The Variation of the *ortho* Electrical Effect with Solvent

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Twelve sets of pK_A values for 2-substituted benzoic acids in various solvents have been correlated with the extended Hammett equation

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$$

where α is a constant independent of the solvent (average value is -2.39) and β is a function of the solvent, increasing with increasing solvent polarity. The variation of β with the solvent is given by the equation

$$\beta = mS + c$$

where S is the Brownstein solvent parameter. Correlation of pK_A values for the corresponding sets of 3- and 4-substituted benzoic acids with the simple Hammett equation shows that ρ (and therefore both α and β) varies with solvent, ρ increasing as solvent polarity decreases. The constancy of α is ascribed to a localized substituent effect due to a direct field effect between substituent and reaction site, which owing to the geometry of the 2-substituted benzoic acids are in virtual contact. The decrease in β is believed to be due to an interplanar angle between carboxyl group and ring, the magnitude of which is solvent dependent. The results show that the composition of the *ortho* electrical effect at least in some systems is a function of the solvent.

We have for some time been interested in the nature of the electrical effect of *ortho* substituents on chemical reactivity. Previously, we have applied the Hammett equation,[1] eq 1, to the study of the *ortho* effect in sets in which the reaction site and the benzene ring are separated by some group.[2] We have also investigated

$$Q_X = \rho\sigma_X + h \tag{1}$$

the *ortho* effect in 2-substituted pyridines,[3] quinolines,[3] imidazoles,[4] and benzimidazoles.[4] Watkinson, Watson, and Yates[5] have reported on the effect of solvent upon the *ortho* electrical effect in the alkaline hydrolysis of ethyl phenylacetates. It seemed of interest to examine the *ortho* electrical effect over a wider range of solvent variation than that reported by these workers. As we are interested in the electrical effect of *ortho* substituents rather than the over-all *ortho* effect, we have chosen to examine the ionization of benzoic acids. The mechanism of the alkaline hydrolysis of esters requires a rate-determining addition of hydroxide ion to the carbonyl group. In the process, the carbonyl carbon changes its hybridization state from sp^2 to sp^3 and therefore significantly increases its bulk. By comparison, the carboxyl group in ionizing does not undergo a significant change in size or shape. Thus, we have examined the correlation of ionization constants, extant in the literature of 2-substituted benzoic acids, in various solvents and solvent mixtures with the equation[6]

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{2}$$

Two types of substituent which were excluded from the correlations are (1) groups which form intramolecular hydrogen bonds with the carboxyl group such as the amino and hydroxy substituents, and (2) groups which are exceptionally large such as tertiary butyl and trifluoromethyl. The unsubstituted compound has also been omitted from the correlations, as in it the benzene ring and carboxyl group are coplanar, whereas in most 2-substituted benzoic acids the plane of the carboxyl group is rotated about its carbon–carbon bond to the ring so that it makes an angle greater than zero with the plane of the ring. This point will be considered in greater detail in the discussion.

The values of pK_a used are given in Table I, sets 01 through 012. The σ_I values were taken from our compilation;[7] values of σ_R were obtained from[6]

$$\sigma_R = \sigma_P - \sigma_I \tag{3}$$

The results of the correlations are given in Table II. For purposes of comparison, we have also correlated ionization constants of the 3- and 4-substituted benzoic acids with eq 1. Some of these have previously been examined by Jaffé.[1] The values of pK_a for the *meta*- and *para*-substituted acids are given in Table III, sets 1 through 12. The σ_m and σ_p constants used are those of McDaniel and Brown.[8] The results of these correlations are reported in Table IV. The values for 3- and 4-hydroxybenzoic acids were not included in the correlations for solvents other than water since the OH substituent seems particularly susceptible to solvation effects.

Results

2-Substituted Benzoic Acids.—Our results are unfortunately limited to substituents which are electron donors by resonance. Of the 12 sets of 2-substituted benzoic acids studied, excellent correlations (CL $\geqq$ 99.0) were obtained in seven sets, good correlations (CL = 97.5) in three sets, and poor, although significant, correlations (CL = 90.0) in two sets. The two sets which gave poor correlations consisted of only four data points. We believe that, over-all, the results are very good. The success of the correlations with eq 2 seems to indicate that *only electrical effects are necessary to account for the substituent effect in these sets.* There is no detectable steric effect.

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(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co. Inc., New York, N. Y., 1940; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956; V. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(2) M. Charton, *Can. J. Chem.*, **38**, 2493 (1960).

(3) M. Charton, *J. Amer. Chem. Soc.*, **86**, 2033 (1964).

(4) M. Charton, *J. Org. Chem.*, **30**, 3146 (1965).

(5) J. G. Watkinson, W. Watson, and B. L. Yates, *J. Chem. Soc.*, 5437 (1963).

(6) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958).

(7) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(8) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

TABLE I

pK_a VALUES OF 2-SUBSTITUTED BENZOIC ACIDS (ALL DATA AT 25°)

	Set					
	01[b]	02[c]	03[c]	04[c]	05[d]	06[d]
		Dioxane–water			10%	25%
Substituent	H_2O	26.5%[a]	43.5%	73.5%	MeAc–H_2O	MeAc–H_2O
F	3.267				3.796	4.394
Cl	2.9215	3.735	4.498	6.193	3.334	4.020
Br	2.854	3.689	4.465	6.144		
I	2.863	3.817	4.596	6.277		
Me	3.9083	4.785	5.548	7.243	4.304	4.895
Et	3.793					
OMe	4.094	4.873	3.873	5.254	4.511	5.022
Ph	3.460					

	Set					
	07[e]	08[f]	09[g]	010[g]	011[f]	012[h]
	80% Methyl Cellosolve–H_2O	Ethylene glycol	MeOH	EtOH	BuOH	PrOH
F	6.03	6.958	7.683	7.83	7.683	7.643
Cl	5.70	6.510	7.476	7.74	7.534	7.517
Br	5.62	6.449	7.413	7.70	7.519	7.441
I	5.73	6.542	7.495	7.78	7.571	7.507
Me		7.601	8.594	8.84	8.607	8.562
OMe	6.76	7.468	8.511	8.62	8.328	8.348

[a] All solvent–water ratios are weight/weight. [b] G. Kortum, W. Vogel, and K. Andrussow, *Pure Appl. Chem.*, **1**, 190 (1961). [c] J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 485 (1941). [d] J. F. J. Dippy, S. R. C. Hughes, and B. C. Kitchiner, *J. Chem. Soc.*, 1275 (1964). [e] W. Simon, G. H. Lyssy, A. Morilofer, and E. Heilbrunner, "Zusammenstellung von scheinbaren Dissoziationkonstanten im Losungsmittelsystem Methylcellosolve/Wasser," Juris-Verlag, Zurich, 1959. [f] J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 472 (1941). [g] J. H. Elliott and M. Kilpatrick, *ibid.*, **45**, 454 (1941). [h] J. H. Elliott, *ibid.*, **46**, 221 (1942).

TABLE II

RESULTS OF CORRELATION OF 2-SUBSTITUTED BENZOIC ACIDS

Set	$-\alpha$	$-\beta$	h	R[a]	F[b]	r[c]	s_{estd}[d]	s_α[d]	s_β[d]
01	2.40	2.31	3.474	0.997	475.4	0.503	0.0426	0.0796	0.112
02	2.47	1.96	4.449	0.994	80.87	0.101	0.0933	0.218	0.286
03	2.42	1.74	5.240	0.994	88.16	0.101	0.0853	0.200	0.262
04	2.36	1.34	6.978	0.996	136.9	0.101	0.0643	0.150	0.197
05	2.34	2.36	3.892	0.9985	165.9	0.531	0.0502	0.132	0.183
06	2.07	1.94	4.578	0.9986	184.2	0.531	0.0417	0.109	0.152
07	2.44	1.90	6.389	0.992	64.64	0.300	0.0819	0.413	0.252
08	2.35	1.78	7.219	0.983	43.55	0.295	0.120	0.265	0.328
09	2.61	1.69	8.272	0.9981	394.5	0.295	0.0431	0.0954	0.118
010	2.48	1.23	8.581	0.9985	512.7	0.295	0.0353	0.0780	0.0906
011	2.32	1.12	8.343	0.9990	738.5	0.295	0.0274	0.0606	0.0750
012	2.39	1.29	8.282	0.998	360.2	0.295	0.0406	0.0898	0.111
Set	s_h[d]	n[e]	CL[f]	t_α[g]	CL[f]	t_β[g]	CL[f]	t_h	CL[f]
01	0.0284	8	99.9	30.15	99.9	20.62	99.9	122.3	99.9
02	0.100	5	97.5	11.33	99.0	6.863	95.0	49.49	99.9
03	0.0916	5	97.5	12.10	99.0	6.641	95.0	57.21	99.9
04	0.0690	5	99.0	15.73	99.0	6.802	95.0	101.1	99.9
05	0.0580	4	90.0	17.72	95.0	12.90	95.0	67.10	99.0
06	0.0482	4	90.0	18.99	95.0	12.76	95.0	94.36	99.0
07	0.213	5	97.5	5.908	95.0	7.540	98.0	30.00	99.0
08	0.119	6	99.0	8.968	99.0	5.427	98.0	60.66	99.9
09	0.0426	6	99.9	27.36	99.9	14.32	99.9	194.2	99.9
010	0.0349	6	99.9	31.80	99.9	12.73	99.0	245.9	99.9
011	0.0271	6	99.9	38.28	99.9	14.93	99.9	207.9	99.9
012	0.0401	6	99.9	26.61	99.9	11.62	99.0	206.5	99.9

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R. [d] Standard errors of the estimate, α, β, and h. [e] Number of points in set. [f] Confidence levels of the regression, α, β, and h. [g] Student "t" test for significance of α, β, and h.

It is interesting to consider the variation of α and β for the 2-substituted benzoic acids with solvent. The average value of α is -2.39. Let us define the quantities

$$\Delta_\alpha = |\bar{\alpha} - \alpha| \quad \Delta_\beta = |\bar{\beta} - \beta| \tag{4}$$

Values of Δ_α and Δ_β are given in Table V. The average values of Δ_α is 0.08. Of the twelve values of Δ_α, ten are less than or equal to 0.09. We conclude that for the 2-substituted benzoic acids α *is constant and is independent of solvent.* The average value of β is -1.72; the average value of Δ_β is 0.33. Of the twelve values of Δ_β, nine are greater than 0.15 and six are greater than 0.33. By inspection β is seen to be dependent on the solvent; β *seems to decrease as the bulk dielectric constant of the solvent increases.*

TABLE III[a–h]
pK_a VALUES OF 3- OR 4-SUBSTITUTED BENZOIC ACIDS

	Set							
	1[b]		2[c]		3[c]		4[c]	
	3-	4-	3-	4-	3-	4-	3-	4-
Substituent	H_2O		26.5% dioxane–H_2O[a]		43.5% dioxane–H_2O		73.5% dioxane–H_2O	
F	3.867	4.142	4.409	4.670	5.057	5.249	6.541	6.775
Cl	3.830	3.977	4.379		4.986	5.089		6.639
Br			4.387		4.999	5.094	6.502	6.602
I			4.448		5.072	5.091	6.573	6.654
NO_2	3.494	3.425	3.931	3.846	4.496	4.369	5.969	5.849
OMe	4.088	4.471		5.152		5.794		7.390
H	4.203		4.820		5.469		7.029	
Ac	3.827	3.701						
Me	4.272	4.373	4.944	5.049	5.611	5.684	7.174	7.239

	Set							
	5[d]		6[d]		7[e]		8[f]	
	3-	4-	3-	4-	3-	4-	3-	4-
	10% MeAc–H_2O		25% MeAc–H_2O		80% methyl Cellosolve–H_2O		Ethylene glycol	
F	4.064	4.305	4.620	4.796	6.07	6.37	7.199	7.478
Cl	4.043	4.207	4.565	4.698	5.99	6.13	7.128	7.343
Br					5.97	6.10	7.103	7.279
I					6.05	6.15	7.157	7.290
NO_2	3.695	3.585	4.182	4.039	5.44	5.29	6.716	6.682
OMe	4.311	4.813	4.830	5.203	6.55	7.00		7.971
NH_2					6.96	7.70		
CF_3					5.79			
H	4.454		4.996		6.63		7.647	
Ac	4.062	3.925	4.565	4.458				
Me	4.486	4.656	5.040	5.137			7.237	7.819

	Set							
	9[g]		10[g]		11[f]		12[h]	
	3-	4-	3-	4-	3-	4-	3-	4-
	MeOH		EtOH		*n*-BuOH		*n*-PrOH	
F	8.944	9.256	9.53	9.90	8.193	8.394	8.081	8.390
Cl	8.856	9.033	9.52	9.62	8.024	8.215	7.997	8.214
Br	8.851	9.024	9.47	9.64	8.031	8.188	7.973	8.171
I	8.884	9.039	9.47	9.62	8.043	8.213	7.986	8.153
NO_2	8.366	8.349	8.88	8.85	7.509	7.468	7.450	7.463
OMe		9.749		10.52		8.969		8.966
NH_2								
CF_3								
H	9.41		10.25		8.609			8.603
Me	9.507	9.624	10.20	10.32	8.704	8.802	8.698	8.814

[a–h] References are identical with those in Table I.

TABLE IV
RESULTS OF CORRELATIONS. 3- OR 4-SUBSTITUTED BENZOIC ACIDS

Set	$-\rho$	h	r[a]	s[b]	t[c]	s_ρ[d]	n[e]	CL[f]
1	0.985	4.198	0.9996	0.00426	1121.8	0.00809	15	99.9
2	1.24	4.829	0.996	0.0388	34.63	0.0357	11	99.9
3	1.33	5.453	0.990	0.0607	23.84	0.0558	14	99.9
4	1.44	7.005	0.991	0.0612	25.55	0.0562	14	99.9
5	1.10	4.452	0.995	0.0369	33.26	0.0330	13	99.9
6	1.08	4.949	0.992	0.0434	27.82	0.0388	13	99.9
7	1.68	6.596	0.993	0.0760	30.56	0.0549	16	99.9
8	1.26	7.614	0.997	0.0312	43.85	0.0286	14	99.9
9	1.38	9.378	0.998	0.0302	48.32	0.0284	13	99.9
10	1.60	10.05	0.996	0.0447	37.93	0.0421	13	99.9
11	1.44	8.572	0.994	0.0493	31.80	0.0453	14	99.9
12	1.50	8.556	0.996	0.0410	39.66	0.0377	14	99.9

[a] Correlation coefficient. [b] Standard deviation. [c] Student "t" test. [d] Standard deviation of ρ. [e] Number of points in the set. [f] Confidence level.

TABLE V
VALUES OF Δ_α AND Δ_β

Set	Δ_α	Δ_β	Set	Δ_α	Δ_β
01	0.01	0.49	07	0.05	0.18
02	0.08	0.24	08	0.04	0.06
03	0.03	0.02	09	0.22	0.03
04	0.03	0.48	010	0.09	0.51
05	0.05	0.64	011	0.07	0.60
06	0.32	0.22	012	0	0.43

3- or 4-Substituted Benzoic Acids.—The results obtained from correlation with eq 1 are excellent as can be seen from the confidence levels. According to Taft and Lewis[6]

$$\sigma_p = \sigma_I + \sigma_R \qquad (5)$$

Then from eq 1 and 2, $\rho = \alpha = \beta$. For these sets, ρ, and therefore α and β, increases as the solvent dielectric constant decreases. Not only are both α and β in-

TABLE VI

VALUES OF D AND S

Solvent	D	S	Solvent	D	S
Water	78.54,[a] 80.37[b]	0.1540[d]	Propanol	20.1[a]	−0.0158[d]
Ethylene glycol	37.7[a]	0.0679[d]	Butanol	17.1[a]	−0.0240[d]
Methanol	32.63[a]	0.0499[d]	26.5% dioxane–H_2O	57.0[c]	0.130[e]
Ethanol	2.43[a]	0[d]	43.5% dioxane–H_2O	41.1[c]	0.109[e]
			73.5% dioxane–H_2O	17.2[c]	0.0365[e]

[a] A. A. Maryott and E. R. Smith, National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951. [b] D. DeCroocq, *Bull. Soc. Chim. Fr.*, 127 (1964). [c] Interpolated from a plot of D *vs.* % H_2O. Data from footnote *b*. [d] Ref 10. [e] Calculated from eq 7.

TABLE VII

RESULTS OF CORRELATIONS WITH EQ 6 AND 8

Set	m	d	r[a]	s[b]	s_m[c]	t[d]	n[e]	CL[f]
061	18.3	−2.35	0.927	0.187	5.24	3.485	4	90.0
61	−7.59	−1.04	0.806	0.141	3.94	1.926	4	80.0
062	25.8	−2.51	0.957	0.146	3.93	6.563	6	99.0
62	−10.5	−0.976	0.807	0.143	3.85	2.737	6	90.0
62A	−21.8	−0.702	0.999	0.0163	0.802	27.13	4	99.0
081	−7.77	−1.00	0.969	0.122	1.39	5.575	4	95.0
81	3.36	−1.61	0.879	0.113	1.29	2.603	4	80.0
082	−6.59	−1.32	0.991	0.0665	0.441	14.93	6	99.0
82	2.99	−1.48	0.931	0.0887	0.589	5.083	6	99.0
82A	3.96	−1.58	0.992	0.0397	0.357	11.09	4	99.0

[a] Correlation coefficient. [b] Standard error of the estimate. [c] Standard error of the slope. [d] Student "t" test for significance of regression. [e] Number of points in set. [f] Confidence level.

creasing as the solvent dielectric constant decreases, *they are doing so at the same rate.*

The Correlation of ρ and β with Solvent Parameters.—In order to determine quantitatively the nature of the dependence of ρ (for sets 1–12) and β (for sets 01–012) upon the solvent we have examined the correlation of these quantities with eq 6 where D is the bulk dielectric

$$\rho = m/D + c \text{ and } \beta = m/D + c \tag{6}$$

constant of the solvent. The values of D used in the correlations are set forth in Table VI. Results of the correlations are reported in Table VII. For the β values in aqueous dioxane (set 061) a poor correlation was obtained. The ρ values in this solvent system did not give a significant correlation (set 61). In the pure hydroxylic solvents (water and the alcohols) the β values (set 062) gave an excellent correlation whereas the ρ values gave poor results (set 62). Exclusion of the ρ values for 1-propanol and 1-butanol gave an excellent correlation however (set 62A).

A number of authors[9] have proposed solvent parameters of various types as a measure of the effect of solvent upon reaction rates and equilibria. As these solvent parameters are believed to be related to the "solvating power" of the solvent it seemed of interest to examine a relationship between them and the β or ρ values. In general, the solvent parameters proposed by various authors are at least crudely related to each other. There is, therefore, no reason to prefer one of these parameters to the others. We have chosen the Brownstein solvent parameters[10] for the purposes of correlation, since values were available for a more extensive range of solvents and mixed solvents. We find that solvent parameters for mixed solvents can be calculated from the equation

$$S = mf + c \tag{7}$$

where m and c are obtained by simple linear regression analysis of a correlation of observed S values for the mixed solvents with the mole fraction, f, of one of the solvents.

Values of β and ρ were therefore correlated with

$$\beta = mS + d \quad \rho = mS + d \tag{8}$$

The values of S required are given in Table VI; results of the correlations are presented in Table VII. The correlation obtained for the ρ values in aqueous dioxane is not significant (set 81); the β values in this medium gave fair results (set 081). In hydroxylic solvents, excellent correlation was obtained for the β values (set 082) and to a lesser extent, for the ρ values (set 82). Exclusion of the ρ values for 1-propanol and 1-butanol (set 82A) gave somewhat improved correlation.

Over-all, correlations of ρ and β with eq 8 gave better results than correlations with eq 6. The values of D used for the aqueous dioxane sets were at 20°; the ρ and β values were obtained at 25°. We do not believe that the use of D values at 20° made a significant difference in the extent of correlation. Our most significant conclusion from these correlations is that resonance effects in 2-substituted benzoic acids respond in a direction opposite to that of resonance effects in 3- or 4-substituted benzoic acids when the solvent polarity varies.

Reaction of 2-Substituted Benzoic Acids with 1,3-Diphenylguanidine.—Davis and Hetzer[11] have reported equilibrium constants for the reaction of substituted benzoic acids with 1,3-diphenylguanidine in benzene

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(9) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961); C. G. Swain, R. B. Mosely, and D. E. Brown, *ibid.*, **77**, 3731 (1955); E. M. Kosower, *ibid.*, **80**, 3253 (1958); J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, **84**, 297 (1962); K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963); E. sz. Kovats and P. B. Weiss, *Ber. Bunsenges. Phys. Chem.*, **69**, 812 (1965).

(10) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

(11) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Stand.*, **60**, 569 (1958).

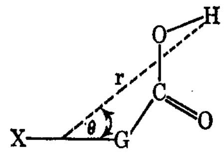

Figure 1.

to form the salt. Their data are given in Table VIII. The data have been correlated with eq 2 for purposes of comparison with the results obtained for the ionization of benzoic acids in protonic solvents. The results of the correlations are given in Table IX. The 2-substituted benzoic acids (set 021) gave a correlation significant at the 95% confidence level. Exclusion of the values for X = OMe and X = NO$_2$ gave very much improved results, with α = 2.07 and β = 0.713 (set 021A). These results seem to be in accord with those reported above for the ionization of 2-substituted benzoic acids in protonic solvents. Correlation of the equilibrium constants for the 3- and 4-substituted benzoic acids (sets M21 and P21, respectively) gave excellent results.

TABLE VIII

EQUILIBRIUM CONSTANTS FOR THE REACTION OF 1,3-DIPHENYLGUANIDINE WITH SUBSTITUTED BENZOIC ACIDS IN BENZENE AT 25°

	$10^3K''$		
X	2-	3-	4-
H		183	183
F	591	876	411
Cl	1200	1160	656
Br	1480	1160	728
I	1650	1120	708
Me	863	134	106
OMe	4.72	239	83.1
NO$_2$	27400	6600	6280
OH		224	87.0
CN		3650	3380
NH$_2$	87.8	84.5	28.0
Me$_2$N		77.9	
OAc	526		

Discussion

The Variation of α with Solvent.—We have found that α for 2-substituted benzoic acids is independent of solvent. For 3- or 4-substituted benzoic acids, ρ, and therefore α, increases with decreasing solvent polarity. In order to account for these observations, we must determine the nature of the localized effect. It is generally believed that the localized effect of a substituent is due to inductive and/or field effects. We have presented arguments based on the ratio of ρ_{cis}/ρ_{trans} for 3-substituted acrylic acids[12] which seem to preclude the inductive effect as the major contributor to the localized effect in these compounds. In view of the similarity in geometry between 2-substituted benzoic acids and *cis*-3-substituted acrylic acids, it seems likely that inductive effects are unimportant in the former. In considering the field effect of a substituent, we may make use of the Kirkwood-Westheimer equation[13]

$$\log K_X/K_H = (e\mu_X \cos\theta)/(2.303RTD_Er^2) \qquad (9)$$

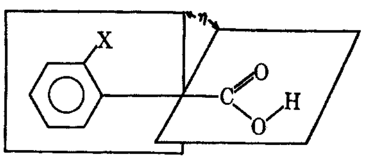

Figure 2.

where e is the charge on an electron, μ_X the bond moment of the X-ring bond, R the gas constant, T the temperature, D_E the effective dielectric constant, and r and θ are defined in Figure 1. In the case of the 3- or 4-substituted benzoic acids the field is exerted through both the skeleton of the benzoic acid molecule and the surrounding sheath of solvent molecules. The effective dielectric constant will therefore vary with change in solvent. As the bulk dielectric constant of the solvent decreases, D_E will decrease.

From eq 1 and 9 we may write for ρ in some reference solvent

$$\rho_{Sv} = \frac{(e\mu_X \cos\theta)}{(2.303RTD_{E,Sv}r^2)} \quad \rho_{Sv^0} = \frac{(e\mu_X \cos\theta)}{(2.303RTD_{E,Sv^0}r^2)} \qquad (10)$$

and as $\rho = \alpha$

$$\alpha_{Sv} = \frac{(D_{E,Sv^0}\alpha_{Sv^0})}{D_{E,Sv}} \qquad (11)$$

Let us now consider the geometry of the 2-substituted benzoic acids. In these compounds the substituent and the carboxyl group are in very close proximity, in many of these compounds they are actually in contact. Thus there is neither solvent nor skeletal group intervening between substituent and reaction site. We conclude that, as a first approximation, for 2-substituted benzoic acids

$$D_{E,Sv} = D_{E,Sv^0} \qquad (12)$$

and therefore α_{Sv} remains constant.

The Variation of β with Solvent.—For a 4-substituted acid, $\beta = \rho$, and for a 3-substituted acid, $\beta = \rho/3$. Then

$$\beta_{Sv} = \frac{(D_{E,Sv}\beta_{Sv^0})}{D_{E,Sv}} \qquad (13)$$

We have observed that the variation in β for 2-substituted benzoic acids is given by eq 6 and 7. If our previous discussion is correct, then $D_{E,Sv} = D_{E,Sv^0}$ and the variation of β with solvent polarity observed represents a decreased delocalization in the system. This can be accounted for in terms of an increase in the interplanar angle η (between the plane of the carboxyl group and the plane of the ring, Figure 2) with decrease in solvent polarity. We may write for β

$$\beta = \beta^0 \cos^2 \eta \qquad (14)$$

Then as the solvent polarity decreases, η increases. A somewhat analogous phenomenon is observed for biphenyl which exhibits an interplanar angle of 45° in the vapor state and 0° in the crystal.[14] Even in water, the most polar medium for which data are available, the interplanar angle in 2-substituted benzoic acids is not zero. Values of η found for various crystalline 2-substituted benzoic acids by X-ray diffraction studies are given in Table VIII. These values

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[12] M. Charton, *J. Org. Chem.*, **30**, 974 (1965).

[13] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

[14] A. Almenningen and O. Bastiansen, *Kgl. Norske Videnskab. Selskabs, Skrifter*, [4], 1 (1958); D. Steele and E. R. Lippincott, *J. Mol. Spectrosc.*, **6**, 238 (1961).

TABLE IX[a]

RESULTS OF CORRELATIONS OF EQUILIBRIUM CONSTANTS

	α	β	h	R	F	r	s_{estd}	s_α	s_β	s_h
021	2.58	1.79	2.22	0.842	7.305	0.436	0.657	1.15	0.988	0.625
021A	2.07	0.714	2.22	0.927	12.16	0.173	0.252	0.482	0.436	0.240
M21	2.05	0.748	1.30	0.998	916.9	0.402	0.0491	0.0677	0.0479	0.0337
P21	1.95	1.42	1.28	0.998	878.2	0.308	0.0539	0.0745	0.0618	0.0371

	n	CL	t_α	CL	t_β	CL	t_h	CL
021	9	95.0	2.243	90.0	1.812	80.0	3.552	98.0
021A	7	97.5	4.294	98.0	1.638	80.0	9.250	99.9
M21	12	99.9	30.28	99.9	15.62	99.9	38.58	99.9
P21	11	99.9	26.17	99.9	22.98	99.9	34.50	99.9

[a] Symbols are the same as those in Table II.

show that the magnitude of η is a function of the van der Waals radius of the *ortho* substituent.

We have attempted to calculated *average* values of η for sets 01 through 012 in the following manner. Values of η were estimated for the groups F, OMe, Me, Et, and I from the smooth curve drawn through a plot of η *vs.* van der Waals radii for the substituents H, OAc, Cl, Br, and SO_3^-. As the points for the CO_2H and CO_2^- substituents do not lie on the smooth curve, it would seem that planar π-bonded substituents have values which are a different function of the van der Waals radius than are the η values of the other substituents. The value of η for the phenyl group was therefore assumed to be equal to that of the carboxyl group. These estimated η values are reported in Table X. Values of $\cos^2 \eta$ for the eight members of set 01 were averaged. It was assumed that this average value of $\cos^2 \eta$ obtained for the crystalline 2-substituted benzoic acids was equal to the *average* value which would have been observed for these acids in a hypothetical solvent of infinite dielectric constant. A value of β for this solvent can be calculated from the correlation of β with eq 6 (set 062). When $D_E = \infty$, $\beta = c = 2.51$. From eq 14 a value of -2.77 for $\beta°$ was then calculated. From eq 14 and the known values of β and $\beta°$, *average* values of η were calculated for each set. They are presented in Table XI. These average values of η *are not applicable to individual acids.* If our arguments as to the cause of the decrease in β are correct, then the $\bar{\eta}$ values represent an estimate of the degree of noncoplanarity in 2-substituted benzoic acids in solution.

TABLE X

PHENYL–CARBOXYL INTERPLANAR ANGLE IN CRYSTALLINE 2-SUBSTITUTED BENZOIC ACIDS

X	η	Ref	r_v[a]	X	η	Ref	r_v[a]
H	0	*b*	1.20	F	1.3	*i*	1.47
Cl	13.7	*c*	1.75	OMe	2.0	*i*	1.52
Br	18.3	*d*	1.85	Me	11.	*i*	1.72[k]
SO_3^-	50.7	*e*	2.19[h]	Et	11.	*i*	1.72[k]
OAc	2.0	*f*	1.52	I	28.	*i*	1.98
CO_2H	33.0	*g*	1.70	Ph	33.	*j*	1.77
CO_2^-	31.77	*g*	1.70				

[a] From A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964), unless otherwise noted. [b] G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Cryst.*, **8**, 157 (1955). [c] G. Ferguson and G. A. Sim, *ibid.*, **14**, 262 (1961). [d] G. Ferguson and G. A. Sim, *ibid.*, **15**, 346 (1962). [e] Y. Okaya, *ibid.*, **22**, 104 (1967). [f] P. J. Wheatley, *J. Chem. Soc.*, 6036 (1964). [g] Y. Okaya, *Acta Cryst.*, **19**, 879 (1965). [h] Minimum radius perpendicular to the axis through the S–C bond. [i] Estimated by interpolation from the smooth curve drawn through a plot of η *vs.* r_v. [j] Assumed equal to η for CO_2H. [k] Minimum radius perpendicular to the axis through the C–C bond.

TABLE XI

CALCULATED AND OBSERVED VALUES OF pK_a FOR 2-NITROBENZOIC ACID

Set	pK_{NO_2}		Δ	$\bar{\eta}$
	Calcd	Obsd[a]		
01	1.657	2.173	0.516	24.1
02	2.613	3.038	0.425	32.7
03	3.455	3.808	0.353	37.6
04	5.266	5.453	0.187	45.9
05	2.112	2.609	0.497	21.8
06	3.015	3.344	0.329	33.2
07	4.578	4.98	0.402	34.1
08	5.479	5.906	0.427	36.7
09	6.362	6.855	0.493	38.6
010	6.796	7.09	0.294	48.2
011	6.676	6.829	0.153	50.5
012	6.554	6.799	0.245	46.9

[a] Taken from the references in Table I.

Hydrogen Bonding in 2-Nitrobenzoic Acid.—We now consider the evidence for an intramolecular hydrogen bond in 2-nitrobenzoic acid. Let us calculate values of pK_{NO_2} for sets 01 through 012 from the values of α, β, and h reported in Table III. To do this, we must take into account the fact that the nitro group is not coplanar with the ring. Although the 2-nitrobenzoic acid has not itself been studied, in 2-nitroperoxybenzoic acid the nitro group makes an angle of 28° with the plane of the ring,[15] while in 2-nitrobenzaldehyde the interplanar angle is reported to be 30°.[16] Thus, assuming an interplanar angle of 30°, from eq 15 we

$$\sigma_{R,NO_2} = \sigma_{R,NO_2} \cos^2 \eta_{NO_2} \qquad (15)$$

calculate $\sigma_R = 0.08$. Values of pK_{NO_2} were calculated and are given in Table IX, as are the observed values, and the differences, Δ between pK calculated and pK observed.

The values reported in Table XI lead to two important conclusions, that pK_{NO_2} (calcd) is invariably less than pK_{NO_2} (obsd) and Δ decreases with decreasing solvent polarity. Models show that an intramolecular hydrogen bond in 2-nitrobenzoic acid is possible if $\eta_{NO_2} = \eta_{CO_2H} = 30°$. An increase in these interplanar angles would increase the distance between the proton and the oxygen atom to which it is hydrogen bonded and therefore decrease the strength of the hydrogen bond. We suggest that as solvent polarity decreases η_{NO_2} and η_{CO_2H} increase; the intramolecular hydrogen

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(15) M. Sax, P. Beurskens, and S. Chu, *Acta Cryst.*, **18**, 252 (1965).

(16) P. Coppens and G. M. J. Schmidt, *ibid.*, **17**, 22, 573 (1964).

bonding decreases; the magnitude of σ_{R,NO_2} decreases; and therefore Δ decreases.

The Exclusion of Benzoic Acid from the 2-Substituted Sets.—The pK values of benzoic acid obviously do not lie on the correlation lines obtained for 2-substituted benzoic acids. We may account for this in part in terms of coplanarity of the carboxyl group with the ring in benzoic acid as compared to the existence of a large average interplanar angle in the 2-substituted benzoic acids. We find[17] that the pK values for carboxylic acids belonging to the set XCO_2H in water at 25° can be correlated with σ_m giving $\rho = -8$. Then from eq 2 for X = Ph

$$pK_{Ph} = -8\sigma_{I,Ph} - 8/3\sigma_{R,Ph} + pK_H \tag{16}$$

As $\sigma_{R,Ph}$ is given by eq 15, for an interplanar angle of 30° we would expect a deviation of 0.08 pK units in water. The remainder of the deviation may be due to the difference in solvation of the carboxyl group in planar benzoic acid as compared with the nonplanar 2-substituted benzoic acids. Values of pK_H calculated, pK_H observed, and Δ, the difference between calculated and observed values, are reported in Table XII. In all sets studied, pK_H calculated is less than pK_H observed.

Table XII

Calculated and Observed pK_H Values for Benzoic Acid

Set	pK_H Calcd	pK_H Obsd	Δ
01	3.474	4.203	0.729
02	4.449	4.820	0.371
03	5.240	5.469	0.226
04	6.978	7.029	0.051
05	3.892	4.454	0.562
06	4.548	4.996	0.448
07	6.389	6.63	0.428
08	7.219	7.647	0.428
09	8.272	9.41	1.14
010	8.581	10.25	1.67
011	8.343	8.609	0.266
012	8.282	8.603	0.321

Composition of the *ortho* Electrical Effect.—The composition of the electrical effect of a substituent may conveniently be described[3] by the parameter ϵ where

$$\epsilon = \beta/\alpha \tag{17}$$

We have previously investigated ϵ for *ortho*-substituted compounds as a function of structure.[3,4] Electrical effects of *ortho* substituents were classified as normal effects (ϵ >0.6) and abnormal effects (ϵ <0.5). From our present results for at least some sets ϵ is a function of solvent as well as of structure. For the 2-substituted benzoic acids eq 8 and 17 give

$$\epsilon = (mS + d)/\alpha \tag{18}$$

and as α is constant

$$\epsilon = m'S + d' \tag{19}$$

This is in contrast to the behavior of 3- or 4-substituted benzoic acids for which ϵ is not solvent dependent.

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[17] M. Charton, unpublished results.

A Linear Free-Energy Relationship for Acceptor Strength in Charge-Transfer Complex Formation. I. Substituted Benzene Donors

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Equilibrium constants for charge-transfer complex formation between 19 sets of substituted benzene π donors and various acceptors are correlated by the linear free-energy relationship

$$\log K_A = \nu\eta_A + \log K^\circ_A$$

where η_A is a constant characteristic of the "strength of acceptor" and ν is a function of donor, solvent, and temperature. Values of η are defined from the reference system p-xylene in CCl_4 at 25° for which $\nu \equiv 1.00$. Fifty values of η are reported for acceptors including substituted 1,4-benzoquinones, nitrobenzenes, cyanobenzenes, anhydrides, and halogens. It is suggested that η_A values for π acceptors of the type $GX_1 \ldots X_n$ may be calculated from the equation

$$\eta_A = \eta_G + \Sigma\eta_{X_i}$$

where η_{X_i} is the increment in η caused by the X_i substituent and η_G is the η value of the parent compound.

In the course of a previous investigation[1] a need arose for a parameter which would serve as a measure of acceptor strength in charge-transfer complex formation. Hammond[2] has shown that the acceptor strengths of 2-substituted 1,4-benzoquinones may be adequately represented by the Hammett equation. A scale of acceptor strength which would comprise all known acceptors including halogens and SO_2, as well as organic acceptors, is required; therefore the Hammett equation cannot be used. To provide such a scale, the linear free-energy relationship (eq 1) has been defined

$$\log K_A = \nu\eta_A + \log K^\circ_A \tag{1}$$

where K_A is the equilibrium constant for charge-transfer complex formation of some acceptor A; η_A is a constant characteristic of the acceptor strength of A; the slope ν is a function of the donor, solvent, and temperature; and the intercept log K°_A represents the logarithm of the calculated value of the formation constant for the reference acceptor A°. To determine values of η a standard donor, solvent, and temperature and a reference acceptor must be chosen. The choice of the standard system was determined by the following considerations. (1) The donor must be sufficiently reactive to permit the determination of "reliable"

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[1] M. Charton, *J. Org. Chem.*, **31**, 2991, 2996 (1966).

[2] P. R. Hammond, *J. Chem. Soc.*, 471 (1964).