Substituent Effects. VII.[1] The ^{19}F Nuclear Magnetic Resonance Spectra of Substituted 1- and 2-Fluoronaphthalenes[2]

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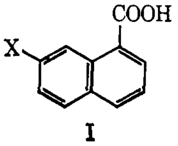
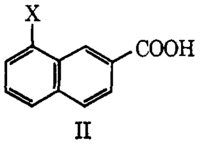
Abstract: The ^{19}F nmr spectra of 55 monosubstituted derivatives of 1- and 2-fluoronaphthalene are reported, some in a variety of solvents. The results confirm the suggestion in part VI,[1] that the effects of substituents on the nmr chemical shifts of fluorine are qualitatively different from their effects on physical and/or chemical properties of other side chains; attempts to explain both sets of phenomena in terms of a common inductive/resonance scheme are therefore incorrect. It is shown that the fluorine chemical shifts can be interpreted in terms of a modified *FM* treatment;[3] in this the major contribution of the field effect is supposed to arise from lengthwise polarization of the C–F bond, so that its magnitude depends on the vector potential of the field along the bond rather than the scalar potential, while the charges on the ring atoms due to mesomeric polarization of the π electrons are calculated by a semiempirical SCF–MO treatment[4,5] instead of the simple PMO approach used previously.

Previous papers of this series[1,3,6,7] have presented evidence implying that the long-range influence of substituents is due essentially to field and mesomeric effects, the classical inductive effect being inappreciable at distances of more than one or two bonds from the substituent. It was shown that the chemical effect of a given substituent in a variety of ring systems could be predicted in these terms, the contributions of the field and mesomeric effects being estimated in a very simple way (*FM* method[3]). This treatment was also successfully extended[1] to the prediction of chemical shifts in the ^{19}F nmr spectra of various derivatives of 4-fluorobiphenyl and 4-fluoroterphenyl.

However, two anomalies remained. First, the effect of substituents (X) in the 7 position of α-naphthoic acid (I) was less than that calculated by the *FM* method; secondly, the effect of substituents on the ^{19}F nmr spectra of fluorobenzene seemed to be out of line with their effect on other systems. A third anomaly, similar to the first, has been reported by Wells and Adcock;[8] the effect of substituents in the 4, 5, 6, and 7 positions on the pK_A of β-naphthoic acid followed the *FM* relation closely, but their effect in the 8 position (II) was again less than that calculated.



I



II

The anomalously small effect of substituents in I and II has been explained in two different ways. Dewar and Grisdale[3] suggested that the effective dielectric constant of the medium separating X from carboxyl might be greater for I than for the other substituted naphthoic acids, on the grounds that in I both X and COOH lie on the same side of the molecule; a line joining X to COOH passes close to the edge of the "cavity" formed by the naphthoic acid in the highly polar solvent (aqueous ethanol) used for the measurements of pK_a. A similar explanation could of course also be used to explain the anomalously small effect of substituents in II.

On the other hand, Wells and Adcock[8] have pointed out that I and II would show a similar anomaly if the field caused by the substituent were dipolar in type. In the *FM* method,[3] the field effect is calculated using a point charge model, the effect of a given substituent being assumed to be inversely proportional to its distance from the reaction center and independent of orientation. The field of a dipole, however, depends also on orientation; at a given distance, the field varies as cos θ, where θ is the angle between the dipole and a line joining it to the reaction center. This factor is fairly close to unity for all the substituted α- and β-naphthoic acids except I and II where it is much smaller; neglect of this factor could account for the failure of the *FM* method in these cases. One would also predict that the resulting error should be greater in the case of II than I, for the values of cos θ for the two series of compounds are roughly in the ratio 2:1. The available data suggest that the anomaly in the case of II is indeed somewhat greater than it is for I, although the difference is less than would be predicted on the basis of a cos θ relationship.

A third alternative would be that both these effects are operating; this would correspond to a model in which the bond linking the substituent to the adjacent carbon atom in the ring is treated as a finite dipole, the potentials owing to the charges at each end of the dipole being calculated independently by some modification of the Kirkwood–Westheimer method.[9] The field effect calculated in this way would have a value intermediate between those predicted by the point charge and point dipole models, and a treatment of this kind has indeed been used with success in certain cases.[10]

The remaining anomaly, *i.e.*, the failure of ^{19}F sub-

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[1] Part VI: M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88**, 3318 (1966).

[2] This work was supported by the Army Research Office through Grant No. DA-ARO-D-31-124-G713.

[3] M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

[4] M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966).

[5] M. J. S. Dewar and T. Morita, unpublished work.

[6] M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3541, 3546 (1962).

[7] M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 354 (1966).

[8] P. R. Wells and W. Adcock, *Australian J. Chem.*, **18**, 1365 (1965).

[9] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

[10] See H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5188 (1964).

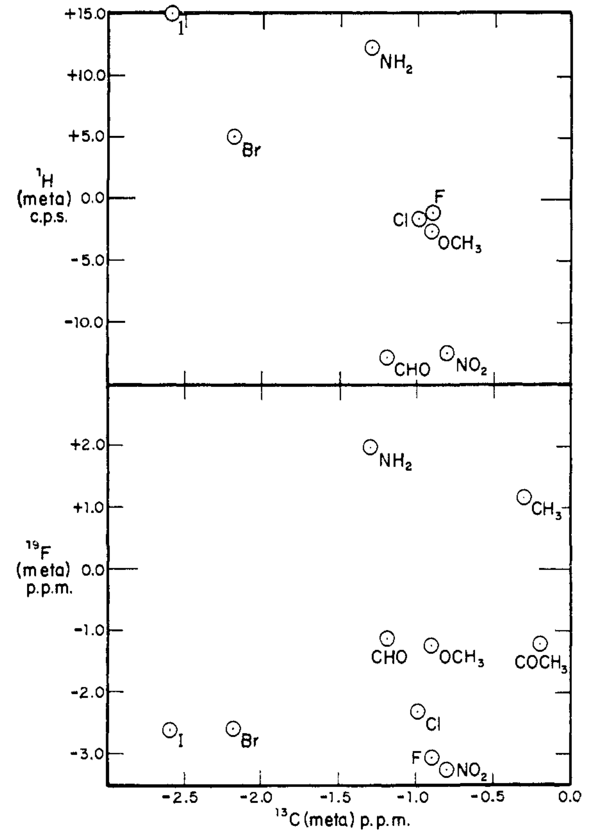
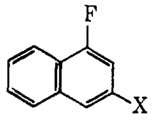


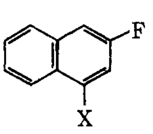
Figure 1. Plot of *m*-fluorine and *meta*-proton shifts *vs.* *m*-carbon shifts in monosubstituted benzenes.

stituent chemical shifts (SCS)[11] for *meta* substituents in fluorobenzene to follow the Hammett relation, was attributed by Dewar and Marchand to deficiencies in the Hückel MO (HMO) method. Consider for example the effect of a $+M$ substituent (*e.g.*, NO_2) in benzene. The HMO method predicts a polarization of the π electrons of the ring, leading to a reduced π density at the positions *ortho–para* to the substituent, but to little change in the π density at the *meta* positions. The SCF–MO method also predicts a reduced π density at the *ortho–para* positions, but it predicts an almost equally large increase in the *meta* π density. Neglect of this *meta*-mesomeric effect would of course lead to errors in any treatment based on the HMO method—and the *FM* method used Hückel π-charge densities as a criterion of the mesomeric effect.

It seemed to us that light could be thrown on both these problems by a study of the ^{19}F nmr spectra of substituted fluoronaphthalenes. Since the π charges calculated by the SCF–MO method for the 3 position of an α-substituted naphthalene, or the 4 position of a β-substituted naphthalene, differ from those calculated for the *meta* position of a substituted benzene, the ^{19}F SCS of 3-substituted α-fluoronaphthalenes (III) and of 4-substituted β-fluoronaphthalenes (IV) should show corresponding variations if the explanation given by Dewar and Marchand is correct. Again, a study of the ^{19}F nmr spectra of 7-substituted α-fluoronaphthalenes (V), and of 8-substituted β-fluoronaphthalenes (VI), in a range of solvents of differing polarity should provide a distinction between the explanations given by Dewar and Grisdale, and by Wells and Adcock, for the anomalously small effect of substituents in I and II; if Dewar and Grisdale are right, the SCS of V and VI should show a large dependence on the effective dielectric constant of the solvent, while, if Wells and Adcock are right, the dependence should be small. The advantage of nmr measurements in this connection is obvious; the SCS for a compound can be determined without difficulty in a wide range of solvents, unlike most other chemical or physical properties.



III



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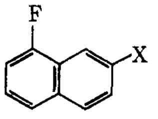
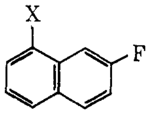


V



VI

These arguments rest of course on the assumption that nmr chemical shifts can be interpreted in the kind of terms used to explain other properties of molecules; there is no good theoretical basis for this and the situation is indeed somewhat confused. Much work has been reported[12,13] on the effects of substituents in benzene on the nmr chemical shifts of protons, ^{13}C, ^{19}F, and ^{15}N, but little attention has been paid to other ring systems. As Gutowsky[12g] and his collaborators first showed, there seems to be a reasonable correlation between the chemical shifts of fluorine *para* to substituents in benzene and the Hammett σ_p constants for the substituents, and similar correlations seem to hold in other cases; however, the chemical shifts of atoms *meta* to a substituent show no good correlation with σ_m, and they do not even correlate with one another. Thus Figure 1 shows plots of published data for the effects of substituents on the chemical shifts of *meta* protons, of *m*-fluorine, and *m*-^{13}C in the ring; clearly the three effects bear little relation to one another.

It is difficult to draw any definite conclusions concerning the effect of substituents from data for benzene alone since these are so limited; there are only two unhindered positions in benzene where a substituent can be placed. We therefore decided to extend our studies of the fluoronaphthalenes to include orientations other than III, IV, V, and VI, in the hope that this additional information might help to clarify the situation. In the following paper we describe the preparation of 55 derivatives of α- and β-fluoronaphthalene, carrying a variety of substituents in most of the unhindered positions; here we report a study of their ^{19}F nmr spectra in a variety of solvents and conclusions that

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(11) The substituent chemical shift for a given substituent in a given compound is defined as the difference between the chemical shift for the compound and the chemical shift for the parent system derived from it by replacing the substituent with hydrogen. Thus the SCS of *m*-NO_2 in fluorobenzene is the difference between the ^{19}F chemical shift in *m*-fluoronitrobenzene and the ^{19}F chemical shift in fluorobenzene.

(12) (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); *Tetrahedron Letters*, 468 (1961); (b) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962); (c) G. Fraenkel, R. E. Carter, A.McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (d) P. C. Lauterbur, *ibid.*, **83**, 1838 (1961); (e) A. Mathias, *Tetrahedron*, **22**, 217 (1966); (f) D. T. Clark and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 745 (1966); (g) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *ibid.*, **74**, 4809 (1952); (h) N. Boden, J. W. Emsley, J. Feeny, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133, 467 (1964); J. W. Emsley, *ibid.*, **9**, 381 (1965); (i) J. Homer and L. F. Thomas, *J. Chem. Soc., Phys. Org. Chem. Sect.*, 141 (1966).

(13) (a) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957); R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5352 (1959); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963); R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965).

Table I. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes in Dimethylformamide, Relative to TCTFB

Substituent	Orientation						
	3α	4α	6α	7α	4β	6β	8β
NO_2	+329.9 ± 4.4	−115.5 ± 0.4	+487.2 ± 3.8	+413.5 ± 1.10	+54.2 ± 2.1	−270.0 ± 2.5	−282.6 ± 1.8
CN	+397.1 ± 2.3	−35.1 ± 0.2	+532.2 ± 0.4	+472.2 ± 0.6	+53.5 ± 0.3	−208.5 ± 2.1	−201.1 ± 1.3
COOH[a]	+547.7 ± 1.2	+142.7 ± 2.0		+518.7 ± 2.6	+139.6 ± 0.5	−105.7 ± 1.1	−96.1 ± 2.0
$COOCH_3$		+103.2 ± 3.2		+510.6 ± 1.2		−131.4 ± 1.4	−124.1 ± 0.8
Br	+424.2 ± 0.6	+569.9 ± 1.6	+557.3 ± 2.9	+583.0 ± 2.0	+39.7 ± 0.1	+29.8 ± 0.7	−92.7 ± 1.0
OH				+680.0 ± 4.0		+373.6 ± 1.6	+153.6 ± 1.5
OCH_3				+641.5 ± 2.8		+308.0 ± 1.2	+99.7 ± 1.0
NH_2	+650.2 ± 0.3	+1444 ± 1.3	+664.1 ± 1.0	+746.4 ± 2.2	+72.2 ± 3.0	+491.5 ± 6.6	+204.8 ± 2.3
$NH \cdot COCH_3$	+557.0 ± 0.7	+776.1 ± 0.5	+629.4 ± 1.7	+623.5 ± 2.8	+44.9 ± 0.4	+229.1 ± 3.3	+53.7 ± 2.4
$N(CH_3)_2$		+981.2 ± 1.5			+41.8 ± 2.6		+63.3 ± 1.5
α-H	+604.7 ± 4.4						
β-H	+98.9 ± 2.0						

[a] Value for 5β-COOH, +93.6 ± 0.7.

seem to follow from them. For brevity these compounds will be designated by the symbol for the substituent, preceded by a numeral giving its position and a Greek letter denoting the position of fluorine; thus 6α-NO_2 implies 1-fluoro-6-nitronaphthalene (VII).

Experimental Section

The fluorine nmr spectra were measured with a Varian DP-60 spectrometer with variable-temperature probe, operating at 56.4 MHz, using solutions containing 29% (w/w) of the fluoro compound together with 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as internal standard. The spectra were calibrated using a Hewlett-Packard 200 JR audio oscillator; each spectrum was swept at least four times in each direction at a maximum rate of 15–20 Hz/sec. The standard deviations of nearly all the measurements were less than 5 Hz.

All the compounds were measured in dimethylformamide at 36°; the results are listed in Table I. Certain of them were also measured in other solvents (Tables II–V) at the same temperature. Difficulties arose in the case of the 6β, 8β, and 7α derivatives, due to their low solubilities; some measurements were therefore made at 74° (Table VI). The SCS values for 6β-NO_2, 8β-NO_2, and 7α-NO_2 in benzene were, however, the same at both temperatures within the limits of experimental error; moreover Taft and his collaborators[13b] have reported that the SCS of *meta*-substituted fluorobenzenes show a similar insensitivity to temperature. It therefore seems reasonable to compare SCS values calculated from the data in Table VI with SCS values calculated from the results at 36°.

Table II. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes in Acetone, Relative to TCTFB

Substituent	Orientation		
	7α	6β	8β
NO_2	+410.9 ± 1.5	−271.8 ± 1.4	−283.4 ± 1.4
CN	+466.0 ± 2.5	−211.4 ± 1.3	−199.0 ± 0.9
$COOCH_3$	+499.6 ± 2.6	−126.1 ± 1.9	−117.9 ± 2.2
Br	+579.7 ± 1.8	+30.9 ± 1.4	−80.4 ± 2.6
OH	+668.0 ± 7.0	+352.5 ± 1.7	+141.5 ± 1.6
OCH_3	+641.6 ± 1.5	+308.6 ± 1.0	+102.6 ± 1.7
NH	+725.0 ± 2.5	+467.4 ± 3.8	+183.5 ± 1.9
$NH \cdot COCH_3$	+609.1 ± 2.1	+217.9 ± 2.7	
$N(CH_3)_2$			+89.2 ± 0.7
α-H	+598.9 ± 2.9		
β-H	+102.6 ± 1.2		

Table III. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes in Benzene, Relative to TCTFB

Substituent	Orientation		
	7α	6β	8β
NO_2	+350.5 ± 2.9	−293.4 ± 2.3	−332.7 ± 5.5
CN	+413.9 ± 1.8		−238.5 ± 1.6
$COOCH_3$	+436.1 ± 4.7	−147.3 ± 2.0	−170.7 ± 3.5
Br	+523.3 ± 3.6	+9.5 ± 0.4	−110.9 ± 1.6
OH	+610.4 ± 2.4		
OCH_3	+612.2 ± 1.2	+246.5 ± 2.6	+66.9 ± 0.9
NH_2	+670.1 ± 3.7	+374.5 ± 1.8	+113.9 ± 1.0
$N(CH_3)_2$			+60.0 ± 0.5
α-H	+554.7 ± 2.3		
β-H	+67.3 ± 1.1		

Table IV. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes in Cyclohexane, Relative to TCTFB

Substituent	Orientation		
	7α	6β	8β
$COOCH_3$	+407.6 ± 3.4		−185.5 ± 1.7
Br	+506.5 ± 2.4	−30.0 ± 1.1	−136.4 ± 1.2
OCH_3	+597.0 ± 0.8	+253.2 ± 1.8	+58.6 ± 0.5
$N(CH_3)_2$			+39.9 ± 0.0
α-H	+528.3 ± 5.6		
β-H	+43.8 ± 1.8		

Table V. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes in Methanol, Relative to TCTFB

Substituent	Orientation		
	7α	6β	8β
CN	+449.8 ± 1.9		
$COOCH_3$	+483.4 ± 1.0		−126.8 ± 0.2
Br	+578.5 ± 3.0		−80.0 ± 1.3
OH		+352.9 ± 1.1	+158.3 ± 3.2
OCH_3	+640.5 ± 4.9	+304.4 ± 1.3	+112.1 ± 0.7
NH_2	+705.1 ± 3.3	+410.5 ± 1.3	+146.8 ± 2.0
$NH \cdot COCH_3$	+600.2 ± 1.9		
$N(CH_3)_2$			+77.8 ± 0.8
α-H	+593.3 ± 4.0		
β-H	+101.1 ± 1.2		

Table VII shows measurements for the various fluoronaphthylammonium ions (substituent, NH_3^+). These were obtained using solutions containing 10% (w/w) of the chloride together with 5% (w/w) of TCTFB.

Discussion

Our primary purpose in this investigation was threefold. First, we wanted to see whether the SCS of the 7α (III) and 8β (IV) compounds would show a dependence on the polarity of the solvent, in order to distinguish between the possible explanations for the anomalous behavior of substituents in the corresponding naphthoic acids. Secondly, we wanted to see if the effects of substituents in naphthalene would support our explanation for the apparently anomalous behavior of the *meta*-substituted fluorobenzenes. Thirdly, we

Table VI. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes Relative to TCTFB in Benzene and Cyclohexane at 73–75°

Compound	SCS	
	Benzene	Cyclohexane
α-H	+565.4 ± 0.9	+544.9 ± 0.8
β-H	+78.0 ± 0.6	+60.2 ± 0.4
6β-NO_2	−280.1 ± 1.2	. . .
8β-NO_2	−324.0 ± 0.9	. . .
7α-NO_2	+358.7 ± 0.8	+340.9 ± 1.2
8β-CN	. . .	−249.4 ± 1.1
7α-CN	. . .	+424.5 ± 1.8
8β-$COOCH_3$	. . .	−144.4 ± 2.1
6β-OH	+278.0 ± 0.7	. . .
8β-OH	+74.0 ± 0.7	. . .
8β-NH_2	. . .	+99.3 ± 0.0
7α-NH_2	. . .	+667.8 ± 1.2

Table VII. Chemical Shifts (Hz) of Substituted Fluoronaphthalenes in 95% DMF–5% H_2O, Relative to TCTFB

Compound	Shift
α-H	+616.5 ± 0.6
β-H	+103.3 ± 1.2
3α-NH_3^+	+411.9 ± 1.3
6α-NH_3^+	+559.9 ± 4.0
7α-NH_3^+	+575.1 ± 2.4
4β-NH_3^+	+56.0 ± 0.5
6β-NH_3^+	+33.3 ± 0.3
8β-NH_3^+	−72.9 ± 0.5

Table VIII. Substituent Chemical Shifts (ppm) in Various Solvents

Compound	DMF	Acetone	Benzene	Cyclohexane	Methanol
6β-NO_2	−6.54	−6.64	−6.39		
8β-NO_2	−6.76	−6.84	−7.09		
7α-NO_2	−3.39	−3.33	−3.62	−3.63	
6β-CN	−5.45	−5.56			
8β-CN	−5.32	−5.35	−5.42	−5.49	
7α-CN	−2.35	−2.36	−2.50	−2.13	−2.54
6β-COOH	−3.62				
8β-COOH	−3.46				
7α-COOH	−1.52				
6β-$COOCH_3$	−4.08	−4.05	−3.80	−3.63	
8β-$COOCH_3$	−3.95	−3.91	−4.22	−4.07	−4.04
7α-$COOCH_3$	−1.67	−1.76	−2.10	−2.14	−1.95
6β-Br	−1.23	−1.27	−1.02	−1.31	
8β-Br	−3.40	−3.24	−3.16	−3.20	−3.21
7α-Br	−0.38	−0.34	−0.56	−0.39	−0.25
6β-OH	+4.87	+4.43	+3.55		+4.46
8β-OH	+0.97	+0.69	+0.07		+1.01
7α-OH	+1.34	+1.23	+0.99		
6β-OCH_3	+3.72	+3.65	+3.18	+3.71	+3.60
8β-OCH_3	0.00	0.00	0.00	+0.26	+0.20
7α-OCH_3	+0.65	+0.76	+1.00	+1.22	+0.84
6β-NH_2	+6.96	+6.47	+5.45		+5.49
8β-NH_2	+1.88	+1.43	+0.83	+0.69	+0.81
7α-NH_2	+2.51	+2.24	+2.07	+2.18	+1.98
8β-$N(CH_3)_2$	−0.63	−0.24	−0.13	−0.07	−0.41
6β-$NH \cdot COCH_3$	+2.31	+2.04			
8β-$NH \cdot COCH_3$	−0.80				
7α-$NH \cdot COCH_3$	+0.33	+0.18			+0.10

hoped to arrive at some general treatment of substituent effects which might help us to rationalize data for ^{19}F SCS in a straightforward manner.

The substituent chemical shifts for the 7α and 8β fluoronaphthalenes (III, IV) in various solvents are listed in Table VIII; values for the 6β series are included for comparison. Some of the compounds could not be studied in certain solvents because their solubility was too small; these appear as blanks in the table. It will be seen that the SCS values for compounds containing $+F+M$ substituents (*e.g.*, NO_2, CN) vary little from one solvent to another in all three series, and that the variations show no obvious correlation with the bulk properties of the solvent. The variations in the case of $-M$ substituents (*e.g.*, MeO, NH_2) are somewhat larger—but, as Taft and his collaborators have pointed out,[13b] one might expect specific interactions between the solvent and substituents of this type to alter the nature of the latter.

The field effect of a neutral $\pm F$ substituent, S, is due to the electrostatic field set up by the polar bond linking it to an adjacent carbon atom. This dipole will have a finite length (l), comparable with the length of the C–S bond. Consider the potential at a distance r from the nearer end of the dipole. If $r \ll l$, the potential will vary as $1/r$; if $r \gg l$, it will vary as $1/r^2$. At short distances the field is therefore similar to that of a point charge. Furthermore, in a polar solvent, where the substituent S is embedded in a medium of high dielectric constant, one might expect the contribution of the S end of the dipole to be selectively attenuated; in this case the potential might vary inversely as $1/r$ even for large values of r. These arguments led Dewar and Grisdale[3] to approximate the field effect by the expression F_S/r_{RS}, F_S being a constant characteristic of the substituent, S, and r_{RS} its distance from the reaction center R.

The results shown in Table VIII suggest that the second part of their argument cannot be correct, for, if it were, the SCS of substituents should be systematically less in cyclohexane than in methanol. The point charge model for the field effect cannot therefore be a good approximation; in any exact treatment, substituents will have to be treated as finite dipoles or multipoles, particularly when the distance between the substituent and the reaction center is large. This conclusion is supported[1] by a comparison of the SCS of 3′-substituted 4-fluorobiphenyls with those of 3′′-substituted 4-fluoroterphenyls; here, where the distance between the substituent and fluorine is large, the SCS varies approximately as the inverse square of distance, rather than as the inverse first power.

These results therefore seem to provide a fairly definite answer to our first problem; the deviations shown by I and II from the *FM* relation are probably due, as Wells and Adcock[8] suggested, to the incorrect form of the expression used to estimate the field effect.

Apart from their bearing on the solvent problem, the data in Table VIII also raise a further very interesting point. The SCS values for $+M+F$ substituents are uniformly much larger in the 8β series than in the 7α series, and similar discrepancies also appear with substituents of other types. These differences cannot be explained in terms of existing theories of substituent effects. They cannot be attributed to mesomeric interactions; for all theories agree in predicting that interactions between the 1 and 7 positions of naphthalene should be small—and if anything, smaller in the 8β orientation than in the 7α. Nor can they be due to an orientational field effect of the kind postulated by Wells and Adcock, for the effect should then be *greater* in the 7α series—as it is in the case of the corresponding

Table IX. Substituent Chemical Shifts (ppm) of Substituted Fluoronaphthalenes in Dimethylformamide

Substituent	Orientation 3α	4α	6α	7α	4β	5β	6β	8β
NO_2	−4.87	−12.77	−2.08	−3.39	−0.79		−6.54	−6.76
CN	−3.68	−11.34	−1.29	−2.35	−0.80		−5.45	−5.32
COOH	−1.01	−8.19		−1.52	+0.72	−0.09	−3.62	−3.46
$COOCH_3$		−8.89		−1.67			−4.08	−3.95
Br	−3.20	−0.62	−0.84	−0.38	−1.05		−1.23	−3.40
OH				+1.34			+4.87	+0.97
OCH_3				+0.65			+3.72	0.00
NH_2	+0.81	+14.88	+1.05	+2.51	−0.47		+6.96	+1.88
$NH{\cdot}COCH_3$	−0.85	+3.04	+0.44	+0.33	−0.96		+2.31	−0.80
$N(CH_3)_2$		+6.68			−1.01			−0.63
NH_3^+	−3.63		−1.00	−0.73	−0.84		−1.24	−3.12

carboxylic acids I and II. And finally, the ^{19}F nmr results entirely exclude any explanation in terms of classical inductive effects since these would be the same in both the 7α and 8β series. This last argument incidentally invalidates Taft's interpretation of substituent effects in the ^{19}F nmr spectra of substituted fluorobenzenes; his correlation of the SCS for *meta*-substituted fluorobenzenes with σ_I must be regarded as fortuitous and irrelevant.

Our next step was to compare the effect of substituents on the ^{19}F nmr spectra of 1- and 2-fluoronaphthalene with their effect on the pK_a of the corresponding naphthoic acids. The substituent chemical shifts, calculated from the data listed in Table I, are shown in Table IX. On comparing these values with the pK_a data,[3,8] a remarkable regularity emerged; in nearly every case a plot of SCS *vs.* pK_a was linear. Table X shows the proportionality factor, *a*, in the following equation, calculated by a least-squares method, together with the corresponding correlation coefficient and the number of compounds for which data were available. The correlation is excellent for every series except 4β.

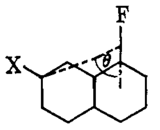
$$\mathrm{SCS} = a(\mathrm{p}K_a) + b \qquad (1)$$

Table X. Comparison of SCS for Substituted Fluoronaphthalenes with pK_a for Substituted Naphthoic Acids

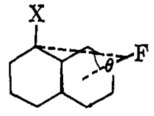
Orientation	No. of compounds	*a* in eq 1	Correlation coefficient
3α	4	−4.6	0.96
4α	5	−11.4	0.99
6α	4	−3.1	0.98
7α	6	−6.1	0.99
4β	5	−0.5	0.63
6β	5	−12.0	0.98
8β	6	−12.0	0.96

These results provide further support for Wells and Adcock's interpretation[8] of the data for I and II. As we have seen, the ^{19}F SCS in substituted fluorobenzenes are almost unaffected by a change in solvent; this insensitivity to the dielectric constant of the surrounding medium shows that they are not subject to a medium effect of the kind envisaged by Dewar and Grisdale. The fact that the pK_a's of I and II correlate so well with the SCS's for III and IV therefore shows that the acids must also be unaffected by the medium, *i.e.*, that the deviations shown by I and II from the *FM* relation cannot be attributed to intervention by the polar solvent.

However, we are still left with the problem of explaining why the value of *a* is twice as great in the 8β series as in the 7α. The only feasible explanation seems to lie in an anisotropic response of fluorine to an applied field. This indeed seems very reasonable, for the change in chemical shift of fluorine is presumably due to a polarization of the electrons forming the C–F bond—and this should depend on the field along the axis of the bond rather than the field perpendicular to it. If then we draw a line from the midpoint of the bond to the polarizing group, and, if this line makes an angle θ with the line joining fluorine to carbon, the SCS should vary as cos θ. Using the naive point charge model,[8] the corresponding diagrams for the 7α and 8β series are as indicated in VII and VIII, respectively; the corresponding values for cos θ are in the ratio 1:2.1, in excellent agreement with the ratio of the corresponding proportionality factors *a* in eq 1. This orientational effect can therefore account quantitatively for the difference between the 7α and 8β series; one might add that the need for postulating such orientational factors provides a decisive confirmation of the suggestion[8] that the long-range nonmesomeric effects of substituents are due to the field effect rather than to the classical inductive effect.



VII



VIII

Next let us consider the "anomalous" behavior of *meta* substituents in fluorobenzene. It is interesting that the one anomaly in Table X is for a series of fluoronaphthalenes (IV) that have exactly the same orientation of fluorine and substituent as a *meta*-substituted fluorobenzene, and that the isomeric series III shows no such anomaly. This difference can be explained qualitatively in the manner outlined in part VI.[1] Figure 2 shows formal charges calculated[5] by the SCF–MO method for benzaldehyde and for α- and β-naphthaldehyde, assuming that the charge arises solely by polarization of the π electrons.

Note that the negative charges in the *meta* position of benzaldehyde, and in the 4 position of β-naphthaldehyde, are only half as great as that in the 3 position of α-naphthaldehyde. Since similar differences will presumably occur also in the case of other substituents,

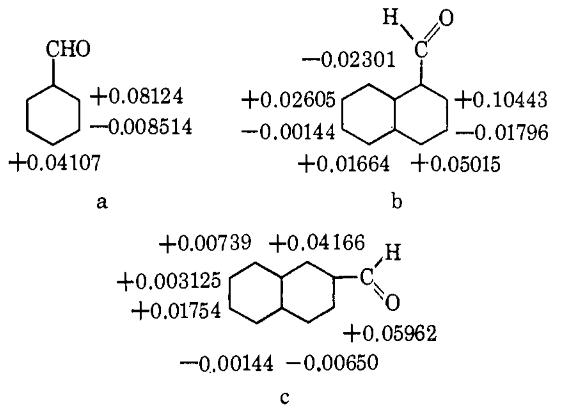


Figure 2. Formal charges calculated[5] by the SCF–MO method for: a, benzaldehyde; b, α-naphthaldehyde; c, β-naphthaldehyde.

one might expect the discrepancies between the effects of substituent on ^{19}F nmr, and their effects on other chemical properties, to be much greater in *meta*-substituted benzenes, and in the 4β-naphthalenes, than in the 3α-naphthalenes. Indeed, it is only in the latter series that one finds a good correlation between the SCS of substituted fluoronaphthalenes and the pK_a of the corresponding naphthoic acids. We next tried to construct a general treatment of ^{19}F substituent chemical shifts, based on the *FM* approach[3] and the considerations outlined above. Several formidable difficulties impede any endeavor of this kind, *e.g.*, a–c below.

(a) If the field effect is to be calculated on the basis of a dipole field due to a finite dipole, the length of the dipole must be known; not only is there no way of estimating this theoretically, but it cannot even be treated as a parameter since the length would be expected to vary from one substituent to another. Moreover, it is difficult to know what values to assume for the effective dielectric constants.

(b) If the π-charge densities are to be calculated by the SCF–MO method, each substituent must be treated separately, for preliminary calculations have shown that the π-charge distributions differ very greatly for substituents of different types.

(c) The arguments given in part VI[1] imply that allowance must be made for the charges at every position in the molecule; if these mesomeric-field contributions are to be included, additional parameters will be involved.

For these reasons it seems unlikely that attempts to develop general and quantitative theories of substituent effects can prove successful. However, we thought it might be interesting to see if a more limited approach could account for the ^{19}F nmr results. It seems reasonable to hope that the mesomeric polarizations due to different $+F+M$ substituents may be similar, and so resemble those induced by formyl; moreover, the arguments of part VI suggest that the main mesomeric effect of a given substituent should correspond to the charge induced by it at the carbon atom adjacent to fluorine. With these assumptions, the mesomeric effect of a given substituent at position i in a given molecule on the SCS of fluorine attached at position j should be given (*cf.* ref 3) by $M_S q_{ij}$ where M_S is a constant characteristic of the substituent, and q_{ij} is the charge at atom j induced by formyl at position i (*cf.* Figure 2). For our limited purpose it seemed sufficient to use the point charge model[3] in estimating the field effect; the vector potential along the C–F bond is then given by $F_S \cos \theta / r_{ij}$, where F_S is another constant characteristic of the substituent, r_{ij} is the distance between atom i and the midpoint of the CF bond, in units of the aromatic C–C bond length (1.40 A), and θ is defined as above. We assumed all bond lengths to be equal and all bond angles to be 120°. With these assumptions, the SCS for a given substituent in a given aryl fluoride should be given by

$$\mathrm{SCS} = \frac{F_S \cos \theta}{r_{ij}} + M_S q_{ij} \qquad (2)$$

Calculations were carried out on this basis for three $+F+M$ substituents, *viz.* NO_2, CN, and COOH. The parameters, F_S, could not be determined unambiguously from data for *meta*- and *para*-substituted fluorobenzenes[13b] since the quantity $\cos \theta / r$ is almost the same for the *meta* and *para* positions. The parameters were therefore chosen to fit the data for fluorobenzene to within ±0.01 ppm and to give the best general fit for the various substituted fluoronaphthalenes; the values so found are shown in Table XI. Table XII compares SCS's calculated from eq 2 for the various fluoronaphthalenes, using the values for F_S and M_S listed in Table XI, with experimental SCS's taken from Table VIII.

Table XI. Values for F and M Calculated from SCS Values in DMF

Substituents	F	M
NO_2	−10.88	−144.78
CN	−9.55	−145.65
COOH	−3.30	−115.21

The agreement between the calculated and observed SCS values in Table XII is surprisingly satisfactory, considering the crudity of our theoretical approach. The differences between the 7α and 8β series, and between the 3α and 4β series, are faithfully reproduced, even for the "abnormal" case of 4β-COOH where the SCS is negative. It seems likely that a more sophisticated treatment of such SCS values might provide a valuable criterion for quantum mechanical treatments of molecular structure.

Equation 2, together with the F and M values in Table XI, can be used to predict SCS for other systems; Table XIII compares values calculated in this way for some 4-fluorobiphenyls with those reported in part VI.[1] The appropriate charge densities q_{ij} (*cf.* Figure 2) are also listed. The agreement is again very satisfactory; in particular, the SCS value for 4′-fluorobiphenyl-3-carboxylic acid is correctly predicted to be greater than that for *m*-fluorobenzoic acid, a surprising result to which attention was drawn in part VI. It will be noticed that the calculated values are uniformly too large; this can be attributed to our oversimplified treatment of the field effect. The discrepancy should be still greater for X″-substituted 4-fluoroterphenyls; the value reported in part VI[1] for 3″-cyano-4-fluoroterphenyl (SCS = −0.71) is considerably less than our calculated value (−1.62).

Table XII. Comparison of SCS Values Calculated by the Modified *FM* Method for Fluoronaphthalenes with Observed Values

Substituent	Orientation							
	3α		4α		6α		7α	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
NO_2	−4.87	−3.64	−12.77	−11.61	−2.08	−1.81	−3.39	−2.48
CN	−3.68	−3.07	−11.34	−11.12	−1.29	−1.57	−2.35	−2.32
COOH	−1.01	−0.64	−8.19	−7.10			−1.52	−1.28

Substituent	Orientation							
	4β		6β		8β		5β	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
NO_2	−0.79	−1.97	−6.54	−5.13	−6.76	−6.70		
CN	−0.80	−1.40	−5.45	−4.91	−5.32	−6.37		
COOH	+0.72	+0.68	−3.62	−2.81	−3.46	−3.89	−0.09	−0.77

Table XIII. Comparison of SCS Values Calculated from Eq 2 for 3′- and 4′-Substituted 4-Fluorobiphenyls with Experimental Values

Substituent	q_{ij}	SCS	
		Calcd	Obsd
3′-NO_2	+0.006008	−2.98	−2.08
3′-CN	+0.006008	−2.72	−1.80
3′-COOH	+0.006008	+1.14	−0.80
4′-NO_2	+0.01006	−3.43	−2.74
4′-CN	+0.01006	−3.20	−2.24
4′-COOH	+0.01006	−1.75	−1.40

A further interesting conclusion follows from the data for the fluoronaphthylammonium ions in Table IX. It will be seen that the SCS for NH_3^+ is greater in the unconjugated 6α series (no first-order π-inductive effect) than it is in the conjugated 7α case. This difference can be explained if NH_3^+ acts predominantly by a field effect (*cf.* part V[7]), the π-inductive effect being unimportant, and if the field effect includes the orientational factor (cos θ in eq 2). Although the distance between the 1 and 7 positions in naphthalene is less than that between 1 and 6 positions, the term cos θ/r is greater in the latter case.

A further amusing feature is the difference between the SCS for 8β-NH_2 and 8β-NMe_2 (+1.88 and −0.63, respectively; Table IX), these differing in sign. Here we are probably dealing with a classic case of steric inhibition of mesomerism, the bulky dimethylamino group being forced out of conjugation with the adjacent ring by steric hindrance due to the adjacent *peri*-hydrogen atom. Both NH_2 and NMe_2 should be of the $+F-M$ type; reduction of the $-M$ mesomeric effect of NMe_2 allows its $+F$ field effect to dominate.

Conclusions

Three main conclusions follow from this work, together with that reported in part VI.[1]

First, it seems clear that the effect of substituents on ^{19}F chemical shifts presents features that are not present in conventional chemical systems, so that any attempt to interpret both sets of phenomena in similar terms is probably doomed to failure. This criticism applies to all previous interpretations of ^{19}F substituent chemical shifts.

Secondly, the results reported here seem to imply that the π-electron distributions in derivatives of benzene and naphthalene differ significantly from those predicted by the Hückel method, but agree, at least qualitatively, with the results of the SCF–MO calculations.[14]

Thirdly, it seems possible to explain the observed ^{19}F data in a reasonably satisfactory manner in terms of a simple scheme involving only field and mesomeric effects. The success of this simple treatment further emphasizes the potential value of ^{19}F nmr data as an aid in the development of improved quantum mechanical treatments of molecules.

(14) *Cf.* M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *J. Am. Chem. Soc.*, **86**, 5698 (1964).