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The Effect of Substituents on the Dissociation Constants of Carboxylic Acids

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The Kirkwood-Westheimer electrostatic theory for relative acid strength has been extended by the use of an oblate spheroidal molecular model and applied to the study of a number of substituted benzoic acids. When reasonable values of certain structural and electrical parameters, describing the acid and base molecules in equilibrium, are used, the agreement between theory and experiment with respect to the meta acids is good. The theoretically calculated and experimentally determined values of log $K_{A_x B_0}$ for the parasubstituted acids, where $K_{A_x B_0}$ is the ratio of the dissociation constant of the substituted acid to that of the parent acid, show differences Δ log $K_{A_x B_0}$ which may be considered measures of the resonance effects operative in the para acids. The quantity Δ log $K_{A_x B_0}$ for each acid changes very little from one single-component hydroxylic solvent to another.

PART I. INTRODUCTION AND THEORETICAL RESULTS

A RECENT investigation[1,2] of the acid strengths of the substituted benzoic acids relative to that of benzoic acid in a number of solvents has yielded a quantity of consistent data to which a theory of substituent effects might profitably be applied.

The groundwork for the type of theory to be considered in this paper was laid out by Bjerrum[3] who suggested that a value of the ratio of the first to the second dissociation constant of an uncharged polybasic acid in any solvent might be estimated by taking account of a statistical effect and the influence of the electrostatic field of the negative charge in the acid-ion on the dissociation of a second proton.

Following a similar line of reasoning Waters,[4] Smallwood,[5] Eucken,[6] and Schwarzenbach and Egli[7] came to regard the change of the dissociation constant of an organic acid due to the substitution of a polar group as largely connected with the electrostatic interaction of an electric dipole, representing the group, with the dissociating proton. In their calculations of electrostatic interaction energies, the three last mentioned authors took cognizance of the low electric polarizability within a molecule by using effective dielectric constants having values between that of the dielectric constant of the solvent and that which the molecules may be presumed to have.

By characterizing the molecules of the related acids and their conjugate bases[8] as sets of charges embedded in equal cavities of low dielectric con-

* Now at the Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland.
[1] J. H. Elliott and M. Kilpatrick, J. Phys. Chem. 45, 454, 466, 472, 485 (1941).
[2] J. H. Elliott, J. Phys. Chem. 46, 221 (1942).
[3] N. Bjerrum, Zeits. f. physik. Chemie 106, 219 (1923).

[4] W. A. Waters, Phil. Mag. 8, 436 (1929).
[5] H. M. Smallwood, J. Am. Chem. Soc. 54, 3048 (1932).
[6] A. Eucken, Zeits. f. angew. Chemie 45, 203 (1932).
[7] G. Schwarzenbach and H. Egli, Helv. Chim. Acta 17, 1183 (1934).
[8] M. Kilpatrick, Chem. Rev. 30, 159 (1942).

277

stant in a continuous solvent medium of high dielectric constant, Kirkwood and Westheimer[9,10] also developed relations between the first two dissociation constants of a polybasic acid and between the dissociation constants of a substituted acid and its unsubstituted parent acid. Their equations, which are similar in form to those of their predecessors in the field, contain an effective dielectric constant which is an explicit function of the dielectric constants of the solvent and the molecular cavities, the distance between the dissociating protons or between dissociating proton and substituent dipole, as the case may be, and of the parameter defining the shape of the cavity.

Two molecular models were set up featuring spherical[9] and prolate spheroidal[10] cavities. The theoretical results were applied to the aliphatic acids[9-11] with considerable success. In the field of benzenoid compounds the theory was applied[12] to experimental data only for the parasubstituted monobasic and the paradibasic acids. Due to resonance effects[13] the application of such a purely electrostatic theory to these acids alone was of limited usefulness.

In the case of the meta benzenoid acids, however, substituent effects have hitherto been considered to be but little complicated by resonance phenomena.[13] Accordingly a theory of the Kirkwood-Westheimer type should probably apply best to this class of acids and should yield information which would be useful in appraising the contributions of the various factors which affect the acid strengths of the para isomers. It is the program of this paper to develop and use such a theory in this manner.

The development follows that of Kirkwood and Westheimer in all fundamentals. There is considered the reaction, $A_1 + B_2 \rightleftharpoons A_2 + B_1$, with equilibrium constant[8] $K_{A_1B_2}$ where A_1 and A_2 are benzenoid acid molecules and B_1 and B_2 their conjugate bases. A_1 and A_2 are described as having point charge configurations identical in

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

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

[11] F. H. Westheimer and M. W. Shookhoff, J. Am. Chem. Soc. 61, 555 (1939).

[12] F. H. Westheimer, J. Am. Chem. Soc. 61, 1977 (1939).

[13] G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941).

every respect except that A_1 possesses a number of charges in excess of A_2. The excess charges reduce to the first dissociating proton, if A_1 is a polybasic acid, or to a point dipole, if A_1 is a substituted acid. The two charge configurations are assumed to lie in cavities of the same shape, size, and internal dielectric constant placed in a continuous medium with a high dielectric constant equal to that of the solvent. The conjugate base molecules B_1 and B_2 are assumed to be formed from A_1 and A_2 by the dissociation of protons without further change in the acid molecules.

With the well-known flat ring structure of benzenoid molecules in mind, it is reasonable to assume the cavities just considered to be oblate spheroids with their charges on the focal disks and all dissociating protons and substituent dipoles on the focal circles. Calculations with this model are facilitated by the use of the oblate spheroidal coordinates ζ, η, and, ϕ, which are defined in terms of Cartesian coordinates x, y, and z by the equations:

$$x = c(1+\zeta^2)^{\frac{1}{2}}(1-\eta^2)^{\frac{1}{2}} \cos \phi,$$

$$y = c(1+\zeta^2)^{\frac{1}{2}}(1-\eta^2)^{\frac{1}{2}} \sin \phi, \qquad (1)$$

$$z = c\eta\zeta.$$

The parameters ζ, η, and ϕ define orthogonal families of oblate spheroids, hyperboloids of one sheet, and half-planes, respectively. The focal ring of the spheroids and hyperboloids has the radius c.

The equilibrium constant, $K_{A_1B_2}$, is then to be approximated by means of the relations

$$2.303kT \log (K_{A_1B_2}/\sigma) = \Delta W$$

and $\qquad\qquad\qquad\qquad\qquad\qquad (2)$

$$\Delta W = W(A_1) + W(B_2) - W(A_2) - W(B_1),$$

where σ is the statistical factor and $W(A_1)$, $W(A_2)$, $W(B_1)$, and $W(B_2)$ each represent the electrostatic work of formation of the corresponding molecule in the solvent. The quantities W and ΔW may be calculated by the use of expressions for the electrostatic potential obtained by the solution of Laplace's equation in the coordinates ζ, η, and ϕ. The calculations are outlined in Part IV of this paper.

For the ratio of the first to the second dissociation constants of a polybasic acid, the considerations of Part IV lead to the following relation which is similar in form to that of Bjerrum,[3]

$$\log [K_1/(K_2\sigma)] = e^2/(2.303kTrD_E),$$

where

$$\frac{1}{D_E} = \frac{1}{D_i} + \left(\frac{1}{D} - \frac{1}{D_i}\right)$$

$$\times \sum_{\substack{n=0 \\ (n+m)\ \text{even}}}^{\infty} \sum_{m=0}^{n} \frac{r}{c} \frac{\alpha_n^m}{1 - (D_i/D) Y_n^m} \cos m\Phi,$$

$$\alpha_n^m = i(2 - \delta_m^0)(2n+1) \qquad (3)$$

$$\times \frac{[(n-m)!(n+m)!]^2}{\left[2^n \left(\frac{n-m}{2}\right)! \left(\frac{n+m}{2}\right)!\right]^4} \frac{Q_n^m(i\zeta_0)}{P_n^m(i\zeta_0)},$$

TABLE I. f_1 and f_2 for dibasic acids.

ζ_0	Ortho f_1	f_2	Meta f_1	f_2	Para f_1	f_2
0.4					0.00004	0.85986
0.5					0.00044	0.75598
0.6					0.00192	0.74652
0.7	0.0380	0.9096	0.0081	0.7815	0.0056	0.7454
0.8	0.0674	0.9028	0.0177	0.7862	0.0118	0.7492
0.9	0.1038	0.8850	0.0304	0.7914	0.0214	0.7544
1.0	0.1446	0.8578	0.0472	0.7933	0.0340	0.7592
1.1	0.1876	0.8240	0.0671	0.7930	0.0492	0.7618
1.2	0.2306	0.7867	0.0894	0.7867	0.0670	0.7618
1.3	0.2724	0.7480	0.1133	0.7782	0.0862	0.7594
1.4	0.3121	0.7096	0.1385	0.7670	0.1072	0.7542
1.6	0.3842	0.6379	0.1897	0.7382	0.1504	0.7362
1.8	0.4467	0.5733	0.2398	0.7048	0.1946	0.7152
2.0	0.4978	0.5185	0.2872	0.6696	0.2376	0.6896
2.2	0.5418	0.4720	0.3401	0.6260	0.2788	0.6618
2.4	0.5793	0.4323	0.3718	0.6012	0.3172	0.6338

and

$$Y_n^m = \frac{m\zeta_0 + (1+\zeta_0^2)^{\frac{1}{2}} P_n^{m+1}(i\zeta_0)/P_n^m(i\zeta_0)}{m\zeta_0 + (1+\zeta_0^2)^{\frac{1}{2}} Q_n^{m+1}(i\zeta_0)/Q_n^m(i\zeta_0)}.$$

In this relation K_1 and K_2 are the first and second dissociation constants of the polybasic acid, and σ is a statistical factor equal to four for symmetric dibasic acids and three for symmetric tribasic acids and their primary acid-ions. e is the protonic charge, k is Boltzmann's constant, T is the absolute temperature, r is the distance between the dissociating protons, and D_E is the effective dielectric constant. D_i and D are the dielectric constants of the molecular cavities and the solvent, respectively, and Φ is the angle between the radii of the focal circle to the dissociating protons. The quantity r/c takes on the values 1, $\sqrt{3}$, and 2 and the quantity Φ the values 60°, 120°, and 180° for ortho, meta, and para (dibasic or substituted monobasic) acids, respectively. δ_m^0 equals zero when $m \neq 0$ or unity when $m = 0$. The parameter ζ_0 defines the molecular cavity. $P_n^m(i\zeta_0)$ and $Q_n^m(i\zeta_0)$ are associated Legendre functions of the first and second kind, respectively, defined for imaginary variable.[14]

Correspondingly, the ratio[8] $K_{A_x B_0}$ of the dissociation constant of the acid A_x, obtained by substituting the polar group X in a parent benzenoid acid A_0, to that of the acid A_0 is given by the equation,

$$\log K_{A_x B_0} = \frac{1}{2.303kT}\left[-\frac{e(\mathbf{\mu}, \mathbf{r})}{D_i r^3} \right.$$

$$+ \left(\frac{1}{D} - \frac{1}{D_i}\right) \sum_{\substack{n=0 \\ (n+m)\ \text{even}}}^{\infty} \sum_{m=0}^{n} \frac{\alpha_n^m}{1 - (D_i/D) Y_n^m} \frac{e}{c^2}$$

$$\times \mathbf{\mu}\{\mathbf{i}_1(n^2 - m^2 + n) \cos m\Phi - \mathbf{i}_2 m \sin m\Phi\} \bigg], \quad (4)$$

where r is the length of the line vector $\mathbf{r}$ from the dissociating proton to the substituent dipole of moment $\mathbf{\mu}$. The moment $\mathbf{\mu}$ equals the difference between the group moment of the substituent X and that of the hydrogen atom replaced and its direction is that of the motion of a small positive charge placed on the dipole axis. The unit vector $\mathbf{i}_1$ is directed from the center of the focal circle along the radius to the dipole $\mathbf{\mu}$ and makes an angle Φ with the radius to the dissociating proton, whereas $\mathbf{i}_2$ is the corresponding unit vector tangent to the focal circle in the direction of increasing ϕ. The other symbols are as in Eq. (3).

Expansion of the quantity $[1 - (D_i/D) Y_n^m]^{-1}$ in a binominal series, followed by rejection of terms in $1/D$ of power higher than the first, makes it possible to convert the formula for $1/D_E$ in Eq. (3) into the form,

$$\frac{1}{D_E} = \frac{f_1}{D_i} + \frac{f_2}{D}. \qquad (5)$$

By the summation of the appropriate series the quantities f_1 and f_2 corresponding to ortho, meta,

[14] W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill Book Company, Inc., New York, 1939).

and para dibasic acids have been computed for a number of values of ζ_0 and are given in Table I.

The corresponding binomial expansion of $[1-(D_i/D)\,Y_n{}^m]^{-1}$ and rejection of terms in $1/D$ of power higher than the first converts Eq. (4) into the form,

$$\log K_{A_xB_0}=\frac{1}{2.303kT}\left[\frac{-e\,|\,\mu_\zeta\,|\cos\,(\mu_\zeta \mathbf{i}_1,\,\mathbf{r})}{r^2 D_\zeta}\right.$$
$$\left.-\frac{e\,|\,\mu_\phi\,|\cos\,(\mu_\phi \mathbf{i}_2,\,\mathbf{r})}{r^2 D_\phi}\right],\quad (6)$$

where

$$\frac{1}{D_\zeta}=\frac{g_1}{D_i}+\frac{g_2}{D},\qquad (6a)$$

and

$$\frac{1}{D_\phi}=\frac{h_1}{D_i}+\frac{h_2}{D},\qquad (6b)$$

where μ_ζ and μ_ϕ are the components of the dipole $\mathbf{\mu}$ along $\mathbf{i}_1$ and $\mathbf{i}_2$, respectively, and D_ζ and D_ϕ are effective dielectric constants corresponding to the dipole components μ_ζ and μ_ϕ, respectively. Equation (6) in its complete form is required in the treatment of metasubstituted benzenoid acids, while for the para isomers the term due to the dipole component μ_ϕ vanishes. Values of g_1, g_2, h_1, and h_2 for meta acids and g_1 and g_2 for para acids computed for various values of ζ_0 are tabulated in Table II. Values of these functions for ortho acids are not tabulated since the series from which they would be calculated converge too slowly to allow of their summation without considerable labor.

By the use of Eqs. (5), (6), (6a), and (6b) and Tables I and II it may be shown that, as ζ_0 and consequently the volume of the acid molecules with given charge configurations increases, the values of D_E, D_ζ, and D_ϕ approach D_i. Again as ζ_0 approaches zero and the cavity degenerates to a disk, immersing the charges in the solvent, the magnitudes of D_E, D_ζ, and D_ϕ go through values higher than the solvent dielectric constant D. These values must accordingly go through a maximum before becoming equal to D at ζ_0 equal to zero. Again for a given value of ζ_0 and Φ, the value of D_E for dibasic acids is greater than that of D_ζ for substituted acids. Corresponding observations have been noted by Kirkwood and Westheimer[9,10] for their models.

Furthermore it is readily seen that the values of D_E for dibasic acids calculated from the data of Table I for a given value of ζ_0 increase in the order ortho, meta, and para. Similarly the values of D_ζ for metasubstituted acids, computed from Table II, are less than those for the para isomer. These orders of the calculated effective dielectric constants of isomeric benzenoid acid molecules have been suggested by Schwarzenbach.[15] Again for a fixed value of ζ_0 the magnitude of D_ϕ for metasubstituted acids is always greater than D_ζ.

PART II. PARAMETERS AND SAMPLE CALCULATIONS

In this section conventions are adopted for consistently fixing the values of the various

TABLE II. g_1, g_2, h_1, and h_2 for substituted acids.

	Meta				Para	
ζ_0	g_1	g_2	h_1	h_2	g_1	g_2
0.4					0.00148	0.8697
0.5					0.00964	0.9103
0.6					0.03112	0.9567
0.7	0.1038	1.0101	0.0334	1.031	0.06844	0.9856
0.8	0.1728	0.9911	0.0640	1.042	0.1192	0.9879
0.9	0.2504	0.9412	0.1042	1.038	0.1792	0.9648
1.0	0.3297	0.8726	0.1546	1.013	0.2432	0.9232
1.1	0.4066	0.7943	0.2086	0.977	0.3088	0.8688
1.2	0.4783	0.7136	0.2650	0.931	0.3716	0.8088
1.3	0.5431	0.6357	0.3232	0.875	0.4312	0.7460
1.4	0.6006	0.5629	0.3790	0.818	0.4864	0.6844
1.6	0.6952	0.4382	0.4828	0.700	0.5828	0.5696
1.8	0.7658	0.3405	0.5728	0.590	0.6612	0.4708
2.0	0.8185	0.2664	0.6472	0.495	0.7232	0.3896
2.2	0.8576	0.2103	0.7084	0.414	0.7728	0.3232
2.4	0.8867	0.1684	0.7574	0.347	0.8124	0.2692

parameters appearing in Eqs. (3)–(6), (6a), and (6b). A typical numerical calculation of the type employed in the application to experimental data is also outlined.

Maximum and intermediate estimates[9] of the proton-proton or proton-dipole distance r for a benzenoid acid may be made by assuming the acid group to be either fully extended or to be executing free internal rotations. For a maximum estimate the dissociating proton is conventionally placed at the projection of its actual position, as calculated by means of x-ray and electron diffraction data, upon the line of the valence bond joining the fully extended acid group to the benzene ring. To obtain the intermediate esti-

[15] G. Schwarzenbach, Helv. Chim. Acta 15, 1468 (1932).

mate the proton is thought to occupy a mean position in time as the acid group rotates internally. For a halogen substituted acid, the point dipole $\mathbf{\mu}$ corresponding to the substituent group is placed at the midpoint of the carbon-halogen bond.[9]

The focal radius c of the oblate spheroidal molecular cavity of a paradibasic or a para-substituted monobasic benzenoid acid is set equal to $r/2$ and takes on the values c_{Ext} and c_{Rot} depending on whether the carboxyl group is considered fully extended or freely rotating. The values of r for the ortho and meta isomers, whose molecules are assumed to have the same shape and focal radius as those of the para acid, are then set equal to c and $\sqrt{3}c$, respectively. The magnitudes of the distances r for the metahalogenated benzoic acids computed in this way and derived directly from the structural geometry of the molecules differ at most by 0.14A.

Further structural calculations indicate that for metasubstituted benzenoid acids the angles $(\mathbf{\mu}, \mathbf{r})$ do not have the values 150° or 30° required when a dipole is situated on the focal circle 120° from the dissociating proton, and directed along a radius. It has therefore been deemed necessary to assign values of the angles $(\mathbf{\mu}, \mathbf{r})$ to the substituent dipoles of the metahalogenated benzenoid acids calculated from diffraction data assuming the acid groups fully extended. For benzenoid acids with composite substituent groups, whose components are placed farther out from the benzene ring than are those of the halogen, the angles $(\mathbf{\mu}, \mathbf{r})$ have been given rounded values close to those of the corresponding iodosubstituted acid. The resulting components of $\mathbf{\mu}$, μ_r and μ_ϕ, along the radius and along the tangent of the focal circle, respectively, are easily calculated by trigonometry.

In order to determine a value for the parameter ζ_0 defining the boundary of an oblate spheroidal molecule it is required to estimate not only the focal radius c but also the molecular cavity volume τ which is related to c and ζ_0 by the equation,

$$\tau/c^3 = (4\pi/3)\zeta_0(1+\zeta_0^2). \tag{7}$$

The molecular cavity of volume τ may be considered to delimit a region of low dielectric constant containing the molecule and a shell of thickness δ roughly corresponding to the relatively empty interstitial space between the molecule itself and the surrounding solvent molecules. Use is made of the concept of van der Waals radii[16] in making estimates of the volumes of the molecules of parasubstituted or unsubstituted benzenoid acids or their conjugate bases which are ellipsoids with axes of different lengths rather than oblate spheroids. The length of the major axis of such an ellipsoid is taken to be equal to the distance between the outermost atoms along the axis of symmetry plus the sum of the van der Waals radii of these atoms. The length of the mean axis is set equal to the distance between the two ortho hydrogen atoms plus twice the van der Waals radius of hydrogen. The length of the minor axis equals the van der Waals thickness of the benzene ring. The ellipsoidal shell around the molecule is assumed arbitrarily to have a thickness δ equal to 0.8A, the average difference between the van der Waals radius and the covalent radius of an atom. The resulting van der Waals volume τ_w including this shell and the molecule within is then considered an approximation to the volume τ of the oblate spheroidal molecular cavity of the present theory. The molecules of the ortho and meta isomers of a para acid or base are assumed to have the same cavity volumes as the molecules of the para compounds. The quantity τ_w as used in the study of relative acid strengths by the electrostatic theory is taken as the average value of τ_w for all four acid and base molecules involved.

To avoid ambiguities concerning the directions of dipole moments, only benzenoid acids with the symmetric substituents NO_2, CN, F, Cl, Br, I, CH_3, and $C(CH_3)_3$ are considered. The values of the dipole moment $|\mathbf{\mu}|$, which is the difference between the moment of the substituent group and that of hydrogen, are set equal to the moments of the correspondingly substituted benzenes in the vapor state. For the substituents mentioned they are, in Debyes, respectively, 4.21, 4.39, 1.57, 1.72, 1.70 as given by Smyth,[17] 1.50 as estimated by Groves and Sugden,[18] 0.37 and 0.70

[16] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition.
[17] C. P. Smyth, J. Phys. Chem. 41, 209 (1937).
[18] L. G. Groves and S. Sugden, J. Chem. Soc., p. 1992 (1937).

as determined by Baker and Groves.[19] The dipole moment vectors for the alkyl groups are directed along radii away from the benzene ring, while those for the other groups mentioned are directed radially into the benzene ring.

D_i has been assigned[9] the value 2.00, while D is the value of the dielectric constant of the solvent medium under consideration. In what follows the values of D for water, glycol, methanol, ethanol, and n-propanol are given by Åkerlof,[20] for n-butanol by Wooten and Hammett,[21] for dioxane-water mixtures by Åkerlof and Short.[22]

As an illustration of the type of calculation used in applications of the theory, the calculation of $\log K_{A_xB_0}$ for m-nitrobenzoic acid in water at 25°C is outlined. For this acid τ_w is 255A^3, $|\mu|$ is 4.21D, the angle (μ, r) is set equal to 140°. c is given the value 3.35A, D_i equals 2.00, and D equals 78.5. From the angle (μ, r) it follows that the angles $(\mu_\zeta i_1, r)$ and $(\mu_\phi i_2, r)$ are 150° and 60°, respectively. $|\mu_\zeta|$, which equals $|\mu| \cos[150° - (\mu, r)]$, and $|\mu_\phi|$, which equals $|\mu| \sin[150° - (\mu, r)]$, are found to be 4.15D and 0.74D, respectively. The proton-dipole distance r, which equals $\sqrt{3}c$, is 5.80A. Since τ_w/c^3 equals 6.78, ζ_0 may be found graphically from Eq. (7) to be equal to 0.90. From ζ_0 are obtained values of g_1, g_2, h_1, and h_2 in Table II which when used in Eqs. (6a) and (6b) with the given values of D_i

TABLE III. Structural parameters[a] for the metasubstituted benzoic acids, $m-XC_6H_4COOH$ in water at 25°C.

x	$\log K_{A_xB_0}$ (Exp.)	τ_w A^3	(μ, r) °	c A	c_{Ext} A	c_{Rot} A	$\log K_{A_xB_0}$ (Calc.)
NO$_2$	0.71[b]	255	140	3.35			0.70
CN	0.52[c]	265	140	3.55			0.52
F	0.34[b]	250	138	3.20	3.25	2.85	0.33
Cl	0.38[d]	255	139	3.20	3.35	2.95	0.37
Br	0.39[b]	260	140	3.20	3.40	3.00	0.37
I	0.35[b]	265	140	3.20	3.45	3.00	0.34
CH$_3$	−0.07[b]	255	40	3.30			−0.07
C(CH$_3$)$_3$	−0.10[e]	265	40	3.40			−0.10

[a] In the table, the values of τ_w are given to the nearest 5A^3, those of (μ, r) to the nearest degree, and those of c, c_{Ext}, and c_{Rot} to the nearest 0.05A.
[b] J. F. J. Dippy, Chem. Rev. 25, 151 (1939).
[c] M. Kilpatrick and R. D. Eanes, J. Am. Chem. Soc. 65, 589 (1943).
[d] B. Saxton and H. F. Meier, J. Am. Chem. Soc. 56, 1918 (1934).
[e] J. B. Shoesmith and A. Mackie, J. Chem. Soc., p. 300 (1936).

[19] J. W. Baker and L. G. Groves, J. Chem. Soc., p. 1147 (1939).
[20] G. Åkerlof, J. Am. Chem. Soc. 54, 4125 (1932).
[21] L. A. Wooten and L. P. Hammett, J. Am. Chem. Soc. 57, 2289 (1935).
[22] G. Åkerlof and O. A. Short, J. Am. Chem. Soc. 58, 1241 (1936).

and D yield the magnitudes 7.3 and 15.1 for D_ζ and D_ϕ, respectively. From Eq. (6) is then obtained the value 0.70 for $\log K_{A_xB_0}$.

The evaluation of $\log K_{A_xB_0}$ for a parasubstituted benzenoid acid and that of $\log[K_1/(K_2\sigma)]$ for a benzenoid polybasic acid follow similar lines. It is possible to reverse all these calculations to obtain the value of any one of the parameters discussed in this section from given values of the other parameters and the appropriate data for dissociation constants.

PART III. APPLICATIONS OF THEORY TO THE SUBSTITUTED BENZOIC ACIDS

In this section the term "structural parameters" will refer to the cavity volume τ, or to its estimate, the van der Waals volume τ_w, the focal radius c, and the angle (μ, r) which characterize the molecules in an acid-base equilibrium, while the term "electrical parameters" will refer to the magnitude of the substituent dipole moment $|\mu|$, the internal dielectric constant D_i of the molecules, and the solvent dielectric constant D.

By means of the electrostatic theory, the experimentally determined values of $\log K_{A_xB_0}$ for the metasubstituted benzoic acids in water at 25°C together with the appropriate values of the electrical parameters and all the structural parameters except the focal radii c have been employed to calculate the magnitudes of c for these acids. The values of c thus computed are given in Table III. The values employed for τ_w, (μ, r), and $\log K_{A_xB_0}$(Exp.) the experimentally determined $\log K_{A_xB_0}$ are also presented in Table III. The values of c_{Ext} and c_{Rot} in the table were computed in the manner outlined in Part II. The quantities $\log K_{A_xB_0}$(Calc.), also tabulated, are the magnitudes of $\log K_{A_xB_0}$ computed from the values of c, τ_w, and (μ, r) in the table.

Inspection of Table III shows that c for the halogen substituted acids takes on values lying between c_{Ext} and c_{Rot}, respectively the upper limit and free-rotation estimates of the focal radius c computed from electron diffraction data. It is further to be noted that the values of c for the halogens are less than those for the other substituent groups while c for the methyl group is less than that for the tertiary butyl group. This observation is consistent with the fact that the polyatomic substituent groups possess bond

dipoles which are not attached directly to the aromatic nucleus[16, 23] so that the point dipoles characterizing these groups should be farther away from the benzene ring than those of the halogens.

TABLE IV. log KA_xB_0(Calc.)/log KA_xB_0(Exp.) for the metasubstituted benzoic acids, $m-XC_6H_4COOH$ in various solvents at 25°C.

Solvent	X =NO$_2$	F	Cl	Br	I	CH$_3$
Glycol	0.83	0.84	0.75	0.74	0.73	0.9
Methanol	0.76	0.71	0.66	0.67	0.67	0.9
Ethanol	0.72	0.72	0.67	0.66	0.63	0.9
n-Propanol	0.76	0.75	0.72	0.71	0.65	0.8
n-Butanol	0.83	0.98	0.78	0.79	0.72	0.8
Dioxane-water, 26.5 wt. %	0.82	0.83	0.86	0.88	0.95	0.6
Dioxane-water, 43.5 wt. %	0.78	0.85	0.81	0.83	0.90	0.5
Dioxane-water, 61.0 wt. %			0.84			
Dioxane-water, 73.5 wt. %	0.90	0.88	0.87	0.90	0.93	0.6
Hypothetical, by extrapolation to $D = \infty$.	1.22	1.08	1.10	1.07	1.17	0.9

The reasonableness of the magnitudes and of the order of the values of the focal radii c of the metasubstituted benzoic acids constitutes good evidence that the electrostatic theory, assuming oblate spheroidal molecules, satisfactorily accounts for the relative acid strengths of these compounds.

The differences in Table III between log KA_xB_0(Exp.) and log KA_xB_0(Calc.) represent unavoidable errors introduced into the computations by rounding-off the values of c and by uncertainties in making and reading the large scale graphs used in the calculations. It is to be noted, however, that the set of structural parameters in the table is not the only possible one. On the average, increases in c of 0.1A, in τ_w of 25A^3, and in D_i of 1 unit cause a decrease in log KA_xB_0 of between fifteen and twenty percent, an increase of between twelve and fifteen percent, and a decrease of thirty percent, respectively. Variations in c and τ of the magnitudes given and in D_i of one-half unit, occurring in such directions as to leave log KA_xB_0(Calc.) unchanged, would yield values of these parameters as reasonable as those in Table III. However, for the sake of consistency, the conventions described in Part II for determining these parameters have been retained.

Values of log KA_xB_0 for the metasubstituted benzoic acids in solvents other than water have been calculated by the use of the same structural and electrical parameters employed to compute log KA_xB_0(Calc.) in water with the exception that

[23] L. E. Sutton, Proc. Roy. Soc. **A133**, 668 (1931).

the dielectric constant of each solvent considered has been substituted for that of water. The ratios of these calculated values to the experimental ones of Elliott[2] in n-propanol and of Elliott and Kilpatrick[1] for all the other solvents are given in Table IV. As has been pointed out by Elliott and Kilpatrick[1] in connection with the work of Westheimer and Kirkwood[10] and as is further indicated by the results in Table IV, the values of log KA_xB_0 calculated by the cavity model theory with the structural parameters successfully used for water solution are lower than the observed values in all actual solvents other than water.

An explanation of this lack of agreement between calculated and experimental values of log KA_xB_0 shown in Table IV may be found in the probability that the cavity volumes τ of acid and base solute molecules in solvents other than water are greater than those in water. Since the solvents other than pure water are made up of molecules which are larger than those of water itself, it would be expected that the interstitial spaces, and consequently the cavity volumes τ, in these solvents should be greater than those in water. The extent of the increase in τ required to bring about agreement between the calculated and experimental values of log KA_xB_0 in solvents other than water may be inferred from the data in Table V. The values of τ in this table have been calculated from the experimental values of log KA_xB_0, the appropriate electrical parameters and the structural parameters c and (μ, r) of Table III.

TABLE V. Values of τ in A^3 for metasubstituted benzoic acids, $m-XC_6H_4COOH$ in various solvents.

Solvent	X =NO$_2$	F	Cl	Br	I	CH$_3$
Water	255	250	255	260	265	255
Glycol	305	325	340	360	370	295
Methanol	340	380	410	420	425	335
Ethanol	370	375	405	425	450	295
n-Propanol	350	360	395	410	460	335
n-Butanol	320	360	360	360	410	335
Dioxane-water, 26.5 wt. %	300	305	300	290	285	450
Dioxane-water, 43.5 wt. %	320	300	320	315	300	535
Dioxane-water, 61.0 wt. %			315			
Dioxane-water, 73.5 wt. %	295	310	300	300	290	535
Hypothetical, by extrapolation to $D = \infty$.	215	235	225	240	225	285

As would be expected, inspection of Table V reveals that, for each acid, τ increases continuously in magnitude in the series of solvents beginning with water and ending with n-propanol, the difference in τ for ethanol and n-propanol not

TABLE VI. $\Delta \log K_{A_xB_0}$ for parasubstituted acids $p-XC_6H_4COOH$ in various solvents at 25°C.

Solvent	X=NO₂	CN	F	Cl	Br	I	CH₃	C(CH₃)₃
Water	0.30	0.30	−0.17	−0.03	−0.03		−0.12	−0.12
Glycol	0.25		−0.18	−0.09	−0.03	0.00	−0.10	
Methanol	0.24		−0.22	−0.11	−0.05	−0.02	−0.11	
Ethanol	0.29		−0.17	−0.05	−0.01	0.01	−0.11	
n-Propanol	0.28		−0.19	−0.08	−0.05	−0.01	−0.13	
n-Butanol	0.29		−0.11	−0.07	−0.04	−0.04	−0.11	
Dioxane-water, 26.5 wt. %	0.34		−0.15				−0.14	
Dioxane-water, 43.5 wt. %	0.40		−0.09	0.01	0.03	0.08	−0.11	
Dioxane-water, 61.0 wt. %				0.02				
Dioxane-water, 73.5 wt. %	0.35		−0.15	−0.03	0.02	0.02	−0.09	
Pure solvent average	0.28		−0.17	−0.07	−0.04	−0.01	−0.11	
Mean deviation	0.02		0.02	0.02	0.02	0.02	0.01	
Mixed solvent average	0.36		−0.13	0.00	0.02	0.05	−0.11	
Mean deviation	0.02		0.03	0.02	0.02	0.03	0.02	

being significant. (The erratic behavior of τ for m-toluic acid arises from the large relative error in the experimental values of $\log K_{A_xB_0}$ for this acid.) The decrease in τ exhibited by each acid on going down the series from the solvent n-propanol to the solvent n-butanol cannot at present be explained. The cavity volume calculated for each acid in the dioxane-water mixtures does not vary greatly with the concentration of dioxane. Unmixing of the solvent giving rise to a relatively constant environment around the acid and base molecules may serve to explain this fact.[24, 25] The free energy increment, due to this unmixing, which contributes to the value of $\log K_{A_xB_0}$ cannot at present be taken into account.[25] In subsequent computations cognizance is taken of the change of τ for an acid from solvent to solvent.

The structural parameters of Tables III and V together with the values of the electrical parameters discussed in Part II have been employed to compute $\log K_{A_xB_0}$ for the parasubstituted benzoic acids. The values thus obtained have been subtracted from the corresponding experimental values[1, 2] to yield the quantities $\Delta \log K_{A_xB_0}$ given in Table VI. The two averages of this quantity for each acid taken over the set of pure and mixed solvents, respectively, together with their mean deviations, are also shown in the table.

The values of $\Delta \log K_{A_xB_0}$ in Table VI for each parasubstituted acid are practically constant from one pure solvent to another. In dioxane-water mixtures the results in the table indicate that $\Delta \log K_{A_xB_0}$ for each acid is algebraically greater than in the pure solvents, although there are insufficient data to make certain of the constancy of that quantity with change of concentration of dioxane. This difference between one-component and mixed solvents may be connected with the possibility of variations in the free energy of unmixing[24, 25] of the mixed solvent by the molecules present in it on going from meta compounds to their para isomers.

It is desirable at this point to compare the results for $\log K_{A_xB_0}$ of parasubstituted benzoic acids obtained by means of the prolate spheroidal model of Westheimer and Kirkwood[10, 26] with those obtained by the author employing the oblate spheroidal model. The assumptions made in the comparison are that the molecule of a parasubstituted benzoic acid is to be represented by either a prolate spheroidal or an oblate spheroidal cavity of a given volume τ and that the length of the focal line of the prolate spheroid equals that of the focal diameter of the oblate spheroid so that the interprotonic distance for each model is the same. On this basis it is found that the absolute magnitudes of $\log K_{A_xB_0}$ as given by the prolate spheroidal model are from zero to fifteen percent greater than those yielded by the oblate spheroidal model. In explanation of this difference it may be shown that the foci of the prolate spheroidal cavity are farther distant from the boundary surface than is the focal circle

[24] J. L. Magee, T. Ri, and H. Eyring, J. Chem. Phys. 9, 419 (1941).
[25] G. Scatchard, J. Chem. Phys. 9, 34 (1941).
[26] Tables of values of functions required for the calculations were kindly supplied by F. H. Westheimer in a private communication to M. Kilpatrick.

in the oblate spheroidal cavity. Thus the effective dielectric constant for the interaction of the substituent dipole with the dissociating proton is nearer the internal molecular constant and therefore lower for the prolate spheroidal cavity model than for the oblate spheroidal model. Accordingly, $|\log K_{A_xB_0}|$ as calculated by the former model would be greater than that computed by the use of the latter.

On the basis of the constancy of $\Delta \log K_{A_xB_0}$ with change of pure solvent, it is possible to use the values of $\log K_{A_xB_0}$ of the meta and para isomers of a substituted benzoic acid with a symmetrical substituent in one pure solvent and the values of $\log K_{A_xB_0}$ for one of the isomers in a number of other solvents to predict $\log K_{A_xB_0}$ of the other isomer in the latter solvents.

During the course of the measurements by Kilpatrick and Eanes[27] of $\log K_{A_xB_0}$ for the cyanobenzoic acids at 25°C, the author predicted the values of $\log K_{A_xB_0}$ for the meta isomer in glycol, methanol, and ethanol from the already determined data for the meta isomer in water and for the para isomer in all four solvents. The structural parameters for the cyanobenzoic acids in water solution determined from $\log K_{A_xB_0}$ for the meta isomer in water are recorded in Table III. From these parameters and the experimentally determined value of $\log K_{A_xB_0}$, for the para isomer in water was calculated the value of $\Delta \log K_{A_xB_0}$ 0.30, given in Table VI, for para-cyanobenzoic acid. This value of $\Delta \log K_{A_xB_0}$, assumed constant in all the alcohols, was subtracted from the experimental values of $\log K_{A_xB_0}$ for the para acid in these solvents to yield new values of $\log K_{A_xB_0}$ consistent with the electrostatic theory developed by the author. From these last results, the values of c and $(\mathbf{y}, \mathbf{r})$ in Table III, and the appropriate electrical parameters, values of D_ζ and thence of ζ_0 were determined for the cyanobenzoic acids in each solvent. These values of ζ_0 permitted the determination of D_ζ and D_ϕ for the meta acid in each alcoholic solvent. These last values of D_ζ and D_ϕ together with the values of c and $(\mathbf{y}, \mathbf{r})$ in Table III and the value of $|\mathbf{y}|$ given in Part II yielded the desired values of $\log K_{A_xB_0}$ which are given in Table VII in the column marked $\log K_{A_xB_0}$(Calc.).

[27] M. Kilpatrick and R. D. Eanes, J. Am. Chem. Soc. 65, 589 (1943).

The agreement between theory and experiment is considered to be good.

The quantity $\Delta \log K_{A_xB_0}$ for a substituted benzoic acid in a one-component solvent at a given temperature may be regarded as providing a numerical measure of the effect on the acid strength of the acid group due to the resonance interaction[13] of the substituent group in the para position with the benzene ring, the acid group, and its conjugate base group. The values of $\Delta \log K_{A_xB_0}$ in Table VI indicate that the acid-strengthening effect of the nitro and cyano groups is practically the same. There is also clearly exhibited the well-recognized[28] decrease of the acid-weakening effect due to resonance interactions of parasubstituted halogens in the order $F > Cl > Br > I$. The almost equal values of $\Delta \log K_{A_xB_0}$ for the methyl and tertiary butyl groups are to be noted. It would be expected that the absolute magnitude of $\Delta \log K_{A_xB_0}$ for

TABLE VII. $\log K_{A_xB_0}$ for cyanobenzoic acids.

Solvent	$\log K_{A_xB_0}$ (Exp.) Para acid	$\log K_{A_xB_0}$ (Exp.) Meta acid	$\log K_{A_xB_0}$ (Calc.) Meta acid
Water	0.65	0.52	
Glycol	0.82	0.72	0.73
Methanol	0.91	0.83	0.82
Ethanol	1.00	0.97	0.94

the tertiary butyl group would be less than that for the methyl group since it is thought[29, 30] that the latter group can conjugate with the benzene ring more readily than the former. This point of disagreement would bear experimental investigation and verification.

The invariance of $\Delta \log K_{A_xB_0}$ with change of solvent can be made to appear quite reasonable on the following basis. It may be presumed[13, 16] that the extra acid-strengthening or acid-weakening effect of a para substituent arises from the difference in contributions of the paraquinoidal structures (more important than the orthoquinoidal structures) to the final fused structures of the para acid and its conjugate base, and the consequent difference in resonance stabilization.

[28] H. B. Watson, *Modern Theories of Organic Chemistry* (Clarendon Press, Oxford, 1941), second edition.
[29] J. W. Baker and W. S. Nathan, J. Chem. Soc., p. 1844 (1935).
[30] R. S. Mulliken, C. A. Ricke, and W. G. Brown, J. Am. Chem. Soc. 63, 41 (1941).

The paraquinoidal resonance should tend to locate an accumulation of charge on the ring carbon atom adjacent to the acid group. The potential energy and, therefore, the relative contribution of the paraquinoidal form to the resonance should then be largely governed by the electrostatic interaction of the acid group dipole or the conjugate base group charge, as the case may be, with the adjacent accumulated charge. This interaction should occur relatively deep within the molecule across a short distance. The solvent dielectric constant should, therefore, contribute little to the effective dielectric constant for the interaction. Accordingly, the relative contributions of the paraquinoidal forms to the resonance should be little affected by change of solvent and the value of $\Delta \log K_{A_xB_0}$ should not change much.

In connection with the constancy of $\Delta \log K_{A_xB_0}$ it is recognized that all the solvents considered in this work have been hydroxylic solvents. Thus there have not occurred any great changes in the type of solvation of the molecules considered. It is probable that change of solvent type might introduce complications.

The author has attempted calculations, similar to those for the substituted benzoic acids, for the substituted phenols, thiophenols, anilinium ions, N, N-dimethylanilinium ions, and phenylboric acids. Some interesting results have been obtained, but the lack of large quantities of consistent experimental data, such as those available for the benzoic acids, introduces considerable ambiguity into the fixing of structural parameters. Accordingly, the whole treatment of these acids by means of the theory has been rendered very uncertain.

For the benzenoid polycarboxylic acids, the situation with respect to the scarcity of consistent experimental data is much the same as for the acids mentioned in the last paragraph. On application to the existing data the electrostatic theory of the author seems to give no more satisfactory results than do those of Bjerrum[3] and of Kirkwood and Westheimer.[9,10,12] The accumulation of more experimental data on the acidity of the substituted benzenoid acids, other than the benzoic acids, and the benzenoid polybasic acids is highly desirable.

PART IV. DERIVATION OF THEORETICAL RESULTS

The results presented in Part I are now to be derived. The electrostatic potential V in charge-free space within and without the oblate spheroidal surface ζ_0, separating a molecule of dielectric constant D_i from a continuous solvent medium of dielectric constant D, must satisfy Laplace's equation,[14]

$$\frac{\partial}{\partial \zeta}\left[(1+\zeta^2)\frac{\partial V}{\partial \zeta}\right]+\frac{\partial}{\partial \eta}\left[(1-\eta^2)\frac{\partial V}{\partial \eta}\right]$$
$$+\frac{\zeta^2+\eta^2}{(1+\zeta^2)(1-\eta^2)}\frac{\partial^2 V}{\partial \phi^2}=0 \quad (8)$$

in the oblate spheroidal coordinates of Eq. (1). The potential inside ζ_0 due to the charges $e_1, e_2, \cdots, e_\nu$ characterizing the charge distribution of the molecule may be written[10,31] in the form,

$$V_i=\sum_{k=1}^{\nu}\frac{e_k}{D_i|\varrho-\varrho_k|}$$
$$+\sum_{n=0}^{\infty}\sum_{m=-n}^{n}A_n^m P_n^{|m|}(i\zeta)T_n^{|m|}(\eta)\exp(im\phi), \quad (9)$$

where the A_n^m are constants, ϱ and ϱ_k are radius vectors from a point, fixed with respect to the molecule, to the field point (ζ, η, ϕ) and to the charge e_k, respectively, and the $T_n^{|m|}(\eta)$ and $P_n^{|m|}(i\zeta)$ are the associated Legendre functions of the first kind defined respectively for real independent variable with absolute magnitude less than unity, and for imaginary independent variable.[14] The first term on the right of Eq. (9) may be expanded[14,31] in the form,

$$\sum_{k=1}^{\nu}\frac{e_k}{D_i|\varrho-\varrho_k|}$$
$$=\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\frac{E_n^m}{D_i}Q_n^{|m|}(i\zeta)T_n^{|m|}(\eta)\exp(im\phi), \quad (10)$$

where

$$E_n^m=\frac{i}{c}(2n+1)\left\{\frac{(n-|m|)!}{(n+|m|)!}\right\}^2(-1)^{|m|}$$
$$\times\sum_{k=1}^{\nu}e_k P_n^{|m|}(i\zeta_k)T_n^{|m|}(\eta_k)\exp(-im\phi_k),$$

[31] T. M. MacRobert, *Spherical Harmonics* (Methuen and Company, Ltd., London, 1927).

where the $Q_n{}^{|m|}(i\zeta_k)$ are the associated Legendre functions of the second kind defined for imaginary independent variable.[14] The charges e_k of Eq. (10) are assumed to be located at the points $(0, \eta_k, \phi_k)$. In order to fulfill the condition that it vanish at an infinite distance from the charges e_k, the potential V_e outside the ellipsoid ζ_0 must take the form,[31]

$$V_e = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} B_n{}^m Q_n{}^{|m|}(i\zeta) T_n{}^{|m|}(\eta)$$
$$\times \exp{(im\phi)}. \quad (11)$$

The quantities V_i and V_e must satisfy the boundary conditions[14] that the potential and normal component of electric displacement be continuous at all points on the spheroid ζ_0, which may be written in the form,

$$V_i(\zeta_0, \eta, \phi) = V_e(\zeta_0, \eta, \phi),$$
$$-1 \le \eta \le 1$$
$$0 \le \phi \le 2\pi \quad (12)$$

and

$$D_i\left(\frac{\partial V_i(\zeta, \eta, \phi)}{\partial \zeta}\right)_{\zeta=\zeta_0} = D\left(\frac{\partial V_e(\zeta, \eta, \phi)}{\partial \zeta}\right)_{\zeta=\zeta_0}.$$

Equations (9) and (11) are substituted into Eq. (12) and advantage taken of the orthogonality of the functions $T_n{}^{|m|}(\eta)$ over the range, $-1 \le \eta \le 1$, and $\exp{(im\phi)}$ over the range, $0 \le \phi \le 2\pi$, to yield a set of linear relations between the constants $A_n{}^m$ and $B_n{}^m$, which by a simple rearrangement become

$$\frac{E_n{}^m}{D_i} Q_n{}^{|m|}(i\zeta_0) + A_n{}^m P_n{}^{|m|}(i\zeta_0)$$
$$= B_n{}^m Q_n{}^{|m|}(i\zeta_0), \quad (13)$$

and

$$E_n{}^m Q_n{}'^{|m|}(i\zeta_0) + A_n{}^m D_i P_n{}'^{|m|}(i\zeta_0)$$
$$= B_n{}^m D Q_n{}'^{|m|}(i\zeta_0),$$

where the quantities $P_n{}'^{|m|}(i\zeta_0)$ and $Q_n{}'^{|m|}(i\zeta_0)$ are the derivatives of $P_n{}^{|m|}(i\zeta)$ and $Q_n{}^{|m|}(i\zeta)$ evaluated at $\zeta = \zeta_0$. The solutions of Eqs. (13) for the quantities $A_n{}^m$ are

$$A_n{}^m = E_n{}^m \left[\frac{1}{D} - \frac{1}{D_i}\right]$$
$$\times \frac{Q_n{}^{|m|}(i\zeta_0) Q_n{}'^{|m|}(i\zeta_0)}{P_n{}^{|m|}(i\zeta_0) Q_n{}'^{|m|}(i\zeta_0)}. \quad (14)$$
$$- (D_i/D) Q_n{}^{|m|}(i\zeta_0) P_n{}'^{|m|}(i\zeta_0)$$

The recurrence formula,[14]

$$i\Theta_n{}'^{|m|}(i\zeta) = \frac{|m|\zeta\Theta_n{}^{|m|}(i\zeta)}{1+\zeta^2} + \frac{\Theta_n{}^{|m|+1}(i\zeta)}{(1+\zeta^2)^{\frac{1}{2}}}, \quad (15)$$

where $\Theta_n{}^m(i\zeta)$ may be replaced by either $P_n{}^m(i\zeta)$ or $Q_n{}^m(i\zeta)$, may be used to transform Eq. (14) into the relation,

$$A_n{}^m = E_n{}^m \left[\frac{1}{D} - \frac{1}{D_i}\right]$$
$$\times \frac{Q_n{}^{|m|}(i\zeta_0)}{P_n{}^{|m|}(i\zeta_0)} \left[1 - \frac{D_i}{D} Y_n{}^{|m|}\right]^{-1}, \quad (16)$$

where

$$Y_n{}^{|m|} = \frac{|m|\zeta_0 + (1+\zeta_0{}^2)^{\frac{1}{2}} P_n{}^{|m|+1}(i\zeta_0)/P_n{}^{|m|}(i\zeta_0)}{|m|\zeta_0 + (1+\zeta_0{}^2)^{\frac{1}{2}} Q_n{}^{|m|+1}(i\zeta_0)/Q_n{}^{|m|}(i\zeta_0)}.$$

The work W required to form the molecule by bringing the charges $e_1, \cdots, e_\nu$ from initial positions of infinite separation in the solvent may be computed by substituting Eqs. (9) and (16) in the relation,

$$W = \frac{1}{2} \sum_{l=1}^{\nu} e_l \psi(0, \eta_l, \phi_l), \quad (17)$$

where $\psi(0, \eta_l, \phi_l)$ is the potential V_i at the location of the charge e_l, assuming e_l to have been removed after all the other charges present are fixed in place.

It is now possible to evaluate the quantity ΔW of Eq. (2) for the equilibrium between the molecules A_1, B_2, A_2, and B_1, where all the molecules are bounded by oblate spheroids ζ_0 and possess identical charge configurations except for the fact that A_1 and B_1 have similarly placed charges $e_1, \cdots, e_s$ in excess over the molecules A_2 and B_2, respectively. On the basis of these assumptions the use of Eqs. (9), (16), (17), and (2), followed by replacement of the quantities $P_n{}^{|m|}(i \cdot 0)$ and $T_n{}^{|m|}(0)$ by their values in terms of n and m, yields the relation,

$$\Delta W = e \sum_{k=1}^{s} \frac{e_k}{D_i r_k}$$
$$+ \frac{i}{c}\left[\frac{1}{D} - \frac{1}{D_i}\right] \sum_{n=0}^{\infty} \sum_{\substack{m=-n \\ (n+m) \text{ even}}}^{n} L_n{}^m (-1)^{(3n+|m|)/2}$$

$$\times \frac{(2n+1)[(n-|m|)!]^2(n+|m|)!}{\left\{2^n\left(\dfrac{n-|m|}{2}\right)!\left(\dfrac{n+|m|}{2}\right)!\right\}^3}$$

$$\times \frac{Q_n^{|m|}(i\zeta_0)}{P_n^{|m|}(i\zeta_0)}\left[1-\frac{D_i}{D}Y_n^{|m|}\right]^{-1}, \quad (18)$$

where

$$L_n^m = e\sum_{k=1}^{s} e_k T_n^{|m|}(\eta_k)\exp(-im\phi_k).$$

The symbol e represents a dissociating proton located at the point $(0,0,0)$ and r_k the distance of the kth among the charges $e_1, \cdots, e_s$ from the proton e. In the case of the symmetrical dibasic acids the charges $e_1, \cdots, e_s$ reduce to the single proton e placed on the focal circle at the point $(0,0,\Phi)$, and r_k in Eq. (18) becomes the single quantity r, the interprotonic distance, while L_n^m may be rewritten in the form,

$$L_n^m = e^2\frac{(-1)^{(n-|m|)/2}(n+|m|)!}{2^n\left(\dfrac{n-|m|}{2}\right)!\left(\dfrac{n+|m|}{2}\right)!}$$

$$\times \exp(-im\Phi). \quad (19)$$

Replacement of the first summation in Eq. (18) by the term $e/(D_i r)$ and use of Eq. (19) yield an expression for ΔW which, after application of Euler's formula for the cosine, may be combined with the form of Eq. (2) applicable to dibasic acids to yield Eq. (3).

When substituent effects are being considered, the charges $e_1, \cdots, e_s$ are replaced by a positive charge q at $(0, \eta, \Phi+\Delta\phi)$ and a negative charge $-q$ at $(0,0,\Phi)$. The line vector from $-q$ to q is written $\Delta\mathbf{s}$. It is then assumed that the positive charge approaches the negative charge, and, at the same time, the absolute magnitude q of each increases in such a way that

$$\lim_{\substack{\Delta s \to 0 \\ q \to \infty}} q\Delta\mathbf{s} = \mathbf{\mu}, \quad (20)$$

where $\mathbf{\mu}$ is a point dipole, representing the substituent dipole, at $(0,0,\Phi)$. The dipole $\mathbf{\mu}$ has components along the unit vector $\mathbf{i}_1$ directed from the center of the focal circle through the point $(0,0,\Phi)$ and along the unit vector $\mathbf{i}_2$ tangent to the focal circle in the direction of increasing ϕ. On this basis, in Eq. (18),

$$e\sum_{k=1}^{s}\frac{e_k}{D_i r_k} \to -\frac{e\mathbf{\mu r}}{D_i r^3}, \quad (21)$$

where $\mathbf{r}$ is the line vector from the dissociating proton to the dipole $\mathbf{\mu}$ and r is its absolute magnitude, while

$$L_n^m = e\mathbf{\mu}\left[\mathbf{i}_1\exp(-im\Phi)\right.$$

$$\times\lim_{\eta \to 0}\frac{T_n^{|m|}(\eta)-T_n^{|m|}(0)}{c(1-\eta^2)^{\frac{1}{2}}-c}+\mathbf{i}_2 T_n^{|m|}(0)$$

$$\times\left.\lim_{\Delta\phi \to 0}\frac{\exp[-im(\Phi+\Delta\phi)]-\exp(-im\Phi)}{c\Delta\phi}\right]$$

$$=\frac{(-1)^{(n-|m|)/2}(n+|m|)!}{2^n\left(\dfrac{n-|m|}{2}\right)!\left(\dfrac{n+|m|}{2}\right)!}$$

$$\times\exp(-im\Phi)\frac{e\mathbf{\mu}}{c}$$

$$\times[\mathbf{i}_1(n^2-|m|^2+n)-\mathbf{i}_2(-1)^{\frac{1}{2}}m]. \quad (22)$$

Substitution of Eqs. (21) and (22) in Eq. (18), followed by the use of Euler's formulas for the sine and cosine, yields a result which, when combined with the appropriate special case of Eq. (2), gives rise to Eq. (4). On account of symmetry, a component of the dipole in a direction perpendicular to the plane of the focal ring makes no contribution to ΔW.