The Electronic Properties of Di-, Tri-, Tetra-, and Hexacoordinate Sulfur Substituents[1]

William A. Sheppard[*2] and R. W. Taft[3]

Contribution from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, and the Department of Chemistry, University of California, Irvine, Irvine, California 92650. Received April 22, 1971

Abstract: Fluorine nuclear magnetic resonance shifts (and derived σ values) have been obtained for the families m- and p-FC_6H_4SX, m- and p-FC_6H_4SOX, m- and p-$FC_6H_4SF_3$, m- and p-$FC_6H_4SO_2X$, and m- and p-$FC_6H_4SF_5$. The effects of substituents, X, at sulfur have been analyzed by use of the polar and resonance substituent parameters σ_I and σ_R. Evidence regarding the relative contributions of π acceptor orbitals (d orbitals) on sulfur *vs.* p–π donation of unshared electron pair to the aromatic ring has been obtained. Comparison with corresponding families of substituents with oxygen or other second row elements has also been made. For the p-FC_6H_4SX family, it is found that substituents (X) of sp hybridization (*i.e.*, $-C\equiv CH$ or $-C\equiv N$) increase the importance of $Ar=S(\pi$–p) donation relative to $Ar=S(\pi$–d) acceptor interaction. With increasing oxidation number of sulfur, acceptor interactions appear to become relatively more important, *i.e.*, SX < SOX < SO_2X.

Substituent effects on chemical and physical properties have been treated in a number of aromatic systems as additive blends of polar (inductive) and π delocalization (resonance) effects.[4–6] The polar effect is characterized by the generalized substituent parameter, σ_I, which is based upon polar effects measured at saturated carbon.[4] The π delocalization effect is characteristic of the substituent but may also depend upon the nature of the aromatic or conjugating system. The substituent parameter σ_R^0 measures the π delocalization effect in systems in which the reaction center is effectively insulated from the aromatic nucleus.[7] Other scales of the π delocalization effect, which are limited by reaction type, include[8] $\sigma_R \equiv \sigma_p - \sigma_I$, $\sigma_R^+ \equiv \sigma_p^+ - \sigma_I$, and $\sigma_R^- \equiv \sigma_p^- - \sigma_I$.

These various substituent parameter scales are all based upon substitution at carbon. Recent evidence of the generality of the treatment, and the transferability of substituent parameters from carbon to other elements, was provided by application to substitution at phosphorus.[9] The values of f_{m-X}^{p-X} and of $\lambda = \rho_R/\rho_I$ for the m- and p-PX_2 families were interpreted as evidence for π(p–d) interactions both from $Ar\overset{=}{-}P$ and $P\overset{=}{-}X$. A similar analysis of sulfur in three oxidation states has now been carried out to obtain the corresponding information on charge distribution associated with its bonding.

The effects of meta and para substituents on fluorine nuclear magnetic resonance (^{19}F nmr) shielding in fluorobenzenes provide sensitive measures of σ parameters (especially of the σ_R scale) by virtue of the generalized correlations[4d]

$$\int_H^{m-X} = (-7.10)\sigma_I + 0.60 \tag{1}$$

$$\begin{aligned} \int_{m-X}^{p-X} &= -29.5\sigma_R^0 \quad \text{(for } -R) \\ &= -29.5\tilde{\sigma}_R \quad \text{(for } +R) \end{aligned} \tag{2}$$

The superscript to the shielding parameter,[10] f, refers to the specific substituent involved and the subscript indicates the fluorobenzene which is the internal reference standard (H, for example, refers to unsubstituted fluorobenzene).

For the substituent group of the general formula SX, the group electronic properties are anticipated to be a function of the polar and π delocalization interactions of the component X. Since the σ_I and σ_R^0 scales from carbon were already shown to apply (approximately) to phosphorus (for the PX_2 substituent group), logical extension of the previous treatment is to test the transferability of the substituent constants to substitution at sulfur. If the dual substituent parameter (DSP) treatment is applicable for the SX family, then

$$\int_{m-SH}^{m-SX} = \rho_I{}^m\sigma_{I(X)} + \rho_R{}^m\sigma_{R(X)}{}^0 \tag{3}$$

and

$$\int_{p-SH}^{p-SX} = \rho_I{}^p\sigma_{I(X)} + \rho_R{}^p\sigma_{R(X)}{}^0 \tag{4}$$

Thus, the present determination and analysis of the ^{19}F nmr shielding terms for m- and p-FC_6H_4SX provide new values for certain substituents (*e.g.*, values of σ_I, σ_R^0, σ_m^0, σ_p^0 from eq 1 and 2), the test of the ap-

(1) A preliminary report of this work was presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract ORGN 85.

(2) Central Research Department, Contribution No. 1532.

(3) This work was supported in part by the National Science Foundation. Grateful acknowledgment is made to the National Science Foundation for the support which made available the nmr spectrometer to the U.C.I. Chemistry Department.

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Table II. ^{19}F Nmr Chemical Shifts[a] of Fluorophenylsulfur Derivatives and Substituted Parameters

Substituent	$\int_{H}^{m-SX}$	$\int_{H}^{p-X}$	$\int_{m-SX}^{p-SX}$	σ_I	$\sigma_R{}^0$ (or $\bar{\sigma}_R$)
Divalent Sulfur					
SCH$_3$[b]	−0.38[c]	4.30[c]	4.68	0.13	−0.16
	−0.30[d]	4.20[d]			
SCH$_2$CH$_3$	−0.30[d]	2.96[d]	3.26	0.13	−0.11
SN(CH$_3$)$_2$	−0.48[d]	1.17[d]	1.65	0.15	−0.06
SH[b]	−0.78[c]	3.50[c]	4.28	0.19	−0.15
	−0.76[d]	3.50[d]			
SCH=CH$_2$	−0.91[d]	1.21[d]	2.12	0.21	−0.07
SCOCH$_3$	−0.92[d]	−1.19[d]	−0.27	0.21	0.01
SC$_6$H$_5$[e]	−0.97[e]	0.99[e]	1.96	0.20	−0.07
S(OCH$_3$)	−1.17[d]	1.14[d]	2.31	0.25	−0.08
SC≡CH	−1.68[d]	2.18[d]	3.86	0.32	−0.13
SSC$_6$H$_4$F[f]	−1.93[d]	.53[d]	2.46	0.36	−0.08
SCl	−2.23[d]	−4.47[d]	−2.24	0.40	0.08
SCF$_3$	−2.36[d]	−4.20[d]	−1.84	0.42	0.06
SCOCF$_3$	−3.00[d]	−4.45[d]	−1.45	0.51	0.05
SCN	−3.90[d]	−2.47[d]	1.43	0.63	−0.05
Sulfonium					
S$^+$(CH$_3$)$_2$[g]	−5.73[g]	−10.62[g]	−4.89	0.89	0.17
S$^+$(Me)BCl$_3$[e]	−4.50	−7.42	−2.92	0.72	0.10
Sulfinyl					
SON(CH$_3$)$_2$	−1.53[d]	−2.40[d]	−0.87	0.30	0.03
SOOCH$_3$	−2.56[d]	−5.22[d]	−2.66	0.45	0.09
SOCH$_3$[b]	−2.90[c]	−3.00[c]	−0.10	0.49	0
SOF	−4.06[d]	−9.06[d]	−5.00	0.66	0.17
SOCF$_3$	−4.22[d]	−7.98[d]	−3.76	0.68	0.13
	−3.60[h]	−7.47[h]			
SOCl	−4.24[d]	−8.64[d]	−4.22	0.68	0.14
Tetravalent					
SF$_3$	−3.67[d]	−9.51[d]	−5.84	0.60	0.20
Sulfonyl					
SO$_3^-$[b]	−1.03[i]	−3.00[i]	−1.97	0.23	0.07
SO$_2$N(CH$_3$)$_2$	−2.36[d]	−5.98[d]	−3.62	0.42	0.12
SO$_2$NH$_2$	−2.50[i]	−6.00[i]	−3.50	0.44	0.12
SO$_2$C$_2$H$_5$[b]	−2.98[c]	−8.30[c]	−5.32	0.50	0.18
SO$_2$CH$_3$[b]	−3.30[c]	−8.00[c]	−4.70	0.55	0.16
SO$_2$F[b]	−4.73	−12.50[c]	−7.77	0.75	0.26
SO$_2$CF$_3$[j]	−4.93[c]	−14.01[c]	−9.08	0.78	0.31
	−5.09[d]	−13.93[d]			
SO$_2$Cl[b]	−5.10[c]	−12.20[c]	−7.10	0.80	0.24
SO$_2$CN	−6.05[d]	−15.37[c]	−9.32	0.94	0.32
Hexavalent					
SF$_5$[b,k]	−3.13[c]	−5.50[c]	−2.37	0.53	0.08

[a] In ppm. Probable error is 0.04 ppm. [b] Reported in ref 4d. [c] In CCl$_4$ solution. [d] At infinite dilution in CCl$_3$F solution. [e] Dr. R. G. Pews, unpublished results with R. W. T.; shielding parameters in CH$_2$Cl$_2$. [f] Fluorine in fluorophenyl substituent has orientation of probe fluorophenyl. [g] J. W. Rakshys, Jr., Ph.D. Thesis, University of California, Irvine, June 1967. Measurements in CH$_3$CN solution on perchlorate salt. In hexamethylphosphoramide and trifluoroacetic acid, $\int_H{}^m$ and $\int_H{}^p$ are −10.14, −16.06 and −3.57, −7.49, respectively. [h] Reported by L. M. Yagupol'skii, V. F. Bystrov, A. U. Stepanyants, and Yu. A. Fialkov, *J. Gen. Chem. USSR*, **34**, 3731 (1964), solvent and conditions of measurement not given. [i] Methanol solvent. [j] L. M. Yagupol'skii and B. E. Gruz, *ibid.*, **31**, 1219 (1961). [k] See also ref 20.

plicability of σ_I and σ_R values for substitution at sulfur (eq 3 and 4), and, if the latter is successful, information on acceptor orbital (presumably d) participation at sulfur ($\lambda = \rho_R/\rho_I$ values). This approach has also been extended to the families SOX and SO$_2$X.

Experimental Section

Synthesis. All the *m*- and *p*-fluorophenyl sulfur derivatives were known compounds, or were prepared by literature procedures reported for the unsubstituted phenyl sulfur analogs. Source or method of preparation, physical data, and, on new derivatives, analytical data are summarized in Table I[11] for all derivatives whose ^{19}F nmr was not reported previously.

(11) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Nmr Calibrations. ^{19}F nmr measurements were carried out at 25° with a Varian HA-60 or A56-60 spectrometer, using techniques previously described.[12] When spectrograde carbon tetrachloride was used as solvent, the concentration of the sulfides was 0.10 *M* or less. Trichlorofluoromethane was also used as solvent (serves as internal calibrant); measurements were made at three concentrations (20, 10, 5%) and the chemical shifts obtained by extrapolation to infinite dilution. Results obtained in these two solvent systems have been shown to agree to within the ±0.04 ppm precision ascribed to the method.[12b]

The fluorine nuclear magnetic resonance (^{19}F nmr) shifts of the *m*- and *p*-fluorophenyl group with all sulfur substituents, measured in this study or reported previously, are tabulated in Table II as well as values for σ_I and σ_R calculated by eq 1 and 2. For comparison purposes similar data for oxygen analogs are tabulated in Table III.

(12) (a) D. Gurka, R. W. Taft, L. Joris, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 5957 (1967); (b) W. A. Sheppard, *ibid.*, **87**, 2410 (1965).
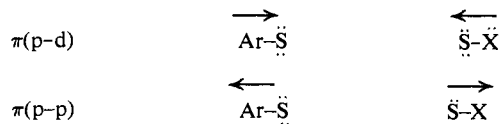
Table III. [19]F Nmr Chemical Shifts[a] of Fluorophenyl Oxygen Derivatives and Substituent Parameters

Substituent	$\int_H^{m-OX}$	$\int_H^{p-OX}$	$\int_{m-OX}^{p-OX}$	σ_I	σ_R^0
OCH₃	−1.05	11.50	12.55	0.23	−0.43
OH	−1.20	11.40	12.60	0.25	−0.43
OCOCH₃	−1.33	4.55	5.88	0.27	−0.20
OCH₂CH₂Br[b]	−1.90	9.86	11.76	0.35	−0.40
OC₆H₅	−1.95	7.40	9.35	0.36	−0.32
OCH=CH₂[b]	−2.07	7.55	9.62	0.38	−0.33
OCH=CHBr[b]	−2.38	6.64	9.02	0.42	−0.31
OC≡CH[b]	−2.94	5.99	8.93	0.50	−0.30
OCF₃	−3.33	2.10	5.43	0.55	−0.18
OCOCF₃[b]	−4.01	1.50	5.51	0.65	−0.19
OCN[b,c]	−5.12	2.46	7.57	0.80	−0.26
O(Me)BCl₃[d]	−3.2	−1.5	1.7	0.54	−0.06

[a] In ppm; unless indicated otherwise, all shielding parameters are in CCl₄ solvent shown from ref 2d. [b] Unpublished results in CCl₃F solvent. [c] D. Martin and W. M. Brause, *Chem. Ber.*, **102**, 2508 (1969), reported values for chemical shifts in CCl₄ as meta −5.00 and para +2.32. [d] Unpublished results of J. W. Carten and R. W. Taft, in CH₂Cl₂.

Discussion

Dicoordinated Sulfur Substituents. At least four π interaction mechanisms must be considered for sulfur in the ArSX compound,[13,14] that is π(p-d) and π(p-p) interactions for both the Ar–S and S–X bonds. The effective electron donation which accompanies these interactions is conveniently represented schematically.

$$\pi(\text{p-d}) \qquad \overrightarrow{\text{Ar–}\underset{\cdot\cdot}{\text{S}}} \qquad \overleftarrow{\underset{\cdot\cdot}{\text{S}}\text{–X}}$$

$$\pi(\text{p-p}) \qquad \overleftarrow{\text{Ar–}\underset{\cdot\cdot}{\text{S}}} \qquad \overrightarrow{\underset{\cdot\cdot}{\text{S}}\text{–X}}$$

For the X substituents used in this study, π(d–d) interactions in the S–X bond are possible for the groups Cl and SC₆H₄F, but we assume that these are not of sufficient importance relative to the other effects to be considered.

The shielding of the p-XC₆H₄F relative to its meta isomer as the internal standard ($\int_{m-X}^{p-X}$) has been proposed as a quantitative measure of the net ground-state delocalization of π charge from the substituent, X (*cf.* eq 2).[4b,d,6,15] This shielding term is positive (shift to higher field) if (net) π electron density is delocalized to the benzene ring and is negative if π electron density is delocalized from the ring to the substituent. From both theoretical considerations[13] and experimental data[14,16,17] the accumulation of positive charge on sulfur (resulting from electron withdrawal by X) will increase Ar–S and S–X π(p-d) acceptor action and generally tend (if sufficiently strong) to decrease Ar–S π(p-p) donor action.

(13) (a) D. P. Craig, *J. Chem. Soc.*, 997 (1959); (b) D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(14) (a) F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, **78**, 87 (1956); (b) G. Cilento, *Chem. Rev.*, **60**, 147 (1960); (c) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); (d) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley New York, N. Y., 1962, Chapter 17; (e) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, Chapter 5; (f) C. E. Griffin, R. P. Peller, K. R. Martin, and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965); (g) L. Goodman and R. W. Taft, *J. Amer. Chem. Soc.*, **87**, 4385 (1965); (h) M. G. Hogben, R. S. Gay, and W. A. G. Graham, *ibid.*, **88**, 3457 (1966); (i) J. E. Bissey and H. Goldwhite, *Tetrahedron Lett.*, 3247 (1966).

(15) (a) R. W. Taft, *J. Amer. Chem. Soc.*, **79**, 1045 (1957); (b) R. T. C. Brownlee and R. W. Taft, *ibid.*, **92**, 7007 (1970).

(16) W. A. Sheppard, *ibid.*, **85**, 1314 (1963).

(17) R. W. Taft and J. W. Rakshys, Jr., *ibid.*, **87**, 4387 (1965).

In the case of the PX₂ family, values of $\int_{m-X}^{p-X}$ were found to be positive for X = NMe₂ and Me, essentially zero for X = C₆H₅, and negative for the electron-withdrawing groups X = OMe, F, Cl, CF₃, and CN. Table II shows a similar pattern for the SX family, although only the very electron-withdrawing groups X = CF₃ and Cl give rise to negative values of $\int_{m-X}^{p-X}$ (or consequently, of small positive σ_R values). This comparison, which is crude because of the different number of substituent groups and unshared electron pairs in the two families, suggests that Ar–S π(p-d) relative to Ar–S π(p-p) interaction is less for sulfur than for the corresponding Ar–P interactions. The results for the 'onium ion substituents, PMe₃⁺ and SMe₂⁺ ($\int_{m-X}^{p-X}$ = −6.42[18] and −4.89, respectively), also support this conclusion.

The application to the SX family of the dual substituent parameter equations (3) and (4) gives results indicating that S–X π(p-d) interaction is very small, definitely less than for P–X π(p-d) interaction in the PX₂ family. Using the σ_R^0 scale[8b] for both PX₂ and SX families, best fit parameters are as follows.

PX₂ $\lambda^m = \rho_R^m/\rho_I^m = -3.34/-5.56 = 0.60$

$\lambda^p = \rho_R^p/\rho_I^p = -5.58/-18.6 = 0.30$

SX $\lambda^m = \rho_R^m/\rho_I^m = -1.51/-4.29 = 0.35$

$\lambda^p = \rho_R^p/\rho_I^p = -0.14/-16.41 = 0.01$

For the PX₂ family the precision of fit by eq 3 and 4 was considered rather poor but adequate (SD/RMS = 11–18%). For the SX family the precision of fit is similar (for m-SX, $f \equiv$ SD/RMS = 0.29/1.46 = 20% and for p-SX, f = 1.01/4.81 = 21%). Actually both meta and para data are best fitted by the σ_R^-(A) scale,[8b] with a small improvement in precision of fit, as expected in terms of S–X π(p-p) interaction between +R substituents and the S unshared electron pairs.

The SCN group, which involves the substituent X with the largest σ_I value, does not have a negative value of $\int_{m-SCN}^{p-SCN}$. Also, the SC≡CH group has an unusually positive value of $\int_{m-SC_2H}^{p-SC_2H}$ (+3.86, compared to values of 1.96 and 2.12 for SC₆H₅ and SCH=CH₂, respectively). For this reason neither substituent is included in the fittings given above for the p-SX family. In contrast, the meta shift values, $\int_{m-SH}^{m-SX}$, become increasingly negative as the hybridization of carbon involves greater s character (−0.38 for SCH₃; −0.91 for SCH=CH₂; −0.97 for SC₆H₅; −1.68 for SC≡CH; −3.90 for SCN). It is clear, therefore, that the para shift values, $\int_{p-SH}^{p-SX}$, involve additional considerations besides the inductive effects of the X substituent. In particular, the results suggest that X substituents with sp carbon bonded to the sulfur increase (compared with other X substituents) the importance of Ar‒S π(p-p) donation relative to Ar‒S π(p-p) acceptor interaction. A similar consideration may be involved in the more positive value of $\int_{m-SX}^{p-SX}$ for SOMe (+2.31) than for SNMe₂ (+1.65). This π electron effect could arise from more effective overlap because the 3p orbitals on S are contracted by the internal inductive effect of sp carbon hybridization. Alternately, the sp carbon hybridization might increase

(18) J. W. Rakshys, Jr., Ph.D. Thesis, University of California, Irvine, June 1967; measured in CH₃CN solution as the BF₄⁻ salt.
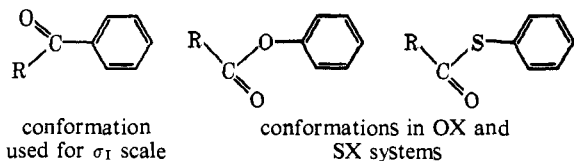
conformation
used for σ_I scale

conformations in OX and
SX systems

Figure 1. Acetyl and trifluoroacetyl conformations.

the promotional energy of the S 3d orbitals resulting in reduced $Ar\overset{-}{=}S$ π(p–d) acceptor action. Certainly, the general conclusion resulting from the failure of eq 4 for the p-SX family (compared to other families, e.g., SOX, and SO_2X, discussed subsequently) is that the pseudo π orbitals of sulfur may be easily polarized with structural changes in substituents.

Comparisons of corresponding shifts for the SX and OX families are also instructive. The meta shifts show nearly a constant difference, i.e., $f_{m-OH}{}^{m-OX} - f_{m-SH}{}^{m-SX} = -0.63 \pm 0.16$, provided that X = $CH_3C{=}O$ and $CF_3C{=}O$ are excluded. The latter two substituents are expected to assume conformations in which the electron withdrawal is reduced compared to the expectations of the σ_I scale (Figure 1). Both of these substituents are accordingly omitted in the fittings given above for the m-SX family. The otherwise constant difference of the meta shifts indicates essentially the same transmission of the polar effect from O and S. The more negative values for oxygen are a manifestation of its greater electronegativity. The dual substituent parameter results for a somewhat limited m-OX family (X = Me, C_6H_5, CF_3, and CN) are quite comparable to those given above for the m-SX family (Table IV).

Table IV. Correlation of Shifts Relative to Inductive Effect of Substituent X in FC_6H_4SX and FC_6H_4OX

| X | σ_I of Substituent[a] | Shifts, ppm, relative to OH or SH derivatives | | | |
| | | OX | | SX | |
		Para	Meta	Para	Meta
CN	0.48	−8.94	−3.92	−5.97	−3.13
$COCF_3$	0.45	−9.99	−2.55	−7.95	−2.23
Cl	0.44			−7.97	−1.46
CF_3	0.41	−9.15	−2.13	−7.70	−1.59
$COCH_3$	0.39	−6.60	−0.13	−4.69	−.15
OCH_3	0.25			−2.36	−.40
$N(CH_3)_2$	0.10			−2.33	0.29
C_6H_5	0.10	−3.95	−0.80	−2.51	−.20
$C{\equiv}CH$	0.10	−5.41	−1.74	−1.32	−0.91
$CH{=}CH_2$	0.05	−3.85	−.87	−2.29	−.14
H	0	(0.00)	(0.00)	(0.00)	(0.00)
CH_3	−0.05	0.30	0.15	0.75	0.43

[a] Values from ref 4d for ^{19}F shielding in normal solvents.

The para shifts do not show a constant difference between corresponding values of $f_{p-OH}{}^{p-OX}$ and $f_{p-SH}{}^{p-SX}$, even if X = $CH_3C{=}O$ and $CF_3C{=}O$ are excluded. This result further supports the conclusion above concerning the feebly interacting and easily polarized pseudo π electrons of sulfur.

Tri-, Tetra-, and Pentacoordinated Sulfur. For all the substituents in these families, $f_{m-SX_n}{}^{p-SX_n}$ is negative (although only very slightly negative for $S(O)CH_3$). The sulfoxides and sulfones have long been considered to involve $Ar\overset{-}{=}S$ and $S\overset{-}{=}O$ π(p–d) interactions[14] as

well as $S^+{-}O^-$ contributing forms. The strongest π electron-withdrawing substituents, X, in this series are trifluoromethylsulfonyl (SO_2CF_3) and cyanosulfonyl (SO_2CN), where the strongly electronegative trifluoromethyl or cyano groups apparently, as expected, enhance d-orbital participation.

Fittings have been carried out with the dual substituent parameter treatment for both the SOX and SO_2X families using (in the absence of results for the H substituent) the CH_3 substituent as reference (i.e., all σ_I and σ_R parameters have been made relative to zero for X = CH_3). For the SOX family, best fits are achieved for both meta and para shifts with the use of the $\sigma_R{}^+$ scale:

$\rho_I{}^m = -2.48$		$\rho_I{}^p = -10.86$	
$\rho_R{}^m = -1.10$		$\rho_R{}^p = 1.05$	
$\lambda^m = 0.44$		$\lambda^p = 0.10$	
$SD = 0.21$		$SD = 0.44$	
$f = 0.177$		$f = 0.100$	

For the SO_2X family, best fits are achieved for both meta and para shifts with the use of the $\bar\sigma_R$ (BA) parameters:

$\rho_I{}^m = -3.58$		$\rho_I{}^p = -10.28$	
$\rho_R{}^m = -1.97$		$\rho_R{}^p = -4.88$	
$\lambda^m = 0.55$		$\lambda^p = 0.47$	
$SD = 0.25$		$SD = 0.39$	
$f = 0.157$		$f = 0.088$	

These fittings may be considered adequate although the precision is generally of rather poor quality. However, it is significant that $f = 0.15 \pm 0.10$ is found for all the fittings with substituents for X at P, S, and O in the various families. Apparently, the σ parameters from carbon are transferable to these elements, at least to this order of precision.

Table V summarizes the ρ_I values obtained in the best fittings for the various families. For meta shifts, $-\rho_I{}^m$ values are 3.5 $\pm$ 1.0 for all families except PX_2, for which a larger value (obsd 5.6) is expected because two X substituents are involved. Within this indicated range of $\rho_I{}^m$ values there appears to be little or no systematic relationship to or dependence upon structural considerations. Significantly larger $-\rho_I{}^p$ values are obtained for the SX or OX families than for the CH_2X, COX, SOX, and SO_2X families. This result indicates that the largest substituent polar effects on σ_R values are for those family groups which involve an unshared pair of electrons, e.g., OX, SX, PX_2, SOX. The SO_2X, CH_2X, and COX families have distinctly smaller values of $-\rho_I{}^p$.

Table VI summarizes values of λ and ρ_R from the best fitting results. Since different σ_R scales are involved (e.g., $\sigma_R{}^-$ for SX, σ_R (BA) for SO_2X and $\sigma_R{}^+$ for COX), the comparisons are only qualitative. Nonetheless it is apparent that for the groups having central first-row elements, λ values are as expected (near zero for CH_2X, and finite for OX and COX). Finite values of λ (both meta and para) for the SO_2X, SOX, and SX families indicate the presence of significant π electron acceptor orbitals on sulfur, and, presumably, of $S\overset{-}{=}X$

Table V. Summary of Family ρ_I Values from Best Fittings with Dual Substituent Parameter Treatment

	COX	SOX	CH₂X	SO₂X	SX	OX	PX₂
$\rho_I{}^m$	−3.00	−2.48	−3.71	−3.58	−4.01	−4.37	−5.56
$\rho_I{}^P$	−7.49	−10.86	−9.87	−10.28	−16.44	−16.98	−18.6

Table VI. Summary of Family ρ_R and λ Values from Best Fittings with Dual Substituent Parameter Treatment

	CH₂X	SX	SOX	PX₂	OX	SO₂X	COX
λ^m	−0.02	0.42	0.44	0.60	0.86	0.55	0.64
$\rho_R{}^m$	0.06	−1.70	−1.10	−3.34	−3.78	−1.97	−1.90
λ^P	−0.21	0.05	0.10	0.30	0.14	0.47	0.65
$\rho_R{}^P$	2.11	−0.82	−1.05	−5.58	−2.30	−4.88	−4.90

Table VII. Fits with the σ_R(BA) Scale

	Meta			Para		
	SOX	SO₂X	COX	SOX	SO₂X	COX
ρ_I	−2.78	−3.58	−2.91	−11.10	−10.28	−8.09
ρ_R	−2.04	−1.97	−2.73	−1.84	−4.88	−8.50
λ	0.73	0.55	0.94	0.17	0.47	1.05
SD	0.29	0.25	0.34	0.54	0.39	0.75
f	0.245	0.157	0.305	0.122	0.088	0.193

π(p–d) bonding. The λ values tend to increase with increased oxidation state of sulfur.

In order to compare ρ_R and λ values for the SOX, COX, and SO₂X families, fitting parameters have been compared in Table VII for fits for each with σ_R (BA) scale. The ρ_R values are seen to generally increase in the sequence SOX < SO₂X < COX, indicating poorer conjugation of X with sulfur than with carbonyl carbon. Two additional points are noteworthy. Except for the COX family, λ^m is consistently larger than the corresponding λ^P value. This result probably reflects the conjugating influence of the p-FC₆H₄ as compared to the m-FC₆H₄ moiety.[19]

The SF₅ group shows only a relatively small value (−2.37) for $f_{m\text{-SF}_5}{}^{p\text{-SF}_5}$[4d,20] in contrast to the much larger negative values (−9.47 and −5.84, respectively) for $f_{m\text{-PF}_4}{}^{p\text{-PF}_4}$ and $f_{m\text{-SF}_3}{}^{p\text{-SF}_3}$. Two d orbitals are already used for σ bonding in the hexacovalent sulfur so that the remaining d orbitals may now be of too high energy for effective π(p–d) interactions; but PF₄, where one d orbital is used in σ bonding, does not show this effect. This difference is not attributed to the different geometry of the two groups (octahedral for SF₅ and trigonal bypyramidal for PF₄ and SF₃; see Figure 2), since two of the remaining d orbitals (d$_{xy}$, d$_{xv}$, and d$_{yz}$) should be in the best possible orientation for overlap with the aromatic π orbitals. The remaining possibility is that S–X π(p–d) overlap with the unshared p electrons on the five fluorines saturates the d orbitals. The relatively short S–F bond compared to C–S

would also help this interaction (see Figure 2). Presumably the balance of four empty d orbitals with four fluorines does not prevent Ar–P π(p–d) in ArPF₄, whereas the SF₅ group has only three empty d orbitals with five fluorines.
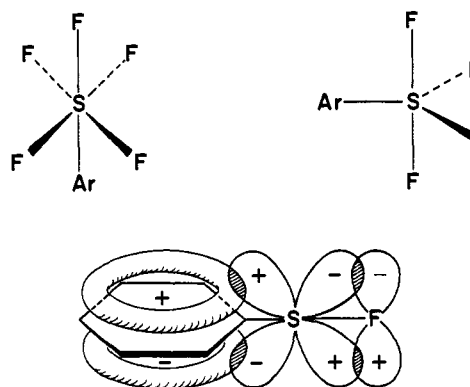
Figure 2. Geometry and orbital overlap of aryl sulfur fluorides.

Interestingly, the various factors contribute in such a manner that the SF₃ group shows a net π electron-withdrawing effect of about the same size as that for the PF₂ group: $f_{m\text{-PF}_2}{}^{p\text{-PF}_2} = -6.19$, $f_{m\text{-SF}_3}{}^{p\text{-SF}_3} = -5.84$.

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