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THE NMR SPECTRA OF 1,2,3,4-TETRAFLUORO-DIBENZOFURAN AND SOME OF ITS DERIVATIVES[1]

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Abstract—The ^{1}H–^{19}F and ^{19}F–^{19}F coupling constants determined from analysis of the ^{1}H and ^{19}F spectra of the derivatives of tetrafluoro-dibenzofuran, obtained by nucleophilic substitution of the parent compound, were contradictory and thus the position of substitution was ambiguous. The spectrum of the 1,2,4-trifluoro-dibenzofuran, prepared by unambiguous synthesis, is discussed in detail and the presence of very large *para* FF coupling is revealed; the spectra of the derivatives are then consistent with substitution having occurred in the 3-position

INTRODUCTION

THE magnitude of the fluorine-fluorine and proton-fluorine coupling constants, in aromatic systems, has been established as being in the order *ortho* > *meta* > *para* for HF coupling and *ortho* > *para* > *meta* for FF coupling. Thus it is usually possible to establish the presence of *ortho* fluorine atoms from the magnitude of the *ortho* F-F coupling which is in the range of 18–22 c/s.[2,3] The magnitude of *para* FF coupling is smaller, and a range of 0–15 c/s has been suggested[2] but more usually this coupling is 5–8 c/s.[3] Similarly the application of ^{1}H resonance spectra, based upon the methoxy and thiomethyl to *ortho* fluorine coupling in substituted fluoroaromatics, has been established.[4] Thus, based upon the ^{1}H and ^{19}F spectra, it should be possible to establish unequivocally the position of the thiomethyl substituent in the product (I) obtained from reaction (1).

^{1}H *and* ^{19}F *spectral features of* I

The thiomethyl resonance at 7·44 τ is a triplet with J_{SMe-F} being 0·7 c/s; the presence of the triplet structure shows that there are two fluorine atoms *ortho* to the thiomethyl group which must be in either the 2- or 3-position (II and III respectively). The ^{19}F spectrum shows three signals at 133·5, 138·2 and 147·8 ϕ^* and analysis of these separate signals affords two large couplings of 18·4 and 22·4 c/s, and, apart from the F–SMe coupling, one additional small coupling of 1·4 c/s. The larger coupling constants being in the range expected for *ortho* F-F couplings implies that the structure of I must have a 2,3,4 or 1,2,3-trifluoro-structure (IV and V respectively)—this conclusion is in obvious conflict with that deduced from the S–Me resonance since, in IV and V, it is not possible to have two fluorine atoms *ortho* to the thiomethyl group, similarly

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[1] P. J. N. Brown, R. Stephens, and J. C. Tatlow, *Tetrahedron* **23**, 4041 (1967).

[2] J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy* Vol. II; p. 903. Pergamon Press, London (1966).

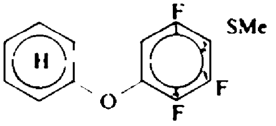
[3] I. J. Lawrenson, *J. Chem. Soc.* 1117 (1965).

[4] J. Burdon, *Tetrahedron* **21**, 1101 (1965).

neither II nor III have three adjacent fluorine atoms. It is thus clear that the NMR spectra of this compound do not permit the structure to be assigned to any of the structures II–V.

(1)

I



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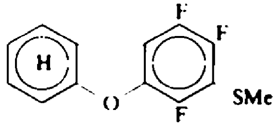

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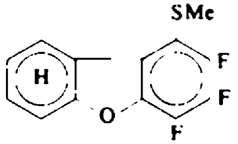

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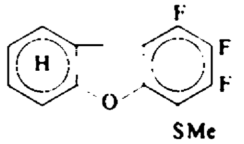
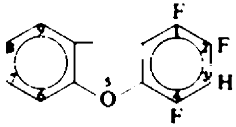


V



VI

The ^{1}H *and* ^{19}F *spectrum of the* 1,2,4-*trifluorodibenzofuran*

On account of the difficulty experienced in relating the spectrum of the thiomethyl derivative with structures II–V the 1,2,4-trifluorodibenzofuran (VI) was prepared by unambiguous synthesis from 2,3,5,6-tetrafluoro-2′-hydroxydiphenyl,[1] the structure of which was confirmed by its NMR spectra.

The proton spectrum of VI showed a low field signal equivalent to one proton at 2·05 τ from H_6, a multiplet between 2·4 and 2·7 τ from H_7, H_8 and H_9, and an eight line multiplet at 3·04 τ from H_3 (Fig. 1) giving J-values of 9·6, 10·6 and 6·3 c/s. The first two values are readily assigned, from the magnitudes, to *ortho* H-F coupling and the latter coupling constant is that of the *meta* H-F coupling. The ^{19}F spectrum of VI consisted of three sets of signals of relative intensity 1 : 1 : 1 with chemical shift values of 138·15, 143·1 and 149·0 ϕ^*. The two low field signals each consisted of four lines while the high field signal consisted of eight lines, and apart from the H-F coupling constants only two couplings of 19·4 and 20·5 c/s. can be attributed to F-F coupling both of which are of the magnitude expected for *ortho* F-F coupling constants. The ^{19}F chemical shifts of F_1, F_2 and F_4 are assigned on the following basis: the two lowest field signals are assigned to the fluorine atoms *ortho* to the hydrogen atom as, based on shielding parameters, the 2 and 6-fluorines in 2,3,4,5,6-pentafluorobenzene (VII) are deshielded by ~23·8 ppm giving the shift of the 2 and 6 fluorines in VII as

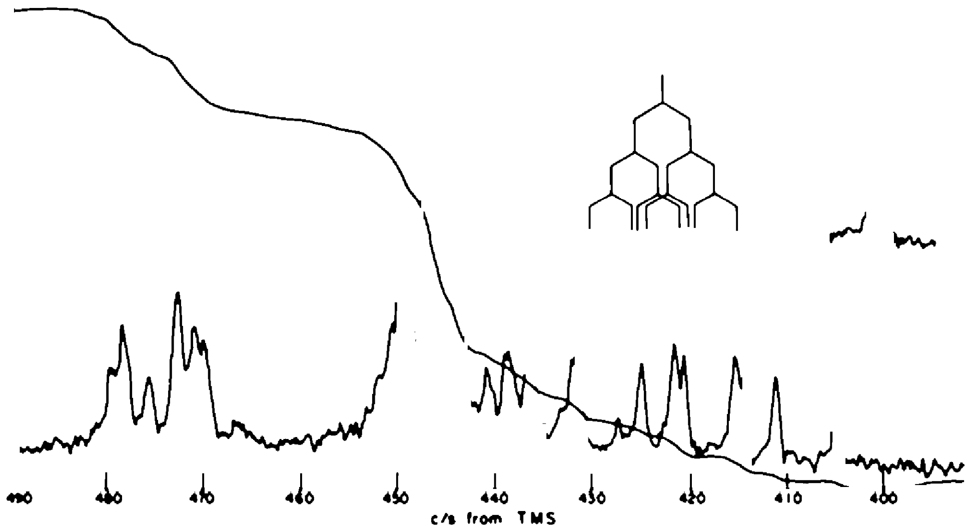


FIG. 1. ^1H Spectrum of 1,2,4-trifluoro-dibenzofuran. The coupling pattern of 3-H is shown.

139·1 ϕ^*.[3] Thus the signal at 138·15 ϕ^* in VI is assigned to F_4 and because F_2 has another fluorine in the *ortho* position it would be shielded and thus the signal at 143·1 ϕ^* is assigned to F_2 and the final signal at 149·0 ϕ^* is assigned to F_1. On this basis the coupling of 20·5 c/s is assigned to the *ortho* F_1F_2 coupling and that of 19·4 c/s is assigned to the *para* F_1F_4 coupling, a most unexpected order of magnitude for a *para* FF coupling.

The NMR spectra of the products of substitution of tetrafluoro-dibenzofuran

Having established that the *para* FF coupling in fluorinated dibenzofuran is abnormally large, it is possible to interpret the spectra of the substitution products in terms of substitution having occurred in the 3-position, this was further established chemically as described in the preceding paper[1] for reduction of the thio compound afforded the trifluoro compound which was identical to VI.

The NMR parameters of the parent tetrafluorodibenzofuran and the 3-thiol- and 3-thiomethyl-1,2,4-trifluorodibenzofurans are shown in Table 1, and it will be noted that in each instance the *para* FF coupling, i.e. J_{14}, is in the range of 15–20 c/s, which is very similar to the *ortho* FF coupling, i.e. J_{12}, of 20–23 c/s. The occurrence of abnormally large *para* FF coupling constants may be more frequently encountered than realised as similar large couplings have been observed between F_1 and F_4 of 1,2,3,4-tetrafluoronaphthalenes.[5]

The chemical shift of F_1 is fairly constant in the four compounds namely 148·3 ± 0·9 ϕ^*. The variation in the shifts of F_2 and F_4 are due to the shielding by the substituent group X. From the study[6] of a series of thioalkyl and thiophenyl penta- and tetra-fluorobenzenes the shielding parameter of the alkyl (or aryl) thio group are

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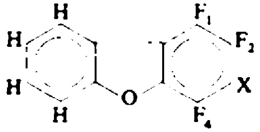
[5] P. L. Coe, Private communication.

[6] C. R. Marsh and E. F. Mooney, unpublished work.

shown in Table 2 together with the shielding parameter for hydrogen and further these shielding parameters are additive as previously demonstrated;[7] these parameters are obtained from the differences in shift of the substituted pentafluorobenzenes from that of hexafluorobenzene. Thus the calculated shifts for F_2 and F_4 on replacing F_3 by hydrogen are (161·5 − 23·8 = 137·7) and (164·6 − 23·8 = 140·8) compared with the experimental values of 138·1 and 143·05 respectively. Similarily the calculated shifts for F_2 and F_4 on substitution of F_3 by the thiomethyl group are (161·5 − 29·3 = 132·2) and (164·6 − 29·3 = 135·3) compared with the corresponding experimental values of 133·5 and 138·2. There is reasonable agreement between the calculated and experimental shifts of F_4 but the calculated values for F_2 are 2–3 ppm too low. This may be due to the variation of the electronegativity of the ether oxygen in the substituted dibenzofurans as it has been found that variation in the electronegativity has a very profound effect upon the chemical shift of the *para* fluorine, e.g. in substituted acetpentafluoroanilides $C_6F_5NHCOCXYZ$, X or Y or Z = H, Cl, Br or F the range of chemical shifts of the *ortho* fluorine vary only by 0·7 ppm while the variation in the *para* fluorine shifts is as much as five ppm.[8]

TABLE 1. NMR PARAMETERS OF 1,2,4-TRIFLUORODIBENZOFURAN DERIVATIVES



VIII

	Chemical shifts*									
X	F_4	F_2	F_1	X	J_{34}	J_{24}	J_{14}	J_{23}	J_{13}	J_{12}
F	161·5	164·6	147·4	157·9	19·2	2·0	15·3	18·5	0·0	20·2
H	138·15	143·1	149·0	3·04τ	9·6	0·0	19·4	10·6	6·3	20·5
SH	136·5	140·8	148·0	6·33τ	0·0	2·2	17·9	0·0	0·0	21·4
SMe	133·5	138·2	147·8	7·44τ	0·7†	1·4	18·4	0·7†	0·0	22·4

* All shifts are given in ϕ^* values unless otherwise shown.
† J_{23} and J_{34} refer to the F–SMe coupling.

TABLE 2. SHIELDING PARAMETERS FOR THIOALKYL, HYDROGEN AND TRIFLUOROMETHYL SUBSTITUENTS IN FLUOROAROMATICS

	−SR	H	CF_3
ortho	−29·3	−23·8	−22·9
meta	−0·2	−0·3	−2·9
para	−8·1	−8·9	−15·0

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[7] J. Homer and L. F. Thomas, *J. Chem. Soc.* B, 141 (1966).

[8] E. F. Mooney, unpublished results.

NMR spectra of fluorinated diphenyls

Related to this work is the spectroscopic investigation of the precursors to the formation of the dibenzofurans, namely the 2'-hydroxy- and 2'-methoxy-2,3,4,5,6-penta- and 2,3,5,6-tetrafluorodiphenyls. The chemical shifts of the relevant compounds are shown in Table 3.

In the case of the 2'-methoxydiphenyls the calculated shifts, using the shielding parameters given in Table 2, are shown below:

	Calculated shifts for δ_{35}	Calculated shifts for δ_{26}
X = H	163·95 − 23·8 = 140·15	140·65 − 0·3 = 140·35
X = CF_3	163·95 − 22·9 = 141·05	140·65 − 2·9 = 137·75

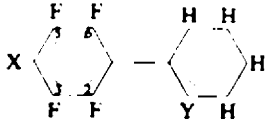
and similarly the calculated shifts for the 2'-hydroxydiphenyl are:

	δ_{35}	δ_{26}
X = H	164·4 − 23·8 = 140·6	140·55 − 0·3 = 140·25

There is fair agreement between the calculated and experimental shift values.

The shielding parameters of the 2-hydroxyphenyl, the 2-methoxyphenyl and 2-bromomethylphenyl groups are shown in Table 4. Again it will be noticed that there is considerable variation in the shielding parameter of the *para*-fluorine atom.

TABLE 3. CHEMICAL SHIFT DATA OF FLUORODIPHENYLS



IX

		Shifts*			
X	Y	δ_{26}	δ_{35}	δ_X	δ_Y
F	OMe	140·65	163·95	156·9	6·21 τ
F	OH	140·55	164·4	157·95	4·81 τ
H	OMe	141·3	141·3	~3·3 τ	6·21 τ
H	OH	139·5	140·8	~3·3 τ	4·81 τ
CF_3	OMe	139·8	143·0	57·0	6·18 τ
F	CH_2Br	139·65	161·6	154·1	5·77 τ

* Shifts in φ* values unless indicated.

TABLE 4. SHIELDING PARAMETERS OF 2-HYDROXY,-METHOXY AND -BROMOMETHYL-PHENYL GROUPS

	−OH	−OMe	$-CH_2Br$
ortho	−22·35	−22·25	−23·25
meta	+1·5	+1·05	−1·3
para	−6·95	−6·0	−8·8

EXPERIMENTAL

The ^1H and ^{19}F spectra were recorded on a Perkin-Elmer spectrometer operating at 60·0 and 56·4Mc/s respectively. The resonance line positions were determined with precision using the calibrated decade-shift facility. The analyses of the spectra were checked using K-code NMR programmes on the University KDF-9 computer.

The spectra of the diphenyls and the dibenzofurans were recorded in CCl_4 soln, except for the furan VIII, X = SH for which chloroform-d was used. TMS (1 %) and fluorotrichloromethane (5 %) were added as internal reference standards for the ^1H and ^{19}F shifts which are given in τ and ϕ^* values.

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