196. *High-resolution Fluorine Magnetic Resonance Spectra of Some Pentafluorophenyl Derivatives.*

By I. J. LAWRENSON.

The high-resolution nuclear magnetic resonance spectra of ten compounds of the type C_6F_5X have been recorded, and the values of the chemical shifts and spin-coupling constants obtained. The chemical shifts of the fluorine nuclei *meta* and *para* to the substituent X have been related to the reactivity parameters of the substituent, and factors responsible for the values of the chemical shift of the fluorine nuclei *ortho* to the substituent are discussed.

SOME details of the nuclear magnetic resonance spectra of certain fully fluorinated aromatic compounds of the type C_6F_5X where X is a halogen, a methyl group, a methoxy-group, or a group containing a metal atom, have recently been reported,[1] following the synthesis of these compounds.[2]

Fluorine chemical shifts have been measured for many substituted monofluorobenzenes,[3-5] and the values correlated with the inductive and resonance reactivity parameters of the substituents.[4,5] In such molecules the chemical shifts of the fluorine nuclei have proved to be a sensitive measure of changes in π-electron charge density in the aromatic ring. In an extension of studies of this type, measurements have now been made of chemical shifts and spin-coupling constants for the molecules C_6F_5X, where X is F, H, CH_3, CF_3, Cl, Br, I, OCH_3, CN, or NH_2.

For every compound examined except pentafluoroanisole, the bands due to the fluorines *ortho*, *meta*, and *para* to the substituent X were well separated, so that a simple analysis of the spectrum could be made; in each of these spectra, the band due to the *para* fluorine was easily recognisable, because its intensity was half that of each of the other bands. The band due to the *para* fluorine consisted of a triplet of triplets, as was to be expected from spin coupling with two pairs of fluorine nuclei. The larger splitting must be due to the pair of fluorine nuclei *meta* to the substituent, and the smaller to the pair *ortho* to the substituent, because the coupling between two fluorine nuclei *ortho* to each other is much greater than that between two fluorine nuclei *meta* to each other.[6,7] Each of the other bands yielded one of the coupling constants obtained from the *para* band and could, therefore, be unambiguously assigned to fluorine nuclei *ortho* or *meta* to the substituent.

The *para* and *meta* bands of pentafluoroanisole were so close that a simple analysis of the spectrum was not valid. Values of the fluorine–fluorine coupling constants are, therefore, not given for this compound. The measured values of the chemical shift of the *para* and *meta* fluorines in pentafluoroanisole are approximate, but should not be in error by more than 0·2 p.p.m.

The measured values of the spin–spin coupling constants are shown in Table 1, where the ± values are standard deviations about the mean. The numbering sequence is in one

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[1] Bourn, Gillies, and Randall, *Proc. Chem. Soc.*, 1963, 200; Massey, Randall, and Shaw, *Chem. and Ind.*, 1963, 1244.

[2] Tatlow, *Endeavour*, 1963, **22**, 89.

[3] Gutowsky, McCall, McGarvey, and Meyer, *J. Amer. Chem. Soc.*, 1952, **74**, 4809.

[4] Taft, *J. Amer. Chem. Soc.*, 1957, **79**, 1045; *J. Phys. Chem.*, 1960, **64**, 1805.

[5] Taft, Price, Fox, Lewis, Anderson, and Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709, 3146.

[6] Gutowsky, Holm, Saika, and Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 4596.

[7] Evans, *Mol. Phys.*, 1963, **6**, 179.

TABLE 1.

Spin-coupling constants [a] (c./sec.) for fluorine nuclei in C_6F_5X, and constants for coupling between fluorine nuclei and magnetic nuclei in the substituent X.

X	J_{23}	J_{24}	J_{25}	J_{34}	J_{26}, J_{35}	J_{2X}	J_{3X}	J_{4X}
H	20·6	1·3	8·8	18·8 [b]	2·4, 1·2	10·2 [d]	6·9 [d]	2·7 [d]
CH_3	20·3	~0	8·5	18·9	1·8, 0·6	2·3 [d]		1·4 [d]
CF_3	20·2	5·7 [b]	8·4	18·9 [b]	7·6, ≤1	22·5 [c]		1·4
Cl	20·8	1·0	6·3	19·5	5·4, 2·0			
Br	21·0	1·1	6·3	19·3	5·6, 1·8			
I	22·9 [b]	2·1	7·3 [b]	19·8	5·2, 1·4			
OCH_3						1·1 [t]		
CN	19·9	5·9 [b]	8·2	19·0 [b]	7·8, ≤1			
NH_2	20·4	6·9	4·9	20·8	4·6, 2·6			

[a] ±0·1 c./sec. unless otherwise noted. [b] ±0·2 c./sec. [c] ±1·0 c./sec. [d] In agreement with values quoted in ref. 1.

direction around the ring, the fluorines *ortho* to the substituent being numbered 2 and 6. It was impossible to distinguish between the values for J_{26} and J_{35}. No signs are given for the coupling constants in Table 1, although it is probable that the coupling constant of fluorine nuclei *ortho* to each other is of opposite sign to those of nuclei *meta* and *para* to each other, as in the trifluorobenzenes studied by Evans.[7]

Coupling constants involving magnetic nuclei in the substituent are also shown in Table 1. These values were obtained from the fluorine spectrum, and, when the magnetic nucleus was hydrogen, from the proton spectrum also. Several examples of long-range spin coupling are shown. Coupling through six bonds is observed between the *para* fluorine nucleus and the CF_3 or CH_3 group in octafluorotoluene and pentafluorotoluene. Five-bond coupling is observed between the hydrogen and *para* fluorine in pentafluorobenzene, and between the hydrogen and the *ortho* fluorine in pentafluoroanisole.

Values of the chemical shift, obtained from measurements on 15% v/v solutions in trichlorofluoromethane, are shown in Table 2, where positive values indicate that resonance occurs at higher field than for the reference compound. The values are accurate within ±0·1 p.p.m. Since the difference in chemical shift between the undiluted liquid and a 15% solution was always less than 1 p.p.m., the tabulated values are probably close to those which would be obtained with infinitely dilute solutions. The chemical shifts of the fluorine nuclei in perfluorobenzene, chloropentafluorobenzene, bromopentafluorobenzene, and pentafluoroiodobenzene, obtained from measurements on the pure liquids, agreed with previously published values.[1]

TABLE 2.

Chemical shifts in C_6F_5X (p.p.m. relative to CCl_3F).

X	*ortho*	*meta*	*para*	X	*ortho*	*meta*	*para*
F	162·9	162·9	162·9	Br	132·7	160·9	154·9
H	139·1	162·6	154·0	I	119·3	159·9	152·8
CH_3	144·0	164·3	159·3	OCH_3	158·5	164·9	164·6
CF_3	140·0	160·6	147·9	CN	132·5	159·2	143·5
Cl	140·9	161·6	156·3	NH_2	163·6	165·7	174·1

The chemical shifts of the fluorines *meta* and *para* to the substituent show a considerable resemblance to the fluorine chemical shifts in *para*- and *meta*-substituted monofluorobenzenes.[4,5] Taft has related the chemical shifts in monofluorobenzenes to the reactivity parameters of the substituent; [4,5] for example, he related the chemical shift, δ_p, in a *para*-substituted monofluorobenzene, relative to fluorobenzene, by the equation [5]

$$\delta_p = -29{\cdot}5\,\sigma_R{}^{\circ} - 7{\cdot}1\,\sigma_I + 0{\cdot}60$$

with a mean deviation between calculated and observed values of 0·6 p.p.m. $\sigma_R{}^{\circ}$ is the resonance-effect parameter obtained from chemical reactivities,[8] and σ_I is the inductive

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[8] Taft, *J. Amer. Chem. Soc.*, 1959, **81**, 5352.

effect parameter.[9] For *meta*-substituted fluorobenzenes his equation [5] for the chemical shift, δ_m, is

$$\delta_m = -7{\cdot}1\ \sigma_I + 0{\cdot}60,$$

with a mean deviation of 0·4 p.p.m. between calculated and observed values.

The chemical shifts of the fully fluorinated compounds listed in Table 2, can also be related to the reactivity parameters, $\sigma_R{}^\circ$ and σ_I. A least-squares analysis of the experimental values reported here shows that the chemical shift, ϕ_p, of the fluorine nucleus *para* to the substituent in the compounds C_6F_5X obeys the relation

$$\phi_p = -39{\cdot}7\ \sigma_R{}^\circ - 12{\cdot}9\ \sigma_I + 154{\cdot}4$$

with a mean deviation between experimental and calculated values of 1·0 p.p.m.

The chemical shifts of the fluorines *meta* to the substituent in C_6F_5X depend on the resonance parameter $\sigma_R{}^\circ$ as well as on σ_I, in contrast to the chemical shifts in monofluorobenzenes, which depend only on σ_I. The chemical shift of the *meta* fluorine found in the present study lies close to that given by the equation

$$\phi_m = -5{\cdot}3\ \sigma_I - 7{\cdot}2\ \sigma_R{}^\circ + 162{\cdot}9$$

the mean deviation between calculated and observed values being 0·5 p.p.m. The chemical shifts of the *meta* fluorines in the halogen-substituted compounds (X = Br or I) show the greatest deviations (0·97 and 1·84 p.p.m. respectively towards low field) between calculated and observed values. It seems likely that a paramagnetic effect, discussed below for the *ortho* fluorines, is responsible for this deviation.

In all the compounds studied here, except pentafluoroaniline and perfluorobenzene, the *para*-fluorine band occurs at lower field than the *meta*. Recent studies [10,11] of monofluorobenzenes indicate that the chemical shift of the fluorine atom, which measures the electron shielding of the fluorine nucleus, can be related to the π-electron charge density on the fluorine atom or on its bonded carbon atom. Thus, the chemical-shift values suggest that most of the molecules studied here have a greater electron charge density in the *para* than in the *meta* position. The *para*- and *meta*-fluorine bands of pentafluoroanisole, however, lie close together, suggesting that in this compound the electron densities at the *meta* and para positions are almost equal. In pentafluoroaniline, on the other hand, the order of the chemical shifts is reversed, suggesting a greater electron density in the *para* than in the *meta* position. This agrees with the known properties of pentafluorophenyl derivatives, which indicate that, in many molecules of this type, the position *para* to the substituent is most susceptible to attack by nucleophilic reagents.[2] In the pentafluoroaniline molecule, the considerable conjugation of the lone pair with the ring deactivates the *ortho* and *para* positions most, so that the *meta* position of pentafluoroaniline is most susceptible to nucleophilic attack.[2]

The chemical shifts of the fluorine nuclei *ortho* to the substituent depend on many factors. It has been suggested [1] that in some compounds of the type C_6F_5X these chemical shifts may be partly the result of a paramagnetic effect similar to that reported for some perfluoroalkyl derivatives.[12,13] This effect depends on the presence of low-lying excited states mixed with the ground state by the magnetic field. This mixing produces a paramagnetic contribution to the chemical shift,[1] so that resonance occurs at a lower value of the applied field. This effect might be expected to occur in the halogen-substituted compounds (X = Cl, Br, or I) and should be greatest for the fluorines in the *ortho* position. The paramagnetic contribution will *increase* from the chloro- to the bromo- to the iodo-compound,

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[9] Taft, " Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, Inc., New York, 1956, pp. 594—597.

[10] Karplus and Das, *J. Chem. Phys.*, 1961, **34**, 1683.

[11] Prosser and Goodman, *J. Chem. Phys.*, 1963, **38**, 374; Taft, Prosser, Goodman, and Davis, *ibid.*, p. 380.

[12] Tiers, *J. Amer. Chem. Soc.*, 1956, **78**, 2914.

[13] Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.

so that the chemical shifts of the *ortho* fluorines should *decrease* in this order. This behaviour is observed in the values of the *ortho*-fluorine chemical shifts for these three compounds (Table 2). It seems likely that this paramagnetic effect is transmitted to the *meta*-fluorine atoms in bromopentafluorobenzene and pentafluoroiodobenzene, because, as was shown above, the chemical shifts of the *meta* fluorines in these two compounds show a significant deviation towards low field from the simple relation between the chemical shift and the reactivity parameters.

Karplus and Das [10] have made a theoretical calculation of the chemical shift of the *ortho*-fluorine nuclei in pentafluorobenzene, including a correction for the " *ortho* effect " which they found in *o*-difluorobenzene. They calculated the chemical shift relative to fluorobenzene to be 23·8 p.p.m. Since the chemical shift of fluorobenzene, relative to trichlorofluoromethane, is 113·1 p.p.m.,[14] their value corresponds to a chemical shift of 136·9 p.p.m. from trichlorofluoromethane, and this value is close to the experimental value of 139·1 p.p.m. found here for the chemical shift of the *ortho* fluorine nuclei in pentafluorobenzene.

EXPERIMENTAL

All samples, and the reference compound, trichlorofluoromethane, were supplied by the Imperial Smelting Corporation. The compounds were used without further purification except for the sample of pentafluoroiodobenzene, which was vacuum-distilled to remove an intense purple colour. No peaks due to impurities were observed in the spectra, which were obtained at 60·0 Mc./sec. with an Associated Electrical Industries Ltd. RS2 spectrometer with flux stabilisation and a spinning sample tube 4·5 mm. in diameter. The temperature of measurement was *ca.* 20°. The positions of the lines were measured by the sideband technique with an audio-oscillator (Muirhead type D880A) monitored by a frequency counter (Venner type 3336).

Coupling constants were calculated from the spectra of pure liquids, mixed with about 5% v/v of CCl_3F; as pentafluoroaniline is a solid, a saturated solution in $CClF_3$ was used. Chemical shift values were obtained from the most dilute solutions that would give signals of acceptable intensity, namely 15% v/v solutions in CCl_3F, except for pentafluoroaniline, for which a solution with a concentration 15% of the saturated value was used.

For compounds containing hydrogen, the proton spectrum was recorded also.

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NATIONAL CHEMICAL LABORATORY, TEDDINGTON, MIDDLESEX. [*Received, June 26th*, 1964.]

[14] Filipovich and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.