Substituent Effects. X.[1] An Improved Treatment (FMMF) of Substituent Effects[2]

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Abstract: An improved version (FMMF) of the earlier FM treatment of substituent effects is described in which explicit allowance is made for the mesomeric–field effect and in which the field effect of neutral substituents is calculated by a finite dipole model instead of a point charge one. The results are shown to account very well for the effects of substituents on side-chain reactions in a number of ring systems. Deviations were observed when this treatment was extended to ^{19}F nmr chemical shifts, confirming earlier suggestions that they cannot be treated in the same terms as chemical reactivity.

Most of the attempts to develop a quantitative calculus of substituent effects have been based on the Hammett relation; they have consequently been purely empirical in nature and for the most part have been confined to benzene derivatives. The trouble with this kind of approach is that it involves too many parameters; different empirical ρ constants must be determined for each position in each different molecule, apart from the σ constants for the substituents themselves. Because of the plethora of parameters, it is difficult to draw any definite conclusions concerning the mode of operation of substituents from this kind of empirical approach.

An earlier paper[3] of this series described a general treatment of substituent effects, based on the assumption that a substituent can affect a distant reaction center only by direct electrostatic interactions across space (field effect) or by polarization of intervening π electrons (mesomeric and π-inductive effects, not usually distinguishable from one another). Using a point charge model to calculate the field effect, and a simple HMO treatment of the π polarization, a general treatment of substituent effects (FM method; FM $\equiv$ field–mesomeric) was developed which allowed them to be calculated in conjugated molecules of all kinds, in terms of just two parameters per substituent and one ρ constant for each type of reaction center. This treatment proved surprisingly successful, a circumstance taken as evidence for the thesis[3] that long-range "inductive" effects are due to direct electrostatic interactions across space rather than to successive polarization of intervening bonds, *i.e.*, to the field effect rather than to the classical inductive effect, a conclusion which has been strongly supported by numerous subsequent studies.

However, although the FM method proved surprisingly successful in spite of its simplicity and relative lack of parameters, it suffered from a serious inconsistency. The data for aromatic systems required $-$E groups such as OH or NH_2 to have *negative F* constants, implying that the field effect of such a substituent should be qualitatively similar to that of a negative charge; this is exactly opposite to that predicted on the basis of the polarities of the CN and CO dipoles, or observed in the case of saturated molecules where π polarization is absent. Logically the field parameters (*F*) should be found from data for such molecules since they should run parallel to Taft's inductive parameter (σ_I).

It was pointed out[3] that this discrepancy almost certainly arises from neglect of the mesomeric–field effect. In aniline, for example, the mesomeric interaction between NH_2 and the ring leads to charge transfer from nitrogen to the positions ortho–para to it; the resulting negative charges can then influence a reaction center by a field effect. If the reaction center is attached to the meta position, where direct mesomeric interactions are inoperative, the resulting apparent electron release of the substituent (NH_2) will appear as a negative contribution to the empirically determined field effect constant *F*. This argument has been strengthened by a number of recent studies[4–8] which have confirmed the importance of the mesomeric–field effect (also referred to as the meta resonance[4] and secondary resonance[5] effect); the purpose of the present study was to see if an allowance for it could be included in the FM treatment without an unreasonable increase in the number of parameters.

Theoretical Approach

In the FM treatment,[3] the σ constant ($\sigma_{im}{}^S$) of a given substituent S, in position i acting on a reaction center at position m, is given by

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[1] Part IX: M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, **89**, 390 (1967).

[2] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-70-1881 and AF-AFOSR-1050-67.

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

[4] R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **81**, 5343 (1959).

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

[6] M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 3318 (1966).

[7] W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967).

[8] M. J. S. Dewar and J. M. Harris, to be published.

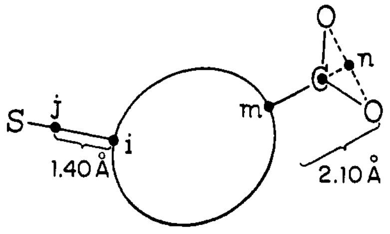

Figure 1. Model used to calculate the field effect

$$\sigma_{\text{im}}{}^{\text{S}} = \frac{F^{\text{S}}}{r_{\text{im}}} + M^{\text{S}}q_{\text{im}} \tag{1}$$

where r_{im} is the distance between the positions (expressed in terms of the CC bond length in benzene), and q_{im} is the formal negative charge at position m when the substituent is replaced by the group CH_2^-, q_{im} being calculated by the NBMO procedure of Longuet-Higgins.[9] The quantity q_{im} is taken as a measure of the transmission of mesomeric effects between positions i and m of a conjugated system; the corresponding term should of course vanish in the case of a saturated or nonconjugated molecule. F^{S} and M^{S} are the substituent parameters which can be calculated from the Hammett σ constants (σ_{m} and σ_{p}) for benzene.

Our purpose is to include an allowance for the field effects due to the secondary charges set up by mesomeric interactions between S and an adjacent conjugated system. As in the original FM method, we can assume that the charge at the various positions (k) will run parallel to the corresponding quantities q_{ik}; our modified expression for the σ constant is then

$$\sigma_{\text{im}}{}^{\text{S}} = \frac{F^{\text{S}}}{r_{\text{im}}} + M^{\text{S}}q_{\text{im}} + M_{\text{F}}{}^{\text{S}}\sum_{\text{k}\neq\text{m}}\frac{q_{\text{ik}}}{r_{\text{km}}} \tag{2}$$

The final sum does not include position m, in cases where q_{im} differs from zero, since the corresponding interaction between substituent and reaction center is included in the term $M^{\text{S}}q_{\text{im}}$. The quantity $M_{\text{F}}{}^{\text{S}}$ is a third substituent parameter, describing its ability to polarize adjacent π systems; if there is no direct resonance interaction between the substituent and reaction center, $M_{\text{F}}{}^{\text{S}}$ should be proportional to M^{S}.

The original FM treatment made the crude assumptions that the field due to the substituent could be approximated by that of a point charge at atom i and the charge on the reaction center by one at atom m. Here we have made the more realistic approximation of treating the substituent as a finite dipole and the reaction center as a point charge at some appropriate position in it. Thus the substituent S is approximated by a point charge q at atom i, together with a second point charge $-0.9q$ at a point one standard bond length (1.40 Å) from atom i along the i–S bond; the factor 0.9 allows empirically for the attenuation of the field due to the S end of the dipole through screening by the solvent.[3] In the case of dissociation of a carboxylic acid RCO_2H, the field effect arises from electrostatic interactions between the substituent and the formal charge on the ion RCO_2^-. Since this charge is evenly shared between the oxygen atoms, we have approximated it by a point charge midway between them, *i.e.*, at a point n, 1.5 standard bond lengths (2.10 Å) from atom m along the line joining it to the carboxyl carbon. This model is illustrated by Figure 1.

In the case of substituent effects on the dissociation of carboxylic acids, eq 2 then becomes

$$\sigma_{\text{im}}{}^{\text{S}} = F^{\text{S}}R_{\text{im}} + M^{\text{S}}q_{\text{im}} + M_{\text{F}}{}^{\text{S}}\sum_{\text{k}\neq\text{m}}\frac{q_{\text{ik}}}{r_{\text{kn}}} \tag{3}$$

where

$$R_{\text{im}} = \frac{1}{r_{\text{in}}} - \frac{0.9}{r_{\text{jn}}} \tag{4}$$

Since this treatment allows for the field, mesomeric, and mesomeric–field effects of substituents, we have termed it the FMMF method.

The parameters F^{S} in eq 3 were calculated from data for 4-substituted bicyclooctane-1-carboxylic acids.[10,11] The parameters M^{S} and $M_{\text{F}}{}^{\text{S}}$ were then found by fitting the Hammett constants, σ_{m} and σ_{p}, for benzoic acids,[10d,12] all bonds being assumed equal in length (1.40 Å), and the distances r_{ij}, r_{in}, r_{jn}, and r_{kn} being expressed in units of this length.

Results and Discussion

A. pK_{A} of Substituted Carboxylic Acids. Table I shows values of r_{im}, R_{im}, and the final sum in eq 3 for various pairs of positions in benzene, biphenyl, anthracene, and naphthalene. Table II shows the constants F, M, and M_{F} for a number of substituents, calculated in the manner indicated above.

Table I. Values of R_{im}, q_{im}, and $\sum_{\text{k}\neq\text{m}} q_{\text{ik}}/r_{\text{kn}}$ for Carboxylic Reactive Centers on Various Hydrocarbons

Compd	i	m	r_{in}	R_{im}	q_{im}	$\sum_{\text{k}\neq\text{m}} q_{\text{ik}}/r_{\text{kn}}$
Bicyclo[2.2.2]-octane	4	1	3.35	0.0916	0	0
Benzene	3	1	3.12	0.0900	0	0.172
	4	1	3.50	0.0857	0.143	0.091
Biphenyl	3′	4	6.06	0.0313	0	0.078
	4′	4	6.50	0.0338	0.032	0.092
Naphthalene	3	1	3.12	0.0900	0	0.154
	4	1	3.50	0.0850	0.200	0.114
	5	1	3.91	0.0690	0.050	0.170
	6	1	3.97	0.0690	0	0.149
	7	1	3.28	0.0662	0.059	0.155
	4	2	3.12	0.0900	0	0.220
	5	2	4.50	0.0447	0	0.151
	6	2	5.07	0.0487	0.059	0.102
	7	2	4.82	0.0476	0	0.143
	8	2	3.91	0.0294	0.050	0.118
Anthracene	8	1	3.55	0.0078	0	0.149

Tables III–V compare calculated and observed σ constants for derivatives of biphenyl-4-carboxylic acid, 8-substituted 1-anthroic acids, and of 1- and 2-naphthoic acids, the observed values being derived from the corre-

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[9] For a review and references see M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[10] (a) C. F. Wilcox, Jr., and J. S. McIntyre, *J. Org. Chem.*, 30, 777 (1965); (b) C. F. Wilcox, Jr., and C. Leung, *J. Amer. Chem. Soc.*, 90, 336 (1968); (c) C. D. Ritchie and E. S. Lewis, *ibid.*, **84**, 591 (1962); (d) C. G. Swain and E. C. Lupton, Jr., *ibid.*, 90, 4328 (1968).

[11] For a discussion of the accuracy of the point-charge model[3] used for the field effect in eq 1 and 2 see H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5188 (1964).

[12] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1957).

Table II. Values of F, M, and M_F Parameters[a]

Substituent	F	M	M_F
CH_3	−0.087	−0.910	−0.355
F[b]	4.85	−2.10	−0.577
Cl	4.95	−1.11	−0.419
Br	4.92	−1.14	−0.303
I[b]	4.57	−1.26	−0.347
OH	2.48	−3.70	−0.593
OCH_3	3.16	−3.14	−0.982
CN[b]	5.57	1.06	0.342
NO_2	7.09	0.927	0.421
CO_2H	3.13	0.944	0.512
$CO_2C_2H_5$	3.18	0.932	0.489
NH_2[b]	0.317	−4.11	−1.10
NHAc[b]	3.22	−1.70	−0.464

[a] Calculated from data for substituted bicyclooctanecarboxylic acids[10] and benzoic acids.[10d,12] [b] Data for the corresponding bicyclooctanecarboxylic acids are not available for the given solvent (50% (w/w) aqueous ethanol); F^S values calculated from log (K_X/K_H) values[c] estimated by Swain and Lupton.[10d] [c] Note that the given equation gives log (K_X/K_H) for the bicyclooctanecarboxylic acids and must be divided by ρ = 1.65 to obtain the σ' value.

Table III. σ Constants for Biphenyl and Anthroic Acids Calculated by the FMMF Method Compared with Experimental Values

	Biphenyl[a]				Anthroic[b]	
	3′,4		4′,4		8,1	
Substituent	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
CH_3			−0.06	−0.02		
Cl			0.09	0.13	−0.02	0.02
Br	0.13	0.12	0.10	0.13		
OH			−0.09	−0.19		
OCH_3			−0.08	−0.07	−0.01	−0.12
NH_2			−0.22	−0.25		
CN					0.10	0.07
NO_2	0.25	0.23	0.31	0.30		
CO_2H					0.06	0.03

[a] E. Berliner and E. A. Blomers, *J. Amer. Chem. Soc.*, **73**, 2481 (1951); **82**, 6427 (1960); measured in 50% aqueous butyl Cellosolve. [b] R. Golden, "Evidence for the Dipolar Field Effect," Doctoral Dissertation, University of Chicago Library, 1969, measured in 50% (w/w) aqueous ethanol.

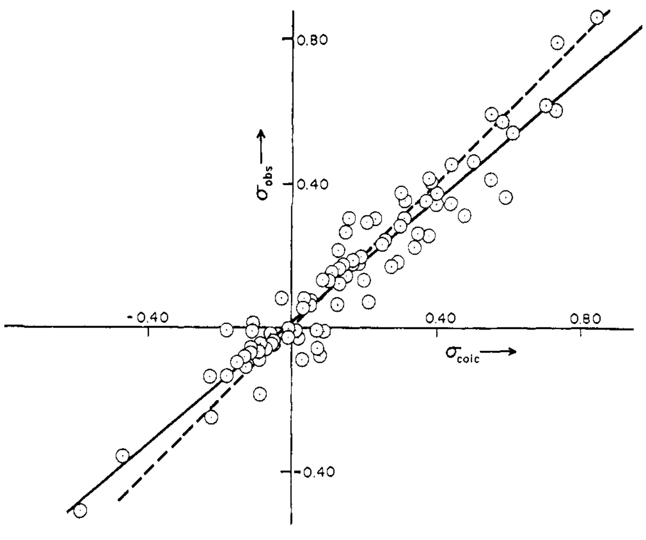

Figure 2. σ constants calculated by the FMMF method (Longuet-Higgins charge distributions) for various substituted 1-naphthoic, 2-naphthoic, 4-biphenyl, and 1-anthroic acids, plotted against experimentally observed values (ρ values identical with those of benzoic acids assumed in all cases). The dotted line has unit slope; the solid line is the least-squares best fit.

Table IV. Calculated σ Constants for α-Naphthoic Acids Compared with Experimental Values[a,b]

Substituent	1,3	1,4	1,5	1,6	1,7
CH_3	−0.06 (−0.05)	−0.23 (−0.14)	−0.11 (0.01)	−0.06 (−0.05)	−0.11 (−0.07)
Cl	0.38 (0.30)	0.15 (0.26)	0.21 (0.29)	0.28 (0.17)	
Br	0.40 (0.34)	0.16 (0.30)	0.23 (0.30)	0.29 (0.18)	0.21 (0.07)
OH	0.13 (0.06)	−0.59 (−0.52)	−0.11 (−0.06)	0.08 (−0.08)	−0.15 (−0.10)
OCH_3		−0.47 (−0.36)	−0.10 (−0.01)	0.07 (−0.06)	−0.13 (−0.08)
CN	0.55 (0.59)	0.73 (0.79)	0.50 (0.46)	0.44 (0.34)	0.48 (0.31)
NO_2	0.70 (0.61)	0.84 (0.86)	0.61 (0.54)	0.55 (0.41)	0.59 (0.36)

[a] Reference 3. [b] Experimental values in parentheses.

sponding pK_A by assuming the constant ρ to be identical with that for benzoic acids in the same solvent.[13] Figure 2 shows a plot of these calculated σ constants against the experimental values.

The calculated and observed values agree closely, the correlation coefficient being 0.96 and the standard deviation 0.069 σ unit. Note that the agreement is equally good for the −E substituents (NH_2, OH, OMe), even though the parameters F^S were determined from data for bicyclooctanecarboxylic acids; evidently the present treatment gives quite a good estimate of the mesomeric–field effect. The agreement between the calculated and observed σ constants is better than that given by the earlier FM treatment[3] (standard deviation, 0.08 unit); this is due partly to the better description of substituent effects generally in cases where the angular dependence of the dipole field is most important (*i.e.*, 7-substituted 1-naphthoic acids and 8-substituted 2-naphthoic acids[5]). In the FM treatment, the field effect was overestimated in such cases through use of the point-charge model.

A least-squares analysis showed that the best fit to the values listed in Tables III–V is given by

$$\sigma_{obsd} = 0.864\sigma_{calcd} + 0.012 \qquad (5)$$

with an uncertainty in the slope (95% confidence limit) of ±0.055. While the intercept is negligible, the slope is significantly less than unity. We suspect that the deviation may be due to small changes in the ρ constant with size of the group R in RCOOH, and with nonplanarity of the acids due to steric effects. Deviations of this kind might be expected, for two reasons. First, the effective dielectric constant in the region between the substituent and the reaction center may well depend on the size and shape of the substrate separating them; secondly, nonplanarity will reduce resonance interactions between the carboxyl group and an adjacent aromatic ring. In the compounds we are considering,

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[13] In 50% (v/v) aqueous ethanol, ρ = 1.52; in 50% (w/w) aqueous ethanol, ρ = 1.65; in 50% (v/v) aqueous butyl Cellosolve, ρ = 1.39.

Table V. Calculated σ Constants for β-Naphthoic Acids Compared with Experimental Values[a,b]

Substituent	2,4	2,5	2,6	2,7	2,8
CH_3	−0.09 (−0.09)		−0.09 (−0.05)	−0.05 (−0.05)	−0.09 (−0.07)
F			0.05 (0.07)	0.15 (0.14)	0.03 (0.08)
Cl	0.35 (0.26)		0.13 (0.16)	0.18 (0.18)	0.04 (0.06)
Br	0.38 (0.25)	0.17 (0.18)	0.14 (0.17)	0.19 (0.19)	0.05 (0.06)
I	0.34 (0.22)		0.11 (0.15)	0.17 (0.18)	0.03 (0.05)
OH	0.09 (−0.11)	0.02 (−0.03)		0.03 (−0.09)	−0.18 (−0.14)
OCH_3	0.07 (−0.01)	−0.01 (−0.01)	−0.13 (−0.11)	0.01 (−0.01)	−0.18 (−0.01)
CN	0.58 (0.57)	0.30 (0.37)	0.37 (0.35)	0.31 (0.35)	0.26 (0.24)
NO_2	0.73 (0.60)	0.38 (0.40)	0.44 (0.45)	0.40 (0.37)	0.30 (0.28)

[a] Experimental values in parentheses. [b] Reference 5.

nonplanarity should be important only in the substituted 1-naphthoic and 1-anthroic acids; it is significant that if the points for these are omitted, the least-squares relation between σ_{obsd} and σ_{calcd} becomes

$$\sigma_{\text{obsd}} = 0.892\sigma_{\text{calcd}} + 0.0087 \qquad (6)$$

with an uncertainty in the slope (95% confidence limit) of ±0.077. The slope is greater than before by an amount which is probably significant, and the standard deviation also falls (0.055 σ unit).

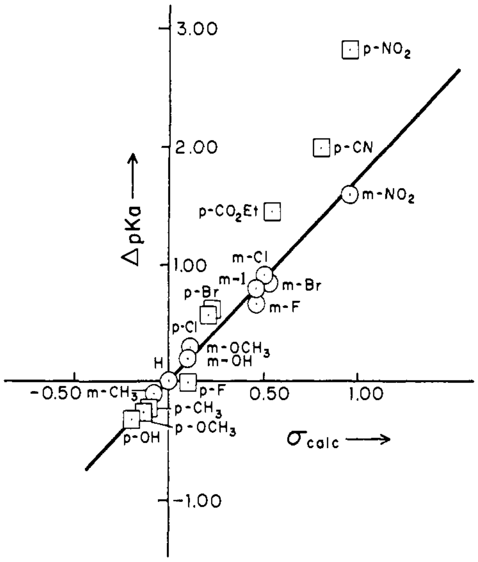

Figure 3. ΔpK_A values for (⊙) meta- and (⊡) para-substituted phenols in aqueous solution at 25° (relative to the unsubstituted compound) plotted against σ constants calculated by the FMMF method. ΔpK_A values for *m*- and *p*-hydroquinone are statistically corrected.

B. Other Chemical Reactions. Since our procedure accounts well for the pK_A of substituted arylcarboxylic acids, it must do so likewise for the equilibrium constants of any reversible reaction, or the rate constants of any irreversible one, in cases where these rate or equilibrium constants correlate with the pK_A of the corresponding carboxylic acids. It was shown previously[3] that the rates of hydrolysis of ethyl arylcarboxylates, and the pK_A of arylammonium ions fall into this category; the present treatment consequently gives a very satisfactory account of both these quantities.

It has long been known[14] that severe deviations from the Hammett relation would be expected to occur, and do indeed occur, in cases where the reaction center can undergo mutual conjugation with the substituent. Two such reactions are the dissociation of phenols and the S$_N$1 solvolysis of arylmethyl esters, a classic example of the latter being the solvolysis of substituted cumyl chlorides.

Figure 3 shows a plot of calculated *vs.* observed σ constants for the pK_A of substituted phenols. The calculations were carried out by an obvious modification of the procedure used for carboxylic acids (Figure 1), the point n being taken to be at the oxygen atom, *i.e.*, one standard bond length from the carbon atom in the ring. It is of course true that the formal negative charge in the phenolate anion will be to some extent delocalized over the ring; as a first approximation we neglected this. The experimental values are from a compilation by Brown, *et al.*[15]

Clearly there is an excellent correlation for the meta-substituted phenols and for phenols carrying a para substituent of other than the +E type. The deviations for +E substituents in the para position can clearly be attributed to mutual conjugation with O^- in the conjugate base of the phenol; however, there does not seem to be any simple relation between the mesomeric parameters M^S and the magnitude of this deviation. Presumably information derived from ionization of benzoic acids, where the reaction center is of +E type, provides a poor guide to the ability of substituents to undergo mutual conjugation with −E groups. Indeed, one would expect the interaction between a +E substituent and an adjacent even alternant conjugated system to be small;[9] in confirmation, the M^S parameters for +E substituents, derived from pK_A's of substituted benzoic acids, are small and show little variation. Evidently groups of this kind possess latent conjugative powers which are only displayed in situations where interaction with a −E center is possible (*i.e.*, mutual conjugation).

A converse situation is seen in the case of the rates of solvolysis of substituted cumyl chlorides; Figure 4 shows a plot of logarithms of the corresponding rate constants[16] against our calculated σ constants. It was assumed that the field effect operates primarily on the nascent carbonium ion in which the charge is again one standard bond length from the ring.

Here the points for meta substituents, and for *p*-nitro, lie very close to a straight line, while the remaining points all show positive deviations, corresponding to rates greater than those expected from the

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(14) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

(15) H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," C. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 589.

(16) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

linear relation. All these points are for para substituents of $-E$ or $-I$ type; the deviations can therefore be attributed to mutual conjugation with the nascent carbonium ion center. In this case, however, the deviations are roughly proportional to the M^S values; thus the deviations for CH_3, Cl, Br, and I are similar, being about one-third that for OMe (see Table II). Evidently the M^S values derived from dissociation constants of substituted benzoic acids do reflect the ability of groups to undergo mutual conjugation with a $+E$ group; the parallel is not exact,[17] as one might expect, since carboxyl is a much less active $+E$ group than $-CMe_2^+$.

It should be pointed out that the σ constants predicted by our procedure vary from reaction to reaction since we explicitly take into account the variation in distance and angular relationship between the substituent and the reaction center. The ρ constants derived by us therefore differ from those given by a simple application of the Hammett equation. Thus, for the dissociation of phenols we find $\rho = 1.75$, instead of 2.11,[18] and for the ionization of cumyl chlorides, 3.5 instead of 4.62.[18] If ρ constants are to be taken as measures of the effective charge at the reaction center, our values will clearly provide a better guide than the Hammett ones since the latter do not allow for variations in the geometrical relationship of the substituent to the reaction center.

C. ^{19}F Nmr Chemical Shifts. Since ^{19}F nmr chemical shifts of aryl fluorides are easy to measure, and since the range of variation with the introduction of substituents is large compared with the possible error in a given measurement, studies of this kind provide an attractive source of data for the analysis of substituent effects.

Taft and his collaborators[19] have reported ^{19}F chemical shifts for a wide range of substituted fluorobenzenes and interpreted them in terms of Taft's σ_I/σ_R approach. They were, however, forced to make the rather surprising assumption that in the case of meta substituents ^{19}F chemical shifts, unlike any other properties studied, depended solely on σ_I, there being no resonance contribution by the substituent.

The trouble with Taft's approach was that it was based solely on data for substituted fluorobenzenes; subsequent studies[7] of substituent effects in a wide range of derivatives of 1- and 2-fluoronaphthalene showed that ^{19}F chemical shifts present special features that are not present in the case of other chemical properties and that attempts to interpret them by a simple application of the Hammett equation are consequently unsound in principle and doomed to failure. In particular, the magnitude of the field effect in the case of ^{19}F chemical shifts was shown not to depend on the scalar potential along the CF bond. It was also suggested that the apparently abnormal effects of $+E$ substituents meta to fluorine 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 PhCOR are predicted to carry quite large negative charges, much larger than those predicted by HMO theory. It was pointed out that such charges would have a much larger effect on the ^{19}F chemical shift of a fluorine meta to carbonyl than on chemical reactions of a side chain at that position, for in the latter case the mesomeric-field effect of the negative charge in the position meta to carbonyl should be outweighed by the larger positive charges in the ortho-para positions.

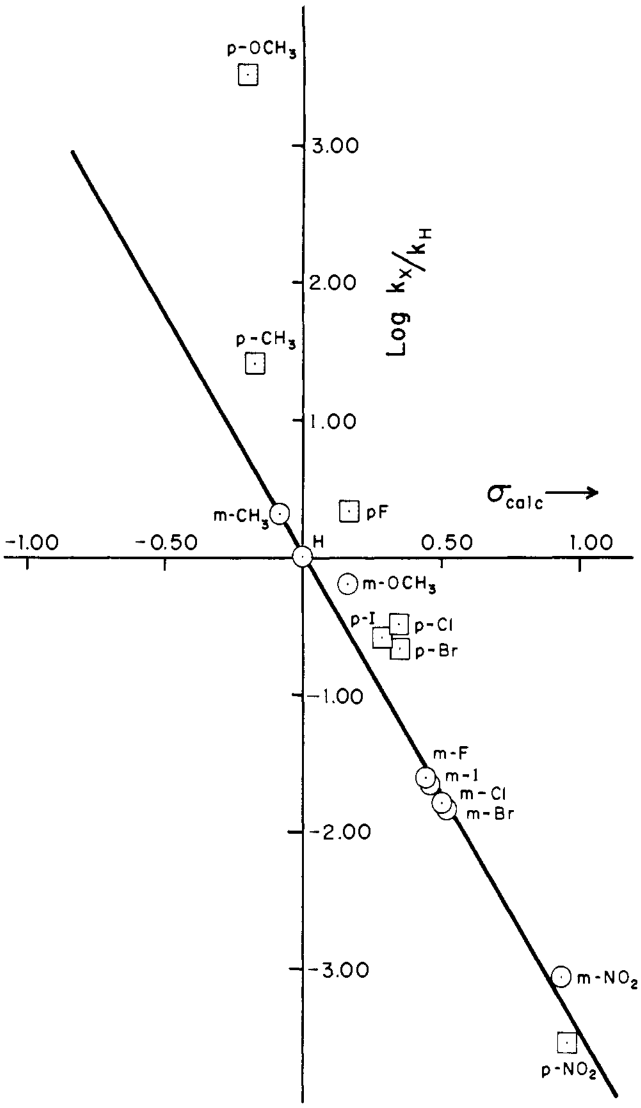

Figure 4. Logarithms of relative rates[18] of solvolysis of (⊙) meta- and (⊡) para-substituted cumyl chlorides in 90% aqueous acetone at 25° (relative to the unsubstituted compound) plotted against σ constants calculated by the FMMF method.

In order to obtain further information concerning these possible phenomena, we have reexamined the problem using an appropriate version of the FMMF treatment.

It has been shown[20] that substituent chemical shifts in aryl fluorides arise primarily by π polarization, rather than by polarization of the CF σ bond; the magnitude of the polarization due to the field effect of a substituent will depend on the component of the electric field along the CF bond, rather than on the scalar potential in that region. Since the field due to a charge q

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(17) See, *e.g.*, *p*-fluoro, the point for which in Figure 4 shows about the same deviation as *p*-methyl although $M^F \sim 2M^{CH_3}$.

(18) H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).

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

(20) M. J. S. Dewar and T. G. Squires, *ibid.*, 90, 210 (1968); G. L. Anderson and L. M. Stock, *ibid.*, 90, 212 (1968); 91, 6804 (1969).

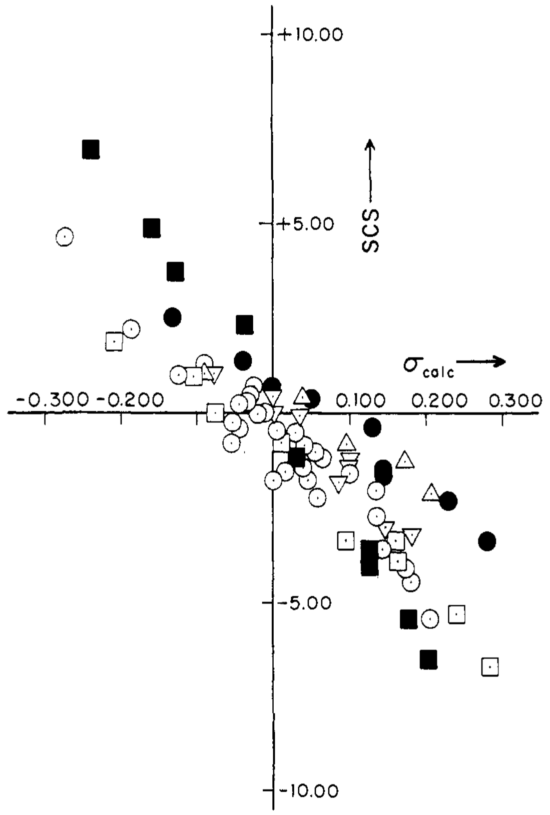

Figure 5. Experimental ^{19}F substituent chemical shifts plotted against σ values calculated by the FMMF method (SCF-π-MO charge distribution): ⊙, biphenyls, terphenyls, and 2,2′,6,6′-tetramethylbiphenyls; ●, 7-substituted α-fluoronaphthalenes; ⊡, 8-substituted β-fluoronaphthalenes; ■, 6-substituted β-fluoronaphthalenes; ◬, 6-substituted α-fluoronaphthalenes; ⊽, 7-substituted β-fluoronaphthalenes. Points for series ⊙ are on double scale.

at distance r is q/r^2, whereas the potential due to it is q/r, eq 3 and 4 need to be modified accordingly. Furthermore, since the published chemical shifts refer to measurements in aprotic solvents, the selective damping effect of the solvent on the substituent end of the i–S (Figure 1) dipole should be small; the factor 0.9 in eq 4 should therefore be replaced by unity. These arguments lead to the following approximate expression for the corresponding σ constant $\sigma_{im}^{S(F)}$ for a substituent S at position i in a given aromatic compound, acting on a fluorine atom at position m

$$\sigma_{im}^{SF} = F^S R_{im}^2 + M^S q_{im} + M_F{}^S \sum_{k \neq m} \frac{q_{ik} \cos \theta_{kn}}{r_{kn}{}^2} \qquad (7)$$

where

$$R_{im}^2 = \frac{\cos \theta_{in}}{r_{in}{}^2} - \frac{\cos \theta_{jn}}{r_{jn}{}^2} \qquad (8)$$

and where θ_{in} is the angle between the CF bond vector and a line drawn from atom i to the midpoint (n) of the CF bond. In view of our earlier conclusions,[7] the mesomeric transmission factors q_{im} were calculated by an SCF–MO procedure[21] rather than by the Longuet-Higgins model used above; the charge distributions calculated for molecules with various substituents at a given position i were numerically very similar, so q_{im} refers to the charge at position m produced by an amino group at position i. This change in the transmission factor leads of course to a corresponding change in the substituent parameters F^S, M^S, and $M_F{}^S$; Tables VI and VII show, respectively, the values of the various quantities in eq 7 and 8 for compounds for which ^{19}F substituent chemical shifts are available and the corresponding values for the substituent parameters. In the case of the 4′-substituted 4-fluoro-2,2′,6,6′-tetramethylbiphenyls, where the rings are virtually orthogonal, it was of course assumed that the mesomeric term ($M^S q_{im}$) in eq 7 vanishes and that the charges q_{ik} in the final term vanish in the ring containing fluorine and have values equal to those in PhS for the ring carrying the substituent S.

Table VI. Values of R_{im}^2, q_{im}, and $\sum_{k \neq m} [q_{ik} \cos \theta_{kn}/r_{kn}{}^2]$

Compd	i	m	R_{im}^2 [a]	q_{im} [b]	$\sum_{k \neq m}[(\cos \theta_{kn} q_{ik})/r_{kn}{}^2]$
Benzene	3	1	0.1044	−0.0079	0.0144
	4	1	0.0784	+0.0114	0.0004
Naphthalene	3	1	0.1044	−0.0074	0.0118
	4	1	0.0784	+0.0120	0.0000
	6	1	0.0247	−0.0023	0.0061
	7	1	0.0346	−0.0031	0.0000
	4	2	0.1044	−0.0086	0.0156
	6	2	0.0201	−0.0044	0.0012
	7	2	0.0219	−0.0016	0.0047
	8	2	0.0321	−0.0027	0.0029
Biphenyl	3′	4	0.00956	+0.0003	0.0016
	4′	4	0.00939	+0.0020	0.0014
2,2′,6,6′-Tetramethylbiphenyl	4′	4	0.00939	0	0.0014
Terphenyl	3″	4	0.00233	+0.0003	0.0003

[a] $R_{im}^2 = \cos \theta_{in}/r_{in}{}^2 - \cos \theta_{jn}/r_{jn}{}^2$. [b] Charge produced at atom m by an amino substituent at atom i. For consistence with the way the LH model was used previously, charges are given as deviations from neutrality in units of one electron, resulting from an amino group at position i.

Table VII. Values of F, M and M_F Parameters Calculated Using an SCF-π-MO Charge Distribution[a]

Substit	F	M	M_F
CH_3	−0.087	−10.67	−8.78
F[b]	4.85	−23.90	−17.39
Cl	4.95	−12.96	−10.54
Br	4.92	−12.87	−9.28
I[b]	4.57	−14.34	−10.44
OH	2.48	−40.66	−25.53
OCH_3	3.16	−36.04	−27.39
CN[b]	5.57	12.20	9.37
NO_2	7.09	11.04	9.63
CO_2H	3.13	11.50	10.80
$CO_2C_2H_5$	3.18	11.30	10.47
NH_2[b]	0.317	−46.56	−33.57
NHAc[b]	3.22	−19.35	−14.05

[a] See footnote *a*, Table II. [b] See footnote *b*, Table II.

Figure 5 shows a plot of the observed ^{19}F chemical shifts for substituted fluoronaphthalenes[7] in which fluorine and the substituent occupy different rings, for 3′- and 4′-substituted 4-fluorobiphenyls,[6] for 3″-substituted 4-fluoroterphenyls,[6] and for 4′-substituted 4-fluoro-2,2′,6,6′-tetramethylbiphenyls,[22] against σ con-

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[21] M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc., Ser. A*, 315, 457 (1970); the calculations were carried out by Dr. N. Trinajstić.

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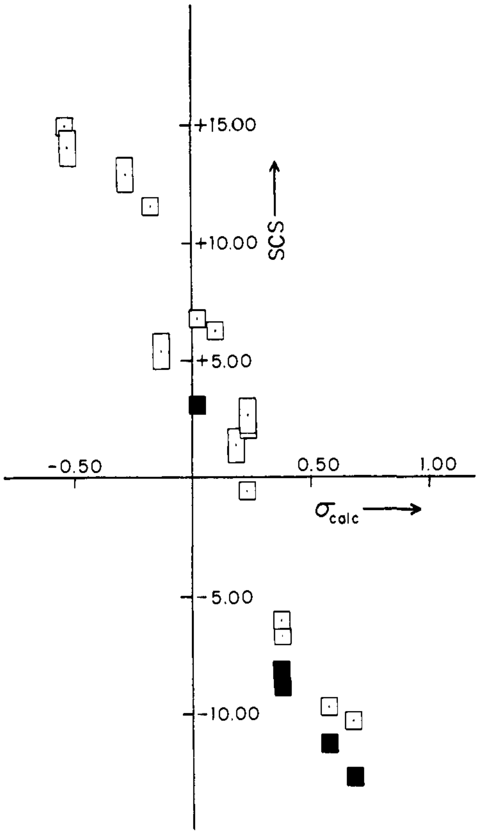

Figure 6. Experimental ^{19}F substituent chemical shifts plotted against σ values calculated by the FMMF method (SCF-π-MO charge distribution): ⊡, para-substituted fluorobenzenes; ■, 4-substituted α-fluoronaphthalenes.

stants calculated from eq 7 and 8 using Tables VI and VII. Figure 6 shows a similar plot for para-substituted fluorobenzenes[21] and 4-substituted 1-fluoronaphthalenes,[7] and Figure 7 one for meta-substituted fluorobenzenes[21] and 3-substituted 1-fluoronaphthalenes.[7]

Table VIII. Correlation of Calculated σ Constants with Experimental ^{19}F SCF Values

Series	ρ	ν_0, ppm	n^a	r^b	SD^c
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	−0.400	−0.39	6	0.185	0.72
6β	−30.6	0.00	9	0.995	0.52
7β^d	−17.8	0.072	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

[a] Number of points. [b] Correlation coefficient. [c] Standard deviation. [d] We thank Professor W. Adcock for a preprint containing the SCF data for the 7-substituted β-fluoronaphthalene system.

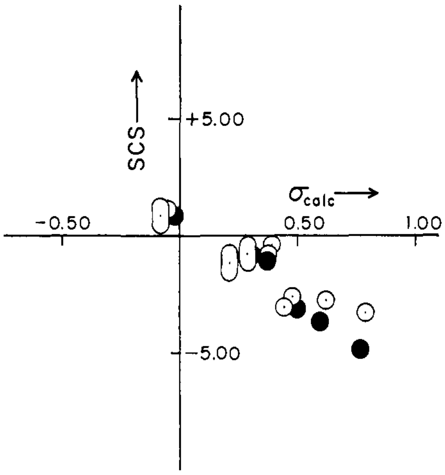

Figure 7. Experimental ^{19}F substituent chemical shifts plotted against σ values calculated by the FMMF method (SCF-π-MO charge distribution): ⊙, meta-substituted fluorobenzenes; ●, 3-substituted α-fluoronaphthalenes.

At first sight the correlation in Figure 5 seems only fair, and comparison of Figures 5–7 shows that the points for compounds in which the substituent is in the same ring as fluorine do not fall on the best line through the points in Figure 5. Closer examination, however, reveals a striking and unexpected regularity; although the points do not obey a single linear relation, the points for any one series of compounds do. Thus the points for each series of substituted 1- and 2-fluoronaphthalenes lie on a straight line, but the lines have different slopes for substituents in different positions. This is true even for compounds in which the substituent is in the same ring as fluorine (Figures 6 and 7). Table VIII shows the slope (ρ) and intercept (ν_0) for the best (least squares) line through the n points for each series of compounds, together with the correlation coefficient (r) and standard deviation (SD).

Obviously the Hammett relation fails completely in this case. The ρ values for fluorine depend on the substrate in question and the positions occupied by fluorine and the substituent; in particular the ρ values for meta- and para-substituted fluorobenzenes are totally different (−5.22 and −23.2!). An extreme example is provided by the 4-substituted 2-fluoronaphthalenes where the chemical shift is essentially independent of the substituent (*i.e.*, $\rho = 0$!). The variations may be due partly to mutual conjugation between the substituent and fluorine but this cannot be the sole factor, for if it were, the highest value of ρ would have to occur in the para-substituted fluorobenzenes and 4-substituted 1-fluoronaphthalenes where such resonance interactions would be far greater than in any of the other series studied. In fact the greatest value of ρ—and that by a wide margin—occurs in the 6 β series where resonance interactions should be relatively small.

These results clearly invalidate entirely any attempt to treat substituent chemical shifts on the same basis as substituent effects on other chemical properties and so refute the whole of Taft's[19] treatment of substituent chemical shifts. Any explanation must await a satisfactory quantum mechanical treatment of chemical shifts in general and of ^{19}F chemical shifts in particular; in view of the success of a recent semiempirical SCF-MO treatment of chemical shifts in fluoro derivatives of aromatic hydrocarbons and heteroaromatics,[23] it seems likely that this goal may soon be attained.

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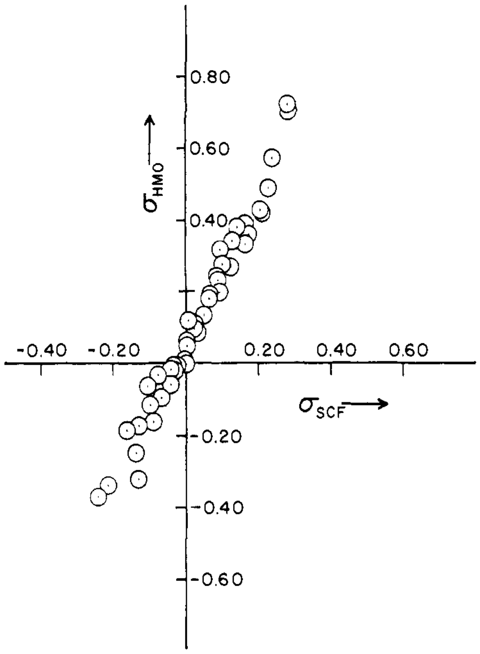

Figure 8. Plot of σ constants from eq 7 and 8 *vs.* σ constants calculated by an analogous treatment in which the charges q_{im} are calculated by Longuet-Higgins' method and the quantities r^2 in eq 7 and 8 are replaced by r.

One particularly striking and curious feature of the analysis in Table VIII is the existence of large and variable intercepts (σ = 0) for the "best" straight lines. These are so large that there can be no doubt that they are real; evidently insertion of *any* substituent into a fluorinated aromatic produces a chemical shift merely by its presence, independent of any specific electronic effect. We believe that this phenomenon must be attributed to geometrical distortion of the aromatic substrate by the substituent, for no other explanation seems feasible, and recent studies[20,24] of fluoro derivatives of saturated cyclic compounds have shown that geometrical and conformational factors can give rise to surprisingly large variations in the ^{19}F chemical shifts.

Further support for this suggestion comes from the fact that the points for the biphenyls and terphenyls, in which the substituent and fluorine are in different rings, lie close to a single straight line with an intercept which is too small to be significant. Note also that the points for the hindered 2,2′,6,6′-tetramethylbiphenyls also lie on this line; our procedure evidently accounts very well indeed for the differences in substituent chemical shift between these and the analogous unhindered biphenyls, in terms of the destruction of resonance coupling between the two rings.

In the original FM treatment[7] of ^{19}F substituent chemical shifts, anomalies were observed in the case of +E substituents meta to fluorine, *e.g.*, *m*-fluorobenzoic acid, 3-fluoronaphthalene-1-carboxylic acid, and 4-fluoronaphthalene-2-carboxylic acid. The observed chemical shifts were smaller than those expected, or even in the opposite direction. It was concluded that these anomalies arose from the use of Longuet-Higgins HMO procedure to estimate the quantities q_{im} and that better results could be obtained by using analogous charges calculated by an SCF-MO procedure. It was for this reason that we used SCF-MO charges in eq 6. However it now appears that the anomalies previously noticed[7] are merely a special case of a more general phenomenon, *i.e.*, the variation in ρ from one series of fluoroaromatics to another. This of course removes the main argument for using SCF-MO charges.

Another problem concerns the dependence of the field effect on distance. In eq 7 and 8 we have assumed, for physical reasons, that an inverse square dependence is involved; the arguments for this are not conclusive and conceivably the apparent variation in ρ could be due to use of an incorrect expression.

We have accordingly repeated the calculations described above using both SCF-MO and HMO values for q_{im}, and with the field effect varying as the inverse first power, or inverse third power, of distance. We also tried replacing the angular factors $\cos^2\theta$ by $\cos\theta$. All these procedures proved comparable in accuracy; thus Figure 8 shows a plot of the σ constants calculated with HMO values for q_{im} and an inverse first power of the distance against the σ constants calculated from eq 7 and 8. Evidently the correspondence is close, the deviations being no greater than those in plots of experimental substituent chemical shifts against either set of σ constants. In view of this correspondence, there seems no point in listing the results of these rather extensive calculations.

Summary and Conclusions

The calculations reported here seem to confirm earlier suggestions concerning the importance of the mesomeric-field effect,[3] concerning the angular dependence of the field effect due to dipolar substituents,[5,7] and concerning the damping of the field effect due to the substituent end of the dipole by solvents of high dielectric constant, in the case of such substituents.[3,7] The success of the FMMF treatment described here also of course provides very strong support for the view that the long-range effects of substituents are to all intents and purposes due solely to a combination of the mesomeric and field effects, the classical inductive effect being wholly unimportant. The agreement between our calculated σ constants and those estimated from a variety of chemical reactions, for a number of aromatic ring systems, is very satisfactory, given that appreciable scatter is bound to be introduced by differential solvent effects. It also seems clear that our procedure will apply equally well to saturated compounds, given that the field effect parameters are determined from the pK_A of 4-substituted bicyclooctane-1-carboxylic acids and given that these are known to correlate very well with Taft's σ_I.

No allowance is made in our approach for mutual conjugation between the substituent and the reaction center; compounds where this is significant show corresponding deviations. In view of the success of our treatment in other cases, these deviations probably provide the best estimate currently available of the magnitude of such resonance interactions.

While our treatment works well for chemical reactions of side chains, it seems to fail badly in the case of ^{19}F chemical shifts. This failure can, however, be quantitatively attributed to variations in ρ^F with the aromatic system in question, and the positions of the fluorine and the substituent in it. In view of the suc-

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cess of our treatment in all other cases, and in view of the large effects of geometry on ^{19}F chemical shifts in saturated fluorides, these correlations seem highly significant. If they are accepted, one must of course conclude that the effects of substituents on chemical properties, and on ^{19}F chemical shifts, present entirely different problems and that attempts to combine the two will prove fruitless.

Experimental and Theoretical Studies of Long-Range H–H Coupling Constants in Ring-Substituted Styrenes

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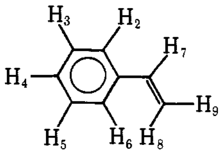
Abstract: Analysis of the proton magnetic resonance spectra of a number of ring-substituted styrenes has yielded the signs and magnitudes of the long-range coupling constants between the protons of the ring and those of the side chain. These parameters are of interest because of their sensitivity to conformational factors and because the relative importance of σ- and π-electron mechanisms in unsaturated compounds of this type is in dispute. To interpret the coupling constant data, theoretical calculations were performed for several values of the dihedral angle between the phenyl ring and the vinyl group. Calculated results for styrene were based on both the semiempirical valence-bond method which includes a sum over triplet states in the second-order perturbation expression for the coupling constants, and by the molecular orbital method which uses finite perturbation theory in the semiempirical INDO approximation. Agreement between experimental and theoretical results is excellent and shows, for example, that the π-electron mechanism is the only important factor for long-range coupling between the vinyl protons and the *p*-hydrogen atom of the ring. On this basis, the experimental and theoretical results permit an estimate to be made of the average angle between the ring and side chain of 2,6-dichlorostyrene.

Although dissection of coupling constants into σ and π contributions is not rigorously valid, this approximation has been found to be useful in both empirical and theoretical studies.[2,3] Proton–proton spin–spin coupling across six or more σ bonds is generally considered to be negligible. However, the relative importance of σ and π contributions to four- and five-bond coupling constants in unsaturated systems is still a subject of debate.[2–6]

Styrene (1) and its derivatives would appear to be potentially useful substrates for testing the relative importance of the various possible mechanisms in determining long-range coupling constants. In particular, the use of bulky substituents to vary the relative orientations of the vinyl and phenyl moieties might be expected to yield useful insights. Many proton magnetic resonance studies of ring-substituted styrenes have been reported,[7–11] but few long-range coupling constants[8,9] and no proton–proton signs have hitherto been noted. Recently a complete analysis of perfluorostyrene was reported.[12]



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In this paper we report the experimental signs and magnitudes found for the long-range proton–proton coupling constants in a series of ring-halogenated styrenes, and compare these results with the values predicted theoretically for styrene by previously developed valence-bond (VB)[5,13,14] and molecular orbital (MO)[15–18] formulations.

Experimental Section

Compounds. 3-Bromo-, 3,4-dichloro-, 2,5-dichloro-, and 2,6-dichlorostyrene were obtained from commercial sources and used without further purification. 3-Bromostyrene was used in preference to 3-chlorostyrene because the larger ring-proton chemical shift differences facilitated the spectral analysis. Any slight traces of impurities in these compounds did not obscure the nuclear magnetic resonance (nmr) spectra. Solutions of these compounds had concentrations which were 5 mol % in carbon disulfide and

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