Phenylsulfur pentafluoride, 2.05 g. (0.010 mole), was mixed with 2.0 g. of the above sulfuric acid in a 15-ml. flask fitted with a magnetic stirrer and a reflux condenser with a Drierite guard tube. The flask was immersed in an oil bath and the contents stirred while the temperature was raised gradually. No reaction was apparent until the oil bath temperature reached 98°, at which point bubbling was observed in the reaction mixture and HF attack was observed on the upper walls of the glass flask. After 5-10 min. heating at 100-103° the reaction was essentially complete, as indicated by the reaction mixture becoming homogeneous. Heating was continued for an additional 40 minutes at 100-103°, and then the reaction mixture was poured over 25 ml. of ice and water. There was obtained a total of 0.75 g. (40%) of oil, characterized by infrared and n.m.r. fluorine spectra as benzenesulfonyl fluoride. Benzenesulfonyl fluoride is hydrolyzed to benzenesulfonic acid under these conditions, and the 60% unrecovered product probably can be accounted for as benzenesulfonic acid which was not isolated in the work-up procedure.

A control hydrolysis of benzotrifluoride was run under the same conditions as above for comparison purposes. It was observed that the benzotrifluoride was hydrolyzed at 90-95° in less than 5 minutes.[18]

(d) Pyrolysis.[19]—Samples (0.10 g.) of phenylsulfur pentafluoride were sealed in evacuated 20 mm. × 15 mm. Pyrex glass tubes constructed with a capillary tip. One of each of these tubes was heated for a 7-hr. period at 400, 450 and 500° in a muffle furnace. The tubes, after cooling, were opened in an evacuated holder and the gaseous products were analyzed in a mass spectrometer. The results are given in Table II.

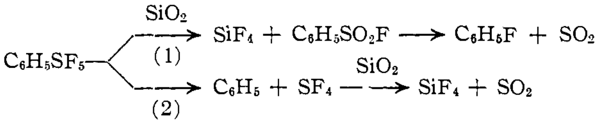
TABLE II

PYROLYSIS OF PHENYLSULFUR PENTAFLUORIDE

	400°	450°[a]
Appearance after heating	Slightly charred deposit. Clear, colorless liquid	Large amount black deposit; clear, colorless liquid
Estimated decomposition[b]	<20%	<40%
Analysis of gaseous products[c]		
SiF_4	49%	29%
SO_2	35%	28%
C_6H_5F	12%	39%
$C_6H_5SF_5$	1%	4%

[a] The tube heated at 500° leaked. It contained very little liquid and was completely black inside; the gaseous product was chiefly air. [b] Estimated from amount of recovered liquid. [c] Liquid product was shown to be chiefly $C_6H_5SF_5$ by spectrometric analysis.

Decomposition could occur at the higher temperature by one of two routes.



$$C_6H_5SF_5 \begin{cases} \xrightarrow[(1)]{SiO_2} SiF_4 + C_6H_5SO_2F \longrightarrow C_6H_5F + SO_2 \\ \xrightarrow[(2)]{} C_6H_5 + SF_4 \xrightarrow{SiO_2} SiF_4 + SO_2 \end{cases}$$

By analogy to decomposition studies on CF_3SF_5,[20] route 2 is favored. Additional pyrolysis studies of gaseous samples in a nickel cylinder also support this conclusion. In this case decomposition became extensive at 500°, but quantitative studies were precluded by reaction of the sample at high temperatures with traces of moisture in the cylinder walls.

Acknowledgments.—The author is grateful to Drs. T. L. Cairns and B. C. McKusick for helpful discussions and suggestions during the course of this work.

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[18] G. M. LeFave, *J. Am. Chem. Soc.*, **71**, 4148 (1949); E. T. McBee and M. R. Frederick, *ibid.*, **71**, 1490 (1949).

[19] A qualitative study of the stability of derivatives of perfluorobenzene recently was described by L. A. Wall, R. E. Donadio and W. J. Pummer, *ibid.*, **82**, 4846 (1960).

[20] R. E. Dresdner, *ibid.*, **77**, 6633 (1955); **79**, 69 (1957).

[CONTRIBUTION NO. 730 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

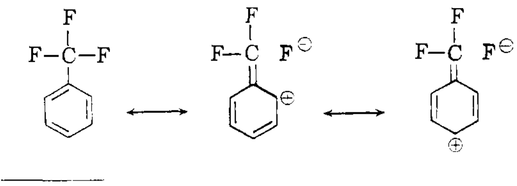
The Electrical Effect of the Sulfur Pentafluoride Group[1]

BY WILLIAM A. SHEPPARD

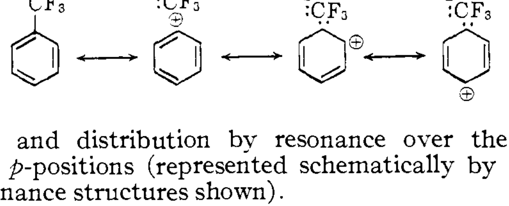
RECEIVED JANUARY 16, 1962

The sulfur pentafluoride group, a new stable substituent on an aromatic ring, has been shown to be strongly electron-withdrawing with measure σ-values, *meta* and *para*, of +0.61 and +0.68 to +0.86, respectively. By ionization constant and dipole moment measurements the electron attracting influence has been shown to be enhanced in the *para* position by a small, but significant, amount of resonance interaction. This resonance effect is discussed relative to a similar effect observed with the trifluoromethyl group and relative to d-orbital participation by sulfur.

The electron-withdrawing power of the trifluoromethyl group on an aromatic ring has been evaluated[2] from dipole moment and σ-parameter data. The strong, inductive electron-withdrawal effect was shown to be enhanced to a significant extent by resonance interaction, and resonance contribution of the following type was suggested



Alternatively, the preferential relay of the electron attracting influence of the trifluoromethyl group to the *o*- and *p*-position may be explained by an induction of a positive charge at C-1 of the aromatic



ring and distribution by resonance over the *o*- and *p*-positions (represented schematically by the resonance structures shown).

Recently, arylsulfur pentafluorides were synthesized for the first time.[3] The sulfur pentafluoride group, like the trifluoromethyl group, was shown to have a strong *meta*-orienting influence in electro-

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[1] This work was presented in part at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

[2] J. D. Roberts, R. L. Webb and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

[3] W. A. Sheppard, *ibid.*, **82**, 4751 (1960) and **84**, 3064 (1962).

philic aromatic substitution. The exceptional stability of the sulfur pentafluoride group when attached to an aromatic ring allowed the preparation of derivatives needed to evaluate its electrical effect. From quantitative determination of the inductive power it was hoped to evaluate and better understand resonance interaction of the type discussed for the trifluoromethyl group and to provide evidence for d-orbital participation by sulfur in the hexavalent state.

Experimental

The arylsulfur pentafluorides used in these measurements were prepared and purified as described in the preceding paper.[3] The other substituted anilines and benzoic acids employed for comparisons and controls were purified commercial products.

Dipole Moments.—The dipole moments were determined by literature methods[2,4] employing a Wissenschaftlich Technische Werkstätten Dipolemeter type DM 01, Cell DFL 1 (20 ml. volume). The data are given in Tables I and II.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES, AND POLARIZATIONS IN BENZENE AT 25°

F_2	E	D	n_D	P_2
Phenylsulfur pentafluoride				
0.00000	2.2740	0.87220		(P_1 = 26.743)[a]
.01010	2.4463	.88425		270.07
.02023	2.6264	.88390		272.75
.04014	2.9563	.91120		258.00
.06028	3.3147	.92836		250.00
m-Aminophenylsulfur pentafluoride				
0.00000	2.2740	0.87220	1.4971	(P_1 = 26.743)[a]
.02015	2.8664	.89660	1.4965	418.08
.04065	3.4924	.91780	1.4959	388.68
p-Aminophenylsulfur pentafluoride				
0.00000	2.2740	0.87220	1.4971	(P_1 = 26.743)[a]
.01015	2.6972	.88620	1.4967	587.05
.02004	3.0998	.89694	1.4964	546.30
.03027	3.5473	.90723	1.4960	520.69

[a] Standardization liquid, benzene; literature values.

TABLE II

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Compound	MRD	P_0 (25°)	μ (Debye)
Phenylsulfur pentafluoride	35.25	277.0	3.44
m-Aminophenylsulfur pentafluoride	38.38[a]	477.0	4.47
p-Aminophenylsulfur pentafluoride	38.38[a]	614.0	5.31

[a] Since these compounds are crystalline solids at room temperature, the MRD could not be determined directly but was estimated by a literature method[4c] and from densities and refractive indices of the benzene solutions.

Ionization Constants.—Apparent ionization constants of *m*- and *p*-carboxyphenylsulfur pentafluoride were obtained at 25° in 50% water–50% ethyl alcohol (by volume) as described by Roberts and co-workers[2,5] using a Beckman pH meter, model G, with glass electrodes.

	Half-point scale reading	Apparent ionization constant[a] × 10^6
Carboxyphenylsulfur		
pentafluoride, *meta*	4.82	15.1
para	4.70	19.8

[a] Calculated assuming unit activities and reading of *p*H meter scale equal to logarithm of reciprocal of hydrogen ion concentration.

Ionization constants of the anilinium ions (pK_a of the reaction $RNH_3^+ \rightleftarrows RNH_2 + H^+$) were determined at 25° in aqueous solution by making spectrophotometric measurements in the ultraviolet region employing a Cary recording spectrophotometer (Model 11) with thermostated cell holder. Two methods were employed for these determinations. In Method A, the procedure of Hammett as described by Roberts and co-workers,[2] pK_a's were determined in aqueous sulfuric acid solutions using *p*-nitroanilinium ion as a reference. In Method B, a procedure described recently by Bryson,[6] acetate and chloroacetate buffer solutions were employed; pH measurements on the buffered solutions of the aniline were made with a Beckman pH meter, Model G, using glass electrodes. In making these measurements at least three results, using buffer solutions within 0.4 pK_a unit of the pK_a of the anilinium ion, were averaged. Agreement of determinations in repeat experiments and of the pK_a's of reference anilines were within the ± 0.03 pK_a unit precision ascribed to the method.[6]

The results of these measurements are reported in Tables III and IV. Method B compared to Method A gives apparent ionization constants lower by 0.1 to 0.2 p*K*a unit for certain *m*- and *p*-substituted anilines. The reason for this discrepancy is not obvious, but it is felt that the use of buffered solution in Method B should be more accurate than the use of *p*-nitroanilinium ion as reference in Method A. In Method A there is a difference of 1 to 2 p*K*a units from the reference and no correction is made for differences in hydrogen ion concentration in the dilute acid solutions.

The ionization constants of the phenols in aqueous solution at 25° were determined also by the spectrophotometric method[7] using borate buffered solutions. The results are reported in Table V.

Polarographic Measurements.—The polarographic half-wave potentials of *m*- and *p*-nitrophenylsulfur pentafluorides were obtained in ethanol at 25° and *p*H 3.0[8] using a Leeds and Northrop Electrochemograph Type E. Concentration and pH studies showed that the reduction was diffusion controlled and that the number of electrons involved in the reaction probably was 4 (5 and 6 are possible, but unlikely; the product from a 4 electron transfer is the hydroxylamine, ArNHOH). It was assumed on the basis of studies reported in the literature that the nitro compounds are reduced irreversibly. The reduction potential, $E_{1/2}$, for the variously substituted nitrobenzenes represents a measurement of the comparative ease of reduction of the aromatic NO_2 group as affected by substituents in the *m*- or *p*-position. The substituents then may be arranged in a series in order of decreasing electron-withdrawing power, or increasingly negative $E_{1/2}$ value

$$NO_2,\ SF_5,\ CO_2H,\ CF_3,\ H,\ CH_3$$

The $E_{1/2}$ values are given in Table VI and have been employed to calculate Hammett σ-values using the equation $E_{1/2} - E^0{}_{1/2} = \sigma\rho$, where $E_{1/2}$ and $E^0{}_{1/2}$ are the half-wave potentials for polarographic reduction of the substituted and unsubstituted nitrobenzenes, respectively. Unfortunately, the reference values for calculation of the ρ for this reduction are limited to a relatively small number of experimental measurements determined in slightly different solvents (8% and 10% ethanol).

Results and Discussion

The ionization constants of the benzoic acids, anilinium ions and phenols quantitatively show

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(4) (a) J. D. Roberts, R. Armstrong, R. F. Trimble and M. Burg, *J. Am. Chem. Soc.*, **71**, 843 (1949); (b) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Physical Methods, Part II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, Chapter XXIV. (c) C. P. Smyth, "Dielectric Behavior and Molecular Structure," Am. Chem. Soc., Monograph Series, Chemical Catalog Co., New York, 1931, p. 409.

(5) J. D. Roberts, E. A. McElhill and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).

(6) A. Bryson, *ibid.*, **82**, 4858 (1960).

(7) A. E. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

(8) J. Pearson, *Trans. Faraday Soc.*, **44**, 683 (1948); J. E. Page, J. W. Smith and J. A. Waller, *J. Phys. Chem.*, **53**, 545 (1949). The effect of substituents on the polarographic reduction of nitrobenzene in acetonitrile solution was carefully investigated by A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

TABLE III

DETERMINATION OF ACIDITY CONSTANTS OF ANILINIUM IONS ($XC_6H_4NH_3^+ \rightleftarrows H^+ + XC_6H_4NH_2$) FROM OPTICAL DENSITY MEASUREMENTS IN AQUEOUS SOLUTIONS (SULFURIC ACID) METHOD A[a]

Substituent	λmax (mμ)	Concn. (g./l.)	D_{ti} (in 30% H_2SO_4)	D_{ui} (in H_2O)	D_{pi}	C_x/C	pK_a
p-NO_2	380	0.200	0.000	1.862	1.737[b]	0.932	(1.11)[e]
					1.615[c]	.867	
					1.420[d]	.763	
m-NO_2	226	.180	.372	1.945	0.885[b]	.326	2.56
					.664[c]	.186	2.57
					.531[d]	.101	2.57
p-CF_3	243.5	.253	.048	1.765	.340[b]	.170	2.94
		.297	.034	1.850	.205[c]	.0944	2.91
p-SF_5	247	.300	.043	1.610	.715[b]	.429	2.37
					.464[c]	.269	2.36
					.274[d]	.147	2.38
m-SF_5	235	.487	.016	1.690	.333[b]	.189	2.88
					.189[c]	.103	2.86
	292		.000	0.440	.081[b]	.184	2.89

[a] The method depends on measurement of the concentration ratio of unionized aniline to ionized aniline in dilute acid solution. The same measurements under the same conditions are made for an aniline whose acidity constant is known, and the unknown acidity constant is then calculated from the relationship

$$pK_a{}^C - pK_a{}^B = \log \frac{C_C}{C_{BH^+}} + \log \frac{C_B}{C_{BH^+}}$$

Where $pK_a{}^C$ and $pK_a{}^B$ are acidity constants for the anilines C and B, C_C and C_B are the concentrations of the unionized form of the anilines C and B, and C_{CH^+} and C_{BH^+} are the concentration of the ionized (protonated) form of the anilines C and B. The appropriate method for measurement of the concentration ratio of unionized to ionized forms is by determination of optical densities of the completely ionized, partially ionized and unionized species of the anilines at the wave length of maximum absorption in the ultraviolet or visible spectra. The calculations were made using the equations:

$$\frac{C_X}{C} = \frac{C_X}{C_{XH^+} + C_X} = \frac{D_{ti} - D_{pi}}{D_{ti} - D_{ui}},\ \frac{C_{XH^+}}{C} + \frac{C_X}{C} = 1,\ \frac{C_X}{C} \Big/ \frac{C_{XH^+}}{C} = \frac{C_X}{C_{XH^+}}$$

where C_X is the concentration of unionized form of aniline X, C_{XH^+} is the concentration of ionized form of aniline X, and C is the total concentration of aniline X in both ionized and unionized form. The optical densities were measured at the wave length for maximum absorption of the unionized species so that D_{ti} is the optical density for the totally ionized form of the aniline measured in 30% sulfuric acid solution, D_{ui} is for the unionized form of the aniline measured in water solution, and D_{pi} is for the partially ionized form of the aniline measured in dilute sulfuric acid solution. [b] Approximate dilute acid concentration 0.01 N. [c] Approximate dilute acid concentration 0.022 N. [d] Approximate dilute acid concentration 0.05 N. [e] Literature value[2]; used as reference aniline.

TABLE IV

ACIDITY CONSTANTS OF ANILINIUM IONS ($XC_6H_4NH_3^+ \rightleftarrows XC_6H_4NH_2 + H^+$) FROM OPTICAL DENSITY MEASUREMENTS IN BUFFERED AQUEOUS SOLUTION—METHOD B[6]

Substituent X	Measured pK_a	Lit. value Method B[6]	Lit. value Method A[2]
H	4.56	4.59	4.57
m-NO_2	2.42	2.47	2.62
m-Cl	3.45	3.46	3.67
m-CF_3	3.20	..	3.49
p-CF_3	2.75	..	2.57 (2.93)[a]
m-SF_5	2.82	..	(2.88)[a]
p-SF_5	2.17	..	(2.37)[a]

[a] Values in parentheses are from present work; see footnote 12 for a discussion of the discrepancies of the values for the p-CF_3 anilinium ion.

TABLE V

IONIZATION CONSTANTS OF PHENOLS ($XC_6H_4CH \rightarrow H^+ + XC_6H_4O^{\ominus}$) IN WATER AT 25°

X	λ_{max} (mμ)	pK_a
m-NO_2	395	8.38 (8.38)[a]
p-NO_2	402	7.19 (7.21)[a]
m-SF_5	300	8.57
p-SF_5	250	8.37

[a] Literature value, ref. 7.

that the sulfur pentafluoride group is more strongly electron-withdrawing than a trifluoromethyl group and approaches a nitro group in inductive power.

TABLE VI

REDUCTION POTENTIALS FOR NITROBENZENE DERIVATIVES IN 8% ETHANOL AT 25° AND pH 3.0

Substituent	$E_{1/2}$
H	−0.34 (−0.34)[a]
m-SF_5	− .262
p-SF_5	− .235
p-CF_3	− .27
m-NO_2	(− .20)
p-NO_2	(− .14)
p-CO_2H	− .23 (−0.235)

[a] Values in parentheses are from literature.[8]

These measurements also show that the sulfur pentafluoride group exerts a stronger electron-withdrawing influence in the *para* compared to the *meta* position.

By use of the Hammett equation,[9] the σ-values for the sulfur pentafluoride group were calculated from the ionization constants and polarographic reduction measurements and are given in Table VII. The σ_m-values from the ionization constants of the benzoic acids, anilium ions and phenols are in excellent agreement (+0.61 to +0.63). The same σ_m-value for the sulfur pentafluoride group was determined recently by Taft from F^{19} n.m.r.

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(9) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry" edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 574.

TABLE VII

HAMMETT SIGMA VALUES

Reaction	Solvent	Temp., °C.	Log k^0	ρ	Log k_{meta}	σ_{meta}	Log k_{para}	σ_{para}
			SF_5 Group					
Ionization of benzoic acids	50% EtOH	25	-5.71^a	$+1.464^a$	-4.82	0.61	-4.70	0.68
Ionization of anilinium ions Method A[2]	H_2O	25	-4.569^a	$+2.730^a$	-2.88	.61	-2.37	.81
Ionization of anilinium ions Method B[6]	H_2O	25	-4.557^b	$+2.767^b$	-2.82	.63	-2.17	.86
Ionization of phenols	H_2O	25	-9.919^c	$+2.229^c$	-8.57	.61	-8.37	.70
Polarographic reduction	8% EtOH	25	-0.341^d	$+0.165^d$	-0.262^d	.48	-0.235^d	.64
						$.41^e$		$.66^e$
			CF_3 Group					
Ionization of anilinium ions Method A[2]	H_2O	25	-4.569^a	$+2.730^a$	......	...	-2.93	.60
Ionization of anilinium ions Method B[6]	H_2O	25	-4.557^b	$+2.767^b$	-3.20	.49	-2.75	.65
Polarographic reduction	8% EtOH	25	-0.341^d	$+0.165^d$	......	...	-0.27	$.44^e$
								.43

[a] Ref. 2. [b] Ref. 11a. [c] Ref. 7. [d] Values of $E^0{}_{1/2}$ and $E_{1/2}$ are given under log k^0 and log k, respectively. The $E^0{}_{1/2}$ and ρ, in units of volts, are from ref. 8. [e] Values read from a plot of $\Delta E_{1/2}(E_{1/2} - E^0{}_{1/2})$ *vs.* known σ values.

chemical shifts.[10] The σ_m-parameter from polarographic reduction measurements was 0.48, but this value is not considered reliable because the ρ-value for this reaction was calculated from insufficient data obtained under different conditions. The σ_m-value for sulfur pentafluoride is intermediate in position between that for trifluoromethyl, σ_m $+0.42$, and the nitro group, σ_m $+0.71$.

The σ_p-parameters are larger positive values than the σ_m-parameters and a single σ_p-value does not suffice for the carboxy (σ_p 0.69) and amino (σ_p 0.85) groups. This enhancement of σ_p- over σ_m-parameters and the need for a σ^* or σ^+ -value[11] is indicative of resonance interaction. The difference in σ_p from the benzoic acids and anilinium ions is 0.18, similar to the 0.12 increment found for the trifluoromethyl group.[12] This increment is smaller than those exhibited by the *p*-nitro (0.49 unit) and *p*-cyano groups (0.34 unit).[11]

Recently Taft and Lewis[13] have proposed a modification of the Hammett free-energy relationship and a method of determining σ_I and σ_R as parameters for defining the extent of inductive and resonance influence, respectively, for a substituent in an aromatic system. By use of the method of Taft and Lewis,[13a] the σ_I and σ_R parameters were calculated and are compared with the parameters for the trifluoromethyl group in Table VIII.

TABLE VIII

COMPARISON OF σ-PARAMETERS FOR THE TRIFLUOROMETHYL AND SULFUR PENTAFLUORIDE GROUPS[a]

	Ionization of (at 25°)					F^{19} n.m.r. chemical shift[b]
	$ArCO_2H$, 50% ethanol		$ArNH_3^+$, H_2O		ArOH, H_2O	
	SF_5	CF_3	SF_5	CF_3	SF_5	SF_5
σ_m	0.61	0.41	0.63	0.49	0.61	0.59
σ_p	.68	.53	.86	.65	.70	0.67
σ_I	.55	.39	.56	.44	.53	0.55 to 0.57
σ_R	.11	.12	.27	.18	.12	0.07 to 0.10

[a] Calculated using ρ_I $+1.50$, α 0.42 for ionization of benzoic and ρ_I $+2.90$, α 0.15 for ionization of anilinium ions, ρ $+2.36$, α 0.07 for ionization of phenols. See ref. 13a. Table II, and equations 1, 6 and 3. [b] See ref. 10.

This treatment of the data clearly demonstrates the strong inductive effect exerted by the sulfur pentafluoride group. This effect is greater than that exhibited by the trifluoromethyl group by an amount slightly less than expected from the inductive effect of two additional fluorines. The resonance influence of the sulfur pentafluoride group compared to the trifluoromethyl group ranges from the same to a proportionately greater amount.

Another comparison between the trifluoromethyl and sulfur pentafluoride groups can be made from the dipole moment data (Table IX). The larger dipole moment of 3.44 D. for phenylsulfur pentafluoride compared to 2.60 D. for benzotrifluoride is again explained easily by the increased inductive effect exerted by the two additional fluorines. The dipole moment of *m*-aminophenylsulfur pentafluoride closely agrees with the value calculated by the vector sum of the moments from phenylsulfur pentafluoride and aniline. However, the measured value of 5.31 D. for *p*-aminophenylsulfur pentafluoride is 0.6 D. larger than the calculated value. This enhancement of dipole moment is again attributed to the resonance interaction and may be compared with 0.4 D. enhancement observed for *p*-aminobenzotrifluoride.

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(10) Private communication from Professor R. W. Taft, Jr. We are indebted to Professor Taft for permission to discuss these results prior to publication. The σ-parameters calculated from F^{19} n.m.r. chemical shifts on the *m*- and *p*-fluorophenylsulfur pentafluoride were σ_m $+0.59$ and σ_p $+0.67$. The σ_I was $+0.55$ to 0.57 and σ_R was $+0.07$ to $+0.10$ (see ref. 13).

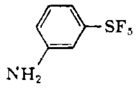
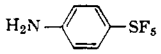
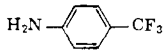
(11) (a) H. H. Jaffe, *Chem. Revs.*, **53**, 222 (1953). (b) C. W. McGary, Jr., Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 3037 (1955).

(12) The value of σp determined by Roberts and co-workers[2] from the ionization constant of *p*-trifluoromethylaniline was found to be in error. In the present work the ionization constant was determined to be 2.75 giving a σ_p of 0.65 which compares favorably with the σ-value of 0.64 reported for *p*-dimethylaminobenzotrifluoride. It was noted that the aqueous solution of *p*-trifluoromethylaniline became cloudy on storage. This instability, in contrast to the behavior of the other anilines studied, could account for the original erroneous value and is perhaps not unexpected in view of the ease of hydrolysis of *p*-hydroxybenzotrifluoride (see R. G. Jones, *ibid.*, **69**, 2346 (1947)).

(13) (a) R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **81**, 5343 (1959); (b) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

TABLE IX

DIPOLE MOMENTS AT 25° (DEBYE)

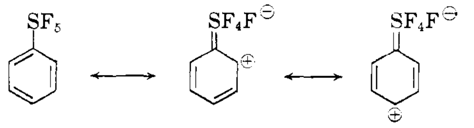
Compound	Measured value	Calculated by vector sum
$C_6H_5NH_2$	1.58	
$C_6H_5SF_5$	3.44	
	4.47	4.47
	5.31	4.73[a]
$C_6H_5CF_3$	2.60[b]	
	4.28[b]	3.86[b]

[a] In this calculation the angle between the vector of the moment of the amino group and the axis of the ring was taken as 42°.[2] [b] Ref. 2.

Several explanations can be considered for this resonance interaction:

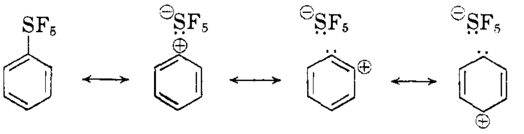
(1) *d*-Orbital participation by sulfur

(2) Fluoride ion no-bond resonance as represented by



An alternative view is the involvement of 3s or higher orbitals of fluorine for stabilization of electrons from an electron-rich substituent.

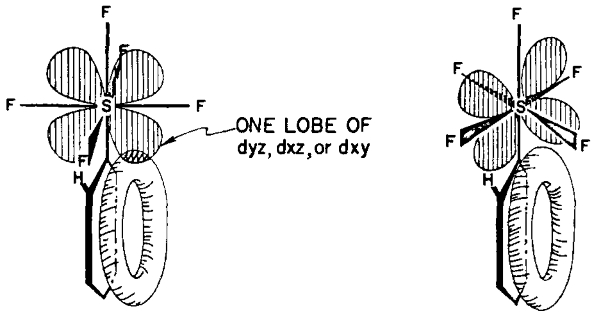
(3) Induced positive charge at C-1 of the ring which is distributed to the *o*- and *p*-positions by resonance. An alternative description of this view is sulfur pentafluoride ion no-bond resonance shown as



(4) Rehybridization about the sulfur, involving the sulfur–fluorine bonds, when energetically favorable for stabilization of electron-rich groups.

First, in considering the d-orbital participation by sulfur as an explanation for this resonance effect, the bonding about sulfur in the arylsulfur pentafluoride is sp^3d^2 hybrid.[3] The d_{z^2} and $d_{x^2-y^2}$ orbitals are used in forming the hybrid because of the favorable geometry.[14] Of the remaining d-orbitals, two of the d_{xy}, d_{yz} and d_{xz} orbitals can be available and in position for partial overlap by one lobe with the π orbital of the benzene ring.

For this d-π overlap to be significant, one axis of the octahedron about sulfur must be parallel to the ring and another is then orthogonal (Form I). The vacant d-orbital should now overlap with the π system. However, the staggered configuration (Form II) for positioning the fluorines with the aromatic ring should be energetically favorable,[15] and this d-π overlap can now occur to only a small extent. Also, the energy of these remaining 3-d-orbitals can be as high as that of the 4-s orbital and hence may not be energetically accessible.[16] Professor Taft proposed that d-orbital participation could be detected by F^{19} n.m.r. chemical shift correlations with solvent for the fluorophenylsulfur pentafluorides by comparison to similar measurements with fluorobenzotrifluorides. However, these measurements showed no evidence for d-orbital participation.[10]



FORM I FORM II

Before considering the other possibilities, the marked similarity of the resonance influence for the trifluoromethyl and sulfur pentafluoride groups should be noted. It seems fortuitous that the size of this effect is the same for the two groups if it occurs by different mechanisms.

The second and third proposals are similar to explanations advanced for the resonance interaction of the trifluoromethyl group (see Introduction) and arguments can be presented in support of each mechanism.[2,17] However, it is felt that this resonance phenomenon also may be described in terms of a rehybridization of bonding orbitals about sulfur (or carbon for the trifluoromethyl group). Rehybridization may be energetically favorable when the opportunity arises to stabilize electron-rich groups supplying electrons by resonance. Such an explanation can be viewed as an elegant elaboration of a combination of the simple explanation as discussed above and will be discussed more fully in subsequent publications.[16]

Acknowledgments.—We wish to acknowledge with thanks the assistance of Miss Ellen Wallace and Mrs. Flora Youngken for carrying out the ionization constant measurements, Mr. Charles Wortz for dipole moment measurements and Miss Lucille Williams for the polarographic study.

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[14] (a) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1960, p. 152. (b) C. A. Coulson, "Valence," Oxford Univ. Press, London, 1952, p. 37. (c) L. E. Orgel, "An Introduction to Transition-Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 2.

[15] The barrier to rotation about the C–S bond by the sulfur pentafluoride group with respect to the benzene ring must be very low. No indication of freezing out this rotation using a *meta*-nitro-substituted ring at very low temperatures could be detected in the F^{19} n.m.r. spectra.

[16] A more detailed discussion of the bonding in the sulfur pentafluoride group will be presented in subsequent publications with Dr. D. R. Eaton of this Laboratory describing F^{19} n.m.r. studies.

[17] One argument against (3) is the lack of significant resonance interaction of the $(CH_3)_3N^+$ group with the ring (σ_m and σ_p are both 0.90^{12a}). If resonance occurred chiefly by mechanism 3 then the σ_p value for the $(CH_3)_3N^+$ group is expected to be at least +1.10, or in other words 0.2 to 0.3 unit more positive than the σ_m-parameter (see J. D. Roberts, R. A. Clement and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2182 (1951)).