The N.m.r. Spectra of Aromatic Fluorocarbons. The Effect of Substituents on J^{FF}_{meta} in Amino- and Nitro-fluorobenzenes

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In a recent study of the ^{19}F magnetic resonance spectra of a range of amino- and nitro-substituted fluorobenzenes[1] it was shown that substituent shielding effects are additive and independent of the degree of substitution. No parallel treatment of coupling constants was then possible but it was noted that, in contrast with the relative constancy of *ortho*-couplings, the magnitude of J_{meta} varied widely over the range of compounds studied and there was some evidence of changes of relative sign. We have now carried out relative sign determinations from which it emerges that, when signs are taken into account, there can be assigned to the substituents position-dependent coupling parameters which are again additive and independent of the degree of substitution.

Relative signs were determined for the asymmetrically substituted compounds by the method of partial decoupling[2] and the absolute J-values obtained were compared with that found in hexafluorobenzene ($J_{meta} = -4\cdot0$ c./sec.),[3] it being assumed that J_{ortho} is negative in all cases (*cf.* $-22\cdot0$ c./sec. for C_6F_6[3]). The change in J_{meta} from the above value may be expressed as the sum of substituent parameters in the three positions in the molecule relative to the fluorine nuclei under consideration:

F, a, F, b, b, c (ring diagram)
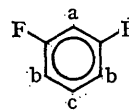
e.g., in 2,4,5-trifluoro-6-nitrophenylene-1,3-diamine $J_{2,4} = +3\cdot7$ c./sec.

so NH_2 (a) $+ NH_2$(b) $+ NO_2$(c) $= +7\cdot7$ c./sec.

Approximate solution of these parameters permits the correct assignment of constants in the symmetrically substituted compounds where previously some ambiguity existed. The final assignments together with data from related H-containing molecules are given in Table 1. The data (A) give thirteen linear equations in the six unknown parameters, a least-squares fit of which yields the values given in Table 2, the mean deviation being $0\cdot5$ c./sec. The data (B) were considered insufficient for inclusion in the computation and the approximate values of H-substitution parameters

Table 1.

J^{FF}_{meta} in derivatives of hexafluorobenzene.

| | \multicolumn{6}{c}{Ring position of substituents} | \multicolumn{4}{c}{J^{FF} (c./sec.)} |
	1	2	3	4	5	6	2,4	2,6	3,5	4,6
(A)	NH₂	—	—	—	—	—	−8·2	+6	−3	−8·2
	NH₂	NH₂	—	—	—	—	—	—	−6·6	−6·6
	NH₂	—	NH₂	—	—	—	0	0	—	—
	NO₂	—	—	—	—	—	+6·0	−10·0	0	+6·0
	NH₂	—	—	NO₂	—	—	—	+9·5	−8·8	—
	NH₂	—	NH₂	—	—	NO₂	+3·7	—	—	—
	NH₂	NO₂	—	—	—	—	—	—	+8·8	−5·9
(B)	NO₂	NH₂	—	—	H	—	—	—	—	+8·6
	NO₂	H	—	—	—	—	—	—	+3·6	+10·5
	NO₂	—	H	—	—	—	+4·9	−6·2	—	+10·0

TABLE 2

Substituent coupling parameters. (c./sec.)

Relative ring positions

		a	b	c
(A)	F	0	0	0
	NH_2	+9·5	−5·0	+1·8
	NO_2	−6·3	+10·5	+3·6
(B)	H	(−0·6)	+3·9	(+4·0)

quoted in Table 2 were obtained by the use of the mean NH_2 and NO_2 values.

It is interesting that the two largest coupling parameters for the NH_2 and NO_2 groups operate in opposite directions for equivalent ring positions. A similar reversal of trend is found in the corresponding shielding parameters.[1] Since the latter can be correlated with the Hammett σ-constants,[4] and hence with the π-electron distribution in the molecules, there is a strong indication that the π-system makes a dominant contribution to the F–F *meta*-coupling mechanism. This should also be the case for *para*-fluorine coupling but, in view of the additional parameters necessary to define the molecular environment of *para*-disposed fluorine nuclei in the present compounds, there is insufficient data for satisfactory correlation.

[1] J. Homer and L. F. Thomas, *J. Chem. Soc. (B),* 1966, 141.
[2] D. F. Evans and J. P. Maher, *Proc. Chem. Soc.,* 1961, 208.
[3] L. C. Snyder and E. W. Anderson, *J. Chem. Phys.,* 1965, **42**, 3336.
[4] I. J. Lawrenson, *J. Chem. Soc.,* 1965, 1117.