A Survey of Hammett Substituent Constants and Resonance and Field Parameters

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I. Introduction

The Hammett equation (and its extended forms) has been one of the most widely used means for the study and interpretation of organic reactions and their mechanisms. Although the Hammett methodology has been criticized by theoreticians because of its empirical foundation, it is astonishing that σ constants, obtained simply from the ionization of organic acids in solution, can frequently predict successfully equilibrium and rate constants for a variety of families of reactions in solution. Almost every kind of organic reaction has been treated via the Hammett equation, or its extended form. The literature is so voluminous and extensive that there is no complete review of all that has been accomplished.

Hammett's success in treating the electronic effect of substituents on the rates and equilibria of organic reactions[1,2] led Taft to apply the same principles to steric and inductive and resonance effects.[3] Then, more recently, octanol/water partition coefficients (P) have been used for rationalizing the hydrophobic effects of organic compounds interacting with biological systems.[4] The use of log P (for whole molecules) or π (for substituents), when combined with electronic and steric parameters, has opened up whole new regions of biochemical and pharmacological reactions to study by the techniques of physical organic chemistry.[5,6]

The combination of electronic, steric, hydrophobic, hydrophilic, and hydrogen-bonding[7] parameters has been used to derive quantitative structure–activity relationships (QSAR) for a host of interactions of organic compounds with living systems or parts thereof. The binding of organic compounds to proteins,[8] their interaction with enzymes[9] and with cells[10,11] and tissues,[12] their inhibition of organelles,[11] and as antimalarials[13] and antitumor agents,[10,14] their action as hypnotics[15,16] and anesthetics,[17] as well as their use in pesticide design,[18] in toxicology,[19] in mutagenicity[20] and carcinogenicity[21] studies, their fate in metabolism,[22,23] in environmental systems,[24] and their behavior in chromatographic systems[25,26] have all been treated via QSAR.

The explosive growth of correlation analysis of biological processes via substituent constants has somewhat changed the focus in the development of σ constants. Until the 1960's the use of substituent constants was almost entirely in the hands of physical organic chemists who generally worked with "well-behaved" substituents to analyze highly refined data from reactions in homogeneous solution. Their goal was to obtain very precise correlations and understanding for clearly defined but limited organic reactions. Applications of QSAR to biological systems, drugs, pesticides, toxicology, etc. brought under consideration much wider structural variations (including less well-behaved substituents) and activity data (dependent variables) of much lower quality. Noise in the biological data in the range of 20 to 100% was common so that small errors in σ and π, became less significant for this work. Researchers in these fields required parameters for a much wider variety of structure and were willing to accept a lower precision if necessary. This shift in emphasis led Hansch and Leo to compile and publish in 1979, a truly comprehensive data base of substituent constants.[4] During the following nine years many new substituent constants have been published, so that in this report we have been able to list both σ_m and σ_p values for 530 different substituents (Table I). With the use of values derived from F NMR shifts of meta- and para-substituted fluorobenzenes, the number is increased to over 660, including many substituents containing metallic atoms and highly interactive neutral and charged substituents. Exner[2] has also compiled an extensive list of σ constants including examples where only σ_m or σ_p is known, and he has attempted to evaluate their reliability. We have attempted to list all examples where both σ_m and σ_p have been reported and where more than one set of values exist we have selected the set which in our judgement is the most reliable. In some instances of very doubtful reliability we have placed the values in parentheses.

The values of σ were defined by Hammett from the ionization constants of benzoic acids as follows

$$\sigma_x = \log K_X - \log K_H \quad (1)$$

where K_H is the ionization constant for benzoic acid in water at 25 °C and K_X is the corresponding constant for a meta- or para-substituted benzoic acid. Some of the benzoic acids are so insoluble in water that mixed solvents such as 50/50 water/ethanol must be used. These secondary values have been linearly related to

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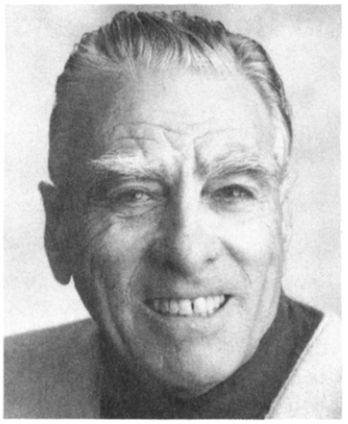
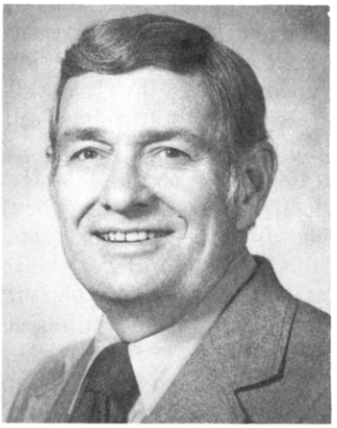


Corwin Hansch in 1944 received his Ph.D. from New York University in the field of synthetic organic chemistry, studying under Professor H. G. Lindwall. After a brief postdoctoral period with Professor H. R. Snyder at the University of Illinois, he joined the du Pont Co. and worked first on the Manhattan project at the University of Chicago and Richland, WA, and then at the experimental station in Wilmington, DE. In 1946 he joined the Chemistry Department at Pomona College, where he has remained except for two sabbatical leaves, one in Professor Prelog's laboratory in Zurich and the other in Professor Huisgen's laboratory in Munich. His main interests in research have been the high-temperature dehydrocyclization reaction and the correlation of chemical structure with biological activity.



Albert Leo was born 1925 in Winfield, IL and educated in southern California. He spent two years in the U.S. Army Infantry, serving in the ETO from 1944 to 1945. He received his B.S. in Chemistry from Pomona College (1948; Phi Beta Kappa, Magna Cum Laude) and M.S. and Ph.D. in Physical Organic Chemistry from the University of Chicago, studying reaction kinetics under Prof. Frank Westheimer. After 15 years in industrial research and development in the area of food chemistry, he returned to Pomona College to initiate and direct the Medchem Project under the leadership of his former professor, Dr. Corwin Hansch. The Project provides software and databases useful in the design of bioactive chemicals and is distributed world wide. His study of partition coefficients as a measure of hydrophobicity resulted in a 1971 paper in *Chemical Reviews* which has become a "Citation Classic". Dr. Leo was given an "Excellence in Science" award by Sigma Xi in 1980 and was chairman of the Gordon Conference on QSAR in Biology in 1981.

the water system by an appropriate scaling factor, ρ. σ values have been obtained also from various organic reactions (rates or equilibria) or from F NMR substituent chemical shifts. All of these methods have been examined in this report. However, in using the values in Table I for developing QSAR, care must be taken to see that the quality of the independent σ constant is commensurate with that of the data being correlated.

One of the early postulates of the so-called "English School of Chemists" was that the electronic effects of

Robert W. Taft is a Professor of Chemistry at the University of California, Irvine. Born in Lawrence, KS, Taft received a B.S. in Chemistry from the University of Kansas and a Ph.D. from the Ohio State University where he worked with Melvin Newman. Following a postdoctoral year with Louis Hammett at Columbia University, Taft spent 15 years at the Pennsylvania State University. He has been at the University of California, Irvine since it began in 1965. Current interests involve extensive studies of the effects of molecular structure on gas-phase proton-transfer equilibria, using ion cyclotron resonance spectroscopy. This work also includes binding studies in the gas phase with a variety of univalent cations. Additional interests include studies of structural and solvent effects on hydrogen-bond acidities and basicities and their applications to treatments of solute partitioning between bilayers and biological activities.

substituents are composed of two main parts: a field/inductive component and a resonance component.[27] Following Hammett's success in placing the discussion in numerical terms with σ constants, efforts were undertaken to factor σ into its component parts. Although progress has been made in showing for distant substituents that the field effect is predominate,[28] there remain questions to be answered[30] as to the magnitude of the contribution of the inductive effect. In this report, reference to either σ_I, σ_F, σ_L, or F, all of which, for present purposes, we show may be taken as essentially equivalent, (cf. Table II) assumes the operation of the combined effects.

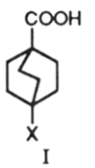
Wider agreement has been accorded the efforts to split the electronic effect of a substituent into field/inductive (σ_I) and resonance (σ_R) components:

$$\sigma_p = \sigma_I + \sigma_R \quad \text{or} \quad \sigma_p - \sigma_I = \sigma_R \quad \text{or} \quad \sigma_p - \sigma_R = \sigma_I \tag{2}$$

These efforts have been reviewed by Charton.[29]

A. Field/Inductive Parameters

There is general agreement that the ionization of bicyclooctane carboxylic acids[31] (I) provides an unambiguous system for *defining* a field/inductive parameter because, in this rigid system, X is held firmly in place and there is little possibility for resonance or polarization interaction between X and the carboxyl functions of COOH and COO^-. It seems safe to assume, therefore, that the only ways X can influence the ionization of the carboxyl group are through space (the predom-



I

inate field effect) and though the intervening σ bonds (inductive). Roberts and Moreland[31] used 50% ethanol as the solvent for these rather insoluble acids and defined the electronic parameter as

$$\sigma' = \log K_X - \log K_H \quad (3)$$

Taft[32] utilized a correlation between σ' and his generalized polar parameter (σ^*) to obtain additional values of σ' (called σ_I) and then calculated σ_R via eq 2. Swain and Lupton[33] used σ' to define F as a basis for separating the resonance and field inductive effects according to eq 4. The coefficients a, b, and ϵ are evaluated via the least squares method. The intercept ϵ, which is close to zero, can be regarded as an error term. In Swain and Lupton's derivations of F they did not attempt to place their F and R values on the same scale as Hammett constants obtained from the ionization of benzoic acids in water at 25 °C. Hansch et al. accomplished this[34] by scaling as follows: $F = \sigma'/1.65$ using the results of Stock et al.[35,36] on the bicyclooctane carboxylic acids.

$$F = \sigma'/1.65 = a\sigma_m + b\sigma_p + \epsilon \quad (4)$$

$$F = \sigma'/1.65 = 1.369\sigma_m - 0.373\sigma_p - 0.009 \quad (5)$$

$$n = 14,\ r = 0.992,\ s = 0.042$$

To evaluate R, Swain and Lupton made the assumptions

$$\sigma_p = \alpha F + R \quad (6)$$

and the further assumption that for $N^+(CH_3)_3$, $R = 0$. Following this procedure and substituting in eq 6 the values for $N^+(CH_3)_3$ of $F = 0.89$ and $\sigma_p = 0.82$, α was found to be 0.921.[34] F and R were then calculated for about 200 substituents. Since, as noted before,[4] the α factor does not differ much from 1, little if anything is lost by using Taft's eq 2 to calculate $R = \sigma_R$ rather than eq 6. Therefore we have recalculated F and R along the lines used by Charton[29] to obtain his σ_L and σ_D parameters using the data in Table I.

In an extensive analysis Charton[29] has concluded that the scaling factor of 1.65 used in eq 5 would be better replaced by 1.56. Accordingly, we have evaluated σ_I, as did Charton, from: $\sigma_I = \Delta pK_a/1.56$, using pK_a values for the 4-X-bicyclooctane carboxylic acid (Table II, third column).

Another excellent system for establishing σ_I values is that of the quinuclidines, II, studied by Grob and Schlageter.[37] In this case, the ionization of the protonated amine is used to obtain σ_I, which has an advantage in that it is significantly more sensitive to X than is the carboxylate group of I. Using substituents for which σ_I can be calculated from ionization constants (entries 1–12, Table II), we have derived eq 7. There

II

$$\sigma_I(\text{Stock}) = 0.191\ (\pm 0.015)\sigma_I(\text{Grob}) - 0.037\ (\pm 0.031) \quad (7)$$

$$n = 14,\ r = 0.992,\ s = 0.029$$

are only three substituents whose σ_I values were determined in the carboxylate system by both Holtz and Stock and by Roberts and Moreland. In eq 7, σ_I(Stock) refers to the scaled values from the carboxylate parent (Roberts and Moreland data included) while σ_I(Grob) values are from unscaled quinuclidine data (Table II, fourth column).

These results in Table II allow the rederivation of eq 5 on the basis of an extended set of σ_I values. The

$$F = \sigma_I = 1.297\ (\pm 0.147)\sigma_m - 0.385\ (\pm 0.089)\sigma_p + 0.033\ (\pm 0.026) \quad (8)$$

$$n = 38,\ r = 0.968,\ s = 0.046$$

parameters of eq 8 are only slightly different from those of eq 5 despite the inclusion of 24 more data points, the new normalization factor of 1.56, and dropping the assumption that R for $N^+(CH_3)_3$ is zero. Note that the quality of fit in eq 8 is the same as eq 5 in terms of the standard deviation. Three substituents in Table II for which σ_I could not be derived from Grob and Schlageter's data have not been used to derive eq 8: $CH_2OSO_2C_6H_4$-4-Me, $CH(OH)_2$, and CO_2^-. For the first two, σ_p and σ_m have not been reported, and hence F can not be calculated via eq 8. The value of F for the CO_2^- group obtained from eq 7 is out of line with that calculated from eq 8. For charged substituents this is not an uncommon result since the simple Hammett equation is poorly applicable.[38] Comparison of F values of some common substituents calculated by eq 5 and eq 8 is made in Table III.

All of the F values in Table I have been *calculated* by using eq 8. That is, we have not listed in Table I any of the experimentally based values of Table II. This seemed to be a more consistent way of presenting the results for correlation analysis although some may prefer to use the values in Tables II and IV insofar as possible.

Ideally, one would like to obtain all values of σ_I from experimentally determined pK_a values of structures like I or II where $R = 0$. This is not feasible because of the great difficulty of synthesizing the necessary structures. Even though the various approaches of evaluating the field inductive parameter from σ_m and σ_p have been criticized by some authors,[39-41] we believe that for many applications the results are precise enough. This conclusion is supported by comparisons of σ values in Tables I, II, and IV.

Table II gives σ_F (σ_I) values obtained for many typical substituents by eight different methods. There are no large differences in the σ_I scale of field/inductive effects for common dipolar substituents, X, as obtained by eqs 5 and 6 (columns 3 and 4, respectively), or, as first obtained by Taft,[32] from the relationship: $\sigma_I = \sigma' = 0.45\sigma^*_{CH2X}$. Furthermore, there are relatively minor differences between any of these σ_I values and the σ_F values given recently by Taft and Topsom[30] (column 2) or F values (column 7). The individual σ_F parameters were obtained by averaging values of determinations by numerous methods[42-44] and have been confirmed[30] by gas-phase proton-transfer equilibria, which are much more discriminating than most solution equilibria.

Charton's review[29] includes numerous examples of solution equilibria for which field/inductive effects are strongly predominant and for which there are both greater sensitivities and varieties of substituents than for the bicyclooctane carboxylic acid pK_a values.

TABLE I. Hammett and Modified Swain-Lupton Constants[a,d]

	substituent	σ_m	σ_p	F^b	R^c	ref(s)
1.	BF_2	0.32	0.48	0.26	0.22	109
2.	Br	0.39	0.23	0.45	−0.22	183
3.	$GeBr_3$	0.66	0.73	0.61	0.12	139
4.	$SiBr_3$	0.48	0.57	0.44	0.13	139
5.	Cl	0.37	0.23	0.42	−0.19	183
6.	HgCl	0.33	0.35	0.33	0.02	74
7.	SO_2Cl	1.20	1.11	1.16	(−0.05)	134
8.	SCl	0.44	0.48	0.42	0.06	74
9.	ICl_2	1.10	1.11	1.03	0.08	110
10.	$P(O)Cl_2$	0.78	0.90	0.70	0.20	74
11.	PCl_2	0.54	0.61	0.50	0.11	164
12.	$P(S)Cl_2$	0.70	0.80	0.63	0.17	74
13.	$GeCl_3$	0.71	0.79	0.65	0.14	139
14.	$SiCl_3$	0.48	0.56	0.44	0.12	139
15.	F	0.34	0.06	0.45	−0.39	183
16.	HgF	0.34	0.33	0.35	−0.02	74
17.	SOF	0.74	0.83	0.67	0.16	74
18.	SO_2F	0.80	0.91	0.72	0.19	142
19.	IF_2	0.85	0.83	0.82	0.01	110
20.	POF_2	0.81	0.89	0.74	0.15	164
21.	PF_2	0.49	0.59	0.44	0.15	109
22.	GeF_3	0.85	0.97	0.76	0.21	139
23.	SF_3	0.70	0.80	0.63	0.17	110
24.	SiF_3	0.54	0.69	0.47	0.22	164
25.	IF_4	1.07	1.15	0.98	0.17	110
26.	PF_4	0.63	0.80	0.54	0.26	110
27.	SF_5	0.61	0.68	0.56	0.12	179
28.	I	0.35	0.18	0.42	−0.24	183
29.	IO	0.58	0.62	0.55	0.07	63
30.	IO_2	0.68	0.78	0.61	0.17	170
31.	NO	0.62	0.91	0.49	0.42	107
32.	NO_2	0.71	0.78	0.65	0.13	183
33.	ONO_2	0.55	0.70	0.48	0.22	74
34.	$N{\equiv}N^+$	1.76	1.91	1.58	0.33	182
35.	$N{\equiv}N^+(BF_4)^-$	1.65	1.79	1.48	0.31	88
36.	NNO_2^-	0.00	−0.43	0.20	−0.63	112
37.	N_3	0.37	0.08	0.48	−0.40	130
38.	O^-	−0.47	(−0.81)	−0.26	(−0.55)	181
39.	SO_2^-	−0.02	−0.05	0.03	−0.08	135
40.	SO_3^-	0.30	0.35	0.29	0.06	81
41.	S^-	−0.36	−1.21	0.03	−1.24	74, 97
42.	AsO_3H^-	0.00	−0.02	0.04	−0.06	74, 87
43.	H	0.00	0.00	0.03	0.00	-
44.	$NHNO_2$	0.91	0.57	0.99	−0.42	112
45.	OH	0.12	−0.37	0.33	−0.70	183
46.	S(O)OH	−0.04	−0.07	0.01	−0.08	74
47.	PO_3H^-	0.20	0.26	0.19	0.07	183
48.	OPO_3H^-	0.29	0.00	0.41	−0.41	74
49.	SH	0.25	0.15	0.30	−0.15	183
50.	$B(OH)_2$	−0.01	0.12	−0.03	0.15	170
51.	NH_2	−0.16	−0.66	0.08	−0.74	183
52.	NHOH	−0.04	−0.34	0.11	−0.45	87
53.	SO_2NH_2	0.53	0.60	0.49	0.11	170
54.	$PO(OH)_2$	0.36	0.42	0.34	0.08	74
55.	PH_2	0.06	0.05	0.09	−0.04	74
56.	$B(OH)_3^-$	−0.48	−0.44	−0.42	−0.02	90
57.	GeH_3	0.00	0.01	0.03	−0.02	74, 280
58.	NH_3^+	0.86	0.60	0.92	−0.32	181
59.	$NHNH_2$	−0.02	−0.55	0.22	−0.77	87
60.	SiH_3	0.05	0.10	0.06	0.04	110
61.	CBr_3	0.28	0.29	0.28	0.01	165
62.	$CClF_2$	0.42	0.46	0.40	0.06	74
63.	5-chloro-1-tetrazolyl	0.60	0.61	0.58	0.03	165
64.	COCl	0.51	0.61	0.46	0.15	164
65.	$N{=}CCl_2$	0.21	0.13	0.26	−0.13	165
66.	CCl_3	0.40	0.46	0.38	0.09	170
67.	$OCCl_3$	0.43	0.35	0.46	−0.11	74
68.	COF	0.55	0.70	0.48	0.22	110
69.	OCF_2O	0.36	0.36	0.36	0.00	153
70.	CF_3	0.43	0.54	0.38	0.16	183
71.	$HgCF_3$	0.29	0.32	0.29	0.03	74
72.	$HgSCF_3$	0.39	0.42	0.38	0.04	74
73.	$I{=}NSO_2CF_3$	1.30	1.35	1.20	0.15	63
74.	$N{=}NCF_3$	0.56	0.68	0.50	0.18	74
75.	OCF_3	0.38	0.35	0.39	−0.04	145
76.	$SOCF_3$	0.63	0.69	0.58	0.11	163
77.	$SeOCF_3$	0.81	0.83	0.76	0.07	74

TABLE I (Continued)

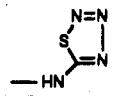
	substituent	σ_m	σ_p	F^b	R^c	ref(s)
78.	SO_2CF_3	0.83	0.96	0.74	0.22	70
79.	SeO_2CF_3	1.08	1.21	0.97	0.24	74
80.	OSO_2CF_3	0.56	0.53	0.56	−0.03	118
81.	SCF_3	0.40	0.50	0.36	0.14	178
82.	$SeCF_3$	0.44	0.45	0.43	0.02	167
83.	HgCN	0.28	0.34	0.27	0.08	74
84.	CN	0.56	0.66	0.51	0.15	183
85.	NC	0.48	0.49	0.47	0.02	74
86.	$CN(BBr_3)$	0.61	0.48	0.64	−0.16	164
87.	$CN(BCl_3)$	0.95	0.86	(0.93)	(−0.05)	164
88.	$CN(BF_3)$	0.72	0.66	(0.71)	(−0.05)	164
89.	N=C=O	0.27	0.19	0.31	−0.12	165
90.	OCN	0.67	0.54	0.69	−0.15	74
91.	SO_2CN	1.10	1.26	0.97	0.29	74
92.	N=C=S	0.48	0.38	0.51	−0.13	156
93.	SCN	0.51	0.52	0.49	0.03	85, 183
94.	SeCN	0.61	0.66	0.57	0.09	173, 87
95.	N=NCN	0.71	1.03	0.56	0.47	72
96.	N(O)=NCN	0.78	0.89	0.70	0.19	281
97.	$C(NO_2)_3$	0.72	0.82	0.65	0.17	74, 190
98.	5-azido-1-tetrazolyl	0.54	0.54	0.53	0.01	165
99.	CO_2^-	−0.10	0.00	−0.10	0.10	183
100.	$CHBr_2$	0.31	0.32	0.31	0.01	74
101.	$CHCl_2$	0.31	0.32	0.31	0.01	74
102.	$OCHCl_2$	0.38	0.26	0.43	−0.17	74
103.	CHF_2	0.29	0.32	0.29	0.03	110
104.	$OCHF_2$	0.31	0.18	0.37	−0.19	146
105.	$SOCHF_2$	0.54	0.58	0.51	0.07	140
106.	SO_2CHF_2	0.75	0.86	0.67	0.19	146
107	$SCHF_2$	0.33	0.37	0.32	0.05	170
108.	$S(O)(=NH)CF_3$	0.72	0.84	0.64	0.20	62
109.	$NHSO_2CF_3$	0.44	0.39	0.45	−0.06	74
110.	CHI_2	0.26	0.26	0.27	−0.01	74
111.	NHCN	0.21	0.06	0.28	−0.22	158
112.	1-(1*H*)-tetrazolyl	0.52	0.50	0.52	−0.02	165
113.	5-(1*H*)-tetrazolyl	0.64	0.56	0.65	−0.09	166
114.	5-hydroxy-1-tetrazolyl	0.39	0.33	0.41	−0.08	165
115.	5-mercapto-1-tetrazolyl	0.45	0.45	0.44	−0.01	165
116.		0.30	0.19	0.35	−0.16	158
117.	CHO	0.35	0.42	0.33	0.09	87, 174
118.	COOH	0.37	0.45	0.34	0.11	183
119.	CH_2Br	0.12	0.14	0.14	0.00	170
120.	CH_2Cl	0.11	0.12	0.13	−0.01	170
121.	OCH_2Cl	0.25	0.08	0.33	−0.25	74
122.	CH_2F	0.12	0.11	0.15	−0.04	110
123.	OCH_2F	0.20	0.02	0.29	−0.27	74
124.	SCH_2F	0.23	0.20	0.25	−0.05	74
125.	CH_2I	0.10	0.11	0.12	−0.01	170
126.	NHCHO	0.19	0.00	0.28	−0.28	156
127.	$CONH_2$	0.28	0.36	0.26	0.10	87, 187
128.	$CSNH_2$	0.25	0.30	0.24	0.06	283
129.	CH=NOH-*t*	0.22	0.10	0.28	−0.18	129
130.	3,4-N=CHNH–	−0.15	−0.15	−0.10	−0.05	116
131.	$N(O)=NCONH_2$	0.59	0.63	0.56	0.07	281
132.	OCH_2O–	−0.16	−0.16	−0.11	−0.05	188
133.	Me	−0.07	−0.17	0.01	−0.18	183
134.	CH_2SO_2R	0.15	0.17	0.16	0.01	170
135.	$SiMeCl_2$	0.31	0.39	0.29	0.10	74
136.	$SiMeF_2$	0.29	0.23	0.32	−0.09	74
137.	HgMe	0.43	0.10	(0.55)	(−0.45)	164
138.	$NHCH_2SO_3$	−0.10	−0.57	0.12	−0.69	89
139.	$NHCONH_2$	−0.03	−0.24	0.09	−0.33	156
140.	$N(Me)NO_2$	0.49	0.61	0.43	0.18	112
141.	$NHCSNH_2$	0.22	0.16	0.26	−0.10	158
142.	OMe	0.12	−0.27	0.29	−0.56	183
143.	CH_2OH	0.00	0.00	0.03	−0.03	133
144.	SOMe	0.52	0.49	0.52	−0.03	183
145.	S(OMe)	0.21	0.17	0.24	−0.07	74
146.	$OS(=O)CH_3$	0.44	0.45	0.43	0.02	74
147.	S(O)OMe	0.50	0.54	0.47	0.07	74
148.	SO_2Me	0.60	0.72	0.53	0.19	183
149.	SSO_2Me	0.43	0.54	0.38	0.16	74

TABLE I (Continued)

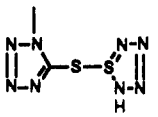
	substituent	σ_m	σ_p	F^b	R^c	ref(s)
150.	OSO_2Me	0.39	0.36	0.40	−0.04	156
151.	SMe	0.15	0.00	0.23	−0.23	183
152.	SSMe	0.22	0.13	0.27	−0.14	74
153.	SeMe	0.10	0.00	0.16	−0.16	183
154.	NHMe	−0.21	−0.70	0.03	−0.73	164
155.	CH_2NH_2	−0.03	−0.11	0.04	−0.15	74
156.	$NHSO_2Me$	0.20	0.03	0.28	−0.25	156
157.	$CH_2NH_3^+$	0.59	0.53	0.59	−0.06	88
158.	$N(COF)_2$	0.58	0.57	0.57	0.00	109
159.	$HgOCOCF_3$	0.50	0.52	0.48	0.04	74
160.	$COCF_3$	0.63	0.80	0.54	0.26	110
161.	$SCOCF_3$	0.48	0.46	0.48	−0.02	74
162.	$OCOCF_3$	0.56	0.46	0.58	−0.12	74
163.	$N(CF_3)C{=}O(F)$	0.50	0.50	0.49	0.01	109
164.	$CF_2OCF_2^-$	0.81	0.81	0.77	0.04	153
165.	CF_2CF_3	0.47	0.52	0.44	0.08	172
166.	OCF_2CF_3	0.48	0.28	0.55	−0.27	74
167.	$SO_2CF_2CF_3$	0.92	1.08	0.81	0.27	76
168.	SCF_2CF_3	0.44	0.48	0.42	0.06	76
169.	$N(CF_3)_2$	0.40	0.53	(0.35)	0.18	145
170.	$S(CF_3){=}NSO_2CF_3$	1.18	1.28	1.07	0.21	62
171.	$SO(CF_3){=}NSO_2CF_3$	1.23	1.40	1.09	0.31	62
172.	$N(SO_2CF_3)_2$	0.61	0.83	0.50	0.33	103
173.	$P(CF_3)_2$	0.60	0.69	0.55	0.14	109
174.	$P(CN)_2$	0.82	0.90	0.75	0.15	74
175.	$C{\equiv}CH$	0.21	0.23	0.22	0.01	171
176.	OCF_2CHFCl	0.35	0.28	0.38	−0.10	146
177.	$NHCOCF_3$	0.30	0.12	0.38	−0.26	156
178.	$CH{=}NSO_2CF_3$	0.76	1.00	0.63	0.37	63
179.	OCF_2CHF_2	0.34	0.25	0.38	−0.13	178
180.	SCF_2CHF_2	0.38	0.47	0.35	0.12	178
181.		0.63	0.64	0.60	0.04	165
182.	$SC{\equiv}CH$	0.26	0.19	0.30	−0.11	74
183.	$SCH{=}CHCl$	0.31	0.24	0.34	−0.10	105
184.	$SeCH{=}CHCl$	0.28	0.26	0.30	−0.04	105
185.	CH_2CF_3	0.12	0.09	0.15	−0.06	109
186.	CH_2SOCF_3	0.25	0.24	0.27	−0.03	162
187.	$CH_2SO_2CF_3$	0.29	0.31	0.29	0.02	162
188.	CH_2SCF_3	0.12	0.15	0.13	0.02	162
189.	CH_2CN	0.16	0.18	0.17	0.01	170
190.	$CH{=}CHNO_2$-*t*	0.32	0.26	0.35	(−0.09)	184
191.	$CH_2CO_2^-$	0.07	−0.16	0.19	−0.35	88
192.	CH_2SCN	0.12	0.14	0.14	0.00	74
193.	$CH{=}CH_2$	0.06	−0.04	0.13	−0.17	85
194.	$NHCOCH_2Cl$	0.17	−0.03	0.27	−0.30	156
195.	$N(Me)SO_2CF_3$	0.46	0.44	0.46	−0.02	74
196.	$HgOCOCH_3$	0.39	0.40	0.39	0.01	74
197.	$C(Me)(NO_2)_2$	0.54	0.61	0.50	0.11	74
198.	oxiranyl	0.05	0.03	0.09	−0.06	74
199.	$OCH{=}CH_2$	0.21	−0.09	0.34	−0.43	96
200.	COMe	0.38	0.50	0.33	0.17	183
201.	SCOMe	0.39	0.44	0.37	0.07	183
202.	OCOMe	0.39	0.31	0.42	−0.11	183
203.	COOMe	0.37	0.45	0.34	0.11	175
204.	2-thiacyclopropyl	0.04	0.01	0.08	−0.07	74
205.	$SCH{=}CH_2$	0.26	0.20	0.29	−0.09	99, 105
206.	$SeCH{=}CH_2$	0.26	0.21	0.29	−0.08	105
207.	1-aziridinyl	−0.07	−0.22	0.03	−0.25	74
208.	2-aziridinyl	−0.06	−0.10	−0.01	−0.09	74
209.	*N*-methyl-3-oxaziridinyl	0.09	0.12	0.10	0.02	74
210.	NHCOOMe	−0.02	−0.17	0.07	−0.24	68
211.	NHCOMe	0.21	0.00	0.31	−0.31	183
212.	CONHMe	0.35	0.36	0.35	−0.01	154
213.	CH=NOMe	0.37	0.30	0.40	0.10	93
214.	CH_2CONH_2	0.06	0.07	0.08	−0.01	74
215.	NHCSMe	0.24	0.12	0.30	−0.18	154
216.	CSNHMe	0.30	0.34	0.29	0.05	154
217.	$CH{=}NNHCSNH_2$	0.45	0.40	0.46	−0.06	93
218.	$OCH_2CH_2O^-$	−0.12	−0.12	−0.08	−0.04	74
219.	Et	−0.07	−0.15	0.00	−0.15	183
220.	$CH{=}NNHCONHNH_2$	0.22	0.16	0.26	−0.10	93
221.	OCH_2CH_3	0.10	−0.24	0.26	−0.50	183

TABLE I (Continued)

	substituent	σ_m	σ_p	F^b	R^c	ref(s)
222.	CH(OH)Me	0.08	−0.07	0.16	−0.23	74
223.	CH_2OMe	0.08	0.01	0.13	−0.12	85
224.	SO_2Et	0.66	0.77	0.59	0.18	74
225.	SEt	0.18	0.03	0.26	−0.23	174, 183
226.	$P(Cl)NMe_2$	0.38	0.56	0.31	0.25	164
227.	$CH_2SC(NH_2)_2^+$	0.13	0.15	0.14	0.01	128
228.	$SiClMe_2$	0.16	0.21	0.16	0.05	74
229.	$SiFMe_2$	0.12	0.17	0.12	0.04	74
230.	NHEt	−0.24	−0.61	−0.04	−0.57	87, 187
231.	$N(Me)_2$	−0.16	−0.83	0.15	−0.98	185, 183
232.	$N(Me)SO_2Me$	0.21	0.24	0.21	0.03	81, 74
233.	SO_2NMe_2	0.51	0.65	0.44	0.21	74
234.	$N(SO_2Me)_2$	0.47	0.49	0.45	0.04	74
235.	$SN(Me)_2$	0.12	0.09	0.15	−0.06	74
236.	$N{=}NNMe_2$	−0.05	−0.03	−0.02	−0.01	72
237.	$N(Me)N^+{=}(Me)N-$	1.17	1.17	1.10	0.07	116
238.	$P(O)Me_2$	0.43	0.50	0.40	0.10	74
239.	$PO(OMe)_2$	0.42	0.53	0.37	0.16	152
240.	PMe_2	0.03	0.06	0.05	0.01	69
241.	S^+Me_2	1.00	0.90	0.98	−0.08	183
242.	$S^+(Me)_2$tosyl	1.06	0.96	1.04	−0.08	88
243.	$CH_2CH_2NH_3^+$	0.23	0.17	0.27	−0.10	74
244.	$SiH(Me)_2$	0.01	0.04	0.03	0.01	74
245.	1-(1,7$(BH)_{10}$-C_2H)	0.25	0.33	0.23	0.10	147
246.	2-(1,7$(BH)_{10}$-C_2H)	0.14	0.15	0.16	−0.01	117
247.	4-(1,7$(BH)_{10}$-C_2H)	−0.02	0.02	0.00	0.02	80
248.	1-(1,2$(BH)_{10}$-C_2H)	0.49	0.43	0.50	−0.07	147
249.	3-(1,2$(BH)_{10}$-C_2H)	0.20	0.19	0.22	−0.03	147
250.	$C{\equiv}CCF_3$	0.41	0.51	0.37	0.14	163
251.	$CF{=}CFCF_3$-*t*	0.39	0.46	0.36	0.10	109
252.	$N{=}C(CF_3)_2$	0.29	0.23	0.32	−0.09	109
253.	$CF_2CF_2CF_3$	0.44	0.48	0.42	0.06	85
254.	$CF(CF_3)_2$	0.37	0.53	(0.31)	0.22	172
255.	$SO_2CF_2CF_2CF_3$	0.92	1.09	0.81	0.28	76
256.	$SO_2CF(CF_3)_2$	0.92	1.10	0.80	0.30	76
257.	$SCF_2CF_2CF_3$	0.45	0.48	0.43	0.05	76
258.	$SCF(CF_3)_2$	0.48	0.51	0.46	0.03	76
259.	$TeCF_2CF_2CF_3$	0.46	0.48	0.45	0.03	76
260.	$C(OH)(CF_3)_2$	0.29	0.30	0.29	0.01	172
261.	$CH(SCF_3)_2$	0.44	0.44	0.43	0.01	74
262.	$CH(CN)_2$	0.53	0.52	0.52	0.00	74
263.	$CH{=}CHCF_3$-*c*	0.16	0.17	0.18	0.01	165
264.	$CH{=}CHCF_3$-*t*	0.24	0.27	0.24	0.03	165
265.	$CH{=}CHSO_2CF_3$	0.31	0.55	0.22	0.33	74
266.	CH=CHCN	0.24	0.17	0.28	−0.11	155
267.	C≡CMe	0.21	0.03	0.29	−0.26	85
268.	$N(Me)COCF_3$	0.41	0.39	0.41	−0.02	74
269.	CH=CHCHO	0.24	0.13	0.29	−0.16	155
270.	cyclopropyl	−0.07	−0.21	0.02	−0.23	177
271.	$C(Me){=}CH_2$	0.09	0.05	0.13	−0.08	85
272.	CH=CHMe-*t*	0.02	−0.09	0.09	−0.18	85
273.	$CH_2CH{=}CH_2$	−0.11	−0.14	−0.06	−0.08	74
274.	$C(Et)(NO_2)_2$	0.56	0.64	0.51	0.13	74
275.	$OCH_2CH{=}CH_2$	0.09	−0.25	0.25	−0.50	105
276.	COEt	0.38	0.48	0.34	0.14	74
277.	COOEt	0.37	0.45	0.34	0.11	183
278.	CH_2OCOMe	0.04	0.05	0.07	−0.02	74
279.	CH_2CH_2COOH	−0.03	−0.07	0.02	−0.09	188
280.	$SCH_2CH{=}CH_2$	0.19	0.12	0.23	−0.11	105
281.	$SeCH_2CH{=}CH_2$	0.21	0.12	0.26	−0.14	105
282.	$CH_2CH_2CH_2-$	−0.26	−0.26	−0.20	−0.06	87
283.	N(Me)COMe	0.31	0.26	0.34	−0.08	74
284.	$CH_2NHCOMe$	0.05	−0.05	0.12	−0.17	85
285.	NHCOOEt	0.11	−0.15	0.23	−0.38	157, 156
286.	$C(NO_2)Me_2$	0.18	0.20	0.19	0.01	74, 190
287.	$OCH_2CH_2CH_2O-$	0.00	0.00	0.03	−0.03	74
288.	isopropyl	−0.04	−0.15	0.04	−0.19	85, 183
289.	$CH_2CH_2CH_3$	−0.06	−0.13	0.01	−0.14	85, 87
290.	$N^+(Me){=}CHN(Me)-$	1.11	1.11	1.05	0.06	116
291.	NHCONHEt	0.04	−0.26	0.19	−0.45	154
292.	NHCSNHEt	0.30	0.07	0.40	−0.33	154
293.	$OCHMe_2$	0.10	(−0.45)	0.34	(−0.79)	183
294.	$OCH_2CH_2CH_3$	0.10	−0.25	0.26	−0.51	183
295.	$CH_2CH(OH)Me$	−0.12	−0.17	−0.06	−0.11	74, 102
296.	$C(OOH)Me_2$	0.06	−0.14	0.17	−0.31	92
297.	$SCHMe_2$	0.23	0.07	0.30	−0.23	74
298.	CH_2NMe_2	0.00	0.01	0.03	−0.02	74

TABLE I (Continued)

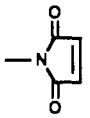
	substituent	σ_m	σ_p	F^b	R^c	ref(s)
299.	$GeMe_3$	0.00	0.00	0.03	−0.03	74
300.	$N^+(Me)_3$	0.88	0.82	0.86	−0.04	183
301.	$CH_2NH^+(Me)_2$	0.40	0.43	0.39	0.04	74
302.	$Si(Me)_2OMe$	0.04	−0.02	0.09	−0.11	74
303.	$OSiMe_3$	0.13	−0.27	0.31	−0.58	74
304.	$SiMe(OMe)_2$	0.04	0.10	0.05	0.05	74
305.	$Si(OMe)_3$	0.09	0.13	0.10	0.03	74
306.	P^+Me_3	0.74	0.73	0.71	0.02	123, 122
307.	$SiMe_3$	−0.04	−0.07	0.01	−0.08	183
308.	$SnMe_3$	0.00	0.00	0.03	−0.03	74, 183
309.	1-(1,2-$(BH)_{10}$-C_2Me)	0.50	0.65	0.43	0.22	111
310.	CH_2-1-(1,7-$(BH)_{10}$-C_2H)	0.00	0.01	0.03	−0.02	67
311.	CH_2-1-(1,2-$(BH)_{10}$-C_2H)	0.12	0.12	0.14	−0.02	67
312.	1-(1,2-$(BH)_{10}$-$C_3H_3HgCH_3$)	0.86	0.85	0.82	0.03	111
313.	2-(hydroxymethyl)carboran-1-yl	0.38	0.49	0.34	0.15	111
314.	$I(OCOCF_3)_2$	1.28	1.34	1.18	0.16	110
315.	cyclo-C_4F_7	0.48	0.53	0.45	0.08	109
316.	$COCF_2CF_2CF_3$	0.63	0.79	0.55	0.24	110
317.	$C(CF_3)_3$	0.55	0.55	0.53	0.02	76
318.	$(CF_2)_3CF_3$	0.47	0.52	0.44	0.08	172
319.	$SO_2C(CF_3)_3$	0.96	1.13	0.84	0.29	76
320.	$SC(CF_3)_3$	0.51	0.58	0.47	0.11	76
321.	$C(SCF_3)_3$	0.51	0.53	0.49	0.04	74
322.	$SeC(CF_3)_3$	0.49	0.54	0.46	0.08	76
323.	$C(CN)_3$	0.97	0.96	0.92	0.04	165
324.	cyclo-1-$(OH)C_4F_6$	0.36	0.37	0.36	0.01	109
325.	$CH{=}C(CN)_2$	0.66	0.84	0.57	0.27	93
326.	2-(5-bromofuryl)	0.15	0.00	0.23	−0.23	94, 95
327.		0.33	0.27	0.36	−0.09	108
328.	3-chloro-1-pyrroline-2,5-dione	0.47	0.46	0.47	−0.01	108
329.	3-pyridazinyl	0.28	0.48	0.21	0.27	61
330.	3,4-CH=CHCH=CH–	0.04	0.04	0.07	−0.03	183
331.	$C(Me)(CN)_2$	0.60	0.57	0.59	−0.02	74
332.	4-pyrimidinyl	0.30	0.63	0.18	0.45	277
333.	2-pyrimidinyl	0.23	0.53	0.13	0.40	277
334.	5-pyrimidinyl	0.28	0.39	0.25	0.14	277
335.	2-furyl	0.06	0.02	0.10	−0.08	114
336.	2-thienyl	0.09	0.05	0.13	−0.08	159
337.	3-thienyl	0.03	−0.02	0.08	−0.10	159
338.	2-selenienyl	0.06	0.04	0.10	−0.06	84
339.	2-tellurienyl	0.06	0.03	0.10	−0.07	84
340.	1-pyrryl	0.47	0.37	0.50	−0.13	93
341.	1-pyrroline-2,5-dione	0.34	0.31	0.36	−0.05	108
342.	CH=CHCOMe	0.21	−0.01	0.31	−0.32	155
343.	$I(OCOMe)_2$	0.85	0.88	0.80	0.08	110
344.	$N(COMe)_2$	0.35	0.33	0.36	−0.03	74
345.	cyclobutyl	−0.05	−0.14	0.02	−0.16	85
346.	$COCHMe_2$	0.38	0.47	0.35	0.12	74, 119
347.	$(CH_2)_4$	−0.48	−0.48	−0.40	−0.08	87
348.	$NHCOCH(Me)_2$	0.11	−0.10	0.21	−0.31	156
349.	$C(Me)_3$	−0.10	−0.20	−0.02	−0.18	183
350.	CH(Me)Et	−0.08	−0.12	−0.02	−0.10	74, 87
351.	$CH_2CH(Me)_2$	−0.07	−0.12	−0.01	−0.11	176, 87
352.	$(CH_2)_3CH_3$	−0.08	−0.16	−0.01	−0.15	174, 87
353.	$O(CH_2)_3CH_3$	0.10	−0.32	0.29	−0.61	183
354.	$CH_2C(OH)Me_2$	−0.16	−0.17	−0.11	−0.06	74, 102
355.	$C(OMe)_3$	−0.03	−0.04	0.01	−0.05	74
356.	$AsEt_2$	0.22	0.00	0.32	−0.32	77
357.	$As(O)Et_2$	0.57	0.44	0.60	−0.16	77
358.	$As(S)Et_2$	0.52	0.44	0.54	−0.10	77
359.	$NH(CH_2)_3CH_3$	−0.34	−0.51	−0.21	−0.30	87, 85
360.	$N(Et)_2$	−0.23	−0.72	0.01	−0.73	113, 82
361.	$PO(Et)_2$	0.37	0.47	0.33	0.14	79
362.	$N{=}NPO(OEt)_2$	(0.16)	0.74	(−0.05)	(0.79)	72
363.	$PO(OEt)_2$	0.55	0.60	0.52	0.08	143
364.	$P(Et)_2$	0.10	0.13	0.11	0.02	124
365.	$P(S)Et_2$	0.39	0.46	0.36	0.10	79
366.	$CH_2N(Me)_3^+$	0.40	0.44	0.38	0.06	74
367.	$CH_2CH_2NH(Me)_2^+$	0.24	0.14	0.29	−0.15	74
368.	$CH_2OSi(CH_3)_3$	−0.04	−0.05	0.00	−0.05	74
369.	$CH_2Si(Me)_3$	−0.16	−0.21	−0.09	−0.12	183
370.	$PO(N(Me)_2)_2$	0.30	0.40	0.27	0.13	78

TABLE I (Continued)

	substituent	σ_m	σ_p	F^b	R^c	ref(s)
371.	$P(N(Me)_2)_2$	0.18	0.25	0.17	0.08	164
372.	2-(methylcarbonyl)carboran-1-yl	0.40	0.63	0.31	0.32	111
373.	2-[(carbonyloxy)methyl]carboran-1-yl	0.70	0.74	0.66	0.08	111
374.	CH_2-1-(1,2-$(BH)_{10}$-C_2Me)	0.10	0.11	0.12	−0.01	67
375.	$C(CN)=C(CN)_2$	0.77	0.98	0.65	0.33	74, 165
376.	2-(5-cyanofuryl)	0.25	0.10	0.32	−0.22	94, 95
377.	2-(5-formylfuryl)	0.22	−0.05	0.34	−0.39	94, 95
378.	2-pyridyl	0.33	0.17	0.40	−0.23	93
379.	3-pyridyl	0.23	0.25	0.24	0.01	71
380.	4-pyridyl	0.27	0.44	0.21	0.23	71
381.	2-(4,6-dimethyl-*s*-triazinyl)	0.25	0.39	0.21	0.18	121
382.	1-cyclopentenyl	−0.06	−0.05	−0.03	−0.02	127
383.	CH=CHCOOEt	0.19	0.03	0.27	−0.24	155
384.	cyclopentyl	−0.05	−0.14	0.02	−0.16	85
385.	$COC(Me)_3$	0.27	0.32	0.26	0.06	74, 119
386.	$NHCO_2(CH_2)_3CH_3$	0.06	−0.05	0.13	−0.18	126
387.	$C(Et)(Me)_2$	−0.06	−0.18	0.03	−0.21	85
388.	$CH_2C(Me)_3$	−0.05	−0.17	0.03	−0.14	85
389.	$(CH_2)_4CH_3$	−0.08	−0.15	−0.01	−0.14	174
390.	$O(CH_2)_4CH_3$	0.10	(−0.34)	0.29	(−0.63)	183
391.	$CH_2PO(OEt)_2$	0.12	0.06	0.17	−0.11	85
392.	$CH_2CH_2N(Me)_3^+$	0.16	0.13	0.19	−0.06	74, 189
393.	$CH_2CH_2Si(Me)_3$	−0.16	−0.17	−0.11	−0.06	74, 132
394.	$Si(Me)_2OSi(Me)_3$	0.00	−0.01	0.04	−0.05	160
395.	C_6Cl_5	0.25	0.24	0.27	−0.03	151
396.	C_6F_5	0.26	0.27	0.27	0.00	151
397.	$P(O)(C_3F_7)_2$	0.95	1.10	0.84	0.26	64
398.	$OP(O)(C_3F_7)_2$	0.66	0.56	0.67	−0.11	64
399.	$NHP(O)(C_3F_7)_2$	0.28	0.18	0.33	−0.15	64
400.	$CH_2Co(CN)_5^{3-}$	−0.53	−0.68	−0.39	−0.29	150
401.	$CH_2Mn(CO)_5$	−0.14	−0.44	0.02	−0.46	150
402.	C_6H_2-2,4,6-$(NO_2)_3$	0.26	0.30	0.26	0.04	170
403.	C_6H_4-3-Br	0.09	0.08	0.12	−0.04	161
404.	C_6H_4-4-Br	0.15	0.12	0.18	−0.06	85
405.	C_6H_4-3-Cl	0.15	0.10	0.19	−0.09	85
406.	C_6H_4-4-Cl	0.15	0.12	0.18	−0.06	85
407.	C_6H_4-3-F	0.15	0.10	0.19	−0.09	85
408.	C_6H_4-4-F	0.12	0.06	0.17	−0.11	85
409.	OC_6H_4-4-F	−0.08	−0.10	−0.03	−0.07	106
410.	C_6H_4-3-I	0.13	0.06	0.18	−0.12	85
411.	C_6H_4-4-I	0.14	0.10	0.18	−0.08	85
412.	C_6H_4-3-NO_2	0.21	0.20	0.23	−0.03	85
413.	C_6H_4-4-NO_2	0.25	0.26	0.26	0.00	85
414.	SC_6H_4-4-NO_2	0.32	0.24	0.36	−0.12	85
415.	SOC_6H_4-4-NO_2	0.58	0.60	0.55	0.05	85
416.	2-benzotriazolyl	0.49	0.51	0.47	0.04	74
417.	C_6H_5	0.06	−0.01	0.12	−0.13	183
418.	$N(O)=NSO_2C_6H_5$	0.69	0.79	0.62	0.17	281
419.	$N=NC_6H_5$	0.32	0.39	0.30	0.09	175
420.	OC_6H_5	0.25	−0.03	0.37	−0.40	183, 87
421.	SOC_6H_5	0.50	0.44	0.51	−0.07	85
422.	2-(5-acetylfuryl)	0.24	0.08	0.31	−0.23	94, 95
423.	2-(6-methylpyronyl)	0.38	0.43	0.36	0.07	115
424.	$SO_2C_6H_5$	0.62	0.68	0.58	0.10	85
425.	$OSO_2C_6H_5$	0.36	0.33	0.37	−0.04	156
426.	SC_6H_5	0.23	0.07	0.30	−0.23	85
427.	NHC_6H_5	−0.02	−0.56	0.22	−0.78	173, 85
428.	$HNSO_2C_6H_5$	0.16	0.01	0.24	−0.23	156
429.	$SO_2NHC_6H_5$	0.56	0.65	0.51	0.14	74
430.	2-(5-ethylfuryl)	0.09	−0.13	0.20	−0.33	94, 95
431.	1-(2,5-dimethylpyrryl)	0.49	0.38	0.52	−0.14	93
432.	1-cyclohexenyl	−0.10	−0.08	−0.07	−0.01	127
433.	cyclohexyl	−0.05	−0.15	0.03	−0.18	85
434.	$N(C_3H_7)_2$	−0.26	−0.93	0.06	−0.99	113
435.	$(CH_2)_4NMe_2$	−0.08	−0.16	−0.01	−0.15	74
436.	PO(isopropyl)$_2$	0.37	0.41	0.36	0.05	79
437.	P(isopropyl)$_2$	0.02	0.06	0.04	0.02	69
438.	$P(O)(OPr)_2$	0.38	0.50	0.33	0.17	152
439.	$Ge(Et)_3$	0.00	0.00	0.03	−0.03	74, 183
440.	$(CH_2)_3N(Me)_3^+$	0.06	−0.01	0.12	−0.13	74
441.	$Si(OEt)_3$	0.02	0.08	0.03	0.05	74
442.	$P(Et)_3^+$	0.99	0.98	0.94	0.04	78
443.	$Sn(Et)_3$	0.00	0.00	0.03	−0.03	74, 183
444.	$P(=NSO_2CF_3)(C_3F_7)_2$	1.24	1.37	1.11	0.26	63
445.	$Si(NMe_2)_3$	−0.04	−0.04	0.00	−0.04	74
446.	2-benzoxazolyl	0.30	0.33	0.30	0.04	138
447.	2-benzthiazolyl	0.27	0.29	0.27	0.02	138

TABLE I (Continued)

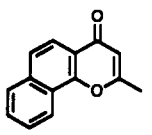
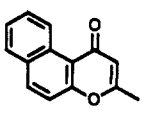
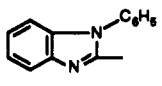
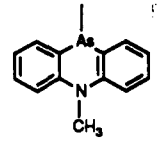
	substituent	σ_m	σ_p	F^b	R^c	ref(s)
448.	COC_6H_5	0.34	0.43	0.31	0.12	180
449.	$OCOC_6H_5$	0.21	0.13	0.26	−0.13	156
450.	$COOC_6H_5$	0.37	0.44	0.34	0.10	128
451.	$N{=}CHC_6H_5$	−0.08	−0.55	0.14	−0.69	156
452.	$CH{=}NC_6H_5$	0.35	0.42	0.33	0.09	136, 137
453.	$NHCOC_6H_5$	0.02	−0.19	0.13	−0.32	156
454.	$CONHC_6H_5$	0.23	0.41	0.17	0.24	74, 175
455.	C_6H_4-4-Me	0.06	−0.03	0.12	−0.15	85
456.	$CH_2C_6H_5$	−0.08	−0.09	−0.04	−0.05	170
457.	$N{=}NC_6H_3$-5-Me-2-OH	0.27	0.31	0.26	0.05	156
458.	C_6H_4-4-OMe	0.05	−0.08	0.13	−0.21	85
459.	$CH(OH)C_6H_5$	0.00	−0.03	0.05	−0.08	74, 175
460.	$CH_2OC_6H_5$	0.06	0.07	0.08	−0.01	128, 282
461.	$CH_2SO_2C_6H_5$	0.15	0.16	0.17	−0.01	128, 282
462.	$C(Et)_3$	−0.07	−0.20	0.02	−0.22	85
463.	$(CH_2)_6CH_3$	−0.07	−0.16	0.00	−0.16	85
464.	$SiMe(OSi(Me)_3)_2$	−0.02	−0.01	0.01	−0.02	160
465.	$CF_2CF_2C_6H_4$-4-F	0.34	0.39	0.32	0.07	109
466.	$C{\equiv}CC_6H_5$	0.14	0.16	0.15	0.01	170
467.	$CH{=}NCOC_6H_5$	0.39	0.51	0.34	0.17	74
468.	$CH{=}CHC_6H_5$	0.03	−0.07	0.10	−0.17	186
469.	$CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$	−0.26	−0.49	−0.11	−0.38	150
470.	$CH{=}NNHCOC_6H_5$	0.39	0.51	0.34	0.17	93
471.	$N{=}CHC_6H_4$-4-OMe	−0.07	−0.54	0.15	−0.69	156
472.	$NHCOC_6H_4$-4-OMe	0.09	−0.06	0.17	−0.23	156
473.	$SCH{=}NSO_2C_6H_4$-4-Me	0.65	0.70	0.61	0.09	74
474.	C_6H_4-4-Et	0.07	−0.02	0.13	−0.15	85
475.	$CH_2CH_2C_6H_5$	−0.07	−0.12	−0.01	−0.11	74
476.	$N{=}C(Me)NHC_6H_5$	0.29	0.08	0.38	−0.30	133
477.	$Si(C_6H_5)(Me)_2$	0.04	0.07	0.06	0.01	74
478.	$S(Me){=}NSO_2C_6H_4$-4-Me	0.65	0.70	0.61	0.09	205
479.	2,4,6-trimethylpyridinium	0.62	0.58	0.61	−0.03	73
480.	$PO(CMe_3)_2$	0.31	0.41	0.28	0.13	79
481.	$PO(C_4H_9)_2$	0.35	0.49	0.30	0.19	152
482.	$PO(OC_4H_9)_2$	0.41	0.57	0.35	0.22	85
483.	$P(CMe_3)_2$	0.01	0.15	−0.01	0.16	69
484.	$C_6H_5Cr(CO)_3$	0.29	0.14	0.36	−0.22	104
485.	2-benzo-4-thiopyronyl	0.34	0.35	0.34	0.01	115
486.	2-(benzothiopyronyl)	0.48	0.45	0.48	−0.03	115
487.	2-(benzo-1,4-pyronyl)	0.41	0.40	0.41	−0.01	115
488.	$CH{=}CHCOC_6H_4$-4-NO_2	0.15	0.05	0.21	−0.16	155
489.	$CH_2Mo(CO)_3(C_5H_5)$	−0.21	−0.45	−0.07	−0.38	150
490.	$CH{=}CHCOC_6H_5$	0.18	0.05	0.25	−0.20	155
491.	C_6H_4-4-$CHMe_2$	0.08	0.01	0.13	−0.12	85
492.	$Si(OSiMe_3)_3$	−0.09	−0.01	−0.08	0.07	160
493.	ferrocenyl	−0.15	−0.18	−0.09	−0.09	141
494.	ferricenium$^+$	0.29	0.29	0.30	−0.01	100
495.	ferrocenonium$^+$	0.05	0.29	−0.01	0.30	101
496.	C_6H_4-4-CMe_3	0.07	0.01	0.12	−0.11	85
497.	1-adamantyl	−0.12	−0.13	−0.07	−0.06	149
498.	1-dibenzarsenyl	0.19	0.13	0.23	−0.10	65
499.	1-dibenzoarsoxyl	0.17	0.09	0.22	−0.13	65
500.	1-dibenzoarsazinyl	0.14	0.09	0.18	−0.09	66
501.	$As(C_6H_5)_2$	0.03	0.09	0.04	0.05	125
502.	$AsO(C_6H_5)_2$	0.54	0.64	0.49	0.15	81
503.	$P(C_6H_5)_2(BCl_3)$	0.67	0.72	0.62	0.10	164
504.	$N(C_6H_5)_2$	0.00	−0.22	0.12	−0.34	168, 169
505.	$PO(C_6H_5)_2$	0.38	0.53	0.32	0.21	144
506.	$P(C_6H_5)_2$	0.11	0.19	0.10	0.09	144
507.	$PS(C_6H_5)_2$	0.29	0.47	0.23	0.24	144
508.	$P(N(C_3H_7)_2)C_6H_4$-3-F	0.20	0.24	0.20	0.04	122, 123
509.		0.37	0.38	0.37	0.01	61
510.		0.38	0.38	0.38	0.00	61
511.		0.17	0.21	0.17	0.04	138

TABLE I (Continued)

	substituent	σ_m	σ_p	F^b	R^c	ref(s)
512.	$CH(C_6H_5)_2$	−0.03	−0.05	0.01	−0.06	74, 102
513.		0.12	0.07	0.16	−0.09	66
514.	$PO(C_6H_5)C_6H_4$-4-Me	0.13	0.30	0.09	0.21	91
515.	$CH_2PO(C_6H_5)_2$	0.14	0.01	0.21	−0.20	85
516.	$PS(C_6H_5)C_6H_4$-4-Me	0.09	0.30	0.03	0.27	91
517.	$P^+(Me)(C_6H_5)_2$	1.13	1.18	1.04	0.14	91
518.	$Si(Me)(C_6H_5)_2$	0.10	0.13	0.11	0.02	74
519.	$COOCH(C_6H_5)_2$	0.36	0.56	0.28	0.28	175
520.	$PO(C_6H_4$-4-Me$)_2$	0.17	0.30	0.14	0.16	91
521.	$PS(C_6H_4$-4-Me$)_2$	0.20	0.23	0.20	0.03	91
522.	$P^+(Me)(C_6H_5)(C_6H_4$-4-Me)	1.09	1.11	1.02	0.09	91
523.	$P^+(Me)(C_6H_4$-4-Me$)_2$	1.13	1.18	1.04	1.14	91
524.	$Ge(C_6H_5)_3$	0.05	0.08	0.07	0.01	98
525.	2-methyl-4,6-diphenylpyridinium	0.65	0.70	0.61	0.09	61
526.	$N{=}P(C_6H_5)_3$	−0.33	−0.77	−0.10	−0.67	83
527.	$Si(C_6H_5)_3$	−0.03	0.10	−0.04	0.14	132
528.	$Sn(C_6H_5)_3$	(0.53)	(0.27)	(0.62)	(−0.35)	164
529.	$C(C_6H_5)_3$	−0.01	0.02	0.01	0.01	131
530.	2,4,6-triphenylpyridinium	0.34	0.33	0.35	−0.02	73

[a] Values in parentheses are suspected of being inaccurate. [b] Calculated from eq 8. [c] Calculated from eq 2. [d] Substituents are arranged by molecular formula, C_xH_y; other elements in alphabetical order.

TABLE II. Substituent Field/Inductive Parameters for Primary Dipolar Substituents Obtained from Various Sources

substituent X	$\sigma_I = 0.45\sigma^*$ CH_2X Taft[a]	σ_F Taft[b]	σ_I Stock[c]	σ_I Grobb[d]	σ_I Charton[e]	σ_I Taylor[f]	F^g	σ_I (F NMR) Taft[h]
NO_2	0.63	0.65	0.68	0.63	0.67	0.64	0.65	0.64
H	0.00	0.00	0.00[b,c]	0.00	0.00	0.00	0.00	0.00
CH_3	−0.05	0.00	−0.01	−0.02	−0.01	0.01	0.01	−0.01
C_2H_5	−0.05	0.00	−0.01		−0.01	−0.03	0.00	0.06
CH_2OH			0.05	0.09	0.11		0.03	0.13
OH	0.27	0.30	0.26[b,c]		0.24		0.33	
OCH_3	0.23	0.25 (0.28)	0.30[b]	0.31	0.30	0.29	0.29	0.30
OC_6H_5	0.38				0.40		0.37	0.42
$CO_2C_2H_5$	0.31	0.24 (0.31)	0.29[b,c]	0.29	0.30	0.31	0.34	0.19
Cl	0.47	0.45	0.47[b]	0.44	0.47		0.42	0.43
Br	0.45	0.45	0.45[b,c]	0.47	0.47		0.45	0.49
CN	0.59	0.60	0.54[c]	0.55	0.57	0.63	0.51	(0.53)
$CH(CH_3)_2$		0.00		−0.05	0.01		0.04	
$C(CH_3)_3$	−0.07	0.00		−0.07	−0.01		−0.02	0.09
CH_2OCH_3		0.14		0.09	0.11		0.13	0.09
CH_2OCOCH_3				0.13	0.15		0.07	
tosylmethyl				0.21	0.23			
CH_2Cl	0.17	0.23		0.15	0.17		0.13	0.23
CH_2Br				0.16	0.20		0.14	0.23
CH_2I				0.16	0.17		0.12	0.26
$CH(OH)_2$				0.20	0.22			
$CH{=}CH_2$		0.06		0.07	0.11		0.13	0.07
$C(CH_3){=}CH_2$				0.08	0.10		0.13	
$C{\equiv}CH$		0.23		0.28	0.29		0.22	(0.15)
C_6H_5	0.10	0.10		0.15	0.12		0.12	0.14
$COCH_3$	0.27	0.26 (0.30)	0.26	0.29	0.30	0.26	0.33	0.25
COC_6H_5		0.28				0.30	0.31	0.29
$CONH_2$				0.30	0.28	0.26	0.26	0.23
NH_2	0.10	0.14 (0.19)		0.15	0.17	0.14	0.08	0.09
$NHCH_3$		0.12		0.12	0.13		−0.03	
$N(CH_3)_2$	0.10	0.10 (0.19)		0.15	0.17		0.15	(0.17)
$NHCOCH_3$	0.28			0.27	0.28	0.27	0.31	0.34
$NHCO_2C_2H_5$				0.26			0.23	
$OCOCH_3$				0.37	0.38		0.42	0.34
SCH_3	0.25	0.25		0.28	0.30		0.23	0.24
SO_2CH_3	0.59	0.59 (0.65)		0.58	0.59		0.53	0.61
SO_2CF_3		0.84			0.71		0.74	0.83
F	0.50	0.44		0.46	0.54		0.45	(0.57)
I	0.38			0.41	0.40		0.42	(0.47)

[a] Reference 32. [b] Reference 30. [c] Calculated as $\Delta pK_a/1.56$. ΔpK_a values from refs 35 and 36. [d] Calculated from eq 8. [e] Reference 45. [f] Calculated as 0.0415 ΔpK_a for $XHN{=}C(NH_2)_2^+$. Reference 41. [g] From Table I. [h] Calculated from the meta-substituted fluorobenzene F NMR shift (relative to fluorobenzene). Reference 43 using eq 10. Values in parentheses are thought to involve magnetic or other complications.

TABLE III. Comparison of F Values Calculated via Eq 5 and 8

	F calcd via eq 5	F calcd via eq 8	|eq 5 − eq 8|
1. F	0.43	0.45	0.02
2. Br	0.44	0.45	0.01
3. CF_3	0.38	0.38	0.00
4. C≡CH	0.19	0.22	0.03
5. $CONH_2$	0.24	0.26	0.02
6. NO_2	0.67	0.65	0.02
7. NH_2	0.02	0.09	0.06
8. $NHCONH_2$	0.04	0.09	0.05
9. OH	0.29	0.33	0.04
10. OCH_3	0.26	0.29	0.03
11. SO_2NH_2	0.41	0.49	0.08
12. SCH_3	0.20	0.23	0.03
13. CN	0.51	0.51	0.00
14. $CH_2C_6H_5$	−0.08	−0.04	0.04
15. $OCOCH_3$	0.41	0.42	0.01

In a different approach to evaluating σ_I, Charton elected to use ionization constants of substituted acetic acids (XCH_2COOH) as a basis for its definition.[29] As he notes, this does not constitute a method beyond reproach, but it does allow the definition of σ_I for 294 substituents whose pK_a's have been measured. A limitation of this method is that of the 294 substituents, only 125 have known values of σ_p so that only 125 σ_R values can be estimated via eq 2.

Despite the quite different methods used to obtain secondary σ_I values by Charton and the method of obtaining F values via eq 7, there is generally satisfactory agreement between the two types of field/inductive constants as shown by the comparison of the fifth and seventh columns of Table II or by eq 9. Equation 9

$$F = 0.888\ (\pm 0.054)\sigma_I(\text{Charton}) + 0.017\ (\pm 0.017) \quad (9)$$

$$n = 129,\ r = 0.944,\ s = 0.067$$

is based on 129 substituents common to both data sets. Bear in mind that not only are the two approaches for obtaining inductive constants grossly different, but also the individual values come from a variety of different laboratories and hence, have different degrees of reliability. Given these conditions, one could hardly expect a better correlation. Table VIII contains σ_I from the acetic acid system by Charton for substituents not contained in Table I.

A recent report by Taylor and Wait[45] of substituent effects based on ΔpK_a for N-substituted guanidinium ions, H_2O at 25 °C, is of particular importance with respect to biologically important substituents. For 15 common substituents with known σ_F values,[30] $\sigma_I = 0.0415\Delta pK_a$, $r = 0.996$, $s = 0.03$. Values of σ_I calculated from this equation are given in the sixth column of Table II. The very great sensitivity of these particular aqueous solution proton transfer equilibria is shown by the very small (0.0415) coefficient to their ΔpK_a. This value is even smaller than the coefficient obtained in the gas phase for the relative acidities of nine 4-substituted bicyclooctane carboxylic acids[30] (for these, $\sigma_F = 0.106\Delta pK_a$).

The eighth column of Table II lists σ_F values calculated from the meta substituent F NMR shielding effect, $f_H^{m\text{-}X}$ for meta-substituted fluorobenzene, in dilute hydrocarbon solvents.[43] A correlation obtained herein for 33 substituents with well-established σ_F values[30] ($C(CF_3)_3$, $C(CN)_3$, CH_2Cl, CH_2CF_3, CH_2OMe, CH_3, C_2H_5, $CH_2SO_2CF_3$, $CHCl_2$, CHF_2, CF_3, CH=CH_2, C_6H_5, CO_2R, COMe, COC_6H_5, CHO, $COCF_3$, COCN, NH_2, NO_2, NO, OMe, OC_6H_5, Cl, Br, $Si(Me)_3$, SCH_3, SC_6H_5, SCF_3, SF_5, SO_2Me, SO_2CF_3) is

$$\sigma_F = 0.16 + 0.137\left(-f_H^{m\text{-}X}\right) \quad (10)$$

$$n = 33,\ r = 0.990,\ s = 0.034$$

Equation 10 has been utilized to obtain σ_F values listed in Tables II and IV.

For ease of determination, the F NMR measurement is a method of choice for estimation of the σ_F value of a new substituent. There is adequate signal-to-noise ratio in this method, a great breadth is allowed in the permissible substituent structural variation, preparation is relatively simple, and there is essentially no dependence upon nonspecific solvent dielectric constant variation.[43] Nevertheless, the F NMR method has given σ_F values for some substituents which appear to involve some relatively small specific magnetic contributions (usually less than 0.10 unit of σ_F) that are not observed in proton-transfer equilibria or other reactions. (Examples are the substituents CN, C≡CH, F, and t-C_4H_9 and others given in parentheses in the last column of Table II). However, variations in σ_F values due to substituent H-bonding solvation assisted field effects[42] are well established and predictable.[46] A few typical examples are given in Table II of enhanced σ_F values resulting from the hydrogen-bond acceptor substituent interacting with the HBD solvent water (cf. σ_F values given in parentheses in the second column of Table II). Another solvent effect on field/inductive parameters involves the fall-off factor for transmission of dipolar effects in a homologous straight chain. For gas-phase equilibria, the factor is 1/1.95 per methylene carbon,[30] but in certain solution equilibria the attenuation factor has been thought to be as large as 1/2.8 per methylene. For CH_2X type substituents in Table II, the σ_F values are generally larger than the corresponding F values.

In spite of these and other complications, the σ_F values from the F NMR method are in generally satisfactory agreement with F values obtained from eq 8. There are 146 substituents common to Tables I and IV. These 146 sets of F and σ_F(F NMR) are collected in Table IV. Only 10 substituents have $|\sigma_F - F|$ differences of 0.20 or greater. Excluding these substituents SO_2Cl, $CN{\cdot}BCl_3$, HgMe, $SnMe_3$, $N(CF_3)_2$, $^+P(CH_3)_3$, OCF_3, $CF(CF_3)_2$, $C(CF_3)_3$ and $P^+Me(C_6H_5)_2$ the standard deviation for equality between corresponding F and σ_F(F NMR) values (for a range of −0.12 to 1.15 in the latter), is only 0.076. Correlation by least-squares gives eq 11.

$$F = 0.924\ (\pm 0.023)\sigma_F - 0.006\ (\pm 0.11) \quad (11)$$

$$n = 136,\ r = 0.960,\ s = 0.067$$

These results further support the conclusion that field/inductive parameters can, with care, be obtained reliably from a number of useful sources.

It is clearly of interest to confirm this kind of agreement for many additional substituents present in one, but not the other, of Tables I and IV. We have commenced a literature search for a more complete tabulation of substituent F NMR chemical shifts for

meta- and para-substituted fluorobenzenes. The results of this search and of experimental determinations of additional substituents shifts will be reported subsequently.

B. Resonance Effect Parameters

Taft used eq 2 to obtain σ_R values. To evaluate R, Swain and Lupton[33] made the assumption that eq 6 applies in the following form

$$\sigma_p = \alpha F + R \quad \text{or} \quad R = \sigma_p - \alpha F \qquad (12)$$

and that for $N^+(CH_3)_3$, $R = 0$. By using eq 12 and the values of $F = 0.89$ and $\sigma_p = 0.82$, α was found to be 0.921. By using this value for α, F and R were then calculated for about 200 substituents.[34] Since, as noted before,[4] α does not differ much from 1, little, if anything, is lost by using Taft's eq 2 to calculate R ($= \sigma_p - F$) rather than eq 12. Therefore, we have recalculated F (using eq 8) and R (using eq 2). The values of R given in Table I generally compare well with Charton's σ_D as shown in eqs 13 and 14.

$$R = 0.864\ (\pm 0.066)\sigma_D - 0.004\ (\pm 0.018) \qquad (13)$$

$$n = 117,\ r = 0.923,\ s = 0.085$$

$$R = 0.877\ (\pm 0.050)\sigma_D - 0.002\ (\pm 0.013) \qquad (14)$$

$$n = 105,\ r = 0.959,\ s = 0.057$$

Equation 13 is based on all 117 substituents common to both data sets, and for eq 14, the 12 most poorly fit data points were dropped. The slopes and intercepts of eqs 13 and 14 are essentially identical. However, eq 14 is a sharper correlation.

Current expertise accepts the need for special parameterization for instances where strong resonance interaction occurs between reaction center and substituent. Two types of parameters σ^- and σ^+ (R^- and R^+) are widely used for such situations; however, Swain et al.[47] argue that this is unnecessary and have derived a set of optimized F and R from 14 selected reactions for all electronic substituent effects. Equations 15 and 16 compare these values of F and R based in part on reactions where π-donor and π-acceptor substituents are conjugated with the reaction centers.

$$F_{\text{Swain}} = 1.63\ (\pm 0.11)F_{\text{Table I}} + 0.45\ (\pm .033) \qquad (15)$$

$$n = 43,\ r = 0.978,\ s = 0.163$$

$$R_{\text{Swain}} = 3.44\ (\pm 0.43)R_{\text{Table I}} - 0.44\ (\pm 1.0) \qquad (16)$$

$$n = 43,\ r = 0.947,\ s = 0.455$$

The correlation between the two field/inductive parameters is fair, although the standard deviation is 3 times greater than that for either eqs 9 or 11, which apply to about 3 times as many substituents.

Swain's values were optimized for all of his selected reaction series including those involving through resonance effects that have been normally correlated by σ^+ and σ^-. Also included were charged substituents (CO_2^-, $S(Me)_2^+$, PO_3H^-, SO_3^-, N_2^+, and $N(Me)_3^+$) which often correlate poorly when included in sets of neutral substituents.[38] Thus, Swain has viewed the situation from the worst possible position so that it is perhaps surprising that the correlation is as good as it is. Still, we do not recommend using these normalized values since it is clear from many, many examples that σ_p^- and σ_p^+ not only give better correlations, but they often afford insight into the reaction mechanism which is lost when the normalized Swain constants are used.

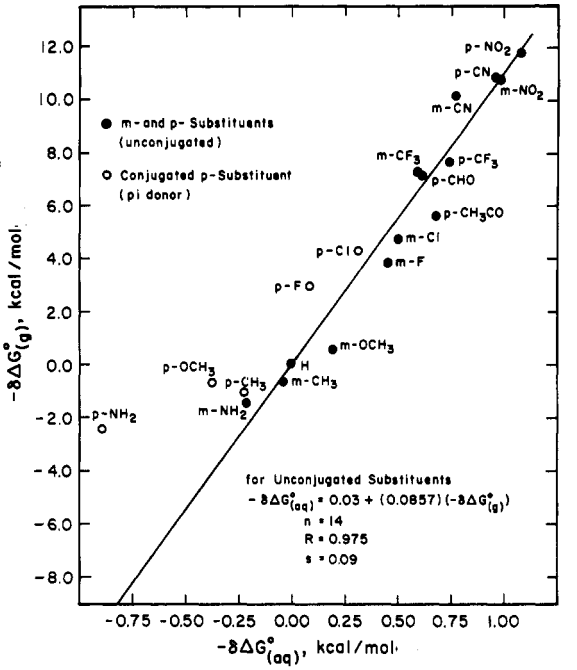


Figure 1. Meta- and para-substituted benzoic acid acidities gas phase vs aqueous.

Gas-phase proton-transfer equilibria for a variety of reaction series have been recently reported.[30] The very large accompanying substituent effects have been examined for rigid substituents at a fixed carbon position in saturated and unsaturated chains or cycles.[48] The series includes substituent effects at tetrahedral, trigonal, planar, or linear carbon positions. Linear free energy relationships of good precision were found to be much less common than in solution. However, σ_F and σ_R values with proper application give generally very good correlations of the substituent field/inductive and resonance effects (substituent polarizability effects were also found to be generally important in the gas phase).[30,48] In many series, it was found necessary to treat π-electron donor and acceptor substituents by using separate reaction constants, ρ_R^d and ρ_R^a in accord with ideas of Yukawa and Tsuno.[49] A number of gas-phase equilibria have ρ_R and ρ_F reaction constants of opposite signs.[30] Such reactions illustrate that although σ_p values are not applicable, the σ_F and σ_R values are. Certain reaction rate series in solution that involve conjugating para substituents have also been shown to follow this same kind of behavior.[50]

The relative gas-phase acidities of meta- and para-substituted benzoic acids provide important evidence that while aqueous solution solvent effects lead to significantly enhanced negative σ_p values for strong π-donor substituents, the major features of σ_m and σ_p constants do involve inherent electronic effects. Figure 1 shows a plot of $-\delta\Delta G_{(g)}$ [$= 2.303RT \log (K/K_0)_g$] vs $-\delta\Delta G^\circ_{(aq)}$ ($= 1.364\sigma_{(aq)}$) for meta- and para-substituted

TABLE IV. σ_F, σ_R, $c\sigma_m$, and $c\sigma_p$ Constants from F NMR Chemical Shifts of Meta- and Para-Substituted Fluorobenzenes

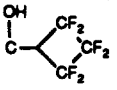
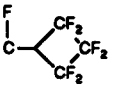
	substituent, Y	solvent	$-f_H^{p\text{-}Y}$	$-f_H^{m\text{-}Y}$	σ_F	σ_R	$c\sigma_m$	$c\sigma_p$
			Carbon Substituents					
			1. CH_2X					
1.	CH_2SnMe_3	c-C_6H_{12}	7.75	0.85	0.04	−0.23	−0.11	−0.35[a]
2.	CH_2GeMe_3	c-C_6H_{12}	7.05	0.90	0.04	−0.20	−0.09	−0.22
3.	CH_2SiMe_3	c-C_6H_{12}	7.00	1.10	0.01	−0.19	−0.12	−0.28
4.	CH_3	c-C_6H_{12}	5.40	1.20	−0.01	−0.13	−0.11	−0.19
5.	CH_2Me	c-C_6H_{12}	5.05	0.75	0.06	−0.13	−0.04	−0.13
6.	CH_2NH_2	c-C_6H_{12}	3.75	0.58	0.08	−0.09	0.00	−0.06
7.	CH_2COMe	C_6H_6	3.22	0.36	0.11	−0.08	0.03	−0.02
8.	CH_2NMe_2	C_6H_6	3.09	0.79	0.05	−0.06	−0.02	−0.06
9.	CH_2SMe	C_6H_6	2.95	0.37	0.11	−0.07	0.04	−0.01
10.	CH_2OMe	Cl_3CF	2.41	0.53	0.09	−0.05	0.03	−0.01
11.	CH_2OH	c-C_6H_{12}	2.15	0.18	0.13	−0.05	0.07	0.03
12.	CH_2CN	c-C_6H_{12}	1.07	−1.20	0.32	−0.06	0.25	0.21
13.	CH_2CF_3	Cl_3CF	0.92	−0.43	0.22	−0.03	0.16	0.14
14.	CH_2SCF_3	Cl_3CF	0.73	−0.92	0.29	−0.03	0.23	0.21
15.	CH_2Cl	Cl_3CF	0.50	−0.53	0.23	−0.02	0.18	0.16
16.	CH_2F	Cl_3CF	0.25	−0.28	0.20	0.00	0.16	0.15
17.	$CHBr$	Cl_3CF	0.22	−0.50	0.23	−0.01	0.18	0.17
18.	$CH_2SO_2CF_3$	C_6H_6	−0.07	−0.67	0.25	0.00	0.21	0.20
19.	CH_2SOCF_3	CCl_4	−0.81	−1.28	0.33	0.00	0.28	0.28
20.	$CH_2SO_2CF_3$	CCl_4	−1.35	−2.14	0.46	−0.01	0.41	0.40
			2. CHX_2					
21.	$CH(SiMe_3)_2$	CCl_4	7.47	0.84	0.04	−0.22	−0.10	−0.24
22.	$CH(C_6H_5)_2$	CH_2Cl_2	2.83	0.20	0.13	−0.07	0.06	0.01
23.	$CH(OMe)_2$	Cl_3CF	1.38	0.50	0.09	−0.01	0.05	0.03
24.	$CH(SCF_3)_2$	Cl_3CF	−2.43	−2.53	0.51	0.02	0.47	0.48
25.	$CHBr_2$	Cl_3CF	−2.21	−1.51	0.37	0.03	0.34	0.35
26.	CHF_2	Cl_3CF	−3.14	−1.48	0.36	0.06	0.34	0.37
27.	$CH(CN)_2$	Cl_3CF	−2.30	−3.29	0.61	−0.02	0.55	0.53
			3. CX_3					
28.	$C(SiMe_3)_3$	CCl_4	6.93	−0.30	(0.20)	(−0.23)	(0.05)	(−0.09)
29.	CMe_3	c-C_6H_{12}	5.55	0.50	(0.09)	(−0.16)	(−0.02)	(−0.13)
30.	CH_3	c-C_6H_{12}	5.40	1.20	0.01	−0.13	−0.11	−0.19
31.	$C(OMe)_3$	Cl_3CF	0.62	0.41	0.10	0.01	0.07	0.06
32.	CBr_3	Cl_3CF	−2.21	−1.26	0.33	0.04	0.30	0.32
33.	CCl_3	Cl_3CF	−2.31	−1.51	0.37	0.03	0.34	0.35
34.	$C(CF_3)_3$	n-C_7H_{16}	−3.44	−3.32	0.61	0.01	0.56	0.56
35.	$C(SCF_3)_3$	Cl_3CF	−3.99	−2.90	0.56	0.04	0.52	0.55
36.	CF_3	c-C_6H_{12}	−5.05	−2.18	0.46	0.09	0.45	0.50
37.	$C(CN)_3$	Cl_3CF	−6.02	−5.75	0.95	0.02	0.90	0.91
								
38.		CCl_4	5.11	1.18	0.00	−0.12	−0.09	−0.17
39.		CCl_4	3.26	0.75	0.06	−0.07	−0.01	−0.06
40.		CCl_4	1.80	0.10	0.15	−0.13	0.10	0.07
41.		CCl_4	1.43	0.11	0.17	−0.02	0.12	0.10
			5. CX_2Z					
42.	$C(C_6H_5)_2N{=}P(C_6H_5)_3$	Cl_3CH	6.12	1.63	−0.07	−0.14	−0.17	−0.26
43.	$C(C_6H_5)_2OH$	CH_2Cl_2	1.31	0.05	0.09	−0.01	0.05	0.03
44.	$C(Me)(CN)_2$	CH_2Cl_2	−2.16	−3.88	0.69	−0.04	0.62	0.59
45.	$C(OH)(CF_3)_2$	Cl_3CF	−2.37	−1.88	0.42	0.02	0.38	0.39
46.		Cl_3CF	−2.50	−1.88	0.42	0.03	0.39	0.40
47.	$CF(CF_3)_2$	Cl_3CF	−4.14	2.93	0.56	0.05	0.53	0.56
48.	CF_2Cl	Cl_3CF	−4.39	−2.09	0.45	0.07	0.43	0.47
49.		Cl_3CF	−4.84	−2.60	0.52	0.07	0.50	0.54
50.	$CF_2(n\text{-}C_3F_7)$	Cl_3CF	−5.58	−2.30	0.47	0.10	0.47	0.52
			6. CXYZ					
51.	C(Me)HOH	c-C_6H_{12}	2.75	0.07	0.15	−0.07	0.08	0.03
			7. C=C					
52.	$C(C_6H_5){=}CH_2$	CH_2Cl_2	1.67	0.60	0.08	−0.02	0.03	0.01
53.	$CH{=}CH_2$	c-C_6H_{12}	1.45	0.63	0.07	−0.01	0.03	0.01
54.	$CH{=}CHCF_3$-c	Cl_3CF	−1.69	−0.25	0.19	0.05	0.17	0.19

TABLE IV (Continued)

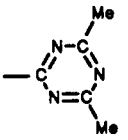
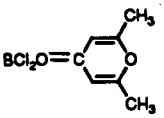
	substituent, Y	solvent	$-\int_H^{p\text{-}Y}$	$-\int_H^{m\text{-}Y}$	σ_F	σ_R	$c\sigma_m$	$c\sigma_p$
55.	$CH{=}CHCF_3$-*t*	Cl_3CF	−2.73	−0.80	0.27	0.06	0.26	0.28
56.	CHCHCN-*t*	Cl_3CF	−4.58	−1.28	0.33	0.10	0.33	0.38
57.	$CH{=}CHNO_2$-*t*	C_6H_6	−5.80	−1.13	0.31	0.14	0.33	0.41
58.	$CH{=}CHSO_2CF_3$-*t*	CCl_4	−8.97	−1.59	0.38	0.22	0.44	0.56
59.	$CH{=}C(CN)_2$	C_6H_6	−10.93	−2.27	0.47	0.25	0.54	0.68
60.	$C(CN){=}C(CN)_2$	C_6H_6	−13.19	−4.12	0.72	0.26	0.79	0.94
61.	C_6H_5	c-C_6H_{12}	3.00	0.15	0.14	−0.08	0.06	0.01
62.	C_6Cl_5	Cl_3CF	−0.83	−1.19	0.32	0.01	0.28	0.28
63.	C_6F_5	Cl_3CF	−1.70	−1.15	0.32	0.03	0.29	0.30
64.		CCl_4	−5.23	−0.01	0.16	0.16	0.20	0.28
			8. C≡C					
65.	1,8-$C_2B_9H_{10}$	CCl_4	−0.34	−0.11	0.17	0.02	0.14	0.14
66.	1,7-$C_2B_{10}H_{11}$	c-C_6H_{12}	−0.46	−0.78	0.27	0.01	0.23	0.23
67.	1,2-$C_2B_{10}H_{11}$	c-C_6H_{12}	−2.14	−2.06	0.44	0.01	0.40	0.40
68.	C≡CH	c-C_6H_{12}	−2.35	0.05	(0.15)	(0.08)	0.15	0.19
69.	$C{\equiv}CCF_3$	CCl_4	−6.25	−1.56	0.37	0.14	0.39	0.47
			9. C≡N					
70.	CN	c-C_6H_{12}	−8.80	−2.80	(0.54)	(0.18)	(0.57)	(0.68)
71.	$CNBCl_3$	CH_2Cl_2	−22.57	−7.40	1.17	0.43	1.30	1.56
			10. COX					
72.	$CONH_2$	MeCN	−4.25	−0.50	0.23	0.12	0.24	0.31
73.	CO_2Et	c-C_6H_{12}	−5.75	−0.25	0.19	0.16	0.22	0.31
74.	COMe	c-C_6H_{12}	−6.10	−0.68	0.25	0.16	0.28	0.37
75.	COC_6H_4Me(p)	C_6H_6	−5.72	−0.81	0.27	0.15	0.30	0.38
76.	COC_6H_4SMe(p)	C_6H_6	−5.90	−0.91	0.28	0.15	0.31	0.39
77.	COC_6H_5	C_6H_6	−6.13	−0.94	0.29	0.16	0.32	0.41
78.	CO(c-C_3H_5)	CCl_4	−6.47	−1.05	0.30	0.16	0.33	0.42
79.	COC_6H_4Cl(p)	C_6H_6	−6.68	−1.30	0.34	0.16	0.37	0.46
80.	$COC_6H_4CF_3$(p)	C_6H_6	−7.55	−1.41	0.35	0.18	0.39	0.49
81.	$CO_2C_6H_5$	c-C_6H_{12}	−7.45	−0.65	0.25	0.20	0.30	0.41
82.	COSMe	MeOH	−8.30	−1.63	0.38	0.20	0.43	0.54
83.	CHO	c-C_6H_{12}	−9.15	−1.38	0.35	0.23	0.41	0.54
84.	COF	c-C_6H_{12}	−11.15	−2.15	0.45	0.26	0.52	0.67
85.	COCl	c-C_6H_{12}	−11.20	−2.10	0.45	0.26	0.52	0.67
86.	$COCF_3$	c-C_6H_{12}	−12.00	−2.62	0.52	0.27	0.60	0.75
87.	COCN	c-C_6H_{12}	−14.13	−3.33	0.62	0.31	0.71	0.89
88.	$C(C_6H_5)OBF_3$	CH_2Cl_2	−17.62	−2.88	0.55	0.42	0.70	0.94
89.	$C(C_6H_5)OBCl_3$	CH_2Cl_2	−21.20	−3.81	0.68	0.50	0.86	1.15
			11. $C(C_6H_5){=}X$					
90.	$C(C_6H_5){=}CH_2$	CH_2Cl_2	1.67	0.60	0.08	−0.02	0.03	0.01
91.	$C(C_6H_5){=}NH$	CH_2Cl_2	−2.51	−0.36	0.21	0.07	0.20	0.23
92.	$C(C_6H_5){=}S$	CH_2Cl_2	−5.93	−0.20	0.19	0.17	0.23	0.32
93.	$C(C_6H_5){=}O$	CH_2Cl_2	−6.69	−0.81	0.27	0.17	0.31	0.40
			Boron Substituents					
			1. BX_2					
94.	$B(NMe_2)_2$	CH_2Cl_2	1.72	1.87	−0.10	0.01	−0.13	−0.14
95.	$B(OMe)_2$	CH_2Cl_2	−2.24	1.10	0.01	0.07	0.01	0.04
96.	BF_2	CH_2Cl_2	−10.04	−0.54	0.23	0.28	0.32	0.48
97.	BCl_2	CH_2Cl_2	−11.86	−0.24	0.19	0.34	0.31	0.50
			2. BX_2Z					
98.	BCl_2-HMPA	CH_2Cl_2	3.91	2.33	−0.16	−0.04	−0.21	−0.25
99.	BCl_2-$OP(C_6H_5)_3$	CH_2Cl_2	3.54	2.21	−0.14	−0.03	−0.19	−0.22
100.			3.08	2.05	−0.12	−0.02	−0.16	−0.19
101.	BCl_3-$(n\text{-}C_7H_{15})_4N^+$	CH_2Cl_2	2.59	1.99	−0.11	−0.01	−0.14	−0.17
102.	BCl_2-NEt_3	CH_2Cl_2	2.23	1.86	−0.10	−0.01	−0.13	−0.14
103.	BCl_2-$P(C_6H_5)_3$	CH_2Cl_2	1.87	1.97	−0.11	0.01	−0.13	−0.14
104.	BCl_2-NC_5H_5	CH_2Cl_2	1.72	1.01	0.02	−0.01	−0.02	−0.04
105.	BCl_2-$N(Me)_2CH_2C_6H_5$	CH_2Cl_2	1.64	1.69	−0.07	0.01	0.10	−0.11
106.	BCl_2-$N(Me)_2C_6H_5$	CH_2Cl_2	1.44	2.37	−0.17	0.04	−0.17	−0.18
107.	BCl_2-THP	CH_2Cl_2	0.86	1.03	0.02	0.01	0.00	−0.02
108.	BCl_2-$S(Me)CH_2C_6H_5$	CH_2Cl_2	0.02	0.75	0.06	0.03	0.04	0.04

TABLE IV (Continued)

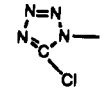
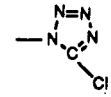
	substituent, Y	solvent	$-\int_H^{p\text{-}Y}$	$-\int_H^{m\text{-}Y}$	σ_F	σ_R	$c\sigma_m$	$c\sigma_p$
			3. Other					
109.	3-$B_{10}C_2H_{11}$(1,2)	$(MeOCH_2)_2$	−1.27	0.52	0.09	0.06	0.08	0.11
			Nitrogen Substituents					
			1. NHX					
110.	NH_2	c-C_6H_{12}	14.40	0.50	0.09	−0.48	−0.18	−0.72[a]
111.	$NHNH_2$	MeOH	12.25	−0.05	0.17	−0.42	−0.07	−0.50[a]
112.	NHC_6H_5	CCl_4	9.15	−1.10	0.31	−0.35	0.10	−0.26[a]
113.	NHCN	Cl_3CF	7.01	−2.06	0.44	−0.30	0.25	−0.06[a]
114.	NHCOMe	MeOH	5.15	−1.35	0.34	−0.21	0.20	−0.04[a]
			2. NXZ					
115.	$N(COF)CF_3$	Cl_3CF	−3.40	−3.36	0.62	0.01	0.57	0.57
			3. NX_2					
116.	NMe_2	c-C_6H_{12}	15.90	−0.08	(0.17)	−0.56	−0.14	−0.42[a]
117.	—N△	n-C_7H_{16}	8.52	0.10	0.15	−0.28	−0.02	−0.32[a]
118.	$N(CN)_2$	Cl_3CF	0.64	−5.75	0.94	−0.21	0.78	0.66
119.	$N(CF_3)_2$	Cl_3CF	−3.19	−2.86	0.55	0.02	0.51	0.52
120.	$N(COF)_2$	Cl_3CF	−3.22	−3.49	0.64	0.01	0.59	0.59
			4. NX_2Z					
121.	NMe_2-BCl_3	CH_2Cl_2	−0.10	−2.78	0.54	−0.08	0.45	0.40
122.	$N^+Me_2O^-$	MeOH	−1.03	−4.03	0.71	−0.09	0.61	0.56
			5. N=Z					
123.	$N{=}P(C_6H_5)_3$	Cl_3CH	15.45	2.02	−0.12	−0.46	−0.37	0.86[a]
124.	$N{=}CCl_2$	Cl_3CF	3.15	−1.42	0.35	−0.14	0.24	0.15
125.	N=C=O	Cl_3CF	3.11	−1.92	0.42	−0.16	0.30	0.20
126.	$N{=}NPt(Cl)(PEt_3)_2$	Cl_3CF	2.27	−0.66	0.25	−0.08	0.17	0.12
127.	$N{=}C(CF_3)_2$	Cl_3CF	1.77	−1.91	0.42	−0.11	0.32	0.25
128.	N=C=S	CCl_4	−0.53	−2.35	0.48	−0.05	0.41	0.37
129.		C_6H_6	−1.61	−3.28	0.61	−0.04	0.54	0.51
130.	$N{=}NC_6H_5$	c-C_6H_{12}	−3.10	−0.70	0.25	0.08	0.25	0.28
131.	N=C	Cl_3CF	−3.21	−2.76	0.54	0.00	0.49	0.49
132.		C_6H_6	−3.63	−3.44	0.63	0.02	0.59	0.60
133.	N=S=O	Cl_3CF	−5.99	−2.25	0.47	0.11	0.47	0.53
134.	NO_2	c-C_6H_{12}	−9.01	−3.50	0.64	0.16	0.66	0.75
135.	N=O	c-C_6H_{12}	−10.50	−1.80	0.41	0.25	0.48	0.62
			6. $N_nP_nF_{2n-1}$					
136.	$N_3P_3F_5$	Cl_3CF	−10.6	−3.3	0.61	0.21	0.66	0.78
137.	$N_4P_4F_7$	Cl_3CF	−10.4	−3.2	0.60	0.21	0.65	0.77
138.	$N_5P_5F_9$	Cl_3CF	−10.2	−3.3	0.61	0.20	0.65	0.77
139.	$N_6P_6F_{11}$	Cl_3CF	−10.1	−3.3	0.61	0.20	0.65	0.77
140.	$N_7P_7F_{13}$	Cl_3CF	−10.0	−3.3	0.61	0.20	0.65	0.77
141.	$N_8P_8F_{15}$	Cl_3CF	−10.0	−3.3	0.61	0.20	0.65	0.77
			Oxygen Substituents					
			1. Y					
142.	OH	CCl_4	11.40	−1.20	0.32	−0.43	0.07	−0.38[a]
143.	OMe	c-C_6H_{12}	11.58	−1.05	0.30	−0.43	0.05	0.40[a]
144.	$O(CH_2)_2Br$	Cl_3CF	9.86	−1.90	0.42	−0.40	0.18	0.23[a]
145.	$OCH{=}CH_2$	Cl_3CF	7.55	−2.07	0.44	−0.31	0.25	−0.09[a]
146.	OC_6H_5	c-C_6H_{12}	7.45	−1.95	0.43	−0.32	0.23	−0.11[a]
147.	OCH_2Cl	CCl_4	7.36	−2.28	0.47	−0.31	0.27	−0.04[a]
148.	$OCH{=}CHBr$	Cl_3CF	6.64	−2.38	0.49	−0.30	0.30	−0.01[a]
149.	$OC{\equiv}CH$	Cl_3CF	5.99	−2.94	0.56	−0.30	0.37	0.06[a]
150.	OCOMe	c-C_6H_{12}	4.55	−1.33	0.34	−0.19	0.20	0.09
151.	$OCHF_2$	CCl_4	4.32	−2.62	0.52	−0.23	0.36	0.22
152.	$OCHCl_2$	CCl_4	3.98	−2.95	0.56	−0.23	0.40	0.26
153.	OCN	Cl_3CF	2.46	−5.12	0.86	−0.25	0.68	0.54
154.	OCF_3	c-C_6H_{12}	2.25	−3.35	0.62	−0.18	0.48	0.37
155.	$OCCl_3$	CCl_4	1.65	−3.04	0.58	−0.15	0.46	0.37
156.	$OCOCF_3$	c-C_6H_{12}	1.58	−3.98	0.71	−0.18	0.57	0.46
			2. OXZ					
157.	$O(Me)BCl_3$	CH_2Cl_2	−1.5	−3.2	0.60	−0.06	0.52	0.48

TABLE IV (Continued)

	substituent, Y	solvent	$-f_H^{p-Y}$	$-f_H^{m-Y}$	σ_F	σ_R	$c\sigma_m$	$c\sigma_p$
		Halogen Substituents						
		1. Y						
158.	F	c-C_6H_{12}	6.72	−3.03	(0.57)	(−0.33)	(0.36)	(0.04[a])
159.	Cl	c-C_6H_{12}	3.10	−2.00	0.43	−0.16	0.31	0.21
160.	Br	c-C_6H_{12}	2.53	−2.43	0.49	−0.16	0.36	0.27
161.	I	c-C_6H_{12}	1.63	−2.30	0.47	−0.12	0.36	0.29
		2. XY_2						
162.	ICl_2	CCl_4	−7.1	−7.2	1.15	0.01	1.09	1.10
		Gold(I) Substituents						
163.	$AuCNC_6H_4F$(p)	C_6H_6	2.59	2.23	−0.15	0.00	−0.18	−0.20
164.	$AuCNC_6H_4F$(m)	C_6H_6	2.66	2.20	−0.14	0.00	−0.17	−0.19
165.	$AuP(C_6H_5)_3$	C_6H_6	3.23	2.32	−0.16	−0.01	−0.20	−0.22
		Magnesium Substituents						
166.	MgC_6H_5	Et_2O	5.61	3.72	−0.35	−0.05	−0.40	−0.45
167.	MgBr	Et_2O	5.39	3.71	−0.35	−0.04	−0.40	−0.43
		Silicon Substituents						
		1. SiX_2Z						
168.	$Si(C_6H_5)_2N{=}P(C_6H_5)_3$	$DCCl_3$	0.84	1.97	−0.11	0.04	−0.12	−0.11
169.	$SiMe_2CH{=}CH_2$	c-C_6H_{12}	−0.73	0.82	0.05	0.05	0.04	0.06
170.	$SiMe_2H$	c-C_6H_{12}	−1.16	0.72	0.06	0.06	0.05	0.08
171.	$SiMe_2CH_2Cl$	c-C_6H_{12}	−2.06	0.16	0.14	0.07	0.13	0.17
172.	$SiMe_2F$	c-C_6H_{12}	−3.09	0.06	0.15	0.10	0.16	0.21
		2. SiX_3						
173.	$Si(NMe_2)_3$	c-C_6H_{12}	0.99	0.90	0.04	0.01	0.01	0.00
174.	$SiMe_3$	c-C_6H_{12}	−0.50	0.90	0.04	0.05	0.03	0.05
175.	SiH_3	c-C_6H_{12}	−2.56	−0.01	0.16	0.08	0.16	0.20
176.	$Si(OEt)_3$	c-C_6H_{12}	−2.57	0.86	0.04	0.11	0.06	0.11
177.	$SiBr_3$	c-C_6H_{12}	−7.46	−2.10	0.45	0.16	0.48	0.57
178.	$SiCl_3$	c-C_6H_{12}	−7.85	−2.14	0.45	0.17	0.48	0.58
179.	SiF_3	CCl_4	−9.57	−2.34	0.48	0.21	0.53	0.65
		Other Group Substituents						
180.	$GeMe_3$	c-C_6H_{12}	0.55	0.70	0.06	0.01	0.03	0.02
181.	$SnMe_3$	c-C_6H_{12}	0.20	0.65	0.07	0.02	0.04	0.04
182.	$PbMe_3$	c-C_6H_{12}	0.20	0.40	0.10	0.02	0.07	0.07
183.	$Sn(C_6H_4F(sym))_3$	c-C_6H_{12}	−2.32	−1.72	0.39	0.03	0.36	0.37
		Phosphorus Substituents						
		1. PX_2						
184.	$P(NMe_2)_2$	c-C_6H_{12}	2.33	0.63	0.07	−0.04	0.01	−0.02
185.	PMe_2	c-C_6H_{12}	1.40	0.05	0.15	−0.03	0.10	0.07
186.	$P(C_6H_5)_2$	c-C_6H_{12}	−0.13	−0.30	0.20	0.01	0.16	0.16
187.	$P(C_6H_4F(sym))_2$	c-C_6H_{12}	−0.85	−1.24	0.33	0.02	0.29	0.30
188.	$P(OMe)_2$	c-C_6H_{12}	−1.94	−0.03	0.16	0.06	0.15	0.17
189.	$P(CF_3)C_6H_4F(sym)$	Cl_3CF	−3.99	−2.29	0.47	0.06	0.45	0.48
190.	PCl_2	Cl_3CF	−7.42	−2.65	0.52	0.14	0.54	0.61
191.	PF_2	Cl_3CF	−8.30	−2.11	0.45	0.18	0.49	0.59
192.	$P(CF_3)_2$	Cl_3CF	−8.82	−3.12	0.59	0.17	0.62	0.71
193.	$P(CN)_2$	CCl_4	−9.33	−4.65	0.80	0.14	0.81	0.89
		2. PX_2Z						
194.	$P(C_6H_4F(sym))_2CH_2$	DMSO	−4.86	−1.47	0.36	0.10	0.36	0.41
195.	$P(C_6H_5)_2O$	CCl_4	−5.01	−1.56	0.37	0.10	0.37	0.42
196.	$P(C_6H_4F(sym))_2O$	CH_2Cl_2	−6.78	−2.47	0.50	0.13	0.51	0.58
197.	$P(C_6H_5)BCl_3$	CH_2Cl_2	−8.69	−4.02	0.71	0.14	0.72	0.80
		3. PX_4						
198.	PF_4	Cl_3CF	−12.09	−2.62	0.52	0.28	0.60	0.76
199.	$P(C_6H_4F(sym))_3{-}N{=}Si(C_6H_5)_2C_6H_4F$(p)	$HCCl_3$	−5.00	−2.07	0.44	0.09	0.43	0.48
		Sulfur Substituents						
		1. SX						
200.	SMe	c-C_6H_{12}	4.40	−0.30	0.20	−0.15	0.09	−0.01
201.	SH	c-C_6H_{12}	3.50	−0.78	0.27	−0.13	0.17	0.08
202.	SEt	Cl_3CF	2.96	−0.30	0.20	−0.10	0.11	0.04
203.	$SC{\equiv}CH$	Cl_3CF	2.18	−1.68	0.39	−0.12	0.29	0.21
204.	$SCH{=}CH_2$	Cl_3CF	1.21	−0.91	0.28	−0.06	0.21	0.17
205.	$SNMe_2$	Cl_3CF	1.17	−0.48	0.22	−0.04	0.16	0.13
206.	S(OMe)	Cl_3CF	1.14	−1.17	0.32	−0.06	0.25	0.21
207.	SC_6H_5	CH_2Cl_2	0.99	−0.97	0.29	−0.05	0.22	0.19
208.	$S(SC_6H_4F(sym))$	Cl_3CF	0.53	−1.93	0.42	−0.06	0.34	0.30
209.	SCOMe	Cl_3CF	−1.19	−0.92	0.29	0.02	0.26	0.26
210.	SCN	Cl_3CF	−3.90	−2.47	0.50	0.05	0.47	0.50

TABLE IV (Continued)

	substituent, Y	solvent	$-\int_H^{p\text{-}Y}$	$-\int_H^{m\text{-}Y}$	σ_F	σ_R	$c\sigma_m$	$c\sigma_p$
211.	SCF_3	Cl_3CF	−4.20	−2.36	0.48	0.06	0.46	0.49
212.	$SCOCF_3$	Cl_3CF	−4.45	−3.00	0.57	0.04	0.54	0.56
213.	SCl	Cl_3CF	−4.47	−2.23	0.47	0.07	0.45	0.49
			2. SXZ					
214.	$S(Me)BCl_3$	CH_2Cl_2	−7.42	−4.50	0.78	0.09	0.76	0.82
			3. SOX					
215.	$SONMe_2$	Cl_3CF	−2.40	−1.53	0.37	0.03	0.34	0.35
216.	SO(OMe)	Cl_3CF	−5.22	−2.56	0.51	0.08	0.50	0.54
217.	$SOCF_3$	Cl_3CF	−7.98	−4.22	0.74	0.12	0.74	0.81
218.	SOCl	Cl_3CF	−8.64	−4.24	0.74	0.13	0.74	0.82
219.	SOF	Cl_3CF	−9.06	−4.06	0.72	0.15	0.73	0.82
			4. SX_3					
220.	SF_3	Cl_3CF	−9.51	−3.67	0.66	0.17	0.69	0.78
			5. SX_5					
221.	SF_5	c-C_6H_{12}	−5.33	−3.14	0.59	0.07	0.57	0.61
			6. SO_2X					
222.	SO_2NMe_2	Cl_3CF	−5.98	−2.36	0.48	0.11	0.48	0.54
223.	SO_2NH_2	MeOH	−6.00	−2.50	0.50	0.11	0.52	0.56
224.	$SO_2C_6H_5$	CCl_4	−7.23	−3.14	0.59	0.12	0.59	0.66
225.	SO_2OEt	c-C_6H_{12}	−8.10	−2.90	0.56	0.16	0.58	0.67
226.	SO_2Me	CCl_4	−8.00	−3.30	0.61	0.14	0.62	0.70
227.	SO_2Cl	c-C_6H_{12}	−11.90	−5.10	0.86	0.20	0.89	1.01
228.	SO_2F	c-C_6H_{12}	−12.20	−4.68	0.80	0.22	0.85	0.97
229.	SO_2CF_3	c-C_6H_{12}	−13.82	−4.86	0.83	0.26	0.89	1.05
230.	SO_2CN	Cl_3CH	−15.37	−6.05	0.99	0.27	1.05	1.21
			Mercury Substituents					
			HgX					
231.	HgMe	CH_2Cl_2	0.24	0.31	0.12	0.01	0.09	0.08
232.	HgC_6H_5	CH_2Cl_2	−0.37	−0.10	0.17	0.02	0.14	0.14
233.	HgC_6H_4F(p)	CH_2Cl_2	−0.56	−0.25	0.19	0.02	0.16	0.16
234.	HgC_6H_4F(m)	CH_2Cl_2	−0.72	−0.27	0.20	0.02	0.17	0.17
235.	HgOH	CH_2Cl_2	−1.11	−1.32	0.34	0.01	0.30	0.30
236.	$HgCCl_3$	CH_2Cl_2	−2.30	−1.53	0.37	0.03	0.34	0.35
237.	HgOCOMe	CH_2Cl_2	−2.32	−1.75	0.40	0.03	0.37	0.38
238.	HgBr	CH_2Cl_2	−2.78	−2.08	0.44	0.03	0.41	0.42
			Platinum(II) Substituents					
			1. $Pt(PEt_3)_2X$					
239.	t-$Pt(PEt_3)_2Me$	c-C_6H_{12}	11.7	4.26	−0.43	−0.24	−0.57	0.83[a]
240.	t-$Pt(PEt_3)_2C_6H_5$	c-C_6H_{12}	10.9	3.72	−0.35	−0.24	−0.49	−0.75[a]
241.	t-$Pt(PEt_3)_2C_6H_4F$(p)	c-C_6H_{12}	10.8	3.44	−0.31	−0.24	−0.45	−0.72[a]
242.	t-$Pt(PEt_3)_2C{\equiv}CC_6H_5$	c-C_6H_{12}	10.4	3.37	−0.30	−0.33	−0.48	−0.85[a]
243.	t-$Pt(PEt_3)_2Cl$	c-C_6H_{12}	10.2	2.50	−0.18	−0.26	−0.33	−0.62[a]
244.	t-$Pt(PEt_3)_2Br$	c-C_6H_{12}	10.0	2.34	−0.16	−0.26	−0.31	−0.60[a]
245.	t-$Pt(PEt_3)_2I$	c-C_6H_{12}	9.70	2.00	−0.11	−0.26	−0.27	−0.55[a]
246.	t-$Pt(PEt_3)_2CN$	c-C_6H_{12}	9.11	2.53	−0.19	−0.22	−0.33	−0.57[a]
247.	c-$Pt(PEt_3)_2C_6H_5$	Me_2CO	11.6	3.55	−0.33	−0.27	−0.48	−0.78[a]
248.	c-$Pt(PEt_3)_2C_6H_4F$(p)	Me_2CO	11.4	3.55	−0.33	−0.26	−0.48	−0.77[a]
249.	c-$Pt(PEt_3)_2Cl$	Me_2CO	9.75	3.37	−0.30	−0.21	−0.43	−0.57
250.	c-$Pt(PEt_3)_2CN$	Me_2CO	9.48	2.85	−0.23	−0.22	−0.36	−0.51
			2. Other Transition-Metal Substituents					
251.	$NiP(C_6H_5)_3(\pi C_5H_5)$	CH_2Cl_2	12.35	3.71	−0.35	−0.29	−0.51	−0.82[a]
252.	$Mn(CO)_3[P(OEt)_3]_2$	CH_2Cl_2	11.75	4.89	−0.51	−0.23	−0.64	−0.89[a]
253.	$Fe(CO)_2(\pi C_5H_5)$	CH_2Cl_2	10.92	2.37	−0.17	−0.29	−0.34	−0.65[a]
254.	$Mn(CO)_4P(n\text{-}C_4H_9)_3$	CH_2Cl_2	9.97	2.63	−0.20	−0.24	−0.34	−0.61[a]
255.	$Mn(CO)_4P(OEt)_3$	CH_2Cl_2	9.78	2.86	−0.23	−0.23	−0.37	−0.62[a]
256.	$Mn(CO)_4P(OMe)_3$	CH_2Cl_2	9.48	2.49	−0.18	−0.23	−0.32	−0.57[a]
257.	$Mn(CO)_4P(C_6H_5)_3$	CH_2Cl_2	9.26	2.08	−0.13	−0.24	−0.28	−0.54[a]
258.	$Mn(CO)_4P(OC_6H_5)_3$	CH_2Cl_2	9.20	2.32	−0.16	−0.23	−0.30	−0.55[a]
259.	$Mn(CO)_4As(C_6H_5)_3$	CH_2Cl_2	9.01	2.02	−0.12	−0.23	−0.26	−0.51[a]
260.	$Mn(CO)_5$	c-C_6H_{12}	7.25	0.14	0.14	−0.23	−0.01	−0.24[a]
261.	$Ti(\pi C_5H_5)_2C_6H_4F$(sym)	C_6H_6	7.14	2.30	−0.16	−0.15	−0.26	−0.36
			Onium Ion Substituents					
262.	9-xanthyl$^+$	CH_2Cl_2	−7.92	−2.91	0.56	0.15	0.58	0.66
263.	(p-anisyl)(Ph)C^+	CH_2Cl_2	−20.8	−3.00	0.57	0.51	0.76	1.05
264.	$(C_6H_5)_2C_3^+$	CF_3COOH	−23.1	−7.0	1.12	0.46	1.26	1.54
265.	$(C_6H_5)_2C^+$	CF_3COOH	−32.9	−6.84	1.10	0.74	1.38	1.82
266.	NMe_3^+	CH_3OH	−3.28	−6.08	0.99	−0.08	0.89	0.84
267.	PMe_3^+	CH_3OH	−10.3	−4.3	0.75	0.18	0.78	0.88
268.	$P(Ph_2)Me^+$	CH_3OH	−11.9	−5.1	0.86	0.20	0.89	1.01
269.	$P^+(Ph)_3$	CH_3OH	−12.83	−5.94	0.97	0.20	1.00	1.12

TABLE IV (Continued)

	substituent, Y	solvent	$-f_H^{p-Y}$	$-f_H^{m-Y}$	σ_F	σ_R	$c\sigma_m$	$c\sigma_p$
270.	$S(Me)_2^+$	CH_3OH	-10.58	-6.19	1.01	0.13	1.01	1.09
271.	$S(Et)_2^+$	CH_3OH	-11.96	-6.5	1.05	0.16	1.06	1.16
272.	$As(Ph)_3^+$	CH_3OH	-10.9	-6.5	1.05	0.13	1.05	1.13

[a] Calculated by using the enhanced σ_R value obtained from eq 18. [b] From a collection of values of F NMR substituent chemical shifts by R. W. Taft no longer kept current after ca. 1973. Both published and unpublished results are included. Results in c-C_6H_{12}, CCl_4, CH_2Cl_2, CH_3OH, and CF_3CO_2H are generally from work of Taft and co-workers, refs 43 and 55, or below. Exceptions in c-C_6H_{12} and CH_2Cl_2 are principally the results with transition-metal substituents from Parshall, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 704, and from Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710. Results in Cl_3CF generally are from W. A. Sheppard and co-workers (below). Many of the shifts in various solvents are summarized in Van Wazer, J. R.; Dungan, C. H. *Compilation of Reported F^{19} NMR Chemical Shifts. 1951-Mid-1967*; Wiley-Interscience: New York, 1970; New York, pp 3889–4223. Positive values of $-\delta_H^{m-Y}$ and $-\delta_H^{p-Y}$ denote upfield shifts (shielding) in ppm for meta and para substituted fluorobenzenes, respectively, relative to internal fluorobenzene in 0.10 (or less) M solutions. Some additional references are as follows: (1) Eaton, D. R.; Sheppard, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 1310. (2) Maciel, G. E. *J. Am. Chem. Soc.* **1964**, *86*, 1269. (3) Taft, R. W.; Carter, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4199. (4) Sheppard, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 2410. (5) Taft, R. W.; McKeever, L. D. *J. Am. Chem. Soc.* **1965**, *87*, 2489. (6) Taft, R. W.; Klingensmith, G. B.; Ehrenson, S. *J. Am. Chem. Soc.* **1965**, *87*, 3620. (7) Fawcett, F. S.; Sheppard, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 4341. (8) Taft, R. W.; Rakskys, J. W. *J. Am. Chem. Soc.* **1965**, *87*, 4387. (9) Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058. (10) Pews, R. G.; Tsuno, Y.; Taft, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 2391. (11) Giam, C. S.; Taft, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 2397. (12) Cairncross, A.; Sheppard, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 2168. (13) Rakskys, J. W.; Taft, R. W.; Sheppard, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 5236. (14) Kitching, W.; Adcock, W.; Hegarty, B. F. *Aust. J. Chem.* **1968**, *21*, 2411. (15) Uschold, R. E.; Taft, R. W. *Org. Magn. Res.* **1969**, *1*, 375. (16) Timberlake, J. W.; Thompson, J. A.; Taft, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 274. (17) Sheppard, W. A.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 1919. (18) Brownlee, R. T. C.; Dayal, S. K.; Lyle, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 7208.

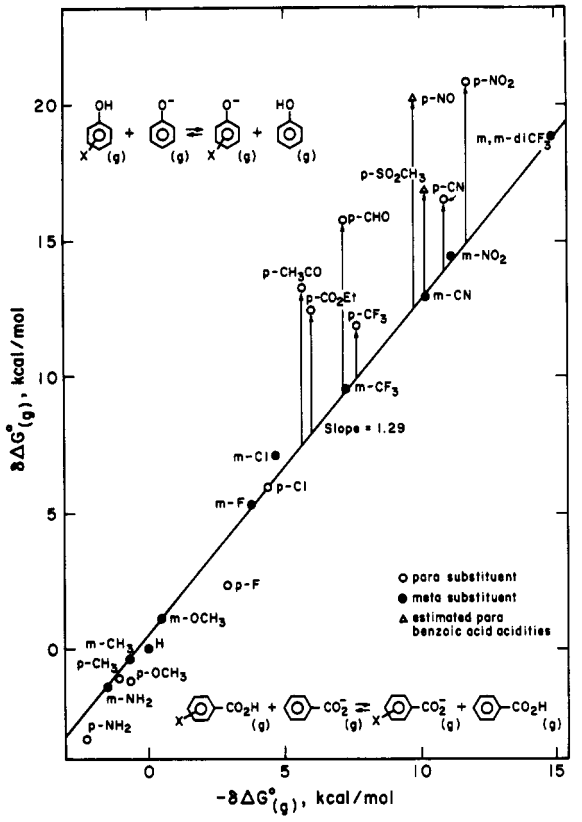


Figure 2. Enhanced resonance effects of para-π acceptor substituents in the gas phase acidities of phenols relative to benzoic acids.

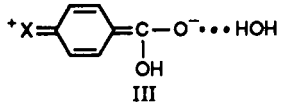
benzoic acids.[30,51] The closed circle points are for unconjugated meta- and para-substituents and these points give

$$-\delta\Delta G°_{(g)} = -0.03 + 11.1(-\delta\Delta G°_{(aq)}) \qquad (17)$$

$n = 14$, $r = 0.974$,

$s = 1.0$ kcal/mol (or 0.09 in σ_m or σ_p)

The open circle points are for conjugated para π-electron donor substituents which all deviate in the direction of enhanced resonance effects in water. The enhancements are most notable for *p*-F, *p*-OMe, and *p*-NH_2, i.e., they tend to increase as π-donation increases. Hydrogen bonding by water to the carbonyl oxygen of the un-ionized benzoic acids (in the high dielectric constant of water) accounts for the enhanced negative σ_p, values probably through transquinoidal resonance of III. The high dielectric constant of water,



III

together with its ability to strongly solvate by hydrogen bonding the COO^- and OH centers of both the ionized and neutral forms of benzoic acids, contributes to the 11-fold reduction of substituent effects in water vs the gas-phase as indicated by eq 17.

Several additional kinds of evidence support these conclusions. Figure 2 shows the gas-phase relative acidities, $-\delta\Delta G°_{(g)}$ of meta- and para-substituted phenols plotted against the corresponding gas-phase relative acidities of meta- and para-substituted benzoic acids. Para π-electron acceptor (+R) substituents show large, but variable, acidity enhancements in the phenol series (σ_p^- type behavior) compared to the approximately linear Hammett relationship followed satisfactorily by all of the other substituents. The failure of Figure 2 to display enhanced resonance effects for para π-electron donor (-R) substituents for the gas-phase benzoic acids indicates the absence of transquinoidal resonance when there is no aqueous medium present. This is also indicated by the relative acidities of meta- and para-substituted benzoic acids in ion-pair formation with 1,3-diphenylguanidine in very dilute benzene solution.[52] A Hammett plot of this series gives a satisfactory linear relationship, except for the para -R substituents. These show significantly smaller acid weakening effects than expected from the aqueous σ_m and σ_p constants (cf. Table IX). Finally, the F NMR substituent chemical shifts of meta- and para-substituted fluorobenzenes show that $-\sigma_R$ values (Table IV) are significantly less than the corresponding (aqueous benzoic acid) $-R$ values (Table I) for the strong π-donor substituents.

A final point that corroborates the interpretation of Figure 1, is that the R values in Table I for -R para substituents are roughly correlated with the gas-phase

TABLE V. Resonance Parameters R^+ and R^-

substituent	σ_p^+	ref	σ_p^-	ref	F	R^+	R^-
1. BCl_2	0.86	267					
2. Br	0.15	194	0.25	206	0.45	−0.30	−0.20
3. $SiBr_3$	0.41	245			0.44	−0.03	
4. Cl	0.11	194	0.19	251	0.42	−0.31	−0.23
5. $P(O)Cl_2$	0.38	208			0.70	−0.32	
6. PCl_2	0.62	208			0.50	0.12	
7. $P(S)Cl_2$	0.33	208			0.63	−0.30	
8. $GeCl_3$	0.57	249			0.65	−0.08	
9. $SiCl_3$	0.57	249			0.44	0.13	
10. F	−0.07	194	−0.03	198	0.45	−0.52	−0.48
11. SO_2F			1.54	109	0.72		0.82
12. SF_5			0.86	179	0.56		0.30
13. I	0.14	194	0.27	251	0.42	−0.28	−0.15
14. NO			1.63	197	0.49		1.14
15. NO_2	0.79	194	1.27	87	0.65	0.14	0.62
16. $N^+{\equiv}N$			3.43	182	1.58		1.85
17. N_3			0.11	130	0.48		−0.37
18. O^-	−2.30	218	−0.82	88	−0.26	−2.04	−0.56
19. SO_2^-			0.08	235	0.03		0.05
20. PO_3^-			−0.16	202			
21. SO_3^-			0.58	239	0.29		0.29
22. S^-	−2.62	269			0.03	−2.56	
23. H	0.00		0.00		0.00	0.00	0.00
24. AsO_3H^-			0.46	244	0.04		0.42
25. OH	−0.92	194	−0.37	251	0.33	−1.25	−0.70
26. SH	−0.03	269			0.30	−0.33	
27. $As(O)(OH)_2$			0.97	244	0.04		0.93
28. $B(OH)_2$	0.38	267			−0.03	0.41	
29. NH_2	−1.30	194	−0.15	195	0.08	−1.38	−0.23
30. SO_2NH_2			0.94	196	0.49		0.45
31. PH_2	0.06	253			0.09	−0.03	
32. NH_3^+			−0.56	74	0.92		−1.48
33. SiH_3	0.14	237			0.06	0.08	
34. 5-chloro-1-tetrazolyl			0.70	165	0.58		0.12
35. COCl	0.79	236	1.24	250	0.46	0.33	0.78
36. CF_3	0.61	194	0.65	178	0.38	0.23	0.27
37. $N{=}NCF_3$	0.74	72			0.50	0.24	
38. OCF_3			0.27	145	0.39		−0.12
39. $S{=}O(CF_3)$			1.05	221	0.58		0.47
40. $SO_2(CF_3)$			1.63	221	0.74		0.89
41. OSO_2CF_3			0.49	221	0.56		−0.07
42. SCF_3			0.64	145	0.36		0.28
43. $SeCF_3$			0.53	221	0.43		0.10
44. CN	0.66	194	1.00	196	0.51	0.15	0.49
45. $N{=}C{=}O$	−0.19	236			0.31	−0.50	
46. $N{=}C{=}S$			0.34	238	0.51		−0.17
47. $SC{\equiv}N$			0.59	251	0.36		0.23
48. $N{=}N{-}C{\equiv}N$	1.03	72			0.56	0.47	
49. CO_2^-	−0.02	194	0.31	200	−0.10	0.08	0.41
50. COOR	0.48	194	0.64	87	0.34	0.14	0.30
51. $OCHF_2$			0.11	221	0.37		−0.26
52. $SOCHF_2$			0.93	221	0.51		0.42
53. SO_2CHF_2			1.44	221	0.67		0.77
54. 1-tetrazolyl			0.57	165	0.52		0.05
55. CHO	0.73	236	1.03	200	0.33	0.40	0.70
56. COOH	0.42	194	0.77	206	0.34	0.08	0.43
57. CH_2Br	0.02	243			0.14	−0.12	
58. CH_2Cl	−0.01	194			0.13	−0.14	
59. SO_2CH_2F			1.17	221			
60. $CONH_2$			0.61	206	0.26		0.35
61. OCH_2O–	−0.68	254			−0.11	−0.57	
62. CH_3	−0.31	194	−0.17	204	0.01	−0.32	−0.18
63. $SiCl_2(CH_3)$	0.08	245			0.29	−0.21	
64. $SiF_2(CH_3)$	0.23	245			0.32	−0.09	
65. OCH_3	−0.78	194	−0.26	198	0.29	−1.07	−0.55
66. CH_2OH	−0.04	243	0.08	200	0.03	−0.07	0.05
67. $S{=}O(CH_3)$			0.73	222	0.52		0.21
68. $S{=}O(OCH_3)$			0.89	235	0.24		0.65
69. SO_2CH_3			1.13	278	0.53		0.60
70. OSO_2CH_3	0.16	241			0.40	−0.24	
71. SCH_3	−0.60	194	0.06	214	0.23	−0.83	−0.17
72. $NHCH_3$	−1.81	269			−0.03	−1.78	
73. $NHC(NH_2){=}NH_2^+$			0.32	247			
74. $C{=}O(CF_3)$	0.85	236	1.09	266	0.54	0.31	0.55
75. CF_2CF_3			0.69	165	0.44		0.25
76. OCF_2CF_3			0.28	178	0.55		−0.27
77. $N(CF_3)_2$			0.53	145	0.35		0.18

TABLE V (Continued)

substituent	σ_p^+	ref	σ_p^-	ref	F	R^+	R^-
78. C≡CH	0.18	171	0.53	223	0.22	−0.04	0.31
79. OCF_2CF_2H			0.21	178	0.38		−0.17
80. SCF_2CF_2H			0.61	178	0.35		0.26
81. $\bar{C}HCN$	−4.67	271					
82. CH_2CF_3			0.14	109	0.15		−0.01
83. CH_2CN	0.16	243	0.11	263	0.17	−0.01	−0.06
84. CH=$CHNO_2$-*t*			0.88	193	0.36		0.52
85. $CH_2CO_2^-$	−0.53	271	−0.16	88			
86. CH=CH_2	−0.16	248			0.13	−0.29	
87. $COCH_3$			0.84	200	0.33		0.51
88. SC=$O(CH_3)$			0.46	195	0.37		0.09
89. $OCOCH_3$	−0.19	265			0.42	−0.61	
90. $COOCH_3$	0.49	194	0.75	74	0.34	0.15	0.41
91. CH_2COOH	−0.01	243	0.05	263			
92. $NHCOCH_3$	−0.60	194	−0.46	251	0.31	−0.91	−0.77
93. CH_2CH_3	−0.30	194	−0.19	251	0.00	−0.30	−0.19
94. OCH_2CH_3	−0.81	256	−0.28	251	0.26	−1.07	−0.54
95. CH_2OCH_3	−0.05	243			0.13	−0.18	
96. CH_2CH_2OH			−0.15	251			
97. $SiCl(CH_3)_2$	0.02	245			0.16	−0.14	
98. $SiF(CH_3)_2$	0.17	245			0.17	0.00	
99. $N(CH_3)_2$	−1.70	194	−0.12	195	0.15	−1.85	−0.27
100. $SO_2N(CH_3)_2$	0.86	275	0.99	215	0.44	0.42	0.55
101. N=$NN(CH_3)_2$	−0.46	72			−0.03	−0.43	
102. $P(O)(CH_3)_2$			0.74	258	0.40		0.34
103. $P(CH_3)_2$			0.22	224	0.05		0.17
104. $P(S)(CH_3)_2$			0.62	224			
105. $S^+(CH_3)_2$			0.83	207	0.98		−0.15
106. $SiH(CH_3)_2$	−0.04	249			0.03	−0.07	
107. 1-(1,7-$(BH)_{10}$-C_2H)			0.32	242	0.23		0.09
108. 1-(1,2-$(BH)_{10}$-C_2H)			0.52	210	0.50		0.02
109. 2-(4,6-dichloro-s-triazinyl)			0.85	240			
110. CF=$CFCF_3$			0.65	221	0.36		0.29
111. $CF(CF_3)_2$			0.68	172	0.31		0.37
112. $SO_2(CF_2)_2CF_3$			1.75	70	0.81		0.94
113. $SO_2CF(CF_3)_2$			1.76	70	0.80		0.96
114. $S(CF_2)_2CF_3$			0.65	70	0.43		0.22
115. $SCF(CF_3)_2$			0.69	70	0.46		0.23
116. $COH(CF_3)_2$			0.48	172	0.29		0.19
117. CH=$CHCF_3$-*t*			0.34	165	0.24		0.10
118. CH=$CHCF_3$-*c*			0.29	165	0.18		0.11
119. CH=$CHSO_2CF_3$			0.83	221	0.22		0.61
120. CH=CHCOOH			0.62	188			
121. cyclopropyl	−0.41	209	−0.09	204	0.02	−0.43	−0.11
122. CH_2CH=CH_2	−0.22	279	−0.18	201	−0.06	−0.16	−0.12
123. CH_2COCH_3	0.03	243					
124. COOEt	0.48	194	0.75	251	0.34	0.14	0.41
125. CH_2COOCH_3			0.07	88			
126. $CH_2CH_2CH_2$–	−0.41	226					
127. $CON(CH_3)_2$			0.70	266			
128. $CH(CH_3)_2$	−0.28	194	−0.16	251	0.04	−0.32	−0.20
129. $CH_2CH_2CH_3$	−0.29	225	−0.06	251	0.01	−0.30	−0.07
130. $OCH(CH_3)_2$	−0.85	254			0.34	−1.19	
131. $OCH_2CH_2CH_3$	−0.83	256			0.26	−1.09	
132. $N^+(CH_3)_3$	0.41	194	0.77	206	0.86	−0.45	−0.09
133. $Si(CH_3)_2OCH_3$	−0.02	245			0.09	−0.11	
134. $SiCH_3(OCH_3)_2$	0.01	245			0.05	−0.04	
135. $Si(OCH_3)_3$	0.13	245			0.10	0.03	
136. $P^+(CH_3)_3$			0.95	258	0.36		0.59
137. $Si(CH_3)_3$	0.02	194			0.01	0.01	
138. $Sn(CH_3)_3$	−0.12	216			0.34	−0.46	
139. $C(CF_3)_3$			0.71	120	0.29		0.42
140. $(CF_2)_3CF_3$			0.73	172	0.44		0.29
141. $SO_2C(CF_3)_3$			1.81	70	0.84		0.97
142. $SC(CF_3)_3$			0.79	70	0.47		0.32
143. CH=$C(CN)_2$	0.82	241	1.20	165	0.57	0.25	0.63
144. 2-furyl	−0.39	228	0.21	228	0.10	−0.49	0.11
145. 2-thienyl	−0.43	228	0.19	159	0.13	−0.56	0.06
146. 3-thienyl	−0.38	228	0.13	159	0.08	−0.46	0.05
147. 2-selenieyl			0.22	84	0.10		0.12
148. 2-tellurienyl			0.25	84	0.10		0.15
149. CH=CH—CH=CH–	−0.14	194	0.12	197	0.19	−0.33	−0.07
150. CH=$CHCOCH_3$	0.39	261			0.31	0.08	
151. cyclobutyl	−0.29	127	−0.07	204	0.02	−0.31	−0.09
152. CH_2COOEt	−0.16	194					
153. $CH_2CH_2CH_2CH_2$–	−0.41	226			−0.40	−0.01	
154. $C(CH_3)_3$	−0.26	194	−0.13	206	−0.09	−0.17	−0.04

TABLE V (Continued)

substituent	σ_p^+	ref	σ_p^-	ref	F	R^+	R^-
155. $CH_2CH(CH_3)_2$			0.01	251	−0.01		0.00
156. $(CH_2)_3CH_3$	−0.29	225	−0.12	251	−0.01	−0.28	−0.11
157. $As(Et)_2$			0.08	219	0.32		−0.24
158. $N(Et)_2$	−2.07	231	−0.43	251	0.01	−2.08	−0.44
159. $CH_2Ge(CH_3)_3$	−0.61	262					
160. $CH_2N^+(CH_3)_3$			0.57	88	0.38		0.19
161. $CH_2Si(CH_3)_3$	−0.62	229	−0.22	132	0.00	−0.62	−0.22
162. $CH_2Sn(CH_3)_3$	−0.92	229					
163. $C(CN)=C(CN)_2$			1.70	165	0.65		1.05
164. 2-pyridyl			0.55	266	0.40		0.15
165. 3-pyridyl			0.58	266	0.24		0.34
166. 4-pyridyl			0.81	266	0.21		0.60
167. cyclopentyl	−0.30	127	−0.18	204	0.02	−0.32	−0.20
168. $CH_2CH=C(CH_3)_2$	−0.26	279					
169. $CH_2C(CH_3)_3$	−0.31	270			−0.09	−0.22	
170. $(CH_2)_4CH_3$			−0.19	201	−0.01		−0.18
171. $CH_2CH_2N^+(CH_3)_3$			0.09	88	0.19		−0.10
172. $CH_2CH_2Si(CH_3)_3$			−0.16	132	−0.11		−0.05
173. $Si(CH_3)_2Si(CH_3)_3$	−0.23	246	0.02	246			
174. C_6F_5	0.23	255	0.43	257	0.32	−0.09	0.11
175. C_6H_4-4-Br	−0.18	226	0.03	212	0.20	0.38	−0.17
176. C_6H_4-3-Cl	−0.15	226			0.19	−0.34	
177. C_6H_4-4-Cl	−0.19	226			0.18	−0.37	
178. C_6H_4-4-NO_2	0.04	260	0.31	212	0.26	−0.22	0.05
179. SC_6H_4-4-NO_2	−0.17	225	0.56	212	0.36	−0.53	0.20
180. $SO_2C_6H_4$-3-NO_2			1.04	217			
181. $SO_2C_6H_4$-4-NO_2			1.06	213			
182. 2-benzotriazolyl			0.57	220	0.47		0.10
183. C_6H_5	−0.18	194	0.02	212	0.12	−0.30	−0.10
184. $N=NC_6H_5$	−0.19	225	0.45	212	0.30	−0.49	0.15
185. OC_6H_5	−0.50	194	−0.10	212	0.37	−0.87	−0.47
186. SOC_6H_5			0.76	266	0.51		0.25
187. $SO_2C_6H_5$			1.21	213	0.56		0.65
188. $SO_2OC_6H_5$			1.11	233	0.37		−1.48
189. SC_6H_5	−0.55	225	0.18	212	0.30	−0.85	−0.12
190. SeC_6H_5	−0.47	268	0.13	212			
191. NHC_6H_5	−1.40	194	−0.29	212	0.03	−1.43	−0.32
192. $NHSO_2C_6H_5$	−0.98	269			0.24	−1.22	
193. $SO_2C_6H_4$-4′-NH_2			1.33	213			
194. cyclohexyl	−0.29	127	−0.14	204	0.03	−0.32	−0.17
195. $CH_2CH_2CH_2N^+(CH_3)_3$			0.09	88	0.12		−0.03
196. $Si(OEt)_3$	0.17	237			0.03	0.14	
197. $Si(Et)_3$	0.04	249					
198. 2-benzoxazolyl			0.68	234	0.30		0.38
199. 2-benzothiazolyl			0.65	234	0.27		0.38
200. COC_6H_5	0.51	236	0.83	74	0.31	0.20	0.52
201. $OCOC_6H_5$	−0.07	272			0.26	−0.33	
202. $N=CHC_6H_5$			0.22	199	0.14		0.08
203. $CH=NC_6H_5$			0.54	199	0.33		0.21
204. $NHCOC_6H_5$	−0.60	194			0.13	−0.73	
205. $CH_2C_6H_5$	−0.28	225	−0.09	212	0.17	−0.45	−0.26
206. $C\equiv CC_6H_5$	−0.03	192	0.30	212	0.15	−0.18	0.15
207. $CH=CHC_6H_5$	−1.00	192	0.13	259	0.10	−1.10	0.03
208. $CH_2CH_2C_6H_5$	−0.28	225	−0.12	212	−0.01	−0.27	−0.11
209. $Si(CH_3)_2C_6H_5$	0.08	273			0.06	0.02	
210. $S(CH_3)=NSO_2C_6H_4$-4′-CH_3			1.00	205	0.61		0.39
211. 2-(benzo-1,4-pyronyl)			0.70	61			
212. ferrocenyl	−1.00	141	−0.03	141	−0.09	−0.91	0.06
213. 1-adamantyl	−0.38	270	−0.14	252	−0.07	−0.31	−0.07
214. $As(C_6H_5)_2$			0.29	219	0.04		0.25
215. $PO(C_6H_5)_2$	0.52	208	0.68	211	0.32	0.20	0.36
216. $P(C_6H_5)_2$	0.70	208	0.26	230	0.10	0.60	0.16
217. $PS(C_6H_5)_2$			0.73	230	0.23		0.50
218. $CH(C_6H_5)_2$	−0.19	264			−0.01	−0.18	
219. $Si(CH_3)(C_6H_5)_2$	−0.04	276			0.11	−0.15	
220. $Ge(C_6H_5)_3$	−0.15	249			0.20	−0.35	
221. $N=P(C_6H_5)_3$	−1.65	232	−0.77	227	−0.10	−1.55	−0.67
222. $Si(C_6H_5)_3$	0.12	237	0.29	132	−0.04	0.16	0.33
223. $C(C_6H_5)_3$	−0.21	264			0.01	−0.22	

σ_R^+ values of Taft and Topsom (cf. extended Table X). On the basis of the para substituents, NMe_2, $N=P(C_6H_5)_3$, OCH_3, $OCH=CH_2$, OC_6H_5, F, c-C_3H_5, Cl, Br, $CH=CH_2$, CH_3, C_6H_5, CH_2OCH_3, $C(OCH_3)_3$, CH_2F, C_6Cl_5 and H, eq 18 is obtained

$$R = 1.41\ (\pm 0.06)\sigma_R^+ + 0.00\ (\pm 0.01) \quad (18)$$
$$n = 17,\ r = 0.989,\ s = 0.04$$

In obtaining eq 18 we have excluded the −R substituents that are hydrogen-bond donors to water: OH,

TABLE VI. Selected Substituents Having Extreme Values of *F* and *R*

substituent	*F*	σ_F (F NMR)	substituent	*R*	σ_R (F NMR)
$N^+{\equiv}N$	1.58		BCl_2		0.34
$I{=}NSO_2CF_3$	1.20		$C(CN){=}C(CN)_2$	0.33	0.26
$I(OCOCF_3)_2$	1.18		$CH{=}CHSO_2CF_3$	0.33	0.22
$P(=NSO_2CF_3)(C_3F_7)_2$	1.11		$N^+{\equiv}N$	0.33	
$SO(CF_3){=}NSO_2CF_3$	1.09		COCN		0.31
$As^+(C_6H_5)_3$		1.05	SO_2CN	0.29	0.27
$P^+(CH_3)(C_6H_5)_2$	1.04	0.86	BF_2	0.26	0.28
ICl_2	1.03	1.15	$CH{=}C(CN)_2$	0.28	0.25
$NHNO_2$	0.99		$SO_2C_2F_5$	0.27	
IF_4	0.98		PF_4	0.26	0.28
S^+Me_2	0.98	1.10	$COCF_3$	0.22	0.27
SO_2CN	0.97	0.99	$CONHC_6H_5$	0.24	
$N(CN)_2$		0.94	4-pyridyl	0.23	
$P(Et)_3$	0.94		SO_2CF_3	0.22	0.26
$C(CN)_3$	0.92	0.95	$P^+(C_6H_5)_3$		0.20
$N^+(CH_3)_3$	0.86	9.99	SiF_3	0.22	0.21
$SO_2C(CF_3)_3$	0.84		SO_2F	0.19	0.22
IF_2	0.82		SO_2CH_3	0.19	
SO_2CF_3	0.74	0.83	$COCH_3$	0.17	0.16
OCN	0.69	0.86	PF_2	0.15	0.18
NO_2	0.65		CN	0.16	
COCN		0.62	SF_3	0.17	0.17
$B(OH)_3$	−0.42		NO_2	0.13	0.16
t-Pt(PEt)$_3$Me		−0.43	S^-	−1.24	
$Ni(C_6H_5)_3(\pi\text{-}C_5H_5)$		−0.35	$N(CH_3)_2$	−0.98	−0.56
NHC_4H_9	−0.21		$OCH(CH_3)_2$	−0.79	
$(CH_2)_3$	−0.20		NHC_6H_5	−0.78	−0.35
OCH_2O–	−0.11		NH_2	−0.74	−0.48
CO_2^-	−0.10		$N{=}CHC_6H_5$	−0.69	
$N{=}P(C_6H_5)_3$	−0.10	−0.12	$N{=}P(C_6H_5)_3$	−0.67	−0.46
ferrocenyl	−0.09		NHEt	−0.57	
1-adamantyl	−0.07		OCH_3	−0.56	−0.43
Me	0.01		$OCH_2CH{=}CH_2$	−0.50	
cyclopropyl	0.02		NHOH	−0.45	
$C^+(C_6H_5)_2$		0.74	$OCH{=}CH_2$	−0.43	−0.31
N=NCN	0.47		N_3	−0.40	
$C_6^+(C_6H_5)_2$		0.46	F	−0.39	−0.33
NO	0.42	0.25	$Fe(CO)_2(\pi C_5H_5)$		0.29
$CH{=}NSO_2CF_3$	0.37				

SH, $NHCOCH_3$, $NHNH_2$, NHC_6H_5, and NH_2. Further, the σ_R^+ values for $N{=}P(C_6H_5)_3$, $OCH{=}CH_2$, $C(OCH_3)_3$, and C_6H_5 have been taken as equal to the σ_R values obtained from F NMR substituent chemical shifts of meta- and para-substituted fluorobenzenes (Table IV).

C. R^+ and R^- Values

One of the shortcomings of the Hammett constant σ_p, which was recognized early,[53] is that correlations obtained with it were poor when the substituents were conjugated with the reaction center. The first case where this problem arose was with phenols and anilinium ions where a lone pair of electrons on the O^- or NH_2 group could be delocalized into substituents such as *p*-NO_2 and *p*-CN. This problem was solved by defining a new constant σ_p^- obtained from the phenol or aniline data. Later H. C. Brown[54] and his colleagues developed σ_p^+ constants for substituents conjugated with a reaction center which could effectively delocalize a positive change. The OCH_3 group in the nitration of anisole is a typical example. The σ_p^+ constants can be used in eq 2 to define R^- and R^+ which are regarded as resonance constants.[4] In Table V we have assembled all of the σ_p^- and σ_p^+ values which we could find and, using the appropriate *F* values we have by eq 12 calculated R^+ and R^-. In a number of examples σ_p^+ and σ_p^- have been listed but no *F* values are yet available for calculating the *R* resonance constants. There are 113 R^+ and 143 R^- values in Table V. In their studies on factoring σ into *F* and *R*, Swain and Lupton argued that a single *R* value should suffice for all kinds of resonance effects. However, we have never accepted this point of view,[4] nor have prominent workers in this field.

In Table V are considered the R^+ and R^- substituent parameters that are made available from the σ_p^+ and σ_p^- values, respectively, through eq 2. Compared to the corresponding values of *R*, (Table I) the R^+ values for *π-electron donor substituents* are significantly enhanced. The enhancements involve changes in electron demand that are produced by solvated π-electron deficient reaction centers, as well as by solvation of certain substituents. Nonetheless, a fairly reasonable correlation is found between corresponding R^+ and *R* values for the π-electron donor substituents.

$$\pi\text{-donors:} \quad R^+ = 1.90\ (\pm 0.26)R - 0.07\ (\pm 0.11) \tag{19}$$

$$n = 29,\ r = 0.945,\ s = 0.170$$

In contrast, R^+ values for the π-electron acceptor substituents in these same reaction series remain nearly equal to their corresponding *R* values (eq 20).

$$\pi\text{-acceptors:} \quad R^+ = 1.16\ (\pm 0.45)R - 0.01\ (\pm 0.07) \tag{20}$$

$$n = 16,\ r = 0.829,\ s = 0.060$$

TABLE VII. Values of σ_I for Various Heterocycles Obtained from the pK_a of Guanidines[41]

substituent	σ_I
1. pyrimidin-2-yl	0.23
2. pyrimidin-4-yl	0.26
3. 1,2,4-triazin-6-yl	0.37
4. 2-furyl	0.17
5. 3-furyl	0.10
6. 2-thienyl	0.19
7. 3-thienyl	0.10
8. pyrrol-2-yl	0.17
9. indol-3-yl	0.01
10. 1-phenylpyrazol-3-yl	0.21
11. oxazol-2-yl	0.38
12. imidazol-2-yl	0.27
13. 1-methylimidazol-2-yl	0.26
14. imidazol-4(5)-yl	0.08
15. 1,2,4-oxadiazol-5-yl	0.49
16. 1,2,4-thiadiazol-5-yl	0.41
17. 2*H*-1,2,3-triazol-2-yl	0.41
18. pyridin-2-yl	0.18
19. 6-methylpyridin-2-yl	0.17
20. quinolin-6-yl	0.17
21. pyrazin-2-yl	0.25
22. 6-methylpyrazin-2-yl	0.24
23. 5,6-dimethylpyrazin-2-yl	0.23
24. quinoxazin-2-yl	0.27
25. 4,6-dimethylpyrimidin-2-yl	0.21
26. 4-phenylpyrimidin-2-yl	0.21
27. 4-methylquinazolin-2-yl	0.22
28. 2-methylpyrimidin-4-yl	0.25
29. 2-phenylpyrimidin-4-yl	0.28
30. pyridazin-3-yl	0.26
31. 3-methyl-1,2,4-triazin-6-yl	0.36
32. 3-phenyl-1,2,4-triazin-6-yl	0.40
33. 4-methyloxazol-2-yl	0.37
34. 4,5-dimethyloxazol-2-yl	0.35
35. benzoxazol-2-yl	0.41
36. thiazol-2-yl	0.34
37. 4-methylthiazol-2-yl	0.32
38. 4,5-dimethylthiazol-2-yl	0.31
39. benzothiazol-2-yl	0.37
40. 4-methylimidazol-2-yl	0.26
41. 1-methylimidazol-2-yl	0.26
42. benzimidazol-2-yl	0.32
43. 1-phenylpyrazol-3-yl	0.21
44. 3-methyl-1,2,4-oxadiazol-5-yl	0.48
45. 3-methyl-1,2,4-thiadiazol-5-yl	0.40
46. 2*H*-1,2,3-triazol-2-yl	0.41
47. tetrazol-5-yl	0.49
48. 3,4-dihydro-4-oxopyrimidin-2-yl	0.41
49. 3,4-dihydro-4-oxoquinazolin-2-yl	0.40
50. 1,6-dihydro-6-oxopyridazin-3-yl	0.27
51. 1,6-dihydro-1-methyl-6-oxopyridazin-3-yl	0.28
52. 4,5-dihydro-4-oxothiazol-2-yl	0.46

($SO_2N(CH_3)_2$ and CHO with deviations of 0.19 and 0.29, respectively, have been excluded). The results of eqs 19 and 20 show that a different resonance effect reaction constant is required for π-donors and π-acceptors. The poor precision of eq 20 reflects uncertainties in the reliability of R^+ values for π-electron acceptors in reaction series with π-electron deficient centers. In gas-phase proton-transfer equilibria that involve strongly π-electron deficient centers, resonance effects for π-acceptors are found to be very small (σ_R^+ for these substituents can reliably be taken as zero).[30]

Comparing corresponding R^- and R values for π-electron acceptor substituents in reactions with π-electron-rich centers shows that there are generally significant enhancements only for the former. Equation 21 gives the relatively crude correlation of the R^- values with corresponding R values (Table I). A major cause

π-donors: $$R^- = 1.93\ (\pm 0.59)R + 0.19\ (\pm 0.11) \quad (21)$$

$$n = 34,\ r = 0.758,\ s = 0.173$$

for the poor precision of eq 21 is that new solvation sites are created for certain substituents (most important for oxy-anionic substituents) as the result of strong conjugation with electron-rich reaction centers (the SSAR effects).[46] This solvation effect is known to be even more important in the solvent dimethyl sulfoxide than in aqueous solvents.[46d,e]

With π-electron donor substituents, no useful general correlation is found between R^- (Table V, reactions with π-electron-rich centers) and corresponding R values (Table I). For some, the expected π-electron saturation effects are observed $|R^-|$ values are significantly smaller than the corresponding $|R|$ values (this is true for N-$(CH_3)_2$, NH_2, I, c-C_3H_5 CH_3, C_2H_5, and SC_6H_5). For others, $|R^-| \cong |R|$ (as for OC_2H_5, OCH_3, OC_6H_5, OH SCH_3, Cl, Br, C_6H_5, and i-C_3H_7). Apparent anomalies are that $|R^-|$ values are significantly larger than corresponding $|R|$ values for $NHCOCH_3$, F, $CH_2Si(CH_3)_3$, and $CH_2C_6H_5$. Again it appears that R^- values for π-donor substituents (just as for R^+ values for π-acceptor substituents) are questionable. These anomalies are probably largely artifacts resulting from the restrictions of the Hammett single parameter treatment.

D. Resonance Effect σ_R Values from NMR Chemical Shifts of Para-Substituted Fluorobenzenes Relative to Their Meta Isomers as Internal References

These chemical shifts (in parts/million) were shown to be very sensitive measures of para-substituent π-electron donor acceptor interactions.[55] Dilutions of 0.05 to a few tenths molar solutions of the two isomers in solvents, such as CCl_4, $FCCl_3$, cyclohexane, benzene, methanol, and others, have been obtained for an extensive number of substituents. Table IV presents a representative summary of F NMR shifts in the indicated solvent relative to internal fluorobenzene for both para ($-f_H^{p\text{-}Y}$) and meta ($-f_H^{m\text{-}Y}$) isomers. Positive values denote upfield shifts (increased shielding) relative to fluorobenzene. The difference, $-f_H^{p\text{-}Y} + f_H^{m\text{-}Y} = -f_{m\text{-}Y}^{p\text{-}Y}$, permits a cancellation of the substituent field/inductive effects,[55] giving essentially the pure resonance effect. A correlation of values of $-f_{m\text{-}Y}^{p\text{-}Y}$ with corresponding values of σ_R^- from Taft and Topsom[30] for the following 18 π-acceptor or inactive substituents, H, $C(CF_3)_3$, C-$(CN)_3$, $C(Cl)_3$, $Si(CH_3)_3$, SF_5, CF_3, SCF_3, SO_2CH_3, $SO_2C_6H_5$, $CO_2C_2H_5$, $SiCl_3$, $COCH_3$, COC_6H_5, NO_2, NO, COCl, and $COCF_3$, gives eq 22.

$$\sigma_{R^-} = -0.0280\ (\pm 0.001)\left(-f_{m\text{-}Y}^{p\text{-}Y}\right) + 0.01\ (\pm 0.01) \quad (22)$$

$$n = 18,\ r = 0.982,\ s = 0.02$$

For the following π-donor (-R) substituents eq 23 is obtained for H and $N(CH_3)_2$, NH_2, OCH_3, OH, OC_6H_5, F, Cl, Br, CH_3, CH_2NH_2, CH_2OCH_3, CH_2CF_3, CH_2Cl, and CH_2F.

TABLE VIII. Values of σ_I for Substituents Not Listed in Table I Derived from Ionization Constants of Acetic Acids[29]

substituent	σ_I	substituent	σ_I	substituent	σ_I
1. $CH_2CH(CH_3)_2$	−0.01	53. $CH_2COOC_2H_5$	0.15	105. $OP[N(C_2H_5)_2]_2$	0.10
2. $(CH_2)_5CH_3$	−0.03	54. $(CH_2)_3CONH_2$	0.04	106. $OP(C_6H_5)C_3H_7$	0.27
3. CH_2-c-C_6H_{11}	−0.03	55. $CH_2N(NO_2)CH_2CH_2N(NO_2)CH_3$	0.14	107. $OP(C_6H_5)C_4H_9$	0.27
4. CH_2CH_2-c-C_6H_{11}	−0.04	56. $CH_2CH_2COOC_2H_5$	0.08	108. $OP(C_6H_5)CH_2CH(CH_3)_2$	0.26
5. $CH_2C{\equiv}CH$	0.14	57. $CH_2P(O)(C_2H_5)_2$	0.14	109. $OP(OC_6H_5)_2$	0.36
6. $C{\equiv}CCH{=}CH_2$	0.35	58. $(CH_2)_3COOC_2H_5$	0.04	110. $SCONH_2$	0.33
7. $CH_2CH_2C{\equiv}CH$	0.05	59. $CH_2CH_2P(O)(C_2H_5)_2$	0.07	111. $SCSCH_3$	0.45
8. $CH{=}C(CH_3)_2$	0.05	60. $CH_2CH_2P(O)(OC_2H_5)_2$	0.05	112. $SC(O)N(CH_3)_2$	0.31
9. $CH{=}CHC_2H_5$	0.07	61. $(CH_2)_4COOC_2H_5$	0.02	113. $SC(S)N(CH_3)_2$	0.36
10. $CH_2CH{=}CHCH_3$	0.02	62. $(CH_2)_3P(O)(OC_2H_5)_2$	0.03	114. $SC(S)OC_2H_5$	0.42
11. $CH_2CH_2CH{=}CH_2$	0.02	63. $CH_2CONHC_6H_5$	0.02	115. $SC(S)SC_2H_5$	0.46
12. $C{\equiv}CC{\equiv}CCH_3$	0.39	64. $CH_2SCH_2C_6H_5$	0.08	116. SC_3H_7	0.25
13. $CH_2CH_2CH_2C{\equiv}CH$	0.05	65. $CH(C_6H_5)COOCH_3$	0.11	117. $SCH_2CH_2CH{=}CH_2$	0.26
14. $CH_2CH{=}C(CH_3)_2$	0.00	66. $CH_2CH_2P(O)(C_6H_5)_2$	0.09	118. $SCH_2COOC_2H_5$	0.28
15. $CH(CH_3)C_6H_5$	0.07	67. $CH_2C(C_6H_5)_2COOCH_3$	0.03	119. SC_4H_9	0.26
16. $C(CH_3)_2C_6H_5$	0.05	68. $CH_2CH_2CH_2P(O)(C_2H_5)_2$	0.04	120. $SCH(CH_3)C_2H_5$	0.25
17. $(CH_2)_3C_6H_5$	0.01	69. $CH_2CH_2CH_2Si(CH_3)_3$	−0.04	121. $S(CH_2)_3CH{=}CH_2$	0.26
18. 1-naphthyl	0.14	70. $(CH_2)_4Si(CH_3)_3$	−0.07	122. $SCH(CH_3)COOC_2H_5$	0.26
19. 2-naphthyl	0.13	71. $Si(CH_3)_2C_6H_5$	−0.12	123. SC_5H_{11}	0.26
20. $(CH_2)_4C_6H_5$	0.00	72. $CON(CH_3)_2$	0.28	124. S-c-C_6H_{11}	0.32
21. methyl-1-naphthyl	0.08	73. $NHC(S)SCH_3$	0.39	125. SC_6H_{13}	0.25
22. $CH{=}CCl_2$	0.18	74. $NHCOC_2H_5$	0.26	126. $SC(CH_3)_2COOC_2H_5$	0.23
23. $C(Cl){=}CH_2$	0.55	75. $N(CH_3)C(S)SCH_3$	0.44	127. $SCH_2C_6H_5$	0.26
24. $CH{=}CHCl$-*c*	0.18	76. $N(NO_2)CH_2CH_2N(NO_2)CH_3$	0.39	128. $SCH_2CH_2C_6H_5$	0.25
25. $CH{=}CHCl$-*t*	0.17	77. $NHC(S)N(CH_3)_2$	0.27	129. $SC(C_6H_5)_3$	0.12
26. CH_2CCl_3	0.14	78. $NHP(O)(OC_2H_5)_2$	0.23	130. SC_6H_4-4′-OMe	0.27
27. $CH(Br)CH_3$	0.19	79. $NHCH_2C_6H_5$	0.28	131. $SO_2C_3H_7$	0.57
28. $CH(Cl)CH_3$	0.15	80. $N(C_6H_5)COCH_3$	0.23	132. $SO_2CH(CH_3)_2$	0.57
29. CH_2CH_2Br	0.05	81. N(1-naphthyl)$COCH_3$	0.27	133. SOC_6H_4-4′-OMe	0.50
30. CH_2CH_2Cl	0.07	82. N(2-naphthyl)$COCH_3$	0.29	134. $SO_2C_6H_4$-4′-NO_2	0.61
31. $CH_2CH{=}CCl_2$	0.05	83. $N(CH_3)C_6H_5$	0.15	135. $SO_2C_6H_4$-4′-OMe	0.71
32. $CH_2CH_2CCl_3$	0.07	84. ONH_2	0.16	136. $CH_2SO_3^-$	0.01
33. $CH_2CH_2CH_2Br$	0.02	85. $ON{=}C(CH_3)_2$	0.30	137. $CH_2CH_2SO_3^-$	−0.03
34. $CH_2CH_2CH_2Cl$	0.02	86. $OCON(CH_3)_2$	0.44	138. $CH{=}CHCH_2COO^-$	0.02
35. $CH_2CH_2CH_2CF_3$	0.15	87. $OCSN(CH_3)_2$	0.47	139. 3,4-diphenyltetrazolium-2-thiyl	0.57
36. CH_2ONO_2	0.20	88. $OCH(CH_3)CH_2CH_3$	0.28	140. $P^+(C_4H_9)_3$	0.60
37. CH_2CH_2OH	0.06	89. O-c-C_5H_9	0.27	141. $P^+(C_6H_5)_3$	0.75
38. $CH_2CH_2OCH_3$	0.00	90. O-c-C_6H_{11}	0.31	142. 2,3,5,6-F_4-C_6H	0.33
39. $CH_2CH(OH)CH(CH_3)_2$	−0.02	91. $OSO_2C_6H_4$-4′-CH_3	0.58	143. SeC_6H_5	0.26
40. $CH(OH)C_6H_5$	0.10	92. OCH_2-c-C_6H_{11}	0.22	144. Se-c-C_6H_{11}	0.40
41. $CH_2OSO_2C_6H_4$-4′-Me	0.23	93. bicyclo[4.4.0]decycloxy	0.28	145. $CH{=}CHCH_2COOH$	0.13
42. CH_2SH	0.12	94. OC_6H_4-4′-NO_2	0.47	146. C_6H_3-3,4-methylenedioxy	0.12
43. CH_2SeCN	0.22	95. $OCH_2C_6H_5$	0.43	147. 3-indolyl	0.01
44. CH_2SCH_3	0.12	96. OC_6H_4-4′-OCH_3	0.39	148. 2-pyridylmethyl	0.10
45. $CH_2NHCONH_2$	0.07	97. $OP(OC_2H_5)CH_3$	0.31	149. 2-pyrrolyl	0.17
46. $CH_2N(NO_2)CH_3$	0.16	98. $OP(OC_2H_5)C_2H_5$	0.30	150. 3-pyrazolylmethyl	0.09
47. CH_2CH_2CN	0.09	99. $OP(C_3H_7)_2$	0.26	151. 4-thiazolylmethyl	0.11
48. CH_2COOCH_3	0.19	100. $OP(C_6H_5)CH_3$	0.30	152. 4(5)-imidazolyl	0.12
49. $CH_2CH_2CONH_2$	0.05	101. $OP(OCH_3)C_6H_5$	0.32	153. 2-furylmethyl	0.05
50. $CH_2CH_2NHCONH_2$	0.03	102. $OP(C_6H_5)C_2H_5$	0.28	154. 2-thienylmethyl	0.06
51. $CH_2N(O)(CH_3)_2$	0.23	103. $OP(C_6H_5)OC_2H_5$	0.30	155. 4(5)-imidazolylmethyl	0.08
52. $CH_2CH_2CO_2CH_3$	0.07	104. $OP(OC_4H_9)C_4H_9$	0.27		

$$\sigma_{R^+} = -0.0359\ (\pm 0.004)\left(-\int_{m-Y}^{p-Y}\right) + 0.02\ (\pm 0.02) \quad (23)$$

$$n = 15, r = 0.978, s = 0.04$$

The coefficient to $-\int_{m-Y}^{p-Y}$ in eq 23 is 1.29 times greater than that for eq 22. That is, π-donor substituents are less sensitive than the π-acceptor substituents. This result is rational since the F detector atom is a π-donor to the benzene ring, giving enhanced donor–acceptor resonance effects, but reduced donor–donor resonance effects.

In Table IV are given the σ_R values calculated from $270\ -\int_{m-Y}^{p-Y}$ values by using eqs 22 and 23. In Table IX these σ_R values are compared with the corresponding R values for 147 substituents common to Tables I and IV. Excluding the 11 strongest –R substituents which have enhanced R values (as discussed above) and the SO_2Cl, HgMe, $CH{=}CHNO_2$-*t*, $P(CH_3)_2$, $P(CH_3)_3^+$, $CH{=}CHCN$, $C(CF_3)_3$, $S(CH_3)_2^+$, and $CNBCl_3$ substituents for which the $|R - \sigma_R|$ exceeds 0.20, eq 24 for R vs σ_R(F NMR) is obtained.

$$R = 0.953\ (\pm 0.050)\sigma_R(\text{F NMR}) + 0.006\ (\pm 0.01) \quad (24)$$

$$n = 125, r = 0.865, s = 0.068$$

For the 11 strong π-donor substituents, F, OH, NH_2, $NHNH_2$, OCH_3, $OCH{=}CH_2$, $NHCOCH_3$, $N(CH_3)_2$, OC_6H_5, NHC_6H_5, $N{=}P(C_6H_5)_3$, and H, eq 25 is obtained.

$$R = 1.68\ (\pm 0.23)\sigma_R(\text{F NMR}) + 0.04\ (\pm 0.09) \quad (25)$$

$$n = 12, r = 0.920, s = 0.13$$

The generality of eqs 24 and 25, indicates that the F NMR shift method can be utilized not only for obtaining reasonably reliable σ_F (or F) and σ_R (or R) values but also for calculation of Hammett σ_m and σ_p values.

TABLE IX. Substituent Parameters for the Gas-Phase Proton-Transfer Equilibria and Appropriate Condensed-Phase Processes and Media[a]

substituent	σ_α	σ_F	σ_{R^+}	σ_{R^-}
1. NEt_2	−0.56	0.10	−0.68	(−0.27)
2. NMe_2	−0.44	0.10	−0.64	−0.26
3. NHMe	−0.30	0.12	(−0.58)	−0.27
4. NH_2	−0.16	0.14	−0.52	−0.28
5. OPr	−0.26	0.25	−0.46	−0.27
6. OEt	−0.23	0.25	−0.45	−0.27
7. OMe	−0.17	0.25	−0.42	−0.27
8. OH	−0.03	0.30	−0.38	−0.28
9. OC_6H_5	−0.38	0.38	−0.32	
10. SEt	−0.74	0.24	−0.27	
11. SMe	−0.68	0.25	−0.27	
12. SH	−0.55	0.28	−0.25	
13. SC_6H_5	−0.88	0.34	−0.10	0.03
14. F	0.13	0.44	−0.25	−0.25
15. C_6H_5	−0.81	0.10	−0.22	0.22
16. Cl	−0.43	0.45	−0.17	−0.12
17. Br	−0.59	0.45	−0.15	−0.10
18. $CH{=}CH_2$	−0.50	0.06	−0.16	(0.16)
19. Me	−0.35	0.00	−0.08	0.03
20. Et	−0.49	0.00	−0.07	0.02
21. Pr	−0.54	0.00	−0.07	0.02
22. *i*-Pr	−0.62	0.00	−0.07	0.01
23. *c*-Pr	−0.62	0.00	−0.15	
24. Bu	−0.57	0.00	−0.07	0.02
25. *i*-Bu	−0.61	0.00	−0.07	0.02
26. *s*-Bu	−0.68	0.00	−0.07	0.01
27. *t*-Bu	−0.75	0.00	−0.06	0.00
28. Pent	−0.58	0.00	−0.07	0.02
29. neo-Pent	−0.67	0.00	−0.07	0.02
30. *t*-Pent	−0.82	0.00	−0.06	0.00
31. $c\text{-}C_6H_{11}$	−0.76	0.00	−0.06	0.01
32. 1-adamantyl	−0.95	0.00	−0.06	0.00
33. Oct	−0.59	0.00	−0.07	0.02
34. $C{\equiv}CH$	−0.60	0.23	(0.00)	(0.00)
35. $(CH_2)_2F$	−0.47	0.12	−0.07	0.02
36. $(CH_2)_2CF_3$	−0.55	0.12	−0.07	0.02
37. $(CH_2)_2Cl$	−0.57	0.12	−0.07	0.02
38. $(CH_2)_2OMe$	−0.52	0.07	−0.07	0.02
39. $(CH_2)_2C_6H_5$	−0.65	0.03	−0.07	0.02
40. $CH_2C_6H_5$	−0.70	0.05	−0.05	0.02
41. CH_2OMe	−0.42	−0.14	−0.06	0.02
42. $CH_2CH{=}CH_2$	−0.57	0.03	−0.07	0.02
43. $CH_2C{\equiv}CH$	−0.61	0.12	−0.07	0.02
44. CH_2CHF_2	−0.45	0.18	−0.06	0.02
45. CH_2Cl	−0.54	0.23	−0.05	0.02
46. CH_2F	−0.30	0.22	−0.03	0.02
47. CH_2CCl_3	−0.65	0.23	−0.05	0.02
48. CH_2CF_3	−0.46	0.23	−0.04	0.02
49. CHF_2	−0.27	0.36	0.00	0.04
50. $CH(CF_3)_2$	−0.57	0.44	0.00	0.01
51. $CHCl_2$	−0.62	0.36	0.00	0.02
52. $C(CF_3)_3$	−0.68	0.61	0.00	0.00
53. H	0.00	0.00	0.00	0.00
54. $SiMe_3$	−0.72	−0.02	0.00	0.06
55. CCl_3	−0.70	0.44	0.00	0.02
56. SF_5	−0.48	0.59	0.00	0.01
57. CF_3	−0.25	0.44	0.00	0.07
58. $SOCH_3$	−0.65	0.40	0.00	0.08
59. SOC_6H_5	−0.83	0.41	0.00	0.09
60. SCF_3	−0.64	0.48	0.00	0.10
61. CN	−0.46	0.60	(0.00)	0.10
62. SO_2Me	−0.62	0.59	0.00	0.12
63. $CONMe_2$	−0.59	0.19	0.00	
64. $SO_2C_6H_5$	−0.80	0.63	0.00	0.14
65. CO_2Me	−0.49	0.24	0.00	0.16
66. CO_2H	−0.34	0.28	0.00	0.16
67. COMe	−0.55	0.26	(0.00)	0.17
68. COC_6H_5	−0.75	0.28	0.00	0.18
69. NO_2	−0.26	0.65	0.00	0.18
70. CHO	−0.46	0.31	(0.00)	0.19
71. SO_2CF_3	−0.58	0.84	0.00	0.21
72. NO	−0.25	0.41	(0.00)	0.26
73. $COCF_3$	−0.51	0.50	0.00	0.26
74. COCN	−0.60	0.66	0.00	0.28

[a] From reference 30 and Taft, R. W., Koppel, I. A., Topsom, R. D., Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047.

TABLE X. Solvent Effects: σ_m and σ_p Values in Gas Phase and Benzene and Aqueous Solutions from Values of log (K/K_0) for Meta- and Para-Substituted Benzoic Acids

	gas phase[a]		benzene solution[b]		aqueous solution[c]	
substituent	σ_m	σ_p	σ_m	σ_p	σ_m	σ_p
1. NH_2	−0.10	−0.17	−0.16	−0.39	−0.16	−0.66
2. OCH_3	0.03	−0.05	0.06	−0.16	0.12	−0.27
3. F	0.25	0.19	0.33	0.17	0.34	0.06
4. Cl	0.31	0.29	0.38	0.27	0.37	0.23
5. CH_3	−0.05	−0.07	−0.06	−0.11	−0.07	−0.17
6. H	0.00	0.00	0.00	0.00	0.00	0.00
7. CF_3	0.49	0.51			0.43	0.54
8. CO_2CH_3		0.43			0.37	0.45
9. CH_3CO		0.37			0.38	0.50
10. HCO		0.47			0.35	0.42
11. CN	0.68	0.72	0.63	0.61	0.56	0.66
12. NO_2	0.72	0.78	0.75	0.74	0.71	0.78

[a] σ = log (K/K_0)/11.1; ref 30 and 51. [b] For ion-pair formation with 1,3-diphenylguanidine, benzene (very high dilution) 25 °C, σ = log (K/K_0)/2.08; ref 52. [c] From Table I.

These calculated values ($c\sigma_m$ and $c\sigma_p$) are given in Table IV and discussed in the next section.

The nearly unit coefficient to σ_R(F NMR) in eq 24 compared to the significantly greater than unit coefficient for the strong −R substituents in eq 25 provides further confirmation of the enhanced resonance effects of substituents of this kind in the aqueous acidities of para-substituted benzoic acids. It should also be noted that the coefficient of σ_R(F NMR) in eq 25 (1.68 ± 0.23) is the same within the confidence limits of the estimates as that for σ_R^+ values in eq 18 (1.41 ± 0.06).

The near equality of R and the corresponding σ_R(F NMR) values shown by eq 24 includes 24 substituents for which R and σ_R values are both zero within ±0.06. These are the π-neutral substituents for which $\sigma_p \cong \sigma_m \cong \sigma_F \cong F$ to very good precision and are as follows: 5-chloro-tetrazolyl, C_6F_5, C_6Cl_5, $CH{=}CHCF_3$ (cis and trans), NC^-, $N(COF)_2$, $HgOCOCH_3$, $P(CH_3)_2$, $SiHMe_2$, $Si[N(CH_3)_2]_3$, $SOCH_3$, CHX_2, CH_2X (where X = NMe_2, OH, F, Cl, Br, CF_3, SCF_3, $SOCF_3$, SO_2R, and SO_2CF_3), CH_2X (where X = F, Cl, Br, CN, and SCF_3), and CX_3 (where X = OCH_3, CN, Cl, Br, and SCF_3). Many other structurally similar substituents that exert little or no resonance effects can be found in Tables I and IV for substituents that are not common to *both* of these tables.

Among commonly used substituents, NO_2 is generally regarded to be strong, both in its field/inductive and π-electron acceptor resonance effects. The results of this survey confirm that NO_2 is moderately strong in its field/inductive effects, but there are a number of substituents that are significantly stronger. The nitro substituent is actually only a moderately strong π-electron acceptor. A significant part of the acceptor affects of NO_2 even in σ_p^- type reactivities has been shown to be a solvation effect.[46b,d] In Table VI are listed selected sets of F, σ_F (F NMR) or R and σ_R (F NMR) values from Table I and IV for substituents that are more extreme in their effects than the NO_2 substituent.

E. Calculated σ_m and σ_p Values and Shortcomings

From the 139 substituents common to Tables I and IV, eqs 26 and 27 have been derived. The calculated

values ($c\sigma_m$ and $c\sigma_p$) given in Table IV are quite reasonable and suggest that this method can be used to obtain σ values for substituents unstable in aqueous solution or other solutions. For individual substituents, values of corresponding σ and $c\sigma$ may be compared by reference to both Tables I and IV. In the case of eq

$$c\sigma_m = 0.971\ (\pm0.05)\sigma_F(\text{F NMR}) + 0.473\ (\pm0.07)\sigma_R(\text{F NMR}) - 0.036\ (\pm0.02) \quad (26)$$

$$n = 135,\ r = 0.972,\ s = 0.064$$

$$c\sigma_p = 0.985\ (\pm0.03)\sigma_F(\text{F NMR}) + 1.058\ (\pm0.03)\sigma_R(\text{F NMR}) - 0.047\ (\pm0.01) \quad (27)$$

$$n = 130,\ r = 0.984,\ s = 0.066$$

26, four data points (SO_2Cl, $CN{\cdot}BCl_3$, HgMe, and $SnMe_2$) were badly fit and hence not used in its derivation. Nine poorly fit data points were excluded in the derivation of eq 27 (NO, $CN{\cdot}BCl_3$, OCOMe, $S(Me)_2^+$, CH=CHCN, $P(NMe_2)_2$, NHC_6H_5).

The standard deviations for eqs 26 and 27 are surprisingly good considering that the σ_m and σ_p values have been obtained by a variety of means in a number of different laboratories. Clearly it is a satisfaction that σ constants obtained by the various methods discussed above are in such good general agreement.

In making the first large compilation of σ constants, it was noted that there was a high degree of collinearity between σ_m and σ_p.[34] By using the present much expanded set of substituents, the collinearity is even more evident as eq 28 shows.

$$\sigma_p = 1.19\ (\pm0.04)\sigma_m - 0.08\ (\pm0.02) \quad (28)$$

$$n = 530,\ r = 0.941,\ s = 0.137,\ F_{1,527} = 4095$$

The resonance and inductive parameters F and R, however, are not highly collinear and can be used as independent variables.

$$F = 0.41\ (\pm0.10)R + 0.34\ (\pm0.02) \quad (29)$$

$$n = 529,\ r = 0.336,\ s = 0.257,\ F_{1,527} = 66.9$$

The collinearity of eq 28 is a result of the large number of substituents which show very little resonance interaction. Of the 529 substituents in Table I, 287 have R values between +0.12 and −0.12. That is, they have very little resonance interaction so that σ_m and σ_p are almost identical.

By comparing only the 38 substituents upon which eq 8 rests, eq 30 is obtained.

$$\sigma_p = 1.46\ (\pm0.27)\sigma_m - 0.20\ (\pm0.08) \quad (30)$$

$$n = 38,\ r = 0.879,\ s = 0.176$$

Although the collinearity in eq 30 is much lower than that of eq 28, it is still high and brings out a shortcoming of the Hammett σ constant: one should draw no firm conclusions about the relative importance of resonance or inductive effects from unfactored σ constants.

II. Discussion

Table I, with over 500 substituents having both σ_m and σ_p values is impressive testimony to the enormous effort which has contributed so much to our understanding of organic reaction mechanisms, both in simple physical organic chemical systems and in biological systems.

In the past two decades there have been increasing efforts to factor σ into its inductive and resonance components, a field which Charton has reviewed.[29] Of these factoring methods, the one proposed by Charton and that of Swain and Lupton offer large data sets for use in correlation analysis. Even though there has been criticism of the exactness of this method, we believe that for many purposes, and especially for biological structure–activity studies, these constants are valuable. This belief is reinforced by eqs 9–11 all of which show that the agreement between the Swain and Lupton's modified F and Chartons's σ_I is good despite the fact that they are derived from completely different systems. The relationship between modified R and σ_D shown by eqs 10 and 11 gives us confidence that R will also be valuable in correlation analysis. However, one must be aware that not all of the values in Table I are of equal quality. One should check the original sources when working with unusual substituents.

One of the features of Table I is that it provides substituents with a wide range of electronic effects as illustrated in Table VI. The NO_2 group is usually thought of as having nearly maximal electron-withdrawing power, but there are many substituents with higher F values in Table I. Furthermore, there are substituents with R values 3–6 times the value of 0.13 for NO_2. Many of these substituents with extreme electronic effects have received almost no attention in QSAR studies, but we believe some of them would be well worth the trouble to synthesize and investigate. Yagupol'skii in particular has designed a most interesting variety of new substituents with unusual electronic properties.[56]

In Table VII, σ_I values for a wide variety of heterocyclic substituents obtained from guanidines by Taylor and Wait[41] have been listed. In Table VIII, σ_I values for substituents not in Table I derived from substituted acetic acids by Charton are given. For many purposes, these could be used along with values from Tables I or IV.

In recent years, considerable interest has developed in the ionization of compounds in the gas phase. Comparison of the gas-phase ionization constants with those obtained in solution clearly brings out the effect of the solvent. Figure 1 compares the substituent effects on the ionization of benzoic acids in water and in the gas phase. Although the substituent effect is very much larger in the gas phase, the correlation between the two types of ionization constants is surprisingly good, except for the conjugated electron-releasing substituents, 4-NH_2, 4-OCH_3, 4-CH_3, and 4-F. Table X gives comparisons of σ_m and σ_p values from benzoic acids obtained in the gas phase and in benzene solution with the corresponding aqueous solution values of Table I.

A point which has generated heated discussions is the assumption of Swain and Lupton that R for $N^+(CH_3)_2$ could be assumed to be zero. It is noteworthy that in Table I where the calculations do not include this assumption, we find R for this group to be −0.04 which for most purposes could be called zero. The value of σ_R(F NMR) of Table IV is −0.08 and Charton has reported a σ_D value of −0.11.

It has been advocated by a number of workers in the field that Swain's original F and R parameters be dropped. We have delineated the principle basis for this criticism as being the inadequate treatment of π-electron-donor/-acceptor interactions. With proper consideration of this matter we have demonstrated that at a level of precision useful for present purposes, field/inductive substituent parameters, F, (as herein modified) are in general not significantly different from corresponding σ_I, σ_F, and σ_L values. For QSAR requiring greater precision, additional modifications of field/inductive parameters due to substituent solvation and solvent effects, such as for the fall-off factor of dipolar effects, need to be considered. Corresponding resonance (π-electron delocalization) effect parameters, R, and corresponding σ_R and σ_D may also not differ significantly if they are based upon similar electron demands for the rate or equilibrium processes. However, care must be taken that proper recognition be accorded to the conditions of both π-electron-donor/acceptor interactions and of substituent solvation effects.

Many practical problems limit the use of carboxylic acid acidities in establishing new electronic parameters: difficult synthesis of exotic structures and low sensitivity of substituent effects coupled with low solubility making pK_a measurements difficult. We have included in this review an analysis of the newer methods which can supplant this "classic" procedure for determination of these constants. It is shown that there is a remarkable consistency at several levels of precision between the results obtained with these methods using proper assumptions. The interested reader is directed also to the C^{13} NMR substituent chemical shift methods given in references.[57-59]

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