^{19}F Nuclear Magnetic Resonance Spectra of 3-Substituted 2,4-Dimethylfluorobenzenes: Possible Steric Effects on Substituent Chemical Shifts

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Summary Possible steric effects on m-SCS$_\text{I}$ are discussed on the basis of comparison of the ^{19}F n.m.r. spectra of some 3-substituted 2,4-dimethylfluorobenzenes with those of m-substituted fluorobenzenes.

CONSIDERABLE attention has been directed to the effect of substituents on ^{19}F chemical shifts in organic fluorides.[1] Theoretically the ^{19}F shieldings of aromatic fluorides depend primarily on the π-charge densities on the fluorine atom and the C–F π-bond order, and a fair agreement is reported between the calculated and experimental Substituent Chemical Shifts (SCS) for *para*-substituted fluorobenzenes.[2] Somewhat conflicting views, however, have been expressed on the m-F SCS$_\text{II}$ of *meta*-substituted fluorobenzenes (II). Taft[3] has suggested that they depend predominantly on the inductive effect. Dewar,[4] on the other hand, suggested that the field effect is relatively important, while Feeney *et al.*[5] report that the ^{19}F shieldings are in general comparable with the electric field effect. Recently, Dewar[6] and Della[7] observed that the field effect seems to contribute little in certain fluorinated alicyclic systems. Instead, Dewar[6] and Stock[8] suggested that the steric environment of the fluorine atom (or its vicinity) would cause a serious effect on the ^{19}F shieldings.

Here we report the effect of sterically hindered substituents on *meta*-fluorine shieldings.[†] We prepared twelve 3-substituted 2,4-dimethylfluorobenzenes (I) and determined their ^{19}F n.m.r. spectra.[‡] The m-F SCS$_\text{I}$ values together with SCS$_\text{II}$ are summarised in the Table. SCS$_\text{I}$ are smaller than the corresponding SCS$_\text{II}$. If NMe$_2$, OMe, and halogens are excluded, the correlation is SCS$_\text{I}$ = 0·91 SCS$_\text{II}$ − 2·20 (r = 0·979). This large and negative intercept can be ascribed to the decrease of C–F π-bond order caused by the skeletal deformation or to the "secondary"

[†] For effects on *para*-fluorine atoms, see: M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1967, **89**, 790.

[‡] Most of the compounds (I) are new. The details of syntheses and physical constants will be given in a full paper. The ^{19}F n.m.r. spectra were determined with a JNM-4H-100 spectrometer operating at 94·077 MHz in a CCl$_4$ or HCONMe$_2$ solution with 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal standard. The signals were calibrated by the side-band technique.

van der Waals effect[9] caused by the buttressing effect of four successive substituents.

The SCS difference is particularly large for halogens, and increases in the order Cl < Br < I. We tentatively assume that this effect is also due, at least in part, to the acceptor $(1p_C\text{–}nd_{\text{halogen}})$ interaction between the *d*-orbital of the halogens concerned and the aromatic ring.§ This interpretation can also account for the similar anomaly in the case of halogens observed for proton shieldings.[9]

It is tempting to assume that SCS_{II} is solely dependent on the inductive (or field) effect of the substituent. The fact that the SCS of 3,5-di-t-butyl-4-nitrofluorobenzene is identical with that of *m*-nitrofluorobenzene,[11] and that the slope of correlation between SCS_{II} and SCS_I is close to unity, agree with this interpretation. But the present results, particularly for NMe_2 and OMe, make it difficult to draw any final conclusion as to the nature of the substituent effect on *meta*-fluorine shieldings.

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^{19}F *Chemical shifts (p.p.m.) and Substituent Chemical Shifts (SCS) of* 3-*substituted* 2,4-*dimethylfluorobenzenes* (I).[a]

Substituent	Solvent	Chemical Shift[b]	SCS_I	SCS_{II}[c]
NH_2	CCl_4	6·98	−2·06	0·4
NMe_2	CCl_4	4·43	−4·61	−0·1
OH	CCl_4	5·58	−3·46	−1·3
OMe	CCl_4	4·57	−4·47	−1·1
Cl	CCl_4	2·62	−6·42	−2·0
Br	CCl_4	1·38	−7·76	−2·30
I	CCl_4	−0·27	−9·31	−2·4
H	CCl_4	9·04	0[d]	0[d]
H	DMF	10·05	0[d]	0[d]
CO_2H	DMF	7·60	−2·45	−0·41
CO_2Me	CCl_4	6·74	−2·30	−0·13
CN	CCl_4	4·77	−4·27	−2·75
NO_2	CCl_4	3·28	−5·76	−3·45

[a] 1 mmole of the sample was dissolved in 0·33 ml of the solvent.

[b] From 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (5% w/w added to solvent).

[c] Data taken from ref. 3.

[d] By definition.

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§ ^{19}F n.m.r. evidence was given for this kind of interaction between the sterically hindered sulphur atom and the aromatic ring.[10]

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