Monomer	[Liv. ends], × 10^5 m./l.	[M], × 10^3 m./l.	Conv., %	k_{ij}, 1. mole^{-1} sec.$^{-1}$
Styrene	3.0	1.4	...	500^a
Styrene	3.7	2.4	...	520^a
p-Methylstyrene	3.3	2.1	6–15	105
p-Methylstyrene	5.9	4.9	12–20	82
p-Methoxystyrene	2.6	2.4	23–57	28^b

^{a} These data, calculated from the V.P.C. analysis of the residual styrene, are lower than those obtained previously (800–1000). We feel that the spectrophotometric technique used in the earlier investigations could be less reliable, since the tetramer solution acquired a slightly yellow color on standing in air. ^{b} This system was studied in a stirred-flow reactor.

in the ordinary anionic polymerization this step apparently involves a negative center.

The low reactivities of α- and β-methylstyrenes reflect the effect of steric hindrance due to the presence of a methyl group located close to the center of reaction. This effect is superimposed upon the inductive effect which also reduces the rate of copolymerization.

The higher reactivity of o-methylstyrene when compared with its p-isomer is unexpected and the cause of this trend is not clear. The lower reactivity of 2,4-dimethylstyrene could be anticipated in view of the enhanced inductive effect of two methyl substituents.

The pattern observed in the rate constants of copolymerization of styrene derivatives with living polystyrene is reflected in the respective rate constants of addition to the living α-methylstyrene tetramer (Na$^+$, $^-$C(CH$_3$)(Ph)CH$_2$CH$_2$[C(CH$_3$)(Ph)]$_2$CH$_2$CH$_2$C(CH$_3$)-(Ph)$^-$,Na$^+$. The pertinent results are collected in Table VI, and it is interesting to notice that all the values given in this table are lower by approximately a factor of 2 than the corresponding values related to the addition to living polystyrene. On the other hand, the addition of styrene to poly-p-methylstyrene$^-$ or poly-p-methoxystyrene$^-$ (see Table V) proceeds as fast as the addition to the living polystyrene. It seems, therefore, that the steric factor is mainly responsible for the lower rate constants of addition to the tetramer of α-methylstyrene.

Finally, it should be pointed out that the results collected in Table V indicate that the polar factors are less important when they operate on the anion than when they act on the monomer (compare the rate constants of copolymerization of the pairs: styrene–p-methylstyrene and styrene–p-methoxystyrene). They become, however, significant when the polarity of the anion is changed considerably, e.g., in the addition of styrene to the living polyvinylpyridine.

F^{19} Chemical Shifts of the Sulfur Pentafluoride, Trifluoromethoxy, Trifluoromethylthio and Trifluoromethylsulfonyl Groups in Aromatic Compounds

BY D. R. EATON AND WILLIAM A. SHEPPARD

The F^{19} n.m.r. spectra have been measured for a series of arylsulfur pentafluorides and aryl trifluoromethyl ethers, sulfides and sulfones substituted in the *meta* or *para* position. The twenty-one line pattern for the sulfur pentafluoride group was analyzed as an AB$_4$ system, and the chemical shift and spin–spin coupling constants determined. The coupling constant of 146 c.p.s. between the base and apex fluorine is independent of the substituent. The F^{19} chemical shifts of these groups have been correlated with Hammett σ-factors and with Taft's inductive and resonance parameters. The magnitudes of the changes in chemical shift with substituent and the correlations with reactivity parameters are discussed.

Introduction

A number of correlations between chemical reactivity and physical properties, such as vibrational band frequencies and intensities, polarographic half-wave potentials and n.m.r. chemical shifts, have been observed and explored in recent years. Of these physical properties, the study of the F^{19} n.m.r. chemical shifts is particularly attractive because of the high precision of the measurements and the relatively direct relationship to chemical bonding. Gutowsky, McCall, McGarvey and Meyer[1] first noted the correlation of the fluorine chemical shifts with Hammett σ-constants for a series of substituted fluorobenzenes. Taft[1b,2,3] has extended and elaborated this correlation by interpreting the shifts in terms of inductive and resonance effects. Theoretical treatments of the problem have been presented recently by several groups.[4]

There is, however, very little experimental data available on the chemical shifts of fluoroaromatics other than the fluorobenzenes.[5] It is the purpose of the present study to investigate the possible correlation of the F^{19} chemical shifts of the SF$_5$, OCF$_3$, SCF$_3$ and SO$_3$CF$_3$ groups and the spin–spin coupling constant of the SF$_5$ group with substituent parameters. Such data should provide a further test of the validity of current theories of aromatic substitution effects and also should give some information on the transmission of inductive and mesomeric interactions through oxygen and sulfur atoms.[6] A concurrent study has been made of the

(4) (a) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961); (b) T. Yonezawa, K. Fukui, H. Kato, H. Kilano, S. Hattori and S. Matsuoka, *Bull. Chem. Soc. Japan*, **34**, 707 (1961); (c) R. W. Taft, F. Prosser, L. Goodman and G. T. Davis, *J. Chem. Phys.*, **38**, 380 (1963).

(5) A limited amount of chemical shift data has been reported on benzotrifluorides[1a] and on aryl trifluoromethyl ethers, sulfides and sulfones; L. M. Yagupolsky, V. F. Bystrov and E. Z. Utyanskaya, *Proc. Acad. Sci. USSR, Phys. and Chem. Sect.* (Engl. Transl.), **135**, 1059 (1960), and *Optics and Spectroscopy*, **10**, 68 (1961). Correlations of proton chemical shift with Hammett σ-parameters for the methyl group of m- and p-substituted anisoles were recently reported by C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962).

(6) The substituent parameters for the groups along with the synthetic

(1) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); (b) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 323.

(2) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(3) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

F^{19} contact interaction shifts of the same groups substituted on the ligands of paramagnetic Ni(II) aminotroponeimines.[7] The chemical shift measurements are indicative of the transmission of charge density, whereas the contact shifts are determined by the transmission of spin density through the conjugated system so that the two studies are in many ways complementary.

Experimental

The compounds used in the present study have the structures I–IV.

SF$_5$ OCF$_3$ SCF$_3$ SO$_2$CF$_3$

X   X   X   X

I   II   III   IV
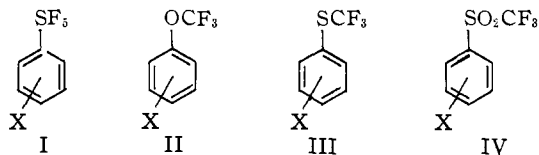
where X is a *meta* or *para* substituent (H, NO_2, NH_2, OH, CH_3 and halogen). The synthesis of these compounds is described elsewhere.[6,8] The spectra were obtained with a Varian high resolution instrument operating at 40 and 56.4 Mc./sec. Reagent grade carbon tetrachloride was used as a solvent and 1,2-difluorotetrachloroethane (Freon 112) as an internal calibrant. The trifluoromethyl sulfones IV were also examined in methanol solution to investigate the possible effects of hydrogen bonding. Calibration was accomplished by superimposing an audiofrequency on the sweep field to produce side band peaks of the reference. In most cases measurements were made at four different concentrations and chemical shifts were obtained by extrapolation to infinite dilution. The corrections involved were of the order of 2–3 c.p.s. in most cases. The *m*- and *p*-hydroxy derivatives of I and IV were only slightly soluble in carbon tetrachloride, and the chemical shifts were obtained directly for the spectra of the saturated solutions. The precision of the measurements is estimated to be ±1 c.p.s. so that the chemical shift measurements are meaningful for even the OCF$_3$ and SO$_2$CF$_3$ groups where the range in shifts is only 30 to 40 c.p.s.

Analysis of the Spectra.—Compounds II, III and IV have only a single F^{19} resonance, and the chemical shift is obtained directly. Compound I has a twenty-one line pattern typical of an AB$_4$ system with the apex fluorine (A) appearing to low field of the basal fluorines (B$_4$). This pattern is consistent with a tetragonal-pyramidal configuration for the sulfur pentafluoride group as ascribed to alkylsulfur pentafluorides and other derivatives of sulfur hexafluoride.[9] The present spectra were analyzed using the perturbation theory of Anderson[10] and satisfactory agreement was obtained between calculated and observed spectra measured both at 56.4 and 40 Mc./sec.

Results

The chemical shifts and spin–spin coupling constants for compounds I are presented in Table I. It is apparent that there is no significant change (less than 2 c.p.s.) of J_{FF} with substituent. The mean value of 146 c.p.s. for the spin–spin coupling constant is very close to the value of 145 c.p.s. reported by Muller, Lauterbur and Svatos[9a] for perfluoroalkylsulfur pentafluoride derivatives.

Chemical shift data for compounds II, III and IV in carbon tetrachloride and for compound IV in methanol are given in Table II. There is a marked dependence of the chemical shift on the substituent for all four series of compounds. Furthermore, in each case there is good correlation with substituent parameters. Gutowsky, McCall, McGarvey and Meyer[1a] originally correlated the chemical shifts of the fluorobenzenes with the Hammett σ-values. Taft[2,3] has pointed out that the relative importance of the inductive and resonance contributions may not be the same for F^{19} chemical shifts as it is for acidity and reactivity functions, and for the fluoro-

chemistry have been described and discussed, W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3064, 3072 (1962); **83**, 4860 (1961), and publications in preparation.

(7) Publication in preparation.

(8) L. M. Yagupolsky and M. S. Marenets, *J. Gen. Chem. USSR* (Engl. Transl.), **24**, 885 (1954), and **26**, 99 (1956).

(9) (a) N. Muller, P. C. Lauterbur and G. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1043 (1957); see, ref. 1b, p. 339; (b) R. K. Harris and K. J. Packer, *J. Chem. Soc.*, 4736 (1961); (c) C. I. Merrill, S. M. Williamson, G. H. Cady and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

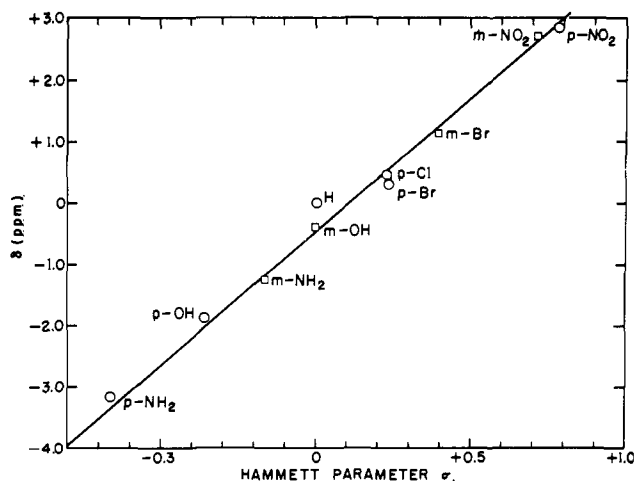(10) W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956); see also ref. 1b, p. 153.

Fig. 1.—Correlation plot of δ for apex fluorine *vs.* Hammett parameter σ for substituted arylsulfur pentafluorides ($\delta = -0.50 + 4.33\sigma$).

benzenes he obtained better correlations with chemical shift data by utilizing separate inductive (σ_I) and resonance (σ_R) parameters. Krueger and Thompson[11]

TABLE I

CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS FOR F^{19} IN ARYLSULFUR PENTAFLUORIDES ($XC_6H_4SF_5$) AT INFINITE DILUTION IN CARBON TETRACHLORIDE

Substituent X	Apex fluorine ν_A, c.p.s.[a]	Apex fluorine δ_A, p.p.m.[b]	Basal fluorines ν_B, c.p.s.[a]	Basal fluorines δ_B, p.p.m.[b]	J_{FF}, cycles/sec.
H	−6035	0.00	−5163	0.00	+147
p-NO$_2$	−5921	+2.85	−5179	− .40	+146
m-NO$_2$	−5926	+2.73	−5193	− .75	+147
p-NH$_2$	−6161	−3.15	−5253	−2.25	+146
m-NH$_2$	−6084	−1.23	−5182	−0.48	+147
p-Br	−6023	+0.30	−5207	−1.10	+145
m-Br	−5990	+1.13	−5193	−0.75	+146
p-Cl	−6017	+0.45	−5204	−1.03	+146
p-OH	−6109	−1.85	−5245	−2.05	(+149)
m-OH	−6049	−0.35	−5188	−0.63	+146

[a] Recorded at 40 Mc./sec. relative to CFCl$_2$CFCl$_2$ (internal). [b] δ relative to phenylsulfur pentafluoride as zero and positive for shift to higher field.

have treated their results on infrared frequencies and intensities in a similar way. The present results for compounds II and III and the basal fluorines of compounds I give satisfactory correlations by plotting the *meta* shifts against σ_I and the difference between the *para* and *meta* shifts against σ_R in the manner described by Taft. (Values used for σ, σ_I, σ_R and $\sigma_R{}^0$ are given in Table II.) Examples of these plots are shown in Fig. 2 and 3. The chemical shifts for compounds IV and the axial fluorine of compounds I plot equally satisfactorily against Hammett σ directly as shown in Fig. 1 and 4. These results, together with those of Taft on the fluorobenzenes, may be summarized by the following equations. The equations (with the exception of eq. 1b) were determined by least squares best fits, $\delta = b_0 + b_1\sigma_I + b_2\sigma_R{}^0$.[12] For these equations $\sigma_R{}^0$ was found more appropriate than σ_R (note, $\sigma_R/\sigma_R{}^0 \cong 1.5$ to 2.0).[3] For comparison, all results have been expressed in terms of σ_I and $\sigma_R{}^0$. The two cases which correlate directly with Hammett σ, namely, SF$_5$ axial and SO$_2$CF$_3$, have the coefficient of σ_I of the same order as $\sigma_R{}^0$. In the remaining cases the dominance of the

(11) P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc.* (London), **A250**, 22 (1959).

(12) W. A. Pavelick and R. W. Taft, *J. Am. Chem. Soc.*, **79**, 4935 (1957). We are indebted to Professor Taft for advice and assistance in carrying out these correlations.
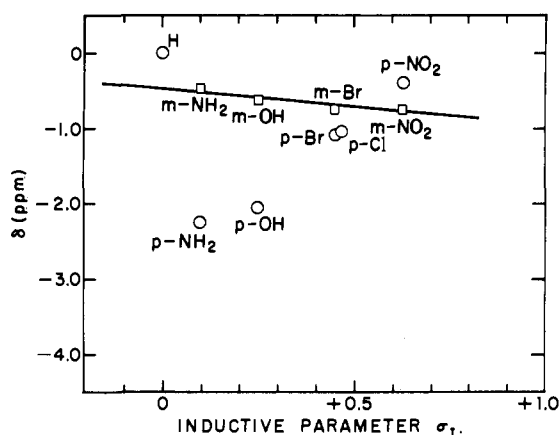
Fig. 2a.—Correlation plot of δ for basal fluorines vs. inductive parameter σ_I for substituted arylsulfur pentafluorides (δ_m = $-0.50 - 0.45\,\sigma_I$).
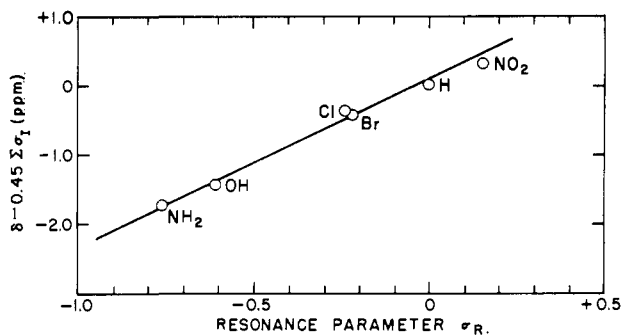

Fig. 2b.—Correlation plot of $\delta - 0.45\Sigma\sigma_I$ for basal fluorine vs. the resonance parameter σ_R for p-substituted arylsulfur pentafluorides ($\delta_p = -0.28 - 0.45\sigma_I + 2.50\sigma_R$).

σ_R^0 term in the p-substituted compounds destroys the simple dependence on Hammett σ.

F	$\delta_m^F = +0.20 - 5.83\sigma_I$
	$\delta_p^F = +0.80 - 5.83\sigma_I - 18.80\sigma_R$ (1)
SF$_5$ apex	$\delta_m^F = 0.00 + 3.79\sigma_I + 3.47\sigma_R^0$
	$\delta_p^F = -0.09 + 3.54\sigma_I + 6.99\sigma_R^0$
basal	$\delta_m^F = -0.01 - 1.38\sigma_I + 0.65\sigma_R^0$
	$\delta_p^F = -0.10 - 0.99\sigma_I + 3.98\sigma_R^0$
OCF$_3$	$\delta_m^F = -0.04 + 0.56\sigma_I + 0.10\sigma_R^0$
	$\delta_p^F = +0.04 + 0.30\sigma_I - 1.35\sigma_R^0$
SCF$_3$	$\delta_m^F = -0.03 - 0.79\sigma_I + 0.00\sigma_R^0$
	$\delta_p^F = +0.04 - 1.32\sigma_I - 3.76\sigma_R^0$
SO$_2$CF$_3$ (in CCl$_4$)	$\delta_m^F = -0.01 - 1.31\sigma_I - 0.45\sigma_R^0$
	$\delta_p^F = 0.00 - 1.04\sigma^I - 1.51\sigma_R^0$
(in CH$_3$OH)	$\delta_m^F = -0.02 - 1.09\sigma_I - 0.82\sigma_R^0$
	$\delta_p^F = +0.01 - 0.87\sigma_I - 1.82\sigma_R^0$

Discussion

It seems clear from the analysis of Karplus and Das[4a] that fluorine chemical shifts are dominated by the second-order paramagnetic term and hence by the nature of the fluorine bonding. There are, however, a variety of inductive, resonance and field effects possible,[13] and an extensive accumulation of various kinds of physical data will probably be necessary before the contributions of the various factors can be disentangled. Ring current effects in these aromatic systems may also have to be considered, but it seems unlikely that these would vary significantly with substituents. In the case of the sulfur pentafluoride compounds in particular, small changes in the hybridization of the sulfur from compound to compound and differences in the proportion of d-orbital contribution to the apex and basal bonds may also be significant.

Several comments can, however, be made from the results of the present study as embodied in eq. 2–6. The

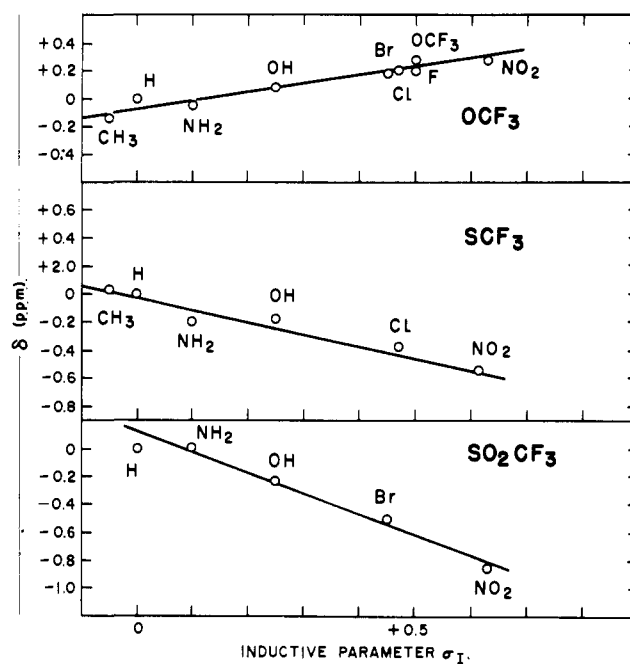(13) M. J. S. Dewar and P. J. Grisdale, J. Am. Chem. Soc., 84, 3540, 3548 (1962).

Fig. 3a.—Correlation plot of δ for F[19] of m-substituted XC_6H_4-OCF$_3$, $XC_6H_4SCF_3$ and $XC_6H_4SO_2CF_3$ vs. inductive parameter σ_I in CCl$_4$.
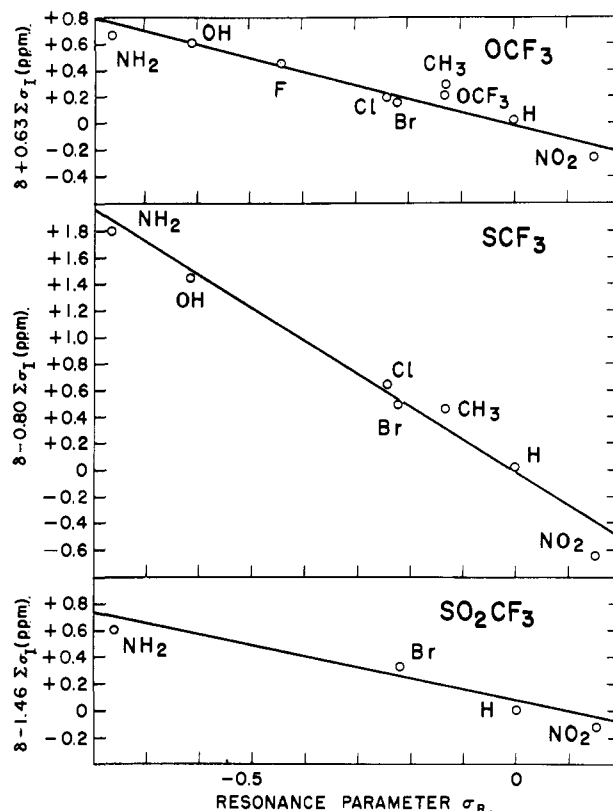
Fig. 3b.—Correlation plot of $\delta + x\sigma_I$ for F[19] of p-substituted $XC_6H_4OCF_3$, $XC_6H_4SCF_3$ and $XC_6H_4SO_2CF_3$ vs. the resonance parameter σ_R in CCl$_4$.

observed correlations demonstrate that substituent effects are indeed transmitted to atoms remote from the ring. As might be anticipated, the magnitude of the effects falls off with increasing number of intervening bonds in the series: fluorobenzenes (one bond), SF$_5$ compounds (two bonds), and OCF$_3$, SCF$_3$ and SO$_2$CF$_3$ compounds (three bonds). Conjugation through –O–, –S–, and –SO$_2$– has recently been demonstrated by the

TABLE II

CHEMICAL SHIFTS FOR F^{19} IN ARYL TRIFLUOROMETHYL ETHERS, SULFIDES AND SULFONES AT INFINITE DILUTION IN CARBON TETRACHLORIDE AND METHANOL

Substituent		Substituent parameter[a]				XC₆H₄OCF₃ In CCl₄		XC₆H₄SCF₃ In CCl₄		XC₆H₄SO₂CF₃ In CCl₄		XC₆H₄SO₂CF₃ In CH₃OH	
		σ	σ_I	σ_R	σ_R^0	ν, c.p.s.[b]	δ, p.p.m.[c]	ν, p.p.m.[b]	δ, p.p.m.[c]	ν, p.p.m.[b]	δ, p.p.m.[c]	ν, p.p.m.[b]	δ, p.p.m.[c]
H		0	0	0	0	−377	0.00	− 984	0.00	+458	0.00	+465	0.00
NO₂	para	.78	0.63	0.15	0.08	−376	+ .03	−1034	−1.25	+425	− .83	+437	− .71
	meta	.71				−366	+ .28	−1010	−0.55	+422	− .90	+434	− .78
NH₂	para[d]	− .66	.10	− .76	− .48	−351	+ .65	−917	+1.68	+482	+ .60	+499	+ .80
	meta	− .16				−379	− .05	−992	−0.20	+459	+ .02	+473	+ .20
CH₃	para	− .17	− .05	− .13	− .10	−370	+ .18	−966	+ .45				
	meta	− .07				−382	− .13	−985	+ .03				
OH	para	− .36	.25	− .61	− .40	−350	+ .68	−937	+1.18			+487	+ .53
	meta	− .02				−374	+ .08	−991	−0.18	+450	−0.20	+469	+ .09
Br	para	.23	.45	− .22	− .19	−363	+ .35	−983	+ .04	+450	− .21	+459	− .16
	meta	.39				−370	+ .18			+440	− .46	+449	− .41
Cl	para	.23	.47	− .24	− .20	−361	+ .40	−977	+ .18				
	meta	.37				−369	+ .20	−999	− .38				
F	para	.06	.50	− .44	− .35	−350	+ .68						
	meta	.34				−369	+ .20						
OCF₃	para	.35	.51	− .13		−360	+ .43						
	meta	.40				−366	+ .28						

[a] Values of σ from H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953); σ_I and σ_R from ref. 1b, 2, 3; σ_R^0 from R. W. Taft, S. Ehrenson, I. C. Lewis and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959). [b] Recorded at 40 Mc./sec. relative to CFCl₂CFCl₂ (internal). [c] Relative to unsubstituted aryl compound as zero and positive for shift to higher field. [d] *ortho* NH₂ for OCF₃ recorded as −388 c.p.s. with δ −0.28 p.p.m.

transmission of spin density through these groups[14]; the non-zero values of the σ_R^0 coefficients in eq. 4, 5 and 6 provide further evidence for this effect. The relative values of the coefficients also are reasonable with −SO₂− being the least effective conjugating group and −S− being significantly more effective than −O−. It is interesting that the signs of the σ_R coefficients alternate on transmission through one bond (negative), two bonds (positive) and three bonds (negative). Whether this is a general effect or a peculiarity of the particular groups studied remains to be established. The different signs of the σ_I coefficients for the OCF₃ and SCF₃ may also be of significance. Differences in the substitutent constants for these groups have been reported previously[6] and attributed to participation of the d-orbitals in the sulfur compound. There is also a reversal in the signs of these coefficients between the basal and apex fluorines of the SF₅ group. It is possible that the basal fluorines may experience a large direct interaction with the ring π-system, giving a negative contribution to the σ_I-coefficient (as in the fluorobenzenes) which opposes the intrinsic positive contribution reflected in the apex fluorine dependence.

In the two cases where the chemical shifts correlate directly with Hammett σ-parameter (SO₂CF₃ and apex SF₅) the fluorines are screened from the π-system of the ring by the SO₂ and SF₄ groups, respectively. It is possible that these groups may have an insulating effect in preventing direct interaction of the fluorine with the π-system of the ring, and the electronic effect transmitted by field and σ- and π-inductive mechanisms[13] is now the major factor influencing the chemical shifts.

The results for the SO₂CF₃ compounds in carbon tetrachloride and in methanol are very similar in their substituent dependence. In each case there is a shift of around 10–20 c.p.s. to high field in methanol compared with carbon tetrachloride. It is deduced from this that although hydrogen bonding with the −SO₂− group can

(14) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

occur, the extent of such solvation does not vary markedly with phenyl substitution.

To summarize, it is concluded that the chemical shift studies provide a sensitive probe for elucidation of the mechanism of transmission of inductive and reso-
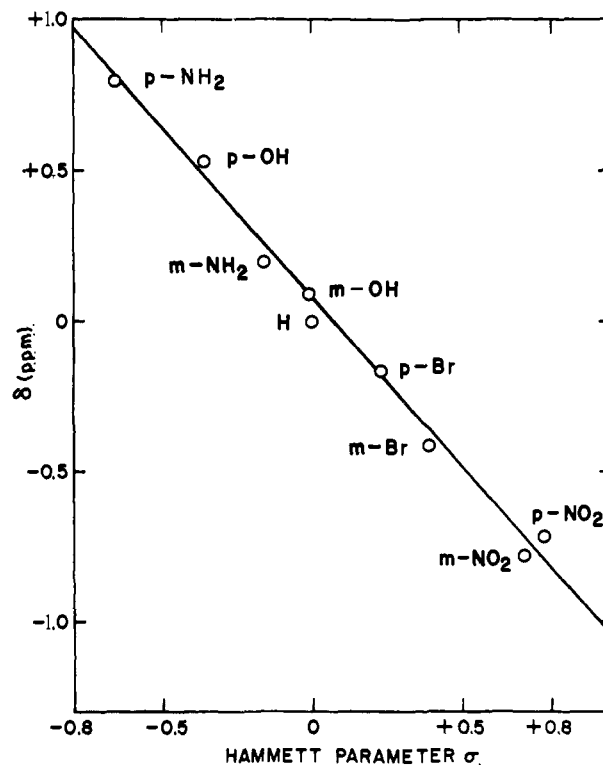

Fig. 4.—Correlation plot of δ vs. Hammett σ parameter for substituted aryl trifluoromethyl sulfones in methanol (δ = +0.08 − 1.12σ).

nance effects. However, a considerable amount of experimental data will probably have to be accumulated before interpretation of these effects is complete.