density at the carbons to which they are attached.[31] This mechanism is not possible for a fluorine substituent because there is no proton on the fluorine, and it may be significant in this connection that chemical-shift changes of the opposite sign may be induced at the fluorine by nonbonded interactions.[32]

The ^{13}C chemical shift of C-8 in 1-fluoronaphthalene is 5.1 ppm upfield of the corresponding shift in naphthalene itself. The two other carbons which are three bonds removed from the fluorine, but which are not in close proximity to it, are shifted downfield by 2.2 and 4.0 ppm. The methyl carbon of 2-fluorotoluene is shifted upfield relative to the methyl carbon in toluene by 7.3 ppm. The corresponding effects on the meta and para derivatives are +1.5 and +0.9 ppm.[33] Clearly, a carbon is shifted upfield by a γ-fluorine which is either eclipsed or gauche to the carbon in question.

The C-1 chemical shift in pentafluoroiodobenzene actually appears upfield of the methyl resonance in methyl fluoride. This large shift can be explained on the basis of additive substituent parameters for fluorobenzene and iodobenzene,[12] where $^1\delta_I$ is the substituent effect of

$$\begin{aligned} \delta &= {}^1\delta_I + 2({}^2\delta_F) + 2({}^3\delta_F) + {}^4\delta_F \\ +63.5 &= +32.3 + 28.6 + 1.8 + 4.4 \end{aligned}$$

iodine on C-1 iodobenzene, $^2\delta_F$ is the substituent effect of fluorine on the *o*-carbon of fluorobenzene, etc. The predicted value of +63.5 ppm agrees fortuitously well with the observed shift. Additivity relations appear to hold reasonably well for ^{13}C chemical shifts in aromatic compounds, but not usually to this precision.

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(31) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967).

(32) J. B. Dence and J. D. Roberts, *ibid.*, **91**, 1542 (1969).

(33) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

The Fluorine-19 Nuclear Magnetic Resonance Spectra of Some Fluoroaromatic Compounds. Studies Using Noise Decoupling of Protons[1a]

M. Ashley Cooper,[1b] Hans E. Weber, and Stanley L. Manatt*

Contribution from the Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103.

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Abstract: The ^{19}F nmr spectra of a number of fluorobenzenes and other fluoroaromatic molecules have been examined at 94.1 MHz under conditions of complete proton decoupling by noise modulation, which allowed ^{19}F chemical shifts and F···F coupling constants to be extracted conveniently without recourse to complete analyses. Details of the digital frequency sweep and the double-tuned probe provisions for a Varian HA-100 spectrometer are given. Where a proton-decoupled spectrum is a single line, the values of $^1J_{^{13}C-F}$ and the ^{13}C–^{12}C isotope shifts may not always be extracted uniquely from the ^{13}C satellites, although the F···F coupling constants can be measured directly. Data on the solvent dependence of F···F couplings and ^{19}F chemical shifts in some polar fluorobenzenes are reported. The behavior of $^3J_{FF}$ in these systems shows no correlation with solvent dielectric constant, which is interpreted to mean that "reaction field" mechanisms are not important here. However, the smaller variations in $^4J_{FF}$ and $^5J_{FF}$ are reasonably correlated with the dielectric constant of the solvent, which suggests that the "reaction field" mechanism is more significant here. No simple dependence of the ^{19}F chemical shifts on solvent dielectric constant was found in contrast to some previous results; possible explanations for this are discussed. Accurate values for the long-range F···F couplings for a number of difluoronaphthalenes, -biphenyls, and -phenanthrenes are presented for the first time.

Because of the difficulties in the theoretical understanding of fluorine–fluorine nmr spin–spin coupling constants, there is continuing interest in the nmr spectra of fluorinated benzenes. To cite but a few examples, there have recently been several careful spectral analyses, including the extraction of F···F coupling relative sign information, on the pentafluorobenzenes.[2,3] It has been shown[4] that a considerable part of the discrepancies found between values of $^3J_{FF}$ in earlier work arises from a large solvent dependence of this coupling. Very recently further evidence from a range of compounds has been presented[5–7] in support of the proposal[8] that the nuclear spin–spin coupling between two fluorine atoms may be transmitted "through space" where the

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(1) (a) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration. Partial support was received from the Jet Propulsion Laboratory Director's Discretionary Fund. (b) NASA Resident Research Associate, 1968–1970.

(2) E. A. Cohen, A. J. R. Bourn, and S. L. Manatt, *J. Magn. Resonance*, **1**, 436 (1969).

(3) R. R. Dean and W. McFarlane, *J. Chem. Soc. B*, 509 (1969).

(4) M. A. Cooper, *Org. Magn. Resonance*, **1**, 363 (1969).

(5) (a) K. L. Servis and K.-N. Fang, *J. Amer. Chem. Soc.*, **90**, 6712 (1968); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **90**, 3577 (1968); (c) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970).

(6) S. L. Manatt and M. T. Bowers, *J. Amer. Chem. Soc.*, **91**, 4381 (1969), and unpublished work of E. A. Cohen and S. L. Manatt quoted therein.

(7) R. A. Fletton, R. D. Lapper, and L. F. Thomas, *Chem. Commun.*, 1049 (1969).

(8) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961).

atoms are spatially close. The details of the ^{13}C spectra of some fluoroaromatics and a number of values of $^{13}C\cdots F$ coupling constants have been presented[9] along with the analyses which allow certain interesting $F\cdots F$ couplings to be estimated. In this paper, as outlined below, we describe results bearing on all these problems.

A considerable simplification in the spectra of systems containing both protons and fluorines may be effected by decoupling one or the other of the nuclear species. In particular, recent studies of decoupling using noise modulation[10,11] have shown that it is quite feasible to decouple completely one of the nuclear species, even when the spectral lines of a nucleus cover a range as large as several kilohertz.[12] In the present work we have concentrated on ^{19}F nmr studies with complete proton decoupling, and under these conditions the resultant ^{19}F spectrum may often be analyzed by inspection to obtain $F\cdots F$ coupling constants and ^{19}F chemical shifts. Thus, these parameters have been extracted for a number of fluorobenzenes, and these new values confirm those from previous full iterative analyses.

A more important reason for our interest in this technique arose out of our recent work[4] on the solvent dependence of $F\cdots F$ coupling constants in some nonpolar molecules. We were interested to see whether similar effects were present in polar systems. To complete a full iterative analysis of a complex six-spin case such as 1,2,4-trifluorobenzene in each of, say, ten solvents would be a prohibitively lengthy task. Admittedly, the labor might be reduced some by employing the techniques of subspectral analysis.[12,13] However, we were primarily interested in $F\cdots F$ couplings and by far the simplest method of extracting these was *via* complete proton decoupling.

As mentioned above, the mechanisms by which long-range $F\cdots F$ coupling constants are transmitted have excited much interest of late. While $^4J_{FF}$ and $^5J_{FF}$ in fluorobenzenes are well documented,[2,14] and there are some data available for fluorobutadienes, there are comparatively few data in other unsaturated systems. This is especially the case for couplings over more than five bonds. The present technique enables values for such couplings to be extracted readily, and a number of examples of long-range $F\cdots F$ coupling constants have been obtained in difluoronaphthalenes, difluorobiphenyls, and one difluorophenanthrene. Although a complete range of model compounds has not been studied and the data shed little immediate light on the mechanisms involved, we believe our results represent some novel data and will serve to stimulate research in this area.

The acquisition of data in the present work was greatly facilitated by employment of a digital frequency sweep spectrometer system which is described in some detail in the following section. In particular, this system was most useful in those cases where molecular symmetry requires the proton-decoupled ^{19}F spectrum to be a singlet, and the $F\cdots F$ coupling constants have to be extracted from the ^{13}C satellite spectra. With this digital sweep system a simple procedure for obtaining precise frequencies of the outermost ^{13}C satellite patterns relative to the main band (^{12}C) signals is outlined. Thus, in this paper we shall discuss a variety of results which illustrate the powerful applications of the techniques of proton noise decoupling and digital frequency sweep, and which we hope will stimulate further, more exhaustive studies of $F\cdots F$ coupling constants in aromatic systems.

Description of the Spectrometer

(a) Digital Frequency Sweep. The spectra were taken on a Varian Associates HA-100 spectrometer, modified as detailed below. The "sweep oscillator amplifier" and "sweep network" cards were removed from the V-4354A unit, and in their place the output from a Hewlett-Packard 5100A synthesizer was fed into the "sweep oscillator out" jack of this unit. Digital frequency sweep was obtained by use of a Barry Research LSC-7A linear sweep controller.[15] This digital programmer is configured to sweep a Hewlett-Packard 5100A frequency synthesizer over sweep widths $10-10^4$ Hz. Of those digit buttons on the synthesizer which are to be swept, only the most significant is placed in the engaged position, while the remainder of the buttons (to the right) are disengaged, and the synthesizer is set in the local mode of operation. The programmer sweeps the frequency downward starting at a frequency one sweep width higher than the most significant of the digits to be swept. The sweep rate may be varied between 5 Hz/sec and 0.01 Hz/sec in convenient multiples.

In the present case, all the signals examined were close to, and downfield from, the hexafluorobenzene (C_6F_6) signal which was used for control. Thus the procedure was to lock on C_6F_6 using the internal-lock system with a frequency of *ca.* 2 kHz, and to sweep an audio side band, which in this instance was never greater than 7 kHz, from the lock. In this range, there is no need to adjust the phases of the locking and observing frequencies independently, although this would be required with a side band of *ca.* 10 kHz or larger. Such a phase adjustment could be made quite easily, and is comonly used[16] in the more usual method of obtaining field-frequency locked ^{19}F spectra. In this method it is the lock frequency which is taken externally, and the internal sweep oscillator, which is restricted to a range of 2500–3500 Hz, is maintained.

We have determined that the times taken by the digital recorder carriage on our HA-100 to traverse are accurate to better than 0.05%. Thus our procedure for taking spectra was to select a sweep range and sweep rate on the digital programmer and to start the latter and the recorder carriage simultaneously. The resultant spectrum is of excellent linearity, and by suitable combination of sweeper and recorder times can be made in a variety of convenient and accurate expansions.

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(9) (a) F. J. Weigert, Ph.D. Thesis, California Institute of Technology, 1968; (b) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 93, 2361 (1971).

(10) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(11) R. R. Ernst, *Mol. Phys.*, **16**, 241 (1969).

(12) E. Lustig, E. A. Hansen, P. Diehl, and H. Kellerhals, *J. Chem. Phys.*, **51**, 1839 (1969).

(13) P. Diehl and J. A. Pople, *Mol. Phys.*, **3**, 557 (1960); for a review on subspectral analysis, see P. Diehl, R. K. Harris, and R. G. Jones, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 1 (1967).

(14) R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Amer. Chem. Soc.*, **90**, 147 (1968).

(15) Available from Barry Research, 934 East Meadow Drive, Palo Alto, Calif. 94303.

(16) E. Lustig, N. Duy, P. Diehl, and H. Kellerhals, *J. Chem. Phys.*, **48**, 5001 (1968).

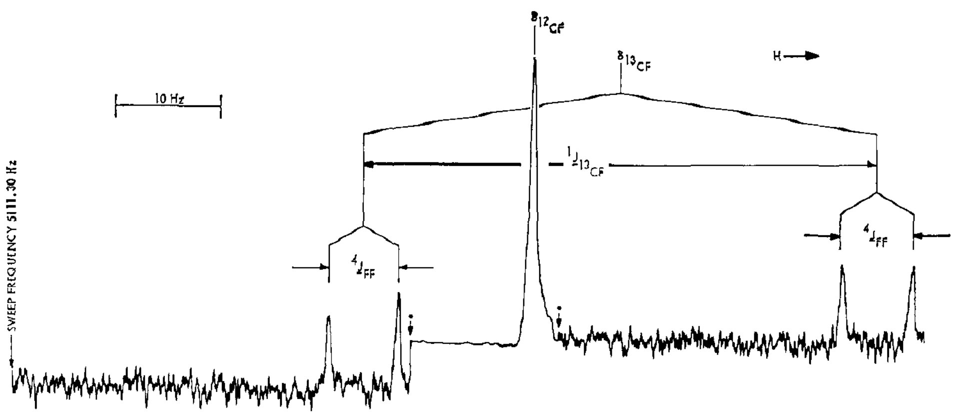


Figure 1. The noise-decoupled ^{12}C and ^{13}C satellite ^{19}F spectra of *m*-difluorobenzene at 94.1 MHz, showing the use made of "switching" the digital sweep (see text). Asterisks indicate positions of switching. Note that in this case $^1J_{^{13}C-F}$ and $(\delta_{^{13}C-F} - \delta_{^{12}C-F})$ may be obtained by inspection (see text). Frequency marker is in hertz from C_6F_6.

Use of the digitally swept spectrometer enables highly accurate measurements of the frequency differences between transitions to be made, for example, of the frequencies of the ^{13}C satellites relative to the main band. We describe this with reference to the proton-decoupled spectrum of *m*-difluorobenzene (see Figure 1). The satellites occur *ca.* 120 Hz either side of the main ^{12}C band, which itself is *ca.* 4960 Hz downfield from C_6F_6. Thus, with a locking side band of 1890 Hz, the main band signal occurs at a sweep frequency of 6850 Hz, which was arranged to be in the center of the digital sweep as the latter decreased from 6900 to 6800 Hz. By sweeping from 7000 to 6900 Hz, or from 6800 to 6700 Hz, the low- and high-field ^{13}C satellites could be obtained, respectively. Thus, the low-field satellites were recorded with the synthesizer set to 6900 Hz, to which the swept width of 100 Hz is added by the programmer. As soon as the low-field satellite had been recorded, the synthesizer was punched manually to give a reading of 6800 Hz, without interrupting the remaining sweep settings, and the ^{12}C band was recorded with suitable reduction in the output controls. Finally, the synthesizer was manually switched to 6700 Hz and the upfield satellites were recorded. Thus all five signals of interest are recorded in one continuous sweep, and their relative positions can be conveniently obtained.

(b) Noise Decoupling. For many of the molecules studied here, *e.g.*, *p*-difluorobenzene, the proton resonances cover a narrow region, and decoupling could be achieved using a single decoupling frequency. In other cases, *e.g.*, 1,2,4-trifluorobenzene, the proton resonances are well spread out and complete decoupling is achieved[10,11] most efficiently using noise modulation of the decoupling frequency. This is also most convenient for the reason that once the optimum conditions for decoupling are found in one case, these need not be changed for decoupling other fluorinated molecules containing protons provided one uses the same locking frequency and control sample molecule. Use of a single decoupling frequency, even when feasible, would require considerable care in the optimization of frequency and power settings.

For the purpose of decoupling and tickling experiments at either 100 or 94.1 MHz, we have developed a stable but settable frequency source, which we now describe. The Hewlett-Packard 5100A synthesizer does not cover the desired 94.1–100 MHz range, but nonetheless we wished to take advantage of the high stability of the synthesizer as a fundamental generator. A block diagram of the frequency converter is shown in Figure 2. Full circuit diagrams are available on request. The 30-MHz frequency was taken from the rear terminal of the synthesizer, was given a preliminary amplification, and was tripled to give 90 MHz. This was then fed into a mixer together with a frequency at either 4 or 10 MHz, selected on the front of the synthesizer. The output of the mixer is an rf at either 94 or 100 MHz, suitably filtered by adjustable tuned circuits. For proton decoupling a frequency of 100.0005 MHz was found to give good results and has the same stability as the synthesizer itself.

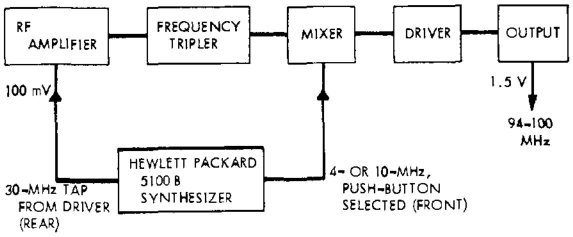


Figure 2. Block diagram of the apparatus for synthesizing a stable 94.1- or 100-MHz frequency, using an HP-5100A frequency synthesizer as source.

For noise decoupling, the 100-MHz frequency was fed into an HP 10514A mixer together with the output from an HP random noise generator. The latter was set to an infinite sequence length with a noise band width setting of 50 Hz and a maximum output setting. The resultant noise-modulated frequency was amplified by a Boonton 230A power amplifier, such that the output meter read 20 V and was fed into the 100-MHz channel of a double-tuned 94.1/100-MHz probe. Details of the probe circuitry are shown in Figure 3. The design of this was developed independently from that given by McFarlane and Charles,[17] and so differs somewhat.

As a check that complete decoupling was in fact achieved, the power level applied to the proton region was varied. At the operating conditions and even at output levels a factor of 5 smaller, an increase in

(17) A. Charles and W. McFarlane, *Mol. Phys.*, **14**, 299 (1968). For other recent descriptions of double-tuned probes, see: G. J. Long and A. G. Moritz, *ibid.*, **15**, 439 (1968) and R. Burton and L. D. Hall, *Can. J. Chem.*, **48**, 59 (1970).

Table I Nuclear Magnetic Resonance Parameters of Some Fluoroaromatic Compounds

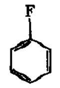
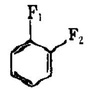
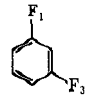
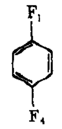
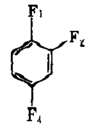
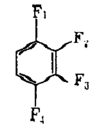
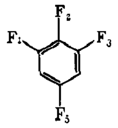
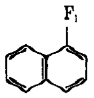
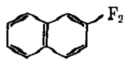
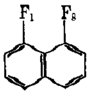
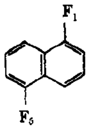
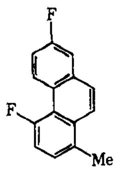
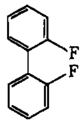
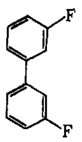
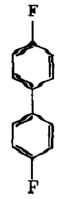
Molecule	$\delta_F{}^a$	$A^{b,m}$	B^{b-d}	$\|J_{FF}\|$,^{c,e} Hz	Remarks
	4685.6 4691.8	245.8^f 244.5^f	8.3^f 8.3^f		50% CCl_4 50% acetone
	2283.7 2305.8 2272.9	249.8^g 249.6^g 248.5^g	8.0^h 7.8^h 7.8^h	20.9 20.5 20.6	50% CCl_4 50% TMS 50% acetone
	4961.3 4894.1	247.2^i 246.5^i	8.0^h 8.0^h	6.64 6.56	50% CCl_4 50% acetone
	4049.9 4095.2	243.4^j 241.9^j	7.9^h 7.9^h	17.64 17.7	50% CCl_4 50% CCl_4
	δ_1 1803.3 δ_2 2758.8 δ_4 4383.4			J_{12} = 20.60 J_{14} = 15.11 J_{24} = 3.15	10% CCl_4
	δ_1 2163.0 δ_2 607.2			J_{12} = 19.72 J_{13} = 2.70 J_{14} = 12.70 ± 0.2 J_{23} = 19.00 ± 0.2	10% CCl_4
	δ_1 2896.8 δ_5 4540.1			J_{12} = 20.36 J_{15} = 1.64 J_{25} = 10.94	10% CCl_4
	3687.4	250.7^j	7.8^j		50% acetone
	4534.7	244.7^j	8.0^j		50% acetone
	4430.8	268.0^k	7.7^k	58.8	50% acetone
	3887.2	250.3^l	7.8^h	4.1	50% acetone
	δ_4 4506.2 δ_7 4672.0			0.8	10% $CDCl_3$
	4524.8	249.6^g	7.9^h	18.2	50% pyridine
	4610.5 4611.4	246.6^j 245.4^j	8.4^j 8.3^j	<0.2 <0.2	50% CCl_4 50% pyridine

Table I (*Continued*)

Molecule	δ_F[a]	A[b,m]	B[b–d]	$\lvert J_{FF}\rvert$,[c,e] Hz	Remarks
	4425.6	246.0[f]	8.2[f]	<0.3	50% pyridine

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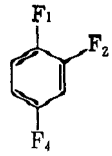
[a] Chemical shifts in hertz downfield from internal C_6F_6 at 94.1 MHz. [b] See test for the significance of these parameters, *A* and *B*, which are first-order approximations to $\lvert {}^1J_{^{13}C-F}\rvert$ and the $^{12}C-^{13}C$ isotope shifts, respectively. [c] In Hz at 94.1 MHz. [d] The chemical shift of the ^{13}C species is upfield of the ^{12}C species. [e] No sign information is available from the present work. [f] These parameters may be equated with the values of $^1J_{^{13}C-F}$ or the isotope shift (see text). [g] The value of *A* is approximately 1.7 ± 0.1 Hz larger than the correct value of $\lvert {}^1J_{^{13}C-F}\rvert$. [h] The value of *B* is within 0.1 Hz of the isotope shift. [i] The value of *A* is approximately 0.2 ± 0.1 Hz larger than the correct value of $\lvert {}^1J_{^{13}C-F}\rvert$. [j] The value of *A* is approximately 1.3 ± 0.1 Hz larger than the correct value of $\lvert {}^1J_{^{13}C-F}\rvert$. [k] For a value of $\lvert J_{BX}\rvert$ of *ca.* 5 Hz the value of *A* is approximately 13.4 ± 0.3 Hz larger than the correct value of $\lvert {}^1J_{^{13}C-F}\rvert$, while *B* is *ca.* 0.4 Hz less than the correct value of the isotope shift. [l] The value of *A* is equal to $\lvert {}^1J_{^{13}C-F}\rvert$ within experimental error. [m] Values of $\lvert {}^1J_{^{13}C-F}\rvert$ quoted in the text have been corrected for second-order effects.

Table II. Solvent Dependence of ^{19}F Spectral Parameters of 1,2,4-Trifluorobenzene



Solvent[a]	$\epsilon_{30°}$[b]	δ_1[c]	δ_2	δ_4	J_{12},[d] Hz	J_{14}, Hz	J_{24}, Hz
Neat liquid		1837.0	2777.6	4477.8	−20.29	15.04	3.16
Pentane	1.83	1843.2	2809.5	4440.5	−20.22	15.10	3.08
TMS	1.88	1833.2	2795.0	4431.2	−20.35	15.08	3.08
CCl_4	2.22	1803.3	2758.8	4383.4	−20.60	15.11	3.15
C_6H_6	2.26	1830.8	2777.1	4452.3	−21.47	15.04	3.25
C_6F_6		1813.4	2778.3	4478.6	−19.40	15.09	3.12
$CFCl_3$	2.27	1819.8	2780.0	4416.2	−20.12	15.08	3.13
CS_2	2.61	1848.8	2783.6	4464.0	−21.37	15.02	3.20
Et_2O	4.14	1802.3	2747.8	4454.6	−20.42	15.24	3.19
$CDCl_3$	4.63	1749.5	2697.0	4367.2	−20.78	15.04	3.20
CH_2Cl_2	8.72	1750.2	2688.6	4390.5	−20.65	15.06	3.24
Me_2CO	20.22	1819.8	2741.0	4508.0	−20.62	15.33	3.29
MeCN	36.50	1800.1	2714.7	4463.1	−20.41	15.20	3.33

[a] Solutions were 10% v/v in solute and 5% in C_6F_6. [b] Dielectric constants of pure solvents at 30° are given. [c] Chemical shifts in hertz downfield for C_6F_6 at 94.1 MHz. [d] Coupling constants in hertz. Signs are by analogy with previous work.

power produced no further change in appearance of the spectrum. The excellent agreement between the present results and those obtained from full analyses also illustrates that complete decoupling was achieved. Figure 4 illustrates the great simplification of the spectrum of F_4 in 1,2,4-trifluorobenzene which is produced by complete proton decoupling.

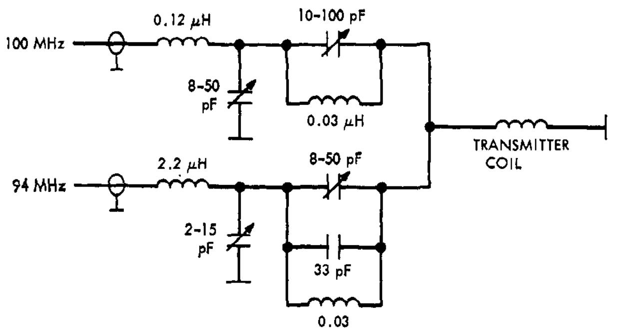


Figure 3. Circuit showing the components used in the 94.1/100-MHz dual-tuned probe.

Experimental Section

The fluorobenzenes were obtained commercially, as were the fluorobiphenyls. The 1,5-difluoro- and 1,8-difluoronaphthalene were kindly loaned by Professor F. B. Mallory, Bryn Mawr College,

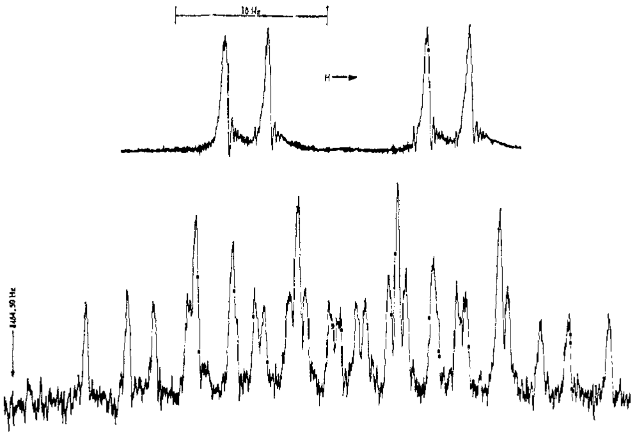


Figure 4. The digitally swept spectra of F_4 in 1,2,4-trifluorobenzene, with and without noise decoupling of protons; TMS solution; frequency marker is in hertz from C_6F_6.

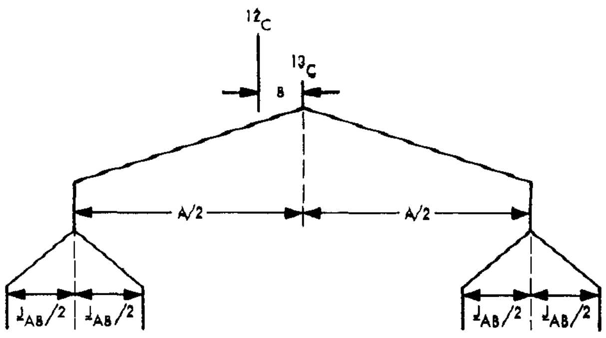


Figure 5. Figure showing the definition of the magnitudes of the quantities *A* and *B* as discussed in the text (Analysis of Spectra).

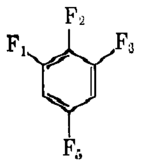
and 1-methyl 4,7-difluoro-phenanthrene was kindly loaned by Professor K. L. Servis, University of Southern California.

In those cases where satellite analyses were performed, the samples were examined as *ca.* 50% solutions. All the fluorobenzenes were initially studied in CCl_4 solution, while the less soluble biphenyls were studied in pyridine solution, and the difluoronaphthalenes were examined in acetone solution. For the studies of solvent dependence, 10% v/v solutions were used. In all cases the reference and locking compound was C_6F_6, present at 5% v/v.

Fluorine chemical shifts are considered accurate to ±0.1 Hz. Except where stated in the next section, coupling constants are considered accurate to at least ±0.05 Hz.

The results are given in Tables I–IV. The latter table also contains some of the data from our earlier work,[4] for convenience in discussion. The parameters "*A*" and "*B*" of Tables I and V are first-order approximations to $^1J_{^{13}C-F}$ and the $^{13}C-^{12}C$ isotope shifts as we shall now discuss.

Table III. Solvent Dependence of ^{19}F Spectral Parameters of 1,2,3,5-Tetrafluorobenzene



Solvent^a	$\epsilon_{30°}$^{b}	δ_1^{c}	δ_5	J_{12},^{d} Hz	J_{15}, Hz	J_{25}, Hz
Neat liquid		2924.4	4647.9	−19.80	1.69	10.99
Pentane	1.83	2937.2	4589.7	−20.00	1.52	11.15
TMS	1.88	2927.3	4576.4	−19.95	1.55	11.08
CCl_4	2.22	2896.8	4540.1	−20.36	1.64	10.94
C_6H_6	2.26	2904.0	4601.0	−21.10	1.81	10.95
C_6F_6		2928.9	4654.9	−18.97	1.67	10.93
$CFCl_3$	2.27	2915.8	4567.6	−19.90	1.60	10.90
CS_2	2.61	2916.8	4607.3	−21.08	1.70	10.95
Et_2O	4.14	2875.1	4632.5	−20.15	1.74	11.00
$CDCl_3$	4.63	2854.8	4535.3	−20.37	1.77	10.85
CH_2Cl_2	8.72	2852.3	4574.5	−20.20	1.80	10.84
Me_2CO	20.22	2887.6	4696.2	−20.16	1.95	10.97
MeCN	36.50	2858.2	4636.2	−19.94	1.94	10.81

[a–d] See Table II. J_{13} is not immediately available from the decoupled spectrum, and was not sought in the satellite spectrum. F_2 is upfield of C_6F_6 and to obtain this would require changing lock frequency, which was not done.

Analysis of Spectra

Where the proton-decoupled spectrum contains magnetically nonequivalent fluorine atoms, *e.g.*, 1,2,4-trifluorobenzene (V) the F···F coupling constants may be extracted from the spectrum of the ^{12}C species (*cf.* Figure 4). Calculation confirmed that in the case of V and 1,2,3,5-tetrafluorobenzene (VII) the spectra were sufficiently first order for the couplings to be extracted directly. The spectrum of 1,2,3,4-tetrafluorobenzene (VI) was analyzed as an AA′XX′ system.

In many of the cases studied here the proton-decoupled fluorine spectra are single lines, and the F···F couplings have to be extracted from the ^{13}C-satellite patterns. We are then concerned with an ABX analysis, where typical values of the coupling constants are $J_{AX} \approx -250$ Hz, $|J_{AB}| \approx$ 0–60 Hz, $J_{BX} \approx -20$ to $+20$ Hz, and $\delta_{AB} \approx 8$ Hz (isotope shift) for the fragment

$$\begin{array}{cc} F_A & F_B \\ | & | \\ {}^{13}C_X\cdots & C \end{array}$$

The inner ^{13}C satellites are often obscured by the intense ^{12}C band, and were in no case sought. Thus we know only the frequencies of the outermost satellites and the ^{12}C band. From these satellites $|J_{AB}|$ may be extracted immediately. No information on the sign of this coupling is presently available, except where obtained by other methods, but this will not affect the rest of the present discussion. It is not possible to find J_{AX} or the isotope shift, δ_{AB}, unless J_{BX} is also known. The latter is contained in the innermost satellites and is not available from the present work. In certain cases, ^{13}C spectroscopy has been used[9] to obtain accurate values of $|J_{AX}|$ and $|J_{BX}|$ for compounds we have studied by ^{19}F nmr. Even where no such data are available, it is often possible to estimate $|J_{BX}|$ to sufficient accuracy from these ^{13}C data.[9]

In an attempt to obtain at least approximately correct values for J_{AX} and δ_{AB} from our data, we have performed a series of calculations using the program LAOCN3[18] on the ABX systems for ranges of values of J_{AB} and $|J_{BX}|$. We define quantities "*A*" and "*B*" as the "first-order" approximations to J_{AX} and δ_{AB}, respectively (see Figure 5). Knowing J_{AB} and having either an experimental value or an estimate for J_{BX}, the appropriate corrections to "*A*" and "*B*" as shown in Table V may be applied to yield accurate values of J_{AX} and δ_{AB}. Note that these corrections are totally independent of the sign of J_{AB}, and are insensitive to δ_{AB}, provided that the latter is approximately 6–10 Hz. Since directly bonded isotope shifts are always close to 8 Hz for C–F bonds, and nonbonded shifts are undoubtedly an order of magnitude smaller than this, the latter restriction is not a severe one.

At this stage we note that the analyses of the ^{13}C spectra of difluoroaromatics are also somewhat approximate.[9] The spectrum of any ^{13}C species is the X region of an ABX system. Extraction of J_{AX}, J_{BX}, and J_{AB} from the frequencies alone of this X region may not always be feasible.[9] However, it has been shown that quite accurate values of these parameters may often be obtained either using the relative intensities, or provided a value of δ_{AB} is assumed.[9]

Consideration of Table V enables the following conclusions to be made. (1) Where there is only one F atom in the molecule, *e.g.*, fluorobenzene (I), or else $|J_{FF}|$ is negligible, *e.g.*, 3,3′-difluorobiphenyl (XIV) or 4,4′-difluorobiphenyl (XV), the values of *A* and *B* are equal to the values of $^1J_{^{13}C-F}$ and δ_{AB}, respectively. (2) Where $|J_{FF}|$ is no greater than 20 Hz and J_{BX} lies within the range −20 to +20 Hz, then the error in δ_{AB} is less

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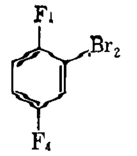
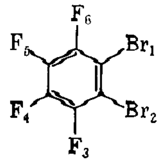
(18) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

Table IV. Solvent Dependence of ^{19}F Spectral Parameters of 1,4-Difluoro-2-bromobenzene and 1,2-Dibromotetrafluorobenzene[a]

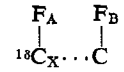




Solvent[b]	$\epsilon_{30°}$[c]	δ_4[d]	J_{14},[e] Hz	δ_4[f]	J_{34}, Hz	J_{35}, Hz	J_{36}, Hz	J_{45}, Hz
Pentane	1.83	4280.0	15.31	486.06	−21.05	2.80	8.30	−19.22
TMS	1.88	4272.5	15.35	486.52	−21.24	2.77	8.33	−19.34
CCl_4	2.22	4230.0	15.25	481.74	−21.53	2.80	8.18	−19.63
C_6H_6	2.26	4309.5	15.53	499.29	−22.34	2.98	7.92	−20.46
$CFCl_3$	2.27	4271.2	15.34	486.49	−21.00	2.85	8.26	−19.09
CS_2	2.61	4333.5	15.46	490.86	−22.30	2.73	8.21	−20.41
Et_2O	4.14	4305.5	15.48	481.27	−21.44	2.78	8.27	−19.41
$CDCl_3$	4.63	4213.4	15.28	485.10	−21.72	2.83	8.00	−19.75
CH_2Cl_2	8.72	4238.5	15.40	486.36	−21.70	2.85	8.02	−19.75
Me_2CO	20.22	4362.0	15.68	499.51	−21.46	3.03	8.05	−19.51
MeCN	36.50	4319.5	15.60	497.42	−21.27	3.02	7.87	−19.17

[a] Results from our previous study.[4] [b] See footnote *a*, Table II. [c] See footnote *b*, Table II. [d] See footnote *c*, Table II. See footnote *d*, Table II. [f] Chemical shift in hertz downfield from C_6F_6 at 56.4 MHz.[4]

Table V. Corrections To Be Applied to "*A*" and "*B*"[a] To Yield Accurate Values of J_{AX} and δ_{AB}, Respectively



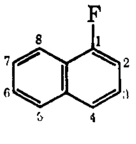
$\overset{F_A}{{}^{13}C_X}\cdots\overset{F_B}{C}$

$J_{AX} \approx -245$ Hz
$\delta_{AB} \approx 8$ Hz

$\lvert J_{AB}\rvert$, Hz	J_{BX}, Hz	Value to be subtracted from "*A*" to yield $\lvert {}^1J_{^{13}C-F}\rvert$, Hz	Value to be *added* to "*B*" to yield δ_{AR}, Hz
0	−20	0.000	0.000
	0	0.000	0.000
	+20	0.000	0.000
5	−20	0.112	0.004
	0	0.103	0.003
	+20	0.094	0.003
20	−20	1.772	0.062
	0	1.629	0.050
	+20	1.506	0.045
50	−20	10.655	0.346
	0	9.845	0.298
	+20	9.148	0.277
60	−20	15.056	0.472
	0	13.950	0.409
	+20	12.990	0.357

[a] See text and Figure 5.

than the experimental error (±0.1 Hz). The error in ${}^1J_{^{13}C-F}$ is only slightly sensitive to J_{BX}, and is known to within ±0.1 Hz, provided the latter is less than |20| Hz. (3) In the sole case studied here where $\lvert J_{FF}\rvert$ is larger than this, *viz.*, molecule X (58.8 Hz), then corrections need to be applied to both *A* and *B*, and the correction in the former case requires a quite accurate value of J_{BX}. We may estimate the latter as being approximately equal to the corresponding C_8–F coupling in 1-fluoronaphthalene, which has been found[9] to be |5.1| Hz.



The corrections to *A* and *B* are found to be 13.4 ± 0.3 Hz, and 0.4 Hz, respectively, with the error in *A* being caused by the sign ambiguity in ${}^4J_{F-F}$. Further discussion of each individual spectrum is given below.

Discussion

Where values of the ^{19}F spectral parameters are already available for the compounds we have investigated, there is in general excellent agreement with the present work. Unfortunately, only a few of the chemical shifts are referenced to C_6F_6, and because use of other fluorine references can produce chemical-shift differences of more than 1 ppm,[19] it is not practical to discuss in detail the chemical shifts other than for those cases where C_6F_6 has been used as the reference.

Values of the isotope shifts[20] fall in the range 7.9–8.3 Hz. Few accurate data are available for comparison, except a value of 7.78 Hz for *p*-difluorobenzene,[21] which is in good agreement with the present work (7.9 Hz). No trends in the values of the isotope shifts with substitution are apparent from the limited data at hand. The values of ${}^1J_{^{13}C-F}$ lie in the range 241.8–254.6 Hz. The highest value, *viz.*, 254.6 ± 0.3 Hz calculated for 1,8-difluoronaphthalene (X) is some 4 Hz larger than any other value, while the values in 1,5-difluoronaphthalene (250.3 Hz), 1-fluoronaphthalene (250.7 Hz, in good agreement with the ^{13}C value[9] of 251.1 Hz), and 2-fluoronaphthalene (244.7 Hz) have been found to be rather smaller. Although the rather larger value in X has had to be corrected for second-order effects by a procedure described above, it seems that the difference between this and the other naphthalenes may be significant. Possibly this is connected with slight molecular distortions[22] occasioned by the juxtaposition of the two peri F atoms. Further specific comments on the values of ${}^1J_{^{13}C-F}$ will be made as we discuss the individual analyses. In general, the agreement with the values obtained from the proton-decoupled ^{13}C spectra is satisfactory (±1 Hz). It is also

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(19) J. W. Emsley and L. Phillips, *Mol. Phys.*, 11, 437 (1966).

(20) For a recent review see H. Batiz-Hernandez and R. A. Bernheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 63 (1967).

(21) J. E. Loemker, J. M. Read, and J. H. Goldstein, *J. Mol. Spectrosc.*, 29, 284 (1969).

(22) *Cf.* the Discussion for the effect of strain-induced molecular distortions in the case of ortho proton–proton couplings in M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 91, 6325 (1969).

pleasing that the same order of the magnitudes of $^1J_{C-F}|$ found in the difluorobenzenes,[9] *viz.*, $^1J_{ortho} > {}^1J_{meta} > {}^1J_{para}$ has been found by us. We also note here that, while linear correlations between $^1J_{^{13}C-F}$ and the isotope shift have been noted[20] in a number of systems, no such correlations are found in the present case. It may be that the correlations are not accurate over small ranges of the parameters On the other hand, it is known that both $^1J_{^{13}C-F}$ and isotope shifts may be solvent dependent,[20] and therefore the present results, obtained in *ca.* 50% solutions, may perhaps not be compared without ambiguity, even for a common solvent. In spite of these limitations, it is seen that the value of $^1J_{^{13}C-F}$ in the polar acetone is generally *ca.* 1 Hz smaller than in nonpolar CCl_4.

We now consider individually the couplings $^1J_{^{13}C-F}$ and J_{FF}, and ^{19}F chemical shifts found in the fluorobenzenes.

Fluorobenzene. Previous values for $J_{^{13}C-F}$ of 265 ± 2 and 252 ± 2 Hz have been given.[23,24] These were from the proton-coupled spectra, and therefore are only expected to be approximate in the absence of a full analysis. In excellent agreement with present work, the ^{13}C spectrum[9] yields a value of 245.3 Hz.

o-**Difluorobenzene**. The chemical shift of 2305.8 Hz downfield from C_6F_6 in TMS solution compares very closely with the only other value of the shift recorded[25] relative to C_6F_6, *viz.*, 2329.5 Hz, also in this solvent. These authors found $^3J_{FF} = -20.43$ Hz, which is in good agreement with the present value of (−) 20.5 Hz. Our value for CCl_4 solution of (−) 20.9 Hz is similarly in good agreement with a value[26] of −21.16 Hz for this solvent. This confirms our previous suggestion[4] that the cause of the discrepancy in these values arises from the solvent dependence of $^3J_{FF}$. A value of |19.0| Hz was found by Weigert for this coupling. A value of 254 ± 3 Hz has been recorded for $^1J_{^{13}C-F}$,[27] again without a complete analysis. Analysis of the proton-decoupled ^{13}C spectrum[9] gives $^1J_{^{13}C-F} = 248.8$ Hz, in good agreement with the present work (248.0 Hz after correction for second-order effects).

m-**Difluorobenzene**. The value of $^1J_{^{13}C-F}$ has been given[27] as 250.8 Hz, but in the absence of a complete analysis this is probably only a rough approximation (±5 Hz). The value from the ^{13}C analysis[9] is 245.4 Hz, which is somewhat smaller[17] than we find (247.0 Hz, with only a small correction for second-order effects required). This difference may arise from solvent effects.

The value of $^4J_{FF}$ of 6.6 Hz is in excellent agreement with that found[28] by Macdonald (6.57 Hz) from a full analysis, and serves to provide further confirmation[29] of this magnitude over that given by Mohanty[30] (3.0 Hz) from a more approximate analysis. The ^{13}C analysis[9] value of 6.6 Hz is also in excellent agreement with the present work.

p-**Difluorobenzene**. The chemical shift of ^{19}F and isotope shift in this molecule were found to be 4087.15 and 7.776 Hz by Goldstein and coworkers,[21] in close agreement with the present work. These workers also obtained $^1J_{^{13}C-F}$ and $^5J_{FF}$ as 241.07 and 17.779 Hz, respectively, as compared to the present values of 242.1 and 17.64 Hz and values from the ^{13}C analysis[9] of 242.0 and 17.5 Hz. It is not certain whether these small differences are significant or not, insofar as they may arise from the different solvents used, *viz.*, neat liquid and 50% in CCl_4.

1,2,4-Trifluorobenzene. The chemical shifts of F_1 and F_2 are very close to the values of 1827.73 and 2761.53 Hz found in a previous study[31] in CCl_4, while the value of F_4 found there, 4152.25 Hz, is substantially smaller than the value found in the present work, *viz.*, 4383.4 Hz, or indeed in any of the solvents used here. Our values for the J_{FF} are in close agreement with the recent results of Lustig, *et al.*[12] ($^3J_{FF} = -20.01$ Hz, $^4J_{FF} = 3.14$ Hz, $^5J_{FF} = 15.03$ Hz), and the only discrepancy in $^3J_{FF}$ is no doubt due to solvent dependence. While the former two values also agree with the results of Abraham, *et al.*,[31] their value of $^5J_{FF}$ is substantially lower (14.57 Hz). The reason for the discrepancy in this work in J_{14} and δ_4 is puzzling, especially in light of the excellent iterative fit obtained previously and the fact that the other parameters are in excellent agreement (±0.1 Hz) with the values of Lustig, *et al.*[12] Substitution of a value for J_{14} of 15.03 Hz in the discussion given by us[4] of the additivity of substituent constant contributions would not, however, invalidate the qualitative conclusions reached.

1,2,3,4-Tetrafluorobenzene. The proton-decoupled spectrum is an AA′XX′ analysis. Unfortunately, not all of the ten lines in each region that are necessary for a complete analysis are fully resolved, and this means that the value of *K* (which is $J_{14} + J_{23}$) is only accurate to ±0.2 Hz. Consequently, J_{14} and J_{23} are only accurate to ±0.2 Hz. Within these limitations, the present values are in good agreement with those found by Lustig, *et al.*[16] ($^4J_{FF} = 2.72$ Hz, $^5J_{FF} = 12.69$ Hz). The values of $^3J_{FF}$ are not strictly comparable because of the large solvent dependence of this coupling. However, we have noted elsewhere[4] that where there are two values of $^3J_{FF}$ in one molecule, their difference remains constant on changing solvent. Since we find $|J_{12}| = 19.72$, $|J_{23}| = 19.0$ Hz, we would expect to find a similar difference between the values in Lustig's work. However, the latter workers find $J_{12} = 19.00$ Hz, $J_{23} = -19.02$ Hz. The reason for the discrepancy is not understood.

1,2,3,5-Tetrafluorobenzene. Lustig, *et al.*,[32] have obtained values of $^3J_{FF} = -19.77$ Hz, $^4J_{FF} = 1.73$ Hz, and $^5J_{FF} = 11.02$ Hz. The latter two values are in good agreement with the present work.

The F···F coupling constant parameters in fluorobenzenes are quite well documented,[15] and need not be further discussed except for their solvent dependence which we shall treat later.

Long-Range F···F Couplings. Long-range F···F couplings in unsaturated systems are not so well understood, and we now present some results for these sys-

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[23] S. Mohanty and P. Venkateswarlu, *Mol. Phys.*, **11**, 329 (1966).

[24] T. F. Page, *ibid.*, **13**, 523 (1967).

[25] J. E. Loemker, J. H. Goldstein, and J. M. Read, *Chem. Commun.*, 744 (1968).

[26] R. J. Abraham and M. A. Cooper, *J. Chem. Soc. B*, 1094 (1968).

[27] G. Aruldhas, *Proc. Indian Acad. Sci., Sect. A*, **63**, 349 (1966).

[28] D. B. Macdonald, *Chem. Commun.*, 687 (1967).

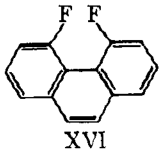
[29] J. E. Loemker, K. M. Pryse, J. M. Read, and J. H. Goldstein, *Can. J. Chem.*, **47**, 209 (1969).

[30] S. Mohanty, *Mol. Phys.*, **13**, 83 (1967).

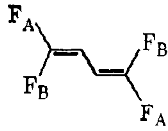
[31] R. J. Abraham, M. A. Cooper, and D. B. Macdonald, *Chem. Commun.*, 1285 (1968).

[32] E. Lustig and P. Diehl, *J. Chem. Phys.*, **44**, 2974 (1966).

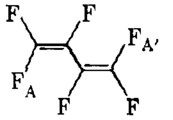
tems. It has been found that F···F couplings over four and five bonds cover an extraordinarily large range. For example, in 4,5-difluorophenanthrenes (XVI) $^{5}J_{FF}$ is found[5a] to be |170| Hz, whereas in planar systems where the fluorines are well separated, *e.g.*, XVII, the value of $^{5}J_{FF}$ may reach[33] 37 Hz, and in nonplanar dienes, *e.g.*, XVIII, a value as large as 11.3 Hz has been found.[6] However, few examples are available for all the bond orientations in these unsaturated systems, and little is known of the magnitudes of couplings over more than five bonds in unsaturated systems.



XVI



XVII, $J_{AA'}$ or $J_{BB'}$ = 37 Hz



XVIII, $J_{AA'}$ = 11.3 Hz

As part of a continuing study of long-range F···F couplings, we have examined the spectra of some additional molecules and these results will now be discussed. These values would be much more difficult to extract by full analyses and the use of noise decoupling of the protons greatly facilitates such studies.

The biphenyls XIII–XV present examples where the fluorine atoms are separated by five, seven, and nine bonds, respectively. It is known from other work that the phenyl rings are not planar in solution.[34] This would be expected to attenuate any coupling *via* the π-electron system. Only in the case of XIII is any significant coupling obtained, and here the value is |18.2| Hz. (A value of 16.5 Hz was given by Servis[5a] for this molecule, from an approximate analysis of the ^{13}C satellites.) In XIV and XV the line width of the ^{13}C satellites ($\lesssim$0.5 Hz) shows that $^{7}J_{FF}$ and $^{9}J_{FF}$ must be $\lesssim$0.2 Hz. As pointed out by Servis,[5a] the values of $^{5}J_{FF}$ in XVI and XIII make an interesting contrast.

Recently, we and other workers have reported[6,7] the large value of $^{4}J_{FF}$ between fluorines substituted at the 1 and 8 position in the naphthalene system. The values obtained range from 59 to 69 Hz in naphthalenes,[7] but are rather smaller than this (*ca.* 30 Hz) when the 4 and 5 positions are bridged.[7] The value of |58.8| Hz reported here for X is believed to be the first recorded in a naphthalene that is not heavily substituted with other fluorine atoms. We have previously noted the rather large value of $^{1}J_{^{13}C-F}$ in this molecule. The value of J_{15} = |4.1| Hz in XI compares with a value of 4.7 Hz found by the ^{13}C analysis.[9] The present value of $^{1}J_{^{13}C-F}$ of 250.3 Hz is also close to the value[9] of 251 Hz found before.

Finally, we have obtained a value of |0.8| Hz for the seven-bond coupling in XII. We know of no other example of $^{7}J_{FF}$ in an unsaturated molecule with which to compare this value.

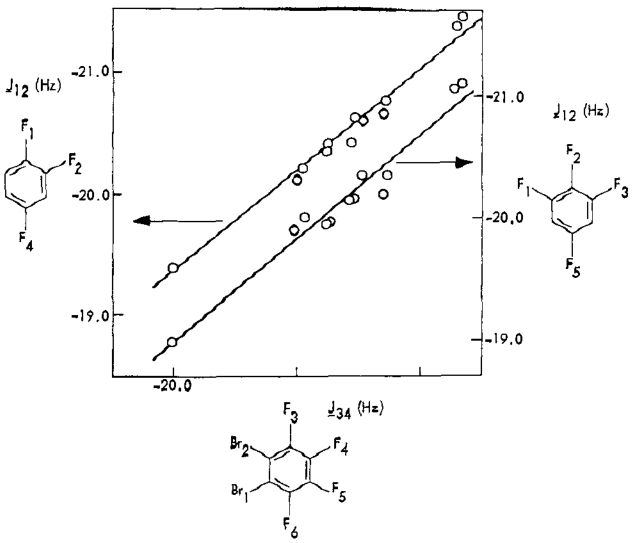


Figure 6. Correlation of J_{12} in 1,2,4-trifluorobenzene and 1,2,3,5-tetrafluorobenzene with J_{34} in 1,2-dibromotetrafluorobenzene for a range of solvents.

Solvent Dependence of Coupling Constants. In our earlier work,[4] it was shown that $^{3}J_{FF}$ in 1,2-dibromotetrafluorobenzene (IX) and also in bromo- and iodopentafluorobenzene exhibits a large solvent dependence (−22.34 to −19.99 Hz for J_{31} in IX). No simple correlation with solvent dielectric constant could be detected. The variations in $^{4}J_{FF}$ and $^{5}J_{FF}$ were much smaller ($\lesssim$0.4 Hz), but here again the correlation with dielectric constant was not particularly good. Because the C–Br and C–F bond dipole moments are very similar (1.70 and 1.52 D in bromobenzene and fluorobenzene, respectively),[35] these mono- and dihaloperfluorobenzenes will have only small resultant dipole moments. Therefore, any solvent dependence of coupling constants arising from a "reaction-field" mechanism[36–38] may well be small. For example, in their study of ^{19}F chemical shifts in some fluorobenzene derivatives,[19] Emsley and Phillips showed that for polar molecules ($\mu \gtrsim$ 1 D) the solvent dependence was well accounted for by a "reaction field" theory. We are not totally in sympathy with this interpretation and we shall discuss below some of our reservations on this point. For nonpolar molecules, *e.g.*, chloropentafluorobenzene, no such solvent dependences were apparent, however. In view of these results, therefore, part of our aim in the present work was to examine the F···F coupling constants and ^{19}F chemical shifts of some polar fluorobenzenes to see whether any solvent dependence arising from the "reaction field" could be clearly singled out. For this purpose, the molecules 1,2,4-trifluorobenzene (V), 1,2,3,5-tetrafluorobenzene (VII), and 1,4-difluoro-2-bromobenzenes (VIII) were examined in ten different solvents. These results, together with those from our previous work on 1,2-dibromotetrafluorobenzene (IX), are shown in Tables I–IV. We now consider the behavior of each type of coupling constant in turn.

$^{3}J_{FF}$. The behavior of $^{3}J_{FF}$ in the polar molecules V and VII parallels that in the much less polar molecule as shown in Figure 6. Because similar behavior is

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[33] K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 1339 (1965).

[34] R. E. Mayo and J. H. Goldstein, *Mol. Phys.*, 10, 301 (1966).

[35] See A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

[36] For a recent review, see P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 231 (1967).

[37] L. Onsager, *J. Amer. Chem. Soc.*, 58, 1486 (1936).

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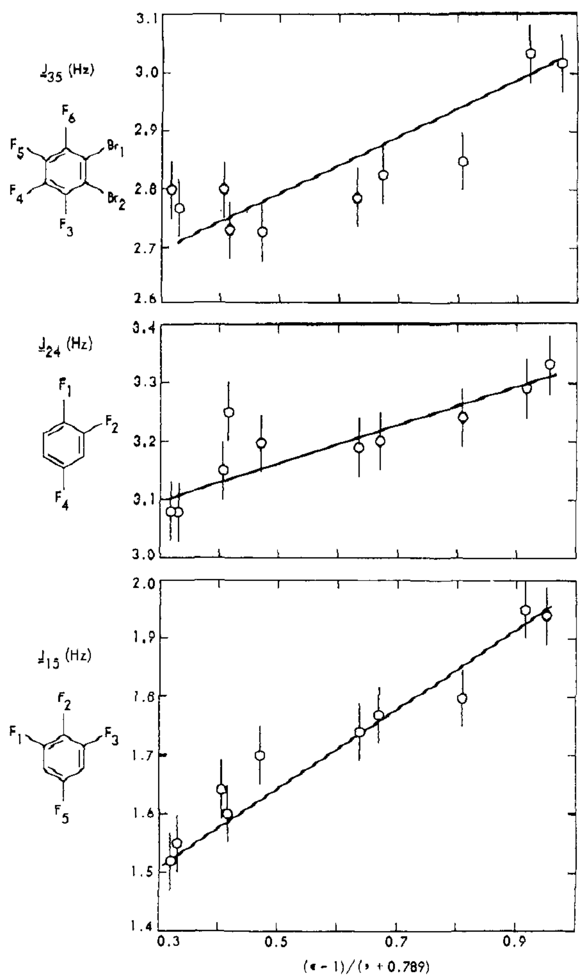
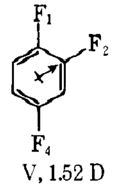


Figure 7. Correlation of $^4J_{FF}$ in 1,2,3,5-tetrafluorobenzene, 1,2,4-trifluorobenzene, and 1,2-dibromotetrafluorobenzene with the "reaction field" expression of Emsley and Phillips.[19] Error bars are ±0.05 Hz.

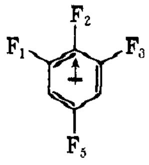
found in both polar and nonpolar molecules and there is no correlation with solvent dielectric constant, these results imply that the "reaction field" mechanism is unimportant for $^3J_{FF}$, as we concluded earlier.[4] A fuller discussion of the possible source of the observed changes has been given elsewhere.[4]

$^4J_{FF}$. In each of the three molecules investigated, it is seen that when "anomalous" solvents (*i.e.*, those known[36,39] to behave contrary to the expectations of the "reaction field" theory) are ignored, $^4J_{FF}$ exhibits an increase on going from nonpolar to polar solvents. Emsley and Phillips have shown[19] that where the "reaction field" mechanism is dominant in the solvent dependence of chemical shifts (and therefore presumably also in the case of coupling constants) and the solute is similar in size to hexafluorobenzene, then a linear correlation should be obtained with the expression $(\epsilon - 1)/(\epsilon + 0.789)$, where ϵ is the solution dielectric constant. Since the dielectric constants of the solutes are unknown here, we shall take ϵ as being approximately the same as that of the pure solvent. Plots of $^4J_{FF}$ against this function of dielectric constant are shown in Figure 7, and there is a very reasonable correlation which is rather better for V and VII than for IX.

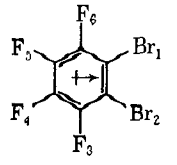
At first sight, therefore, these results suggest that the solvent dependence of $^4J_{FF}$ is dominated by the reaction field term. Some reservations on this proposal must be stated. First, it has been shown that the magnitude and orientation of the solute dipole moment may be critical in determining the sizes of "reaction field" contributions.[40,41] Assuming additivity of bond dipole moments, the net dipole moments of the solutes studied here are as shown. In spite of the great differences in



V, 1.52 D



VII, 1.52 D



IX, 0.3 D

dipole moments and their orientations, the ranges over which $^4J_{FF}$ vary are quite similar in each case, being 0.3, 0.4, and 0.3 Hz in V, VII, and IX, respectively. Second, and as we shall discuss more fully in terms of the chemical shifts, there is some evidence that there is some form of "complexing" by solvent at the hydrogen atoms in V and VII. This might be expected to have an effect on the coupling constants. The third reservation is most conveniently discussed after the behavior of $^5J_{FF}$ is outlined.

$^5J_{FF}$. The variation of this coupling constant with solvent is less than that of $^4J_{FF}$. In VII and IX, $^5J_{FF}$ decreases with increasing solvent polarity, whereas in V and VII it increases with solvent polarity. The correlation with the reaction field term is shown in Figures 8a and 8b. In these cases, there is considerably more scatter than in the case of $^4J_{FF}$. The ranges of variation are *ca.* 0.35 Hz for the polar molecules and *ca.* 0.5 Hz for the nonpolar case.

The scatter observed in the present case of $^5J_{FF}$ suggests that while there is perhaps a substantial contribution to the solvent dependence from a reaction field mechanism, there must also be other mechanisms operating. There is evidence[15] that both $^5J_{FF}$ and $^4J_{FF}$ result from major contributions to the coupling, transmitted *via* the π-electron system. Therefore, we might expect that a component of the solvent dependence should be linked to changes in the π-electron system. This is one reason why we are inclined to view the good correlation of $^4J_{FF}$ with dielectric constant with some suspicion, since the correlation for $^5J_{FF}$ is much poorer. We stress that we do not deny that the reaction field mechanism may well be important or even predominant in causing the solvent dependence of $^4J_{FF}$ and $^5J_{FF}$. In the absence of reliable estimates of other contributions to these couplings, however, and in view of the anomalous results for $^3J_{FF}$ and the chemical shifts (*vide infra*), we think it unwise at the present time to attribute all of the observed variations to one mechanism.

Solvent Dependence of Chemical Shifts. The most extensive investigation of the solvent dependence of ^{19}F chemical shifts in aromatic molecules is that of Emsley and Phillips.[19] These workers gave a detailed discussion of the factors influencing the choice of a reference compound. They concluded that for polyfluoro-

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(40) S. L. Smith and R. H. Cox, *J. Chem. Phys.*, 45, 2848 (1966).

(41) S. L. Smith and A. M. Ihrig, *ibid.*, 46, 1181 (1967).

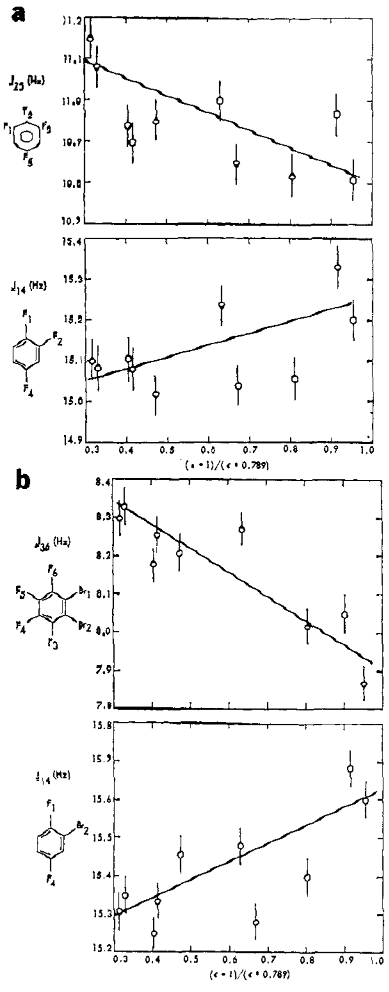

Figure 8. Attempted correlation of $^5J_{FF}$ in (a) 1,2,4-trifluorobenzene and 1,2,3,5-tetrafluorobenzene and (b) 1,4-difluoro-2-bromobenzene and 1,2-dibromotetrafluorobenzene with the reaction field term of Emsley and Phillips.[19] Error bars are ±0.05 Hz.

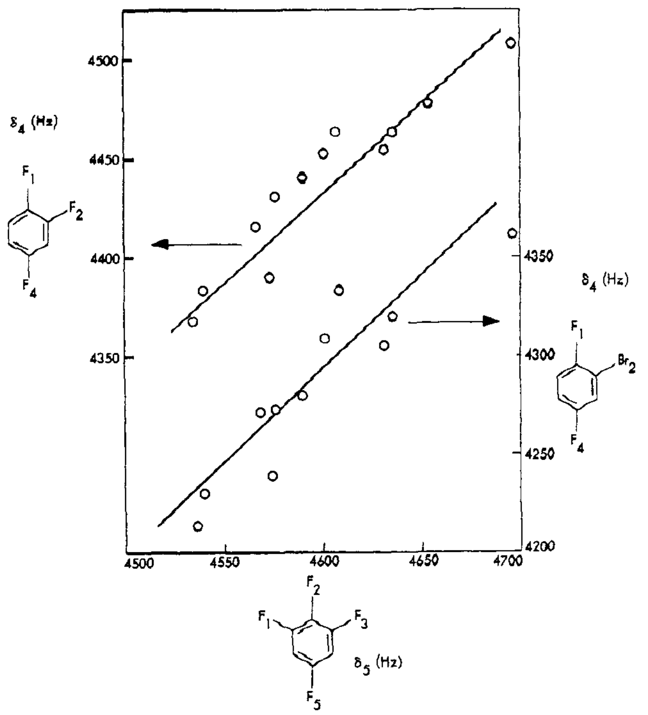

Figure 9. Correlation of the chemical shifts of F_4 in 1,2,4-trifluoro- and 1,4-difluoro-2-bromobenzene with the chemical shifts of F_5 in 1,2,3,5-tetrafluorobenzene. Shifts are downfield from C_6F_6, in hertz at 94.1 MHz.

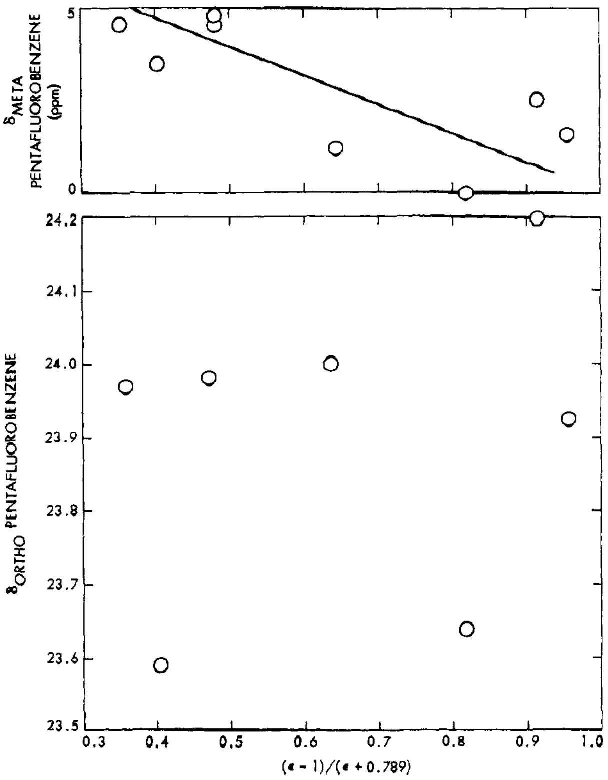

Figure 10. The correlation of the chemical shifts of the *o*- and *m*-fluorines in pentafluorobenzene with the reaction field term of Emsley and Phillips.[19] Data of ref 19.

benzenes the reference hexafluorobenzene best matched up to the requirements of nonpolarity and similarity of size and shape. Hence, this reference was also used in the present work. Those same workers also showed that there was a good correlation between the shifts and the "reaction field" expression $(\epsilon - 1)/(\epsilon + 0.789)$ for a number of polar fluorobenzenes, but that for nonpolar molecules there was no correlation, and the total change in the shift was small. In the present case, it is similarly found that for the nonpolar IX the change in shift is small, only *ca.* 13 Hz at 56.4 MHz, and there is no dependence on dielectric constants. More surprisingly, there is also no correlation for the polar molecules studied here, even though the range of the chemical shift variation is much larger—*ca.* 150 Hz at 94.1 MHz. This is so even when "anomalous" solvents such as benzene are ignored. At the same time, there is consistency in the behavior of similarly situated fluorine atoms in the polar molecules. For example, consider the chemical shifts of F_4 in V and IX, and F_5 in VII (see Figure 9).

There is therefore a direct contradiction between the generally expressed conclusions[19] of Emsley and Phillips that the shifts referenced to C_6F_6 may be correlated with a "reaction field" expression, and the results of the present work. We suggest that the following provides a partial explanation. In the great majority of the molecules studied by the previous workers, fully substituted benzenes or pyridines were considered. In the one case where an H atom is present, pentafluorobenzene, there is a very poor correlation between the "reaction field" expression and the shift of the *o*-fluorines (see Figure 10), while the correlation is much better for the *m*- and *p*-fluorines. Now in the tri- and tetrasubstituted benzenes studied by us, all the fluorines whose shifts have been measured are adjacent to at least one proton. It may be that there is sufficient "complexing" of the solvent around the relatively electron-deficient protons in these molecules to produce large van der Waals shifts which "swamp" the "reaction field" contribution to the shifts. It must also be noted that in some meta- and para-substituted fluorobenzenes[19,42] good agreement with the reaction field term is found, even though there are four "free" proton positions. In this case, however, the reference was monofluorobenzene, so perhaps the effects of "complexing" at the protons are thereby effectively eliminated. This would not be the case for the fully fluorinated C_6F_6.

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Recoil Tritium Reactions with Cyclohexene Including the Pressure Dependence of the Unimolecular Decomposition[1,2]

R. W. Weeks, Jr.,*[3a] and J. K. Garland[3b]

Contribution from the Departments of Chemistry, University of Missouri, Columbia, Missouri 65201, and Washington State University, Pullman, Washington 99163, and the Research Department, American Oil Company, Naperville, Illinois 60540. *Received July 6, 1970*

Abstract: The reaction of recoil tritium with cyclohexene was studied in the liquid phase and at pressures from 9 to 1400 Torr in the gas phase. Products observed in the work were HT, ethene-*t*, 1,3-butadiene-*t*, *n*-hexenes-*t*, methylcyclohexane-*t*, propene-*t*, cyclohexane-*t*, cyclohexene-*t*, and tritiated polymers. Comparison of the recoil tritium–cyclohexene system with known parameters from earlier kinetic studies of the unimolecular decomposition of cyclohexene to ethene plus 1,3-butadiene shows an average excitation energy of 5 eV/molecule for the gas-phase species undergoing this decomposition and 8–12 eV/molecule for the same decomposition in the liquid phase. The observed ratio of cyclohexane-*t*/*n*-hexene-*t* led to an average rate constant of 1.0×10^8 sec^{-1} for decomposition of cyclohexyl-*t* radicals in this system.

Butler and Kistiakowsky[4] have shown the equivalence of different ground electronic state vibrational excitation modes in determining the fate of unimolecular decompositions which proceed by way of an internally equilibrated intermediate. Also similar products have been observed in pyrolysis,[5] shock-tube,[6] and photochemical studies of cyclohexene[7] decomposition. The present work extends these studies to the use of recoil tritium as an excitation source to study the pressure dependence of the unimolecular decomposition of cyclohexene. In this system, the initial locus of excitation is that C–T bond at which tritium has undergone direct substitution for H on the cyclohexene molecule.

Experimental Section

In this work it was necessary to study the cyclohexene decomposition reaction over a wide range of pressures. Samples with vapor pressures above the cyclohexene room-temperature vapor pressure were prepared with the sample ampoule temperature in the range 25–135°. This was done using a specially constructed vacuum system within an oven as was previously described.[8] The oven temperature was the parameter varied to reach the desired cyclohexene vapor pressure. The samples in which the cyclohexene pressure was below 7.0 cm were filled by sequential addition of ^{3}He, moderator gases, and cyclohexene on a vacuum line. LiF (natural abundance ^{6}Li, Riedel-de-Haen, West Germany) was used as the tritium source for liquid-phase studies. Pyrex 1720 sample ampoules were used for both gas and liquid phase studies. All ampoules were "flamed out" *in vacuo* before use.

Neutron irradiations of samples were performed at the Missouri University Research Reactor. The nominal flux was 1.4×10^{12} n cm^{-2} sec^{-1} and irradiations were typically 3–5 min. The γ intensity was $4.2 \pm 0.4 \times 10^7$ rads/hr. When irradiating at a lower flux, the irradiation time was longer so that a similar integral flux was seen by all samples. The external γ radiation and the internal radiation due to the recoil tritium and recoil proton gave radiation damage less than 1%.[8]

The sample holder for the irradiations was an aluminum vessel which contained an aluminum block with bored holes to hold the ampoules. For the samples in which the cyclohexene vapor pressure exceeded 7.0 cm, the sample ampoules were placed in the block holes and heated to the temperature necessary to avoid any condensation before or during irradiation. The block and samples were then placed in the irradiation vessel and its lid was fastened using a polyethylene O-ring to ensure that the vessel was water tight during irradiation. Since the rate of cooling with respect to time was known, it was possible to determine an average temperature and pressure which existed during irradiation.

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[1] Presented in part before the 158th National Meeting of the American Chemical Society, New York, N. Y., 1969.

[2] A portion of the material was submitted by R. W. W. in partial fulfillment of the requirements for the Ph.D. degree, University of Missouri.

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[8] R. W. Weeks, Jr., Ph.D. Thesis, University of Missouri at Columbia, 1969.