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Substituent Effects. XII.[1] Substituent Effects by ^{19}F NMR

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Abstract: FMMF calculations for ^{19}F SCS in the 10-substituted 9-fluoroanthracenes and 4-substituted 3,5-dimethylfluorobenzenes are reported. The analysis strongly supports the idea that polar effects on ^{19}F chemical shifts are enhanced when the fluorine atom is attached to a carbon atom which is part of a π system. Further, a comparison of FMMF calculations for increasingly rigid para-substituted aryl fluorides suggests that σ skeletal deformation can make a significant contribution to the ^{19}F chemical shift, when the substituent and fluorine are in the same ring. ^{19}F chemical shift data for a number of new substituted aryl fluorides are presented which appear to partially support the latter conclusion. In addition, the new data help to throw further light on the factors determining ^{19}F chemical shifts.

In this series of papers, a general theory of substituent effects has been developed on the assumption that only three factors are important, i.e., the field effect (F), the mesomeric effect (M), and the π inductive effect which is usually indistinguishable from the mesomeric effect. In its latest form (FMMF method), allowance is also made for the mesomeric field effect (MF), due to electrostatic interactions with charges set up in a π system through mesomeric interactions with substituents.

Although this improved empirical treatment accounts very well for chemical reactions of side chains, it was found that an analysis of aryl ^{19}F chemical shifts leads to deviations of the hydrogen substituent from the least-squares lines for most of the systems investigated.[3] Since the deviations as well as the scatter of points from the line were greater when the substituent and fluorine are attached to the same ring, it was suggested that ^{19}F chemical shifts in aryl fluorides are sensitive to substituent-induced structural distortions that alter the environment of the fluorine atom, i.e., insertion of any substituent into a fluorinated aromatic produces a chemical shift merely by its presence, independent of any specific electronic effect.

Because this proposal has serious consequences regarding the continued and widespread use of the aryl fluorine atom as a probe for investigating substituent effects,[4] we have extended the analysis (FMMF method) to other available systems, in particular, the 4-substituted 3,5-dimethylfluorobenzenes[6] and the 10-substituted 9-fluoroanthracenes.[7] These two systems are of interest since nonlinear substituent groups must be rotated out of the plane of the ring because of steric interactions with the o-methyl groups or the peri-hydrogen atoms, respectively. Such a rotation destroys π overlaps with the ring so such groups can exhibit only polar effects (electric field and π-inductive effects).

In this paper, we report the results of that study together with the synthesis and ^{19}F spectra of a number of new aryl fluorides, as well as five new fluoromethylnaphthalenes, which shed further light upon the factors determining ^{19}F chemical shifts. Moreover, the new ^{19}F NMR data allow interesting deductions to be made concerning the electronic behavior of alkyl groups in the neutral ground state.

Theory

The FMMF method uses a simplified model in which the dipole moment of the bond CX between a substituent and an adjacent carbon i is represented by equal and opposite point charges on carbon and at a point (j) one standard bond length (1.40 Å) from carbon along the CX bond. The interaction with a fluorine atom attached at atom m is given by the general equation[3]

$$\sigma_{im}^{SF} = F^S R_{im}^2 + M^S q_{im} + M_F^S \sum_{R \neq m} \frac{q_{ik} \cos \theta_{kn}}{r_{kn}^2} \quad (1)$$

where

$$R_{im}^2 = \frac{\cos \theta_{in}}{r_{in}^2} - \frac{\cos \theta_{in}}{r_{jn}^2} \quad (2)$$

θ_{in} being the angle between the CF bond vector and a line of length r_{im} drawn from atom i to the midpoint (n) of the CF bond. q_{im} is the charge produced at atom m by an amino

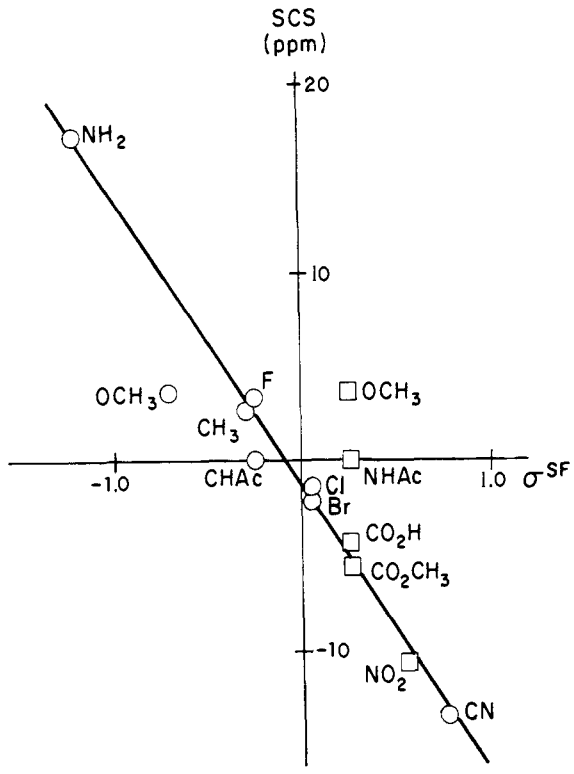


Figure 1. Experimental ^{19}F substituent chemical shifts in the 10-substituted 9-fluoroanthracenes plotted against σ^{SF} values calculated by the FMMF method using SCF-MO charge distributions: σ^{SF} values calculated using eq 3; σ^{SF*} values calculated using eq 5.

substituent attached at atom i and is calculated by an SCF π MO procedure.[8]

Results and Discussion

For the 10-substituted 9-fluoroanthracenes, application of eq 1 gives eq 3. The expression for the 4-substituted 3,5-

$$\sigma_{10,9}{}^{SF} = 0.0784F^S + 0.0263M^S - 0.0001M_F{}^S \quad (3)$$

dimethylfluorobenzenes is the same as that for the fluorobenzenes.

$$\sigma_{4,1}{}^{SF} = 0.0784F^S + 0.0114M^S + 0.0004M_F{}^S \quad (4)$$

The σ^{SF} values calculated using eq 3 were plotted against the ^{19}F SCS values observed for linearly symmetrical substituents in the 10-substituted 9-fluoroanthracenes, giving an excellent linear correlation (Figure 1). The experimentally observed ^{19}F SCS values for groups which could be expected to be rotated completely out of the plane of the anthracene ring (NO_2, CO_2H, CO_2R) were then examined. It was found that the corresponding σ^{SF} values could be attributed entirely to the terms $F^S/R_{im}{}^2$ (eq 5, which applies for any 1,4 interaction across a benzene type ring); viz:

$$\sigma^{SF*} = 0.0784F^S \quad (5)$$

Here the asterisk indicates complete steric inhibition of π-orbital overlap between the substituent and the ring.

While steric interactions with the two peri-hydrogen atoms are insufficient to remove all π-orbital overlap between the methoxy and acetamino substituents and the ring, such interactions do lead to a deviation from eq 3. In the case of NH_2, the steric interactions evidently have little effect since the corresponding point lies exactly on the line.

Accepting the idea that the chemical shifts depend on F^S, if there is no π interaction with the substituent, we plotted the experimental ^{19}F SCS values for the 4-substituted 3,5-dimethylfluorobenzenes against σ^{SF} values calculated from

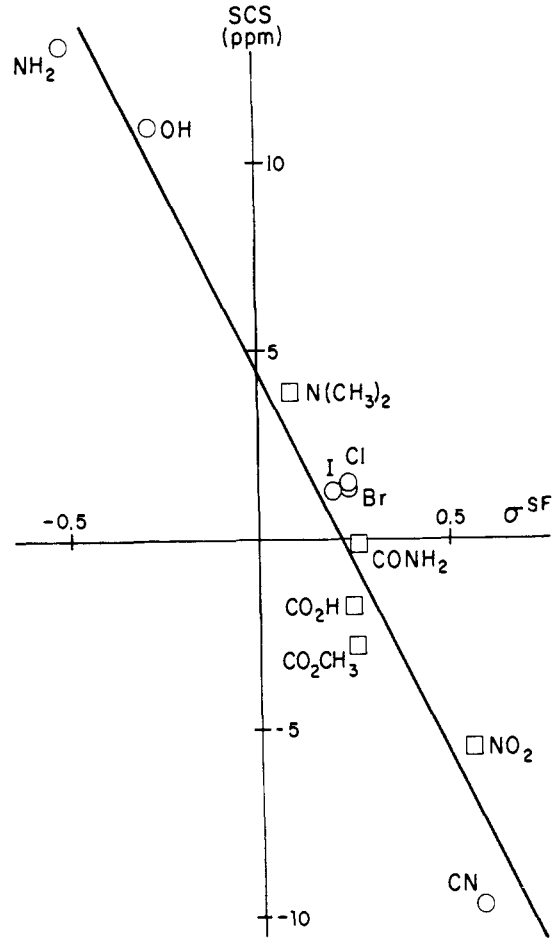


Figure 2. Experimental ^{19}F substituent chemical shifts of 4-substituted 3,5-dimethylfluorobenzenes plotted against σ^{SF} values calculated by the FMMF method (SCF-MO charge distribution): σ^{SF} values calculated using eq 4; σ^{SF*} values calculated using eq 5.[9]

eq 4 and 5. The result is shown in Figure 2.

The correlation is again good though the scatter is greater than in the case of the 10-substituted 9-fluoroanthracenes. This is consistent with our previous suggestion that substitution leads to structural changes in the benzene nucleus, resulting in chemical shifts that cannot be treated in terms of classical substituent effects. Such deformations should be less important in the more rigid anthracene system, a point which will be elaborated presently.

Next we examined the polar effects of substituents in a saturated system by plotting the observed SCS for the acetylenedicarboxylate adducts of 10-substituted 9-fluoroanthracenes[12] (**1**) against the field-effect term $F^S/R_{im}{}^2$ (eq 7). This is equivalent to a plot of SCS vs. σ_I (cf. Anderson and Stock).[12] The F^S value for acetoxy (4.25) was calculated from the σ_I value given by Ritchie and Sager.[10]

$$\sigma^{SF}(1) = 0.0729F^S \quad (7)$$

There is an excellent linear relation (Figure 3) between σ^{SF} and F^S for the five derivatives of **1** for which data are available. Additional measurements in this series would be of interest.

Table I compares the results of the FMMF analysis for the acetylenedicarboxylate adducts (**1**), the 10-substituted 9-fluoroanthracenes (**2**), the 4-substituted 3,5-dimethylfluorobenzenes (**3**), and other systems treated previously.[3] The linear correlations are characterized by the slope (ρ) and intercept (ν_0) for the best (least-squares) line through the n

Table I. Correlation of Calculated σ^{SF} Values with Experimental ^{19}F SCS[a]

Series	ρ	ν_0	n[b]	r[c]	SD[d]
Benzene					
Meta	−5.22	0.47	11	0.887	0.75
Para	−23.2	5.37	13	0.955	2.59
Naphthalene					
3α	−7.61	1.09	6	0.974	0.54
4α	−23.9	2.57	7	0.987	1.73
6α	−10.6	0.34	5	0.968	0.37
7α	−14.1	0.76	9	0.985	0.35
4β	−0.40	−0.39	6	0.185	0.72
6β	−30.6	0.00	9	0.995	0.52
7β	−17.8	0.07	9	0.965	0.43
8β	−17.3	−1.23	9	0.987	0.51
Biphenyls and terphenyls	−18.0	−0.31	32	0.946	0.33
9,10-Anthracenes	−15.7	−1.37	9	0.998	0.61
3,5-Dimethylfluorobenzenes	−19.9	4.42	11	0.970	1.68
Adducts	−5.69	1.35	5	0.984	0.13
Tetramethylbiphenyls	−16.9	0.01	6	0.937	0.13

[a] SCF–MO charge distributions are used in all cases. [b] Number of points. [c] Correlation coefficient. [d] Standard deviation.

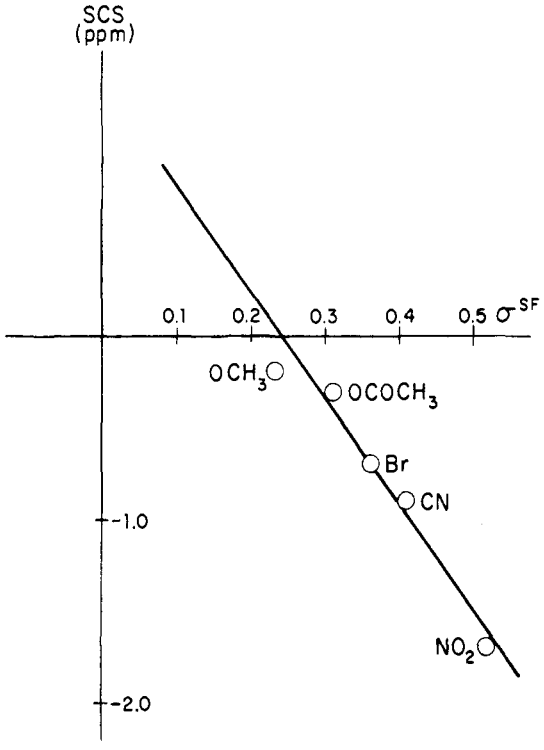
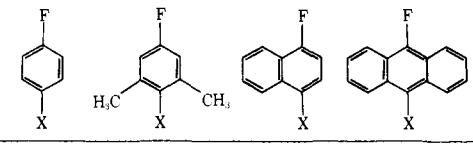
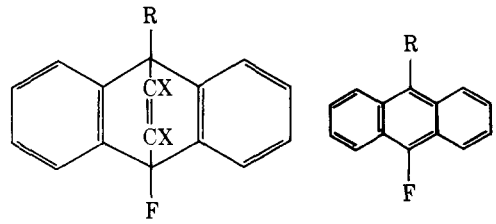


Figure 3. Plot of σ^{SF} vs. F^S (eq 7), for acetylenedicarboxylate adducts (1) of 10-substituted 9-fluoroanthracenes.

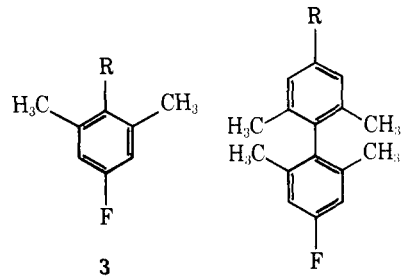
Table II. Effect of Annelation on SCF



ν_0, ppm	+5.37	+4.42	+2.57	−1.37
r	0.955	0.970	0.987	0.998
SD	2.59	1.68	1.73	0.61



1 (X = COOMe) 2



3 4

points for each series, together with the correlation coefficient (r) and the standard deviation.[13]

In the hindered systems **2** and **3**, substituents such as NO_2 or COOEt are of course unable to exercise mesomeric effects since they are twisted out of coplanarity with the ring. The corresponding points lie on the same line as those for axially symmetrical substituents (e.g., CN, Cl), if only the field effect was taken into account in the case of the hindered substituents. Likewise in the case of the 4′-substituted 2,2′,6,6′-tetramethyl-4-fluorobiphenyls[14] (**4**), direct resonance interactions between R and F are blocked by the orthogonality of the rings. Here the surviving terms are those for the field effect, and for the mesomeric field effect due to polarization of the ring carrying the substituent. With this proviso, the results for **4** also gave a good linear plot.

The ρ value for **1** (−5.69) is very much lower than the values for the other series. This supports earlier conclusions[12,15] that the polar (i.e., field) effect of substituents is very much less in most aliphatic fluorides (see later) than in aromatic ones.[1] Thus in **4**, where mesomeric effects are suppressed by the orthogonality of the rings, the ρ value (−16.9) is three times greater than that for **1**. These differences can be ascribed to a greater effective polarizability of the CF bond when the fluorine is attached to a conjugated system.[1] It is also possible that the enhanced response of the ^{19}F SCS to polar effects in aryl fluorides could be due partially to a π inductive (indirect electromeric)[16] effect as suggested by Stock and his associates.[7] Either of these effects could also account for the other curious feature shown by ^{19}F chemical shifts, i.e., the very large variations in ρ between different series of aryl fluorides. Neither factor is included in the FMMF treatment, and it is difficult to see how they could be in any simple way.

Another curious anomaly is seen in the case of substituents in the same ring as fluorine. The linear plots of σ^{SF} against ^{19}F SCS do not as a rule[3] pass through the origin,

Table III. ^{19}F Chemical Shifts (ppm) of Fluorobenzocycloalkenes Relative to Fluorobenzene in Benzene and Dimethylformamide

Number	Compd	Benzene	DMF
1	3, 4-Dimethylfluorobenzene	+5.57	+5.45
2	6-Fluorotetralin	+5.45	+5.22
3	5-Fluoroindan	+5.23	+5.09
4	4-Fluoro-1,2-dihydrobenzocyclobutene	+1.33	+1.27
5	3,4-Di-*tert*-butylfluorobenzene	+5.68	+5.41

the intercepts for $\sigma = 0$ being quite large and positive. In the case of substituents in other rings, the intercepts are of random sign and too small to be significant. The scatter of points from the line is also generally greater when the substituent and fluorine are attached to the same ring. This was attributed[3] to chemical shifts produced by geometric deformation of the fluorine-bearing ring by the presence of *any* substituent in it, implying that hydrogen is the one group out of step. The effect of substituents should on this basis depend on their size; we would therefore expect the plots of σ^{SF} vs. SCS to show scatter, and the scatter should decrease with an increase in rigidity of the ring. Such a decrease is in fact reflected by the correlation coefficients (r) and standard deviations (SD) in Table II. A similar argument has been used by Stock et al.[12] to account for the analogous anomalous chemical shifts in 4-substituted 1-fluorobicyclo[2.2.2]octanes.

If this suggestion is correct, the intercepts (ν_0) should decrease with increasing rigidity of the ring to which fluorine and the substituent are bound. Since the rigidity of a benzene ring should be increased by annelation with additional rings, one would expect a decrease in the value of ν_0 along the series 1,4-phenylene > 1,4-naphthylene > 9,10-anthrylene. Such a decrease is in fact observed (Table II), providing strong support for the idea that ^{19}F chemical shifts depend critically on geometry in the way we have suggested. Further, the analysis indicates that geometrical distortion is absent in the 6β and 7β dispositions of naphthalene as well as the biphenyls and terphenyls, the intercepts (ν_0) being too small to be significant (Table I).

Since no overwhelming physical evidence is available to support these proposals,[17] we have synthesized and measured the ^{19}F NMR spectra of a number of appropriately substituted aryl fluorides in order to provide further information pertinent to the problem. The fluorine chemical shift data for a number of fluoro-substituted benzocycloalkenes[19] are listed in Table III. It can be seen that, similar to 3,4-dimethylfluorobenzene, all the fluorine chemical shifts of the benzocycloalkenes occur upfield from fluorobenzene, implying net electron donation.[20] Neglecting strain effects and on the basis of either a hyperconjugative or an inductive model, this was expected. However, the surprisingly large *downfield* shift of 4-fluoro-1,2-dihydrobenzocyclobutene relative to 3,4-dimethylfluorobenzene is completely incompatible with a purely hyperconjugative model.[21] Although this result is perhaps more explicable in terms of the Streitwieser and coworkers[22] "hybridization effect model," the magnitude of the downfield shift seems far too large for a simple electronegativity change. Since fusing a small cycloalkene ring onto a benzene nucleus gives rise to substantial bond-length and bond-angle perturbations in the aromatic ring,[23] it seems more reasonable to attribute the large downfield shift to skeletal distortions. Interestingly, the fluorine chemical shift of 3,4-di-*tert*-butylfluorobenzene (Table III), a compound where steric effects should be quite severe, is approximately the same as the corresponding dimethyl derivative.

Next we examined a series of alkyl-substituted aryl fluorides, the 4α and 6β alkyl-substituted fluoronaphthalenes[24]

Table IV. Substituent Chemical Shifts (ppm) of Alkyl-Substituted Aryl Fluorides in Benzene

Substituent	Disposition: Para	$4\alpha^{2,4}$	$6\beta^{2,4}$
CH_3	+5.48[a] (+5.44)[c]	+2.96[b]	+1.45[b]
CH_2CH_3	+5.15 (+5.00)[c]	+2.87	+1.36
$CH(CH_3)_2$	+4.93 (+4.75)[c]	+3.01	+1.27
$C(CH_3)_3$	+5.60[a] (+5.55)[c]	+2.52	+1.09

[a] Reference 25. [b] Reference 26. [c] Reference 27. Solvent CCl_4.

Table V. Substituent Chemical Shifts (ppm) of Alkyl-Substituted Aryl Fluorides in Dimethylformamide

Substituent	Disposition: Para	4α	6β
CH_3	+5.45[a]	+2.94[b]	+1.48[b]
CH_2CH_3	+4.98	+2.86	+1.37
$CH(CH_3)_2$	+4.78	+2.96	+1.32
$C(CH_3)_3$	+5.51[a]	+2.40	+1.16

[a] Reference 25. [b] Reference 26.

and the para alkyl-substituted fluorobenzenes, and the data are set out in Tables IV and V. It can be seen that in the 6β disposition, predicted by the FMMF analysis to be "normal," successive replacement of the hydrogen atoms of a methyl group by methyl substituents leads to a progressive *decrease* in the electron-donating power of the alkyl group. Notice the trend in the para position of benzene and the 4α disposition of naphthalene.[1] The effect in the para position parallels that observed in the 6β disposition for two methyl replacements but differs widely on the third replacement. An examination of molecular models indicates that whereas the ethyl and isopropyl substituents can adopt a configuration to minimize steric interactions by placing only a side-chain hydrogen atom in opposition to an ortho-hydrogen atom, the *tert*-butyl group in any configuration produces unfavorable steric interactions with the ortho-hydrogen atoms. We believe the anomalous shift observed for the *tert*-butyl group in the benzene ring system is a manifestation of the greater molecular distortion of the smaller ring system compared with the larger more rigid naphthalene system. Further support for this conclusion is provided by the irregularities in the 4α disposition. Although steric interactions of a side-chain methyl group with a peri hydrogen should be much larger than the corresponding interaction with an ortho hydrogen, the smaller SCS deviation in this orientation compared with the para position of benzene attests to the greater rigidity of the naphthalene ring system.

Our observations here clearly provide a plausible explanation for the recent reports by Sheppard[27] and McBee and coworkers[28] concerning the ^{19}F chemical shift behavior of a series of halogen-containing methyl substituents. They observed that whereas successive substitution on the methyl group by the small fluorine atom effects a progressive increase in the electron-withdrawing power of the group, chlorine and bromine substitution leads to a "saturation effect" on the second substitution. Clearly, the introduction of a third chlorine or bromine substituent will produce steric effects similar to those observed for a methyl group in the *tert*-butyl substituent. Apparently the resulting molecular distortion effects an upfield perturbation of the chemical shift that accidently cancels out any expected downfield shift based on electronic considerations. The results set out in Table VI strongly support this conclusion. Note that in the "normal" 6β disposition, introduction of a third bromine produces the expected substantial increase in the electron-withdrawing power of the halomethyl substituent.

It is appropriate to point out that although the observed order of the total electronic effect by the alkyl groups in the 6β disposition is the so-called Baker–Nathan order (Me >

Table VI. Substituent Chemical Shifts (ppm) of Bromo-Substituted Methyl Groups in the Para Position of Benzene and the 6β Disposition of Naphthalene

Substituent	Para[a]	6β
CH_3	+5.40	+1.48[b]
CH_2Br	+0.13	−1.00[c]
$CHBr_2$	−2.21	−2.35[d]
CBr_3	−2.14	−3.59[d]

[a] Reference 28. [b] Reference 26. [c] Reference 29. [d] W. Adcock and M. A. Zeb, unpublished work.

Table VII. Substituent Chemical Shifts (ppm) of Halogen Substituents Relative to Methyl in the Para Position of Benzene[a] and the 4α Disposition of Naphthalene[a]

Substituent	Para[b]	4α
F	+0.85	+0.99[c]
Cl	−2.97	−3.13[c]
Br	−3.45	−3.56[d]
I	−4.10[e]	−4.02[c]

[a] Solvent DMF. [b] Reference 39. [c] S. Q. A. Rizvi, Ph.D. Thesis. See also ref 7. [d] Reference 40. [e] Solvent MeOH.

Et > *i*-Pr > *t*-Bu),[30] the order cannot be attributed to hyperconjugation since the angular dependence of this mechanism predicts that the effect of a third methyl replacement should be smaller than the first or second.[20,31] The SCS data in Tables IV and V are *not* in accord with this prediction. We believe the observed order can be rationalized in terms of substituent polarizability[32-34] since the presence of the fluorine nucleus as a probe ensures that the alkyl groups in conjugated positions are acting on π electron-rich centers.

A further interesting feature of the data in Tables IV and V is the observation that the SCS for the alkyl groups in the 4α disposition of naphthalene are considerably *less positive* than the values observed in the formally similar para position of benzene;[35] i.e., the net electron-donating power of the alkyl groups, as monitored by the ^{19}F probe, is substantially reduced in the 1,4 disposition of naphthalene.[36,37] Recently, Stock and coworkers[7] have reported a similar observation for halogen substituents and have chosen to rationalize the phenomenon in terms of an enhanced π inductive effect in the 1,4 and 9,10 dispositions of naphthalene and anthracene, respectively, compared with the para position in benzene. However, to accommodate the observations for the alkyl groups within the same framework would require violating the generally accepted belief that alkyl groups donate electrons by a σ inductive effect.[38]

We believe it is indeed possible that structural factors could account for the apparently enhanced shielding effects of the alkyl and halogen substituents in the para-substituted fluorobenzenes. Strong support for this proposition comes from examining the SCS for the halogen substituents listed in Table VII which appear to be perfectly normal. These values have been determined with reference to the methyl substituent rather than hydrogen; therefore, structural factors should be partially compensated for, and the resulting SCS should reflect more normal electronic behavior. This appears to be the case. Examination of the SCS data in Table VIII is further revealing. It can be seen that the SCS for the alkyl substituents in the conjugated 5α and 8β dispositions[42] are *negative*, implying net *electron withdrawal!* Since no other explanation seems reasonable, structural factors may also be responsible for these observations. However, it should be noted that this proposition is not supported by the relative SCS values for the alkyl groups in the 8β disposition since the order parallels that observed in the normal 6β disposition. For example, the bulky *tert*-butyl substituent is downfield from the methyl substituent by approximately the same amount in both dispositions. This was not expected on the basis that substituent-induced structural effects should depend predominantly on the size of the group.

Table VIII. ^{19}F Substituent Chemical Shifts (ppm) of Alkyl-Substituted 5α and 8β Fluoronaphthalenes in Dimethylformamide

Substituent	Disposition 5α	Disposition 8β
CH_3	−1.03[a]	−0.96
CH_2CH_3		−0.87
$CH(CH_3)_2$		−0.90
$C(CH_3)_3$		−1.31

[a] Reference 41.

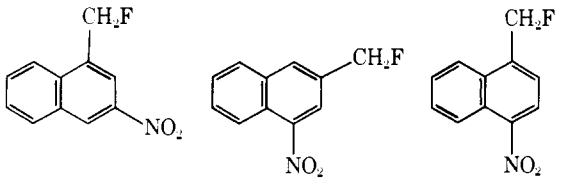
Table IX. Substituent Chemical Shifts (ppm) of +E-Substituted Fluoronaphthalenes in Dimethylformamide[a]

Substituent	Orientation 3α	Orientation 4β	Orientation 4α
NO_2	−4.87	−0.79	−12.77
CN	−3.86	−0.80	−11.34
COOH	−1.01	+0.72	−8.19

[a] Reference 40.

Finally, we examined an unusual phenomenon that we previously observed in an earlier study:[40] namely, that ^{19}F chemical shifts of +E substituents (NO_2, CN, and COOH) meta to the fluorine probe are anomalous, the observed substituent chemical shifts (SCS) in the 4β disposition being much smaller than those expected or even in the opposite direction (Table IX). At the time we suggested that the results might imply that resonance interactions of the substituent with an adjacent aromatic ring may set up a marked alternation of π-electron density around the latter, as predicted by SCF-MO calculations; thus the positions meta to carbonyl in compounds of the type ArCOR are predicted to carry quite large negative charges, much larger than those predicted by HMO theory.[43]

More recently, on the basis of an FMMF analysis, we revised our ideas on the "anomalies" and suggested that they might arise from substituent-induced structural distortions. In order to test this thesis, we synthesized and measured the ^{19}F NMR of three nitro-substituted fluoromethylnaphthalenes (**5**, **6**, and **7**) in which a methylene group is interposed between the aromatic ring and the fluorine probe. We reasoned that this structural manipulation of aryl fluorides should effectively eliminate any perturbation emanating from possible substituent-induced structural changes. Therefore, the ^{19}F SCS in these systems should be an exclusive manifestation of the electronic effect of the nitro substituent.



5 **6** **7**

On this basis, if a structural effect is the predominating factor determining the relative SCS in the 3α and 4β dispositions of the fluoronaphthalenes (Table IX), then the SCS for the nitro group in **5** and **6** should be identical. On the other hand, if the formal negative charge in the meta positions of **5** and **6** is the important factor, then there should be a significant difference between the SCS of **5** and **6** but not as large as that observed in the 3α and 4β dispositions of the fluoronaphthalenes. The latter conclusion follows from the expectation that the relative importance of the formal π charge at the carbon atom to which the probe is attached

Table X. Substituent Chemical Shifts (ppm) of Nitro-Substituted Fluoromethylnaphthalenes

Compd[a] 5	6	7	Solvent
+5.17	+3.92	+7.40	Deuteriochloroform
+5.50	+3.64		*N*-Methyl-2-pyrrolidone
+5.70	+3.70		Dimethylformamide

[a] 1-Fluoromethylnaphthalene (+209.2 ppm relative to $CFCl_3$ in CCl_4); 2-fluoromethylnaphthalene (+209.4 ppm relative to $CFCl_3$ in CCl_4).

should be substantially reduced in systems **5, 6,** and **7** compared with the aryl fluorides.[44] The ^{19}F SCS of **5, 6,** and **7** set out in Table X appear to provide a definite answer to the problem. It can be seen that the difference between the SCS of **5** and **6** is substantial indicating that substituent-induced charge alternation is an important factor determining the magnitude of ^{19}F SCS in aromatic systems. Further, it is clear that the SCS difference between **5** and **7** is much less than the difference observed between the corresponding dispositions (3α and 4α) of the fluoronaphthalenes (Table IX); thus, the charge on the carbon atom attached to the fluorine probe is a predominating factor in aryl fluorides.

It is worth noting two further interesting features about the data in Table X. First, it can be seen that the fluorine chemical shifts of the fluoromethylnaphthalenes respond to the nitro substituent in the *opposite* sense to that observed for aryl fluorides; i.e., electron withdrawal shields the fluorine nucleus in the fluoromethylnaphthalenes (*positive* SCS), whereas deshielding is the norm for aryl fluorides (*negative* SCS). This phenomenon, which has been previously noted with acyclic,[15b,c] cyclic,[15a] and bicyclic fluorides[12] as well as the benzo trifluorides[45] and benzyl fluorides,[46] is not explicable in terms of current theoretical treatments of fluorine chemical shifts. Secondly, in contrast to other structurally rigid aliphatic fluorides, the fluorine nucleus in fluoromethylaryl derivatives is very sensitive to the electronic effect of substituents.[47]

Conclusions

The main point that has emerged from this study is that ^{19}F chemical shifts involve factors different from, and of a different order of complexity to, those encountered in the study of substituent effects on conventional chemical properties. One of the problems seems to be the apparent sensitivity of fluorine chemical shifts to substituent-induced structural distortions. Surprisingly, the results of this study seem to imply that the structural distortions, generally inferred from "anomalous" ^{19}F SCS, are not necessarily a function of substituent size; perhaps structural irregularities are simply an adjustment by the aryl system to changes in the electronic distribution induced by the substituent. However, this question cannot be answered with any degree of certainty because of the paucity of accurate structural information on mono- and di-substituted aryl ring systems.

Finally, the FMMF analysis and the experimental results of this paper suggest that the 6β and 7β orientations of naphthalene offer advantages over the meta and para positions of benzene for assessing the electronic effect of substituents in the ground state by the ^{19}F probe.

Experimental Section

Melting points are uncorrected. The ^1H NMR spectra were recorded for chloroform-*d* solutions with a Varian A-60 spectrometer, while the fluorine NMR spectra were measured with a Perkin-Elmer R12A operating at 56.4 MHz, using solutions containing 10% (w/w) of the fluoro compound together with 3% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as internal standard. The fluorine spectra of the fluoromethylnitronaphthalenes were measured relative to the appropriate fluoromethylnaphthalene as internal standard. 5-Fluoroindan and 6-fluorotetralin were available from a previous study.[48]

5-Fluoro-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide. 3,4-Dimethylfluorobenzene (97.5 g), prepared according to the method outlined by Adcock and coworkers,[49] was brominated at 140° by the method previously used for the preparation of α,α'-dibromo-*o*-xylene.[50] The resulting mixture was distilled under reduced pressure to give crude α,α'-dibromo-4-fluoro-*o*-xylene (129.5 g), bp 68–105° (0.05 mm). This crude product was treated with sodium sulfide according to the method outlined by Oliver and Ongley[51] to yield, after steam distillation, colorless 5-fluoro-1,3-dihydrobenzo[*c*]thiophene (19.5 g). Oxidation of the benzothiophene with 40% peracetic acid[51] gave 5-fluoro-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (19.0 g), which after recrystallization from ethanol formed white needles, mp 101–102°.

Anal. Calcd for $C_8H_7O_2SF$: C, 51.6; H, 3.8. Found: C, 51.8; H, 3.8.

4-Fluoro-1,2-dihydrobenzocyclobutene. 5-Fluoro-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (5.0 g) was pyrolyzed at 700° according to the method outlined by Oliver and Ongley.[51] Distillation of the pyrolysate gave 4-fluoro-1,2-dihydrobenzocyclobutene (3.7 g) as a colorless oil: bp 153–154° (760 mm); $n^{26}D$ 1.5095.

Anal. Calcd for C_8H_7F: C, 78.68; H, 5.74. Found: C, 78.43; H, 5.65.

***p*-Fluoroethylbenzene.** A solution of *p*-fluoroacetophenone[52] (6.9 g; 0.05 mol) in methanol (50 ml) was reduced with hydrogen (40 psi) over activated palladized charcoal (5%). After 2 hr, the solution was filtered and diluted with water, and the oil was extracted with ether. Removal of the ether gave an oil which was distilled to yield a colorless liquid: bp 55–57° (35 mm) [lit.[52] 142–143° (755 mm)]; $n^{19}D$ 1.472.

***p*-Fluoroisopropylbenzene.** 1-Fluoro-4-(1-hydroxy-1-methylethyl)benzene, prepared from *p*-fluoroacetophenone according to the Grignard procedure of Brown, Okamoto, and Ham,[53] crystallized from *n*-pentane in colorless plates, mp 36–37° (lit.[53] 37.8°). The alcohol (6 g) was mixed with finely powdered anhydrous potassium hydrogen sulfate (11 g) and heated on an oil bath at 150° for 2 hr. Distillation of the residue at reduced pressure gave *p*-fluoroisopropenylbenzene as a colorless oil (4.8 g): bp 57–59° (28 mm); $n^{21}D$ 1.5140. The structure was confirmed by ^1H NMR. A solution of the olefin (3.7 g) in ethanol was reduced with hydrogen (50 psi) over palladized charcoal (5%). The product was distilled to yield a colorless oil: bp 72–74° (35 mm) [lit.[4] 164–165° (755 mm)]; $n^{19}D$ 1.471. The structure was confirmed by ^1H NMR.

1-Ethyl-4-fluoronaphthalene. 1-Acetyl-4-fluoronaphthalene was prepared as described by Jacobs, Winstein, Rolls, and Robson.[54] Clemmensen reduction[55] of the ketone gave 1-ethyl-4-fluoronaphthalene. Distillation afforded a colorless oil: bp 53–57° (0.05 mm); $n^{18}D$ 1.5838.

Anal. Calcd for $C_{12}H_{11}F$: C, 82.73; H, 6.36. Found: C, 82.83; H, 6.36.

1-Fluoro-4-(1-hydroxy-1-methylethyl)naphthalene. 1-Acetyl-4-fluoronaphthalene[54] (14.1 g; 0.075 mol) was treated with methylmagnesium iodide as described by Brown and coworkers[53] for the preparation of 1-fluoro-4-(1-hydroxy-1-methylethyl)benzene. The alcohol crystallized from *n*-pentane as colorless plates (13 g), mp 84–85°.

Anal. Calcd for $C_{13}H_{13}OF$: C, 76.45; H, 6.42. Found: C, 76.74; H, 6.49.

1-Fluoro-4-isopropylnaphthalene. Prepared from 1-fluoro-4-(1-hydroxy-1-methylethyl)naphthalene in the way described above for *p*-fluoroisopropylbenzene. Distillation afforded a colorless oil, bp 75–76° (0.4 mm); $n^{23}D$ 1.5740.

Anal. Calcd for $C_{13}H_{13}F$: C, 82.95; H, 6.96. Found: C, 83.08; H, 7.03.

1-Fluoro-4-*tert*-butylnaphthalene. Prepared from 1-fluoro-4-(1-hydroxy-1-methylethyl)naphthalene (10 g) using the procedure outlined by Van Bekkum and coworkers[56] for the preparation of 1,4-di-*tert*-butylnaphthalene. Distillation of the crude product afforded a colorless oil (2.7 g): bp 63–64° (0.1 mm); $n^{19}D$ 1.5710.

Anal. Calcd for $C_{14}H_{15}F$: C, 83.13; H, 7.47. Found: C, 83.65; H, 7.62.

2-Acetyl-6-fluoronaphthalene. A solution of 2-fluoronaphthalene (29 g, 0.2 mol) in nitrobenzene (150 ml) was treated with acetyl chloride (16 ml) in the presence of powdered aluminium

chloride (30 g, 0.22 mol) with mechanical stirring and ice cooling.[57] After 12 hr of stirring at room temperature, the reaction was worked up in the normal manner. Crystallization of the crude residue from *n*-pentane afforded white shining plates (9.0 g), mp 41–42°. This isomer proved to be 2-acetyl-6-fluoronaphthalene by conversion via the oxime to 2-acetamido-6-fluoronaphthalene, mp 142–143° (lit.[58] 146–147°). Hydrolysis afforded the amine which crystallized from light petroleum (bp 60–90°) in light pink plates, mp 108° (lit.[58] 110–111°).

2-Ethyl-6-fluoronaphthalene. Prepared from 2-acetyl-6-fluoronaphthalene in the same way as the 1,4 isomer, the crude solid crystallized from *n*-pentane in colorless flakes, mp 38–39°.

Anal. Calcd for $C_{12}H_{11}F$: C, 82.73; H, 6.36. Found: C, 82.46; H, 6.33.

2-Fluoro-6-(1-hydroxy-1-methylethyl)naphthalene. Prepared from 2-acetyl-6-fluoronaphthalene (5.6 g) in the same way as the 1,4 isomer, the alcohol crystallized from *n*-pentane in colorless plates, mp 59–60°.

Anal. Calcd for $C_{13}H_{13}OF$: C, 76.45; H, 6.42. Found: C, 76.46; H, 6.51.

2-Fluoro-6-isopropylnaphthalene. Prepared from the above alcohol in the same way as the 1,4 isomer, the fluoro hydrocarbon crystallized from *n*-pentane as colorless plates, mp 36–38°.

Anal. Calcd for $C_{13}H_{13}F$: C, 82.95; H, 6.96. Found: C, 82.90; H, 7.27.

2-Fluoro-6-*tert*-butylnaphthalene. 2-Fluoronaphthalene (7.3 g; 0.05 mol) was treated with *tert*-butyl chloride by the method essentially used by Whitmore and James[59] for naphthalene. The crude product was crystallized several times from *n*-pentane as colorless cubes, mp 84–85°. The structure was confirmed by ^{1}H NMR.

Anal. Calcd for $C_{14}H_{15}F$: C, 83.13; H, 7.47. Found: C, 82.85; H, 7.30.

2-Fluoro-8-methylnaphthalene. 7-Fluoro-1-naphthoic acid was prepared in the manner outlined by Adcock and Dewar[58] and recrystallized from aqueous ethanol in needles, mp 224–225° (lit.[58] 224–225°). The acid was reduced to 2-fluoro-8-methylnaphthalene according to the method outlined by Benkeser, et al.[60] Distillation afforded a colorless oil: bp 36° (0.05 mm); n^{17}D 1.5872.

Anal. Calcd for $C_{11}H_9F$: C, 8247; H, 5.66. Found: C, 82.53; H, 5.77.

1-Ethyl-7-fluoronaphthalene. A solution of 2-fluoronaphthalene (14.6 g) in carbon disulfide was treated with acetyl chloride as described by Dziewonski and Sternbach.[61] After standard work-up, the crude residue, after fractional recrystallization from pentane, afforded white plates of 2-acetyl-6-fluoronaphthalene, mp 41–42°, and an additional more soluble isomer, mp 40–41° (lit.[62] 40.5–41°). This isomer proved to be 1-acetyl-7-fluoronaphthalene by conversion via the oxime to 1-acetamido-7-fluoronaphthalene, mp 162–163° (lit.[58] 163–164°).

Clemmensen reduction[63] of this latter ketone afforded 1-ethyl-7-fluoronaphthalene as a colorless oil after distillation: bp 76–78° (0.5 mm); n^{20}D 1.5780.

Anal. Calcd for $C_{12}H_{11}F$: C, 82.73; H, 6.36. Found: C, 82.61; H, 6.33.

2-Fluoro-8-(1-hydroxy-1-methylethyl)naphthalene. Prepared from 1-acetyl-7-fluoronaphthalene in the same way as the 1,4 isomer, the alcohol crystallized from petroleum ether in colorless plates, mp 90–91°.

Anal. Calcd for $C_{13}H_{13}FO$: C, 76.45; H, 6.42. Found: C, 76.45; H, 6.74.

2-Fluoro-8-isopropylnaphthalene. Prepared from the above alcohol in the same way as the 1,4 isomer, the fluoro hydrocarbon distilled as a colorless oil: bp 57–59° (0.07 mm); n^{20}D 1.5723.

Anal. Calcd for $C_{13}H_{13}F$: C, 82.95; H, 6.96. Found: C, 83.00; H, 6.80.

2-Fluoro-8-*tert*-butylnaphthalene. Prepared from the above alcohol in the same way as the 1,4 isomer. Distillation afforded a colorless oil: bp 59–60° (0.1 mm); n^{24}D 1.569.

Anal. Calcd for $C_{14}H_{15}F$: C, 83.13; H, 7.47. Found: C, 83.59; H, 7.37.

1-Fluoromethylnaphthalene. A solution of 1-methylnaphthalene (14.2 g; 0.10 mol) in carbon tetrachloride (150 ml) was heated under reflux with *N*-bromosuccinimide (17.8 g; 0.10 mol) and benzoyl peroxide (0.1 g) for 12 hr. The solution was filtered and solvent removed under reduced pressure to yield crude 1-bromomethylnaphthalene, which crystallized from *n*-pentane in small white crystals, mp 51–52.5° (lit.[64] 53°).

A solution of 1-bromomethylnaphthalene (13.8 g) in *N*-methyl-2-pyrrolidone (40 ml) was added slowly to a stirred suspension of anhydrous potassium fluoride powder (7.5 g) in methylpyrrolidone (15 ml) according to the method outlined by Yokoyama, Wiley, and Miller[65] for the preparation of *m*-trifluoromethylbenzyl fluoride. After 4 hr at 165–170°, the solution was cooled and the reaction mixture poured onto an ice-cold sodium carbonate solution. The oil was extracted with ether, and the ether was washed with water to remove the methylpyrrolidone, dried over magnesium sulfate, and evaporated. Distillation of the residue afforded a colorless oil (2 g): bp 77–78° (1 mm); n^{25}D 1.5970.

Anal. Calcd for $C_{11}H_9F$: C, 82.50; H, 5.62. Found: C, 82.25; H, 5.80.

The fluoride was extremely labile to traces of acid and decomposed violently when subjected to prolonged heat.

2-Fluoromethylnaphthalene. 2-Bromomethylnaphthalene, prepared according to the method outlined above for the 1 isomer, crystallized from *n*-pentane in small white plates, mp 53–54° (lit.[66] 56°).

The fluoride was prepared from 2-bromomethylnaphthalene in the same way as the 1 isomer. Repeated fractional sublimation [50° (0.1 mm)] afforded small white plates, mp 59.5–60.5°.

Anal. Calcd for $C_{11}H_9F$: C, 82.50; H, 5.62. Found: C, 82.39; H, 5.60.

A number of attempts to purify 2-fluoromethylnaphthalene by recrystallization failed. The compound proved to be extremely labile in the presence of trace amounts of acid or base, polymerizing spontaneously.

1-Bromomethyl-3-nitronaphthalene. 4-Methyl-2-nitronaphthalene, prepared according to Sauer, Huisgen, and Hauser,[67] crystallized from ethanol in brown needles, mp 79–81.5° (lit.[67] 79.5–81.5°). Bromination of the methylnitronaphthalene (16.5 g) by the method outlined above for 1-methylnaphthalene gave 1-bromomethyl-3-nitronaphthalene, crystallized from methanol and carbon tetrachloride in pale yellow-brown plates, mp 149–151.5°.

Anal. Calcd for $C_{11}H_8O_2NBr$: C, 49.63; H, 3.01. Found: C, 49.79; H, 2.96.

1-Fluoromethyl-3-nitronaphthalene. Prepared from the above bromo compound (12 g) in the same way as 1-fluoromethylnaphthalene except the reaction mixture was heated for 20 hr. The tarry crude product was extracted with Skellysolve B, and cooling gave 1-fluoromethyl-3-nitronaphthalene (2.5 g) as lemon-yellow needles, mp 90–92.5°.

Anal. Calcd for $C_{11}H_8O_2NF$: C, 64.40; H, 3.9. Found: C, 64.51; H, 3.90.

1-Bromomethyl-4-nitronaphthalene. 4-Nitro-1-methylnaphthalene (18.7 g), mp 67.5–69° (lit.[68] 71–72°), was converted with *N*-bromosuccinimide in carbon tetrachloride (refluxed for 3 days) to 1-bromomethyl-4-nitronaphthalene, pale-yellow needles (10 g; from methanol), mp 87.5–89.5°.

Anal. Calcd for $C_{11}H_8O_2NBr$: C, 49.63; H, 3.01. Found: C, 49.79; H, 2.99.

1-Fluoromethyl-4-nitronaphthalene. An attempt to prepare this compound from the corresponding bromo isomer met with limited success. A considerable amount of tar was formed during the reaction with potassium fluoride in methylpyrrolidone. Extraction of the tarry product with Skellysolve B afforded a limited amount of crude 1-fluoromethyl-4-nitronaphthalene. Fluorine and ^{1}H NMR and mass spectral analysis confirmed the structure of the crude product. A further attempt to prepare the fluoride by shortening the reaction time was no more successful. The crude product was not purified for formal analytical purposes.

Nitration of a sample of 1-fluoromethylnaphthalene in acetic anhydride afforded an isomeric mixture (at least five isomers were detected by ^{19}F NMR) from which pure 1-fluoromethyl-4-nitronaphthalene could not be obtained chromatographically.

2-Bromomethyl-4-nitronaphthalene. 3-Methyl-1-nitronaphthalene (6.5 g), mp 44–45° (lit.[69] 49–50°), prepared according to the method of Marion and McRae[69] with some modification, was brominated in the usual manner (refluxed for 50 hr) to afford crude 2-bromomethyl-4-nitronaphthalene, crystallized from methanol in pale-yellow needles (4 g), mp 114–116°.

Anal. Calcd for $C_{11}H_8O_2NBr$: C, 49.63; H, 3.01. Found: C, 49.86; H, 3.13.

2-Fluoromethyl-4-nitronaphthalene, prepared from the corresponding bromo compound (4 g) in the same manner as outlined above for 1-fluoromethylnaphthalene (0.1 g), crystallized from *n*-pentane as yellow needles, mp 83–85°.

Anal. Calcd for $C_{11}H_8O_2NF$: C, 64.40; H, 3.9. Found: C, 64.57; H, 3.92.

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$$F^S = \sigma_I^S/0.0916 \quad (6)$$

The σ_I value for $N(CH_3)_2$ (0.10) was taken from the compilation of Ritchie and Sager.[10] That for $CONH_2$ (0.30) was calculated from the thermodynamic dissociation constant for the 4-substituted bicyclo[2.2.2]octene-1-carboxylic acid,[11] using eq 2 of ref 11.
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