to their detection system and used a function derived from the response. Thus the free induction decay could be weighted according to the actual characteristics of the system.

Apodisation is another multiplicative weighting process in the time domain which corrects for the finite sampling times. It is particularly important when one interpolates in the time domain by artificially setting to zero data channels corresponding to times after acquisition is complete, see Section X E.

It may even be advantageous to transform frequency spectra into the time domain for the purposes of phase correction. Since the computer complete with FFT programme is already present in a pulse system the implementation of the transforms is easy. Even spectra run under intermediate passage conditions may be phased in this way since the u- and v- mode spectra are still related as Hilbert transforms.[20]

H. Miscellaneous experiments

1. *Overhauser effects*

The improved time scale of Fourier transform NMR may be used to gather spectral information during the time immediately after the spin populations have been perturbed by the presence of a second radiofrequency field.[77]† Transient internuclear Overhauser effects may be measured in the absence of the complicating effects of line displacement caused by the presence of a second coherent radiofrequency field. In practice, the irradiating field is switched off some time, say τ, before the excitation pulse. The transformed spectra, considered as a function of τ, will then display the time evolution of the intensity effects. The molecule studied was acetaldehyde and the effects on the aldehyde proton irradiating the methyl protons is shown in Fig. 15. The top trace (a) shows the sub-multiplets (residual splittings) produced by the presence

† For recent hetronuclear applications of this property probably of considerable practical significance see references 90, 91 and 92.

of the coherent irradiating field during the acquisition of the free induction decay.

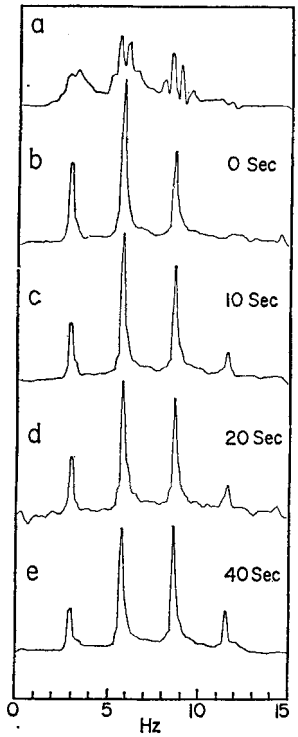

FIG. 15. (a) Acetaldehyde quartet observed by the Fourier transform technique with continuous-wave irradiation of the high-field methyl line. (b to e) The same quartet observed t sec after the irradiation field H_2 has been extinguished.

2. *Heterogeneous systems*

Sternlicht *et al.*[78] have studied the ^{13}C spectra of amino acids bound to cationic exchange resins. The purpose was to shorten the T_1 relaxation times of non-protonated carbon atoms with a view to both aiding their detection and distinguishing them from carbon atoms with attached hydrogen. In practice line widths in the range 1 to 10 Hz were found and it was postulated that these high resolution NMR studies may be very useful with biopolymers in general and in other solid-liquid systems such as those occurring in the fields of catalysis and biological *membranes.*

The increase in sensitivity produced by a shortened T_1 on the resin was offset for moderate T_1 values by the fact that for the amino acid concentration on the resin was low compared to that attainable in solution. Deuterated amino acids bound to the resin produced spectral lines

3 to 4 times narrower than the proton analogues, indicating longer T_2^* values in solution. The spectra were very weak on account of very long T_1 values.

Anisotropic rotational reorientation was postulated to explain the following observations;

(a) The ratio found for $T_{2D}/T_{2H} \sim 3{\cdot}25 \left[= \frac{\gamma_H}{(2\gamma_H)} \right]$.

(b) The Overhauser enhancement factors of ~ 3.

(c) The large differences between T_1 and T_2, with low and high sensitivities to cross-linking in the resin respectively.

Values for T_1 and T_2 for carbon, deuterium and protons and also the Overhauser enhancement factor, are all dependent in different ways on τ_c, the correlation time appropriate to the particular motion involved. It was concluded that a short correlation time of 1×10^{-9} sec or less determined T_1 and enhancement factors but that the line widths, or T_2 values, were determined by a long correlation time which may result from a "wobbling" motion of the resin lattice.

3. *Aqueous solutions*

Redfield and Gupta[76] have described a method which allows observation of weak proton resonances in water solution. The experiment was set up to observe the spectra of protons that are able to exchange slowly with water, resonances that are lost with D_2O as solvent.

The experiment produces signals with large dynamic range and in the time domain,† unlike CW NMR, the large signal is there during the whole acquisition time. In practice selective pulses were applied such that they excited the (NH) resonances of interest but had a zero component at the H_2O resonant frequency, thus effectively eliminating the contribution of H_2O to the free induction decay. Residual H_2O signal due to inhomogeneities in the RF field appear as a baseline distortion for which a correction may be made.

The method was applied to the tryptophan middle N-H resonance. The concentration was 0·03 M and the broadening arising from base catalysed exchange at high pH values was studied. The method included irradiation of the H_2O resonance with a second radiofrequency to determine the exchange time. The N–H resonances in Horse fericytochrome C were also studied (0·006 M, pH 7).

Fourier difference spectroscopy may also be useful in H_2O solutions, see Section IV E 3, if the problem of distinguishing "positive" from "negative" frequencies can be overcome.

† Recently techniques have been reported which utilize differences in T_1's between the solvent and solute to eliminate the reference of the former from the free induction decay. By this method the dynamic range of applications caused by a solvent line are minimized.[93,94]

4. *Polymers*

Recently Schaefer has reported studies using conventional pulsed ^{13}C NMR on the polyelectrolytes poly(methacrylic acid), poly(acrylic acid) and a copolymer of ethylene and maleic anhydride,[79] polyacrylonitrile,[80] acrylonitrile-styrene copolymers[81] and some polymenic gels.[82] None of these systems lend themselves to proton studies. The extra sensitivity provided by the pulse technique for ^{13}C was essential to the work, the experiments often requiring accumulation for several hours. The spectra were of high enough resolution to allow assignments of carbons corresponding to particular segments of the polymers. In the case of the polyelectrolytes the shift differences due to the stereochemical differences were pH dependent; indeed the titration may be followed by the changing shifts of carbonyl carbons. The changes were ascribed to changes in substituent ionisation rather than to changes in local conformation. The free induction decays indicate values of T_2^* of approximately 0·1 sec. Reproducible spectra were obtained with pulse intervals of 1 sec upwards.

It seems that ^{13}C NMR will make a major contribution in the polymer area, the practical application of which has awaited Fourier transformer capabilities.

5. *Gas Phase*

The increase sensitivity provided by the use of Fourier Transform techniques has made the gas more accessible to high resolution NMR techniques.[95] Studies of relaxation parameters in the gas phase as a function of pressure has been reported using Fourier transform techniques.[96]

FINALLY. In this review we would like to stress that we have not attempted to produce a comprehensive list of basic applications of the inherent sensitivity enhancement of Fourier NMR (see ref. 83). We have however, concentrated on those areas when the use of Fourier transform techniques have changed our approach to high resolution NMR.

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AUTHOR INDEX

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