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Substituent Effects on Dissociation of Benzoic Acids and Heteroconjugation of Benzoates with *p*-Bromophenol in Acetonitrile, *N*,*N*-Dimethylformamide, and Dimethyl Sulfoxide. Intramolecular Hydrogen Bonding in *o*-Hydroxybenzoic Acids and Their Anions[1]

I. M. Kolthoff* and M. K. Chantooni, Jr.

Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received October 7, 1970

Abstract: Values of the dissociation constant pK^d_{HA} of a number of mono- and disubstituted benzoic acids were determined potentiometrically, using the glass electrode, in DMF and DMSO. Resulting Hammett plots of pK^d_{HA} *vs.* σ were found linear in these solvents as in AN. The same ρ_{HA} values of -2.4 ± 0.1 were found in the three solvents. Formation constants $K^f_{HR\cdot A^-}$ of the 1:1 and 1:2 heteroconjugates of substituted benzoates A^- with *p*-bromophenol (HR) were found potentiometrically in DMSO and DMF as in AN; linear Hammett plots of log $K^f_{HR\cdot A^-}$ yielded a $\rho_{HR\cdot A^-}$ value equal to -0.61 ± 0.04 in each of the three solvents. Values of $\sigma_{o\text{-}NO_2} = +1.10$ and $\sigma_{o\text{-}Cl} = +0.55$ fitted the above Hammett plots. On the other hand, the value of σ for *o*-OH as read for salicylic acid from the Hammett plot of pK^d_{HA} does not fit similar plots of log $K^f_{HR\cdot A^-}$ in the three solvents and of log $K^f_{HA\cdot Cl^-}$ and log $K^f_{HA_2^-}$ in acetonitrile. The abnormal behavior of salicylic acid and its anion is attributed to intramolecular hydrogen bonding. From infrared spectra in acetonitrile it is concluded that intramolecular hydrogen bonding is much weaker in both salicyclic and 2,6-dihydroxybenzoic acids than in their anions. Chloride ion is postulated to form an intermolecular hydrogen bond with the carboxyl OH group of these acids, the intramolecular hydrogen bond of the phenolic OH group remaining intact.

Parker, *et al.*,[2] found considerable scatter in plots on a logarithmic scale of the dissociation constants of uncharged acids, K^d_{HA}, in aprotic solvents *vs.* the constants in the protic solvents water or methanol. On the other hand, plots of values of pK^d_{HA} in dimethyl sulfoxide (DMSO) *vs.* those in *N*,*N*-dimethylformamide (DMF) were roughly linear with hardly any scatter. In the present study we have tested the relation by determining pK^d_{HA} values potentiometrically with the glass electrode of a group of substituted benzoic acids in the protophobic solvent acetonitrile (AN) and the aprotic protophylic solvents DMF and DMSO. Previously, pK^d_{HA} values of a few substituted benzoic acids have been reported in these solvents.[3-5] Whenever comparison was possible, several of our values have been found to differ considerably from those of Parker, *et al.*,[2] whose constants are approximate and do not refer to an ionic strength of zero.

Also, in the present study the formation constants $K^f_{HR\cdot A^-}$ of the 1:1 and 1:2 heteroconjugates of substituted benzoates, A^-, with *p*-bromophenol (HR) in DMSO and DMF were estimated from potentiometric pa_H data with the glass electrode in equimolar or roughly equimolar mixtures of acid and tetraethyl-

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant No. AF-AFOSR-1223-67.

[2] B. W. Clare, D. Cook, E. C. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966).

[3] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **92**, 7025 (1970).

[4] I. M. Kolthoff, M. K. Chantooni, Jr., and H. Smagowski, *Anal. Chem.*, **42**, 1622 (1970).

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ammonium salt to which HR was added. Previously,[3] $K^{\mathrm{f}}_{\mathrm{HR\cdot A^-}}$ and $K^{\mathrm{f}}_{\mathrm{(HR)_2A^-}}$ values of several benzoates have been reported in AN. Included in the present work are the constants for salicyclic acid in the three solvents. Our quantitative knowledge of the intramolecular hydrogen bonding in salicylic and 2,6-dihydroxybenzoic acids and in their anions is very limited. Dunn[6] states: "Intramolecular hydrogen bonding in salicylic acid has been demonstrated for the solid acid by X-ray crystallography[7] and for solutions of the acid in cyclohexane, ether, and carbon tetrachloride by ultraviolet and infrared spectra,[8–11] and in benzene by ^{13}C nmr shifts."[12] Infrared spectra of salicylic acid in deuterium oxide have been interpreted on the basis of strong intramolecular hydrogen bonding in both acid and anion.[13] No information exists in the literature on the intramolecular hydrogen bonding in solutions of salicylic and 2,6-dihydroxybenzoic acids and their anions in the solvent AN, which forms an intermolecular hydrogen bond with a carboxyl group. Dimerization of salicylic acid *via intermolecular* hydrogen bonding is slight in AN.[14] In the present study no single value of σ for the *o*-hydroxyl group could be found which fitted the linear Hammett plots of $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ and the logarithms of $K^{\mathrm{f}}_{\mathrm{HR\cdot A^-}}$, $K^{\mathrm{f}}_{\mathrm{HA\cdot Cl^-}}$, and $K^{\mathrm{f}}_{\mathrm{HA_2^-}}$ *vs.* σ. This is attributed to intramolecular hydrogen bonding in salicylic acid and salicylate. In order to gain further insight into this hydrogen bonding, infrared spectra of salicylic, 2,6-dihydroxybenzoic, and benzoic acids in AN were compared with those of the chloride heteroconjugates. Infrared spectra of the corresponding simple anions in AN are also reported.

Experimental Section

Chemicals. Solvents. Acetonitrile,[15] *N,N*-dimethylformamide,[4] and dimethyl sulfoxide[16] were purified, stored, and dispensed as described elsewhere.

Acids and Salts. All benzoic acids and their tetraethylammonium salts have been used previously.[3,5,17] *p*-Bromophenol,[18] potassium chloride,[19] and tetraethylammonium chloride[20] were also used previously.

Instrumentation. Details of the conductometric measurements[15] and potentiometric $\mathrm{p}a_{\mathrm{H}}$ measurements[21] have been given elsewhere. Infrared spectra were run on a Perkin-Elmer Model 521 infrared spectrophotometer using 111-μ potassium bromide cells in a similar way as previously.[18]

Results

Conductometric Section. The following ionic mobilities at infinite dilution in AN have been used previously:[3,17,19] $\lambda_{0\mathrm{K^+}} = 76$, $\lambda_{0\mathrm{Na^+}} = 70$, $\lambda_{0\mathrm{Cl^-}} = 89$, $\lambda_{0\mathrm{Sal^-}} = 78$, $\lambda_{0\mathrm{HA\cdot Cl^-}} = \lambda_{0\mathrm{(HA)_2Cl^-}} = 55$. It was assumed that $\lambda_{0\mathrm{HR\cdot Sal^-}} = \lambda_{0\mathrm{(HR)_2Sal^-}} = \lambda_{\mathrm{HSal\cdot Sal^-}} = 56$.[17]

As with other benzoic acids,[3] the two heteroconjugation constants of salicylic acid with chloride in AN were found from the conductometrically determined ionic solubility of potassium chloride in presence of the acid, using a value of K_{sp} of potassium chloride of 1.05×10^{-8}.[3,19] The following values of $f^2[\mathrm{K^+}]^2/K_{\mathrm{sp}}$ were found at the various concentrations of salicylic acid: 21, 0.0354 *M*; 44, 0.0675 *M*; 95, 0.123 *M*; 169, 0.190 *M*; 307, 0.278 *M*; and 495, 0.378 *M* HSal, yielding $K^{\mathrm{f}}_{\mathrm{HSal\cdot Cl^-}} = 5.0 \times 10^2$ and $K^{\mathrm{f}}_{\mathrm{H(Sal)_2Cl^-}} = 2.2 \times 10^3$. In DMF and DMSO the above method is not applicable for determination of $K^{\mathrm{f}}_{\mathrm{HA\cdot Cl^-}}$ as potassium chloride is soluble to a considerable extent, even in absence of HA, $\mathrm{p}K_{\mathrm{sp}}$ being 5.4[22] (molal scale) and 3.9,[23] respectively.

The heteroconjugation constants of salicylate with *p*-bromophenol (HR) in AN were calculated from the ionic solubility of sodium salicylate in presence of HR, as was done with other benzoates.[3] The value of K_{sp} of sodium salicylate was found equal to 1.7×10^{-6} as compared to a previous value of 1.4×10^{-6}.[17] The latter value was used in the calculation of $K^{\mathrm{f}}_{\mathrm{HR\cdot Sal^-}}$. The following values of $f^2[\mathrm{Na^+}]^2/K_{\mathrm{sp}}$ were found at various concentrations of HR: 50, 0.0311 *M*; 104, 0.0653 *M*; 273, 0.111 *M*; and 456, 0.172 *M* HR, yielding $K^{\mathrm{f}}_{\mathrm{HR\cdot Sal^-}} = 1.3 \times 10^2$ and $K^{\mathrm{f}}_{\mathrm{(HR)_2Sal^-}} = 4.7 \times 10^2$. As the solubility of sodium salicylate is appreciable in DMF and DMSO, the heteroconjugation constants of salicylate with HR were found potentiometrically in these solvents (*vide infra*).

Potentiometric Section. Values of $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ of the various benzoic acids were estimated from $\mathrm{p}a_{\mathrm{H}}$ values in DMF and DMSO in equimolar mixtures of the acid and tetraethylammonium salt in a concentration range between 2.5×10^{-3} and 1.2×10^{-2} *M*. As previously,[4,5] activity coefficients were estimated in these solvents using the limiting Debye–Hückel relation with the appropriate constants. In Table I $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ values of benzoic acids found in this work in DMF and DMSO are compared with those reported in these solvents by other investigators. Also listed are values in AN, some of which had been reported previously.[3]

Plots of $\mathrm{p}a_{\mathrm{H}}$ *vs.* C_{HR} (HR = *p*-bromophenol) in equimolar or roughly equimolar mixtures of meta- and para-substituted (Figure 1A) or ortho-substituted (Figure 1B) benzoic acids and their tetraethylammonium salts in DMSO, DMF, and AN are presented in Figure 1. Values of $\log K^{\mathrm{f}}_{\mathrm{HR\cdot A^-}}$ and $\log \beta_{\mathrm{HR\cdot A^-}}$ ($\beta = K^{\mathrm{f}}_{\mathrm{(HR)_2A^-}}/K^{\mathrm{f}}_{\mathrm{HR\cdot A^-}}$) were calculated from the data in Figure 1 as described previously,[24] regarding the solution as equimolar, and are tabulated in Table II. For comparison, values of $\log K^{\mathrm{f}}_{\mathrm{HR\cdot A^-}}$ and $\log \beta_{\mathrm{HR\cdot A^-}}$ of benzoates previously reported in AN[3] are included in Table II.

Infrared Section. Infrared spectra in the –OH stretch region, 3400–2200 cm^{-1}, of 0.18–0.22 *M* benzoic, 2,6-dihydroxybenzoic, and salicylic acids in AN in the absence and presence of 0.23 or 0.73 *M* tetraethylammonium chloride are presented in Figure 2. When

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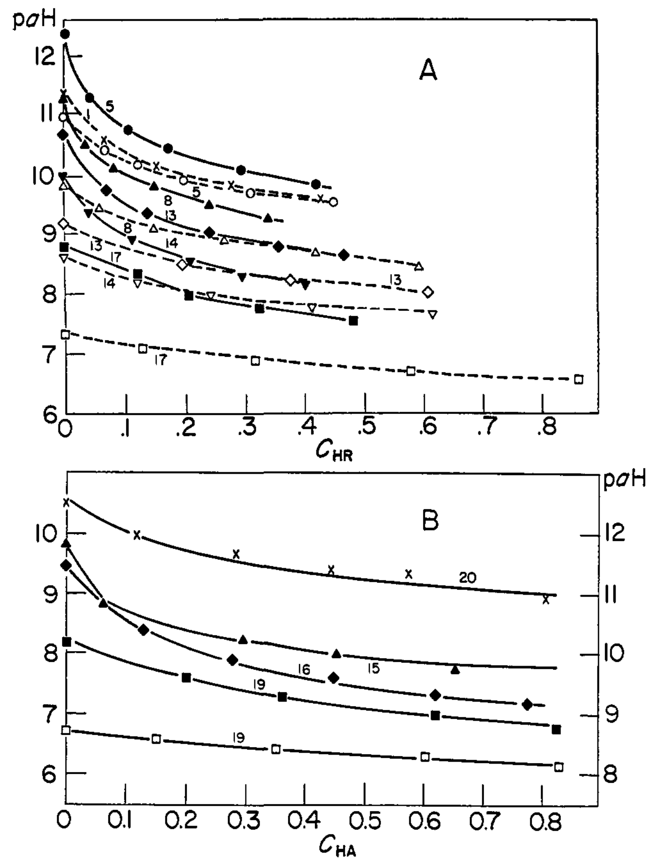

Figure 1. Effect of *p*-bromophenol on pa_H of mixtures of benzoic acids and their tetraethylammonium salts in DMSO, DMF, and AN: A, meta- and para-substituted and B, ortho-substituted benzoic acids. Numbers are the same as those in Table I. A: (1) DMSO, $C_{HA} = C_s = 6.45 \times 10^{-3}\ M$; (5) DMSO, $C_{HA} = 0.965 \times 10^{-2}$, $C_s = 1.14 \times 10^{-2}\ M$; DMF, $C_{HA} = C_s = 3.15 \times 10^{-3}\ M$; (8) DMSO, $C_{HA} = 9.25 \times 10^{-3}$, $C_s = 8.20 \times 10^{-3}\ M$; $C_s = 4.91 \times 10^{-3}\ M$; (13) DMSO, $C_{HA} = 8.96 \times 10^{-3}$, $C_s = 1.06 \times 10^{-2}\ M$; DMF, $C_{HA} = C_s = 4.91 \times 10^{-3}\ M$; (14) DMSO, $C_{HA} = 9.14 \times 10^{-3}$, $C = 8.05 \times 10^{-3}\ M$; DMF, $C_{HA} = C_s = 4.70 \times 10^{-3}\ M$; and (17) DMSO, $C_{HA} = 1.04 \times 10^{-2}$, $C_s = 8.60 \times 10^{-3}\ M$; DMF, $C_{HA} = C_s = 3.08 \times 10^{-3}\ M$. B: (15) DMF, $C_a = C_s = 4.60 \times 10^{-3}\ M$; (16) DMF, $C_a = C_s = 3.75 \times 10^{-3}\ M$; (19) DMSO, $C_{HA} = C_s = 2.40 \times 10^{-3}\ M$; DMF, $C_{HA} = C_s = 4.30 \times 10^{-3}\ M$; and (20) AN, $C_{HA} = C_s = 3.64 \times 10^{-3}\ M$. Open symbols, in DMSO; filled symbols, in DMF. Curve 20 in B, right-hand ordinate; all others, left-hand ordinate.

corrected for the absorption of tetraethylammonium chloride, the spectra of the above acids are identical in 0.23 and 0.73 *M* chloride.

Infrared spectra of tetraethylammonium *m*-bromobenzoate, salicylate, and 2,6-dihydroxybenzoate also in the region 3400–2000 cm^{-1} are presented in Figure 3.

Discussion

Hammett Plots of Dissociation Constants of Benzoic Acids and Heteroconjugation Constants of Benzoates. Miron and Hercules[25] titrated potentiometrically a series of substituted benzoic acids with tetrabutylammonium hydroxide reagent in benzene–methanol in the following aprotic solvents of intermediate dielectric constant: AN, DMF, 2-nitropropane, and nitrobenzene. From Hammett plots of half-neutralization potentials (HNP) they report ρ_{HA} values of -3.0, -2.7, -3.0, and -3.3, respectively, to within ±10%. Very likely the hydrogen bond acceptors and donors water and methanol introduced in these titrations have a nonnegligible effect on HNP[26] as these compounds are weak acids and weak bases. These additives were not introduced in Ritchie's or in our systems. Ritchie[27] titrated substituted benzoic acids in DMSO with dimsylcesium, the Hammett plot of $pK^d{}_{HA}$ yielding $\rho_{HA} = -2.6$. Hammett plots presented in Figure 4 were constructed from $pK^d{}_{HA}$ values in Table I of substituted benzoic acids in AN, DMF, and DMSO. Values of σ for meta and para substituents were those from a com-

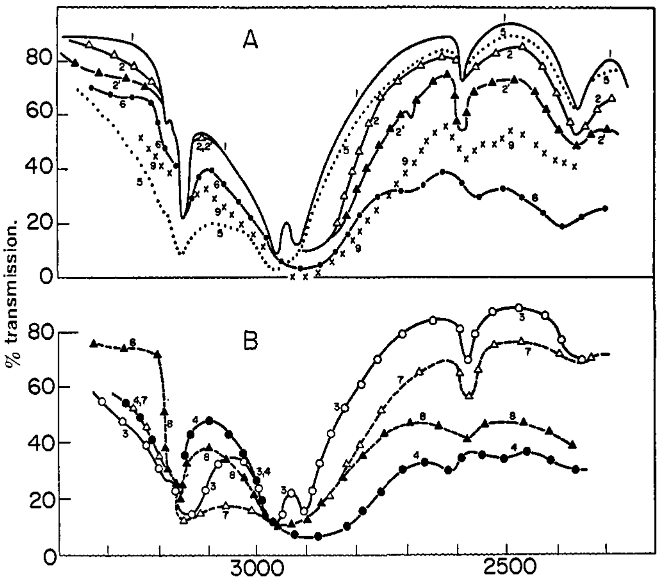

Figure 2. Infrared spectra in AN of benzoic, salicylic, and 2,6-dihydroxybenzoic acids in the absence and presence of tetraethylammonium chloride in the region 3400–3200 cm^{-1}: (1) solvent, (2) 0.23 and (2′) 0.73 *M* Et_4NCl, (3) 0.23 *M* benzoic acid, (4) 0.23 *M* benzoic acid + 0.73 *M* Et_4NCl, (5) 0.19 *M* salicylic acid, (6) 0.19 *M* salicylic acid + 0.73 *M* Et_4NCl, (7) 0.20 *M* 2,6-dihydroxybenzoic acid, (8) 0.18 *M* 2,6-dihydroxybenzoic acid + 0.23 *M* Et_4NCl, and (9) 0.20 *M* *p*-bromophenol + 0.73 *M* Et_4NCl.

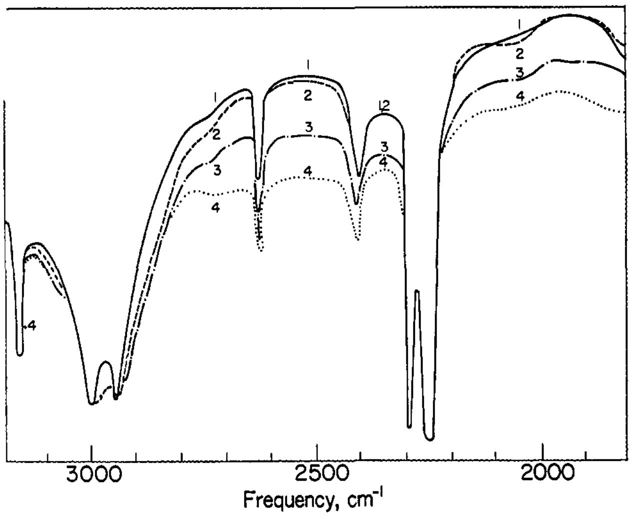

Figure 3. Infrared spectra in AN of tetraethylammonium salts in the region 3200–1800 cm^{-1}: (1) solvent, (2) 0.23 *M* tetraethylammonium *m*-bromobenzoate, (3) 0.26 *M* salicylate, and (4) 0.22 *M* 2,6-dihydroxybenzoate.

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[25] R. R. Miron and D. M. Hercules, *Anal. Chem.*, **33**, 1770 (1961).

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Table I. Dissociation Constants of Substituted Benzoic Acids in Dimethyl Sulfoxide (DMSO), *N*,*N*-Dimethylformamide (DMF), and Acetonitrile (AN)

Acid	DMSO	DMF	AN
(1) 3,4-Dimethyl	11.41[i]	12.98[j]	21.25[i]
(2) *m*-Hydroxy	11.1[d]		
(3) *m*-Methyl	11.0,[d] 11.0[j]		
(4) *m*-Amino	10.4,[h] 11.6[d], 11.0[j]		
(5) Unsubstituted	11.1,[f] 11.0[e], 11.0[g] 11.0,[h] 11.0,[d] 11.0,[i] 10.9[j]	12.27,[a] 12.28[h] 12.20,[c] 12.39[i]	20.7[k]
(6) *p*-Chloro	10.1[d]		
(7) *p*-Bromo	10.5[h]		
(8) *m*-Bromo	9.68[i]	11.29[i]	19.5[k]
(9) *o*-Chloro	9.29[i]	11.18[b]	
(10) 3,4-Dichloro	9.20[i]	10.95[i]	19.04[i]
(11) *m*-Nitro	9.2,[h] 9.17[i]	10.82[i]	19.29[i]
(12) 3,5-Dichloro	8.81[i]	10.43[i]	18.75[i]
(13) *p*-Nitro	9.0,[h] 8.9,[d] 9.04[i]	10.6,[a] 10.63[b]	18.7[k]
(14) 3-Nitro-4-chloro	8.62[i]	10.04[j]	18.55[i]
(15) *o*-Nitro	8.18[i]	10.06,[b] 9.60,[c] 9.90[i]	18.24[i]
(16) 2,6-Dichloro		9.61[i]	
(17) 3,5-Dinitro	7.4,[j] 7.40[i]	8.95,[a] 8.49,[b] 8.87[i]	16.9[k]
(18) 2,4-Dinitro	6.52[i]	8.16[i]	16.19[i]
(19) Salicylic	6.8,[f] 6.6[j]	8.24,[a] 8.24[i]	16.7[k]
(20) 2,6-Dihydroxy	3.1[f]	3.56[a]	12.6[f]

[a] Reference 4. [b] J. Juillard, *J. Chim. Phys. Physicochim. Biol.*, 691 (1970); J. Juillard and A. Mallet, *C. R. Acad. Sci.*, **264**, 2098 (1967). [c] A. Petrov and I. Umanskii, *Zh. Fiz. Khim.*, **41**, 1374 (1967); **42**, 3052 (1968). [d] C. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **90**, 2821 (1968). [e] Reference 2. [f] Reference 5. [g] I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962). [h] I. Jasinski and K. Stefanuk, *Chem. Anal. (Warsaw)*, **10**, 211 (1965). [i] This work. [j] J. Courtot-Coupez and M. Le Demezet, *Bull. Soc. Chim. Fr.*, 1033 (1969). [k] Reference 17.

Table II. Heteroconjugation Constants of Substituted Benzoates (A^-) with *p*-Bromophenol (HR) in DMSO, DMF, and AN

	DMSO		DMF		AN	
Benzoate	Log $K^f_{HR \cdot A^-}$	Log $\beta_{HR \cdot A^-}$	Log $K^f_{HR \cdot A^-}$	Log $\beta_{HR \cdot A^-}$	Log $K^f_{HR \cdot A^-}$	Log $\beta_{HR \cdot A^-}$
(1) 3,4-Dimethyl	1.85	−0.7				
(5) Unsubstituted	1.67	+0.18	2.38	0.75	3.55	0.68
(8) *m*-Bromo	1.42	*a*	2.11	0.5	3.26	1.08
(13) *p*-Nitro	1.23	−0.35	1.92	0.6	3.04	1.12
(14) 3-Nitro-4-chloro	1.11	−0.52	1.88	0.34	2.98	0.81
(15) *o*-Nitro			1.78	0.5	2.90	0.80
(16) 2,6-Dichloro			1.79	0.6		
(17) 3,5-Dinitro	0.72	−0.30	1.57	0.0	2.56	1.04
(19) *o*-Hydroxy	0.30	−0.30	1.02	0.35	2.12	0.55
(20) 2,6-Dihydroxy					1.24	0.00

[a] No detectable $(HR)_2A^-$ formed.

pilation of Brown.[28] Ortho substituents are discussed below. Additivity of σ values was found to hold, as in water, for dissociation of disubstituted benzoic acids.[29] Least-squares ρ_{HA} values in AN, DMF, and DMSO from Figure 4 are −2.4, −2.36, and −2.48. Within experimental error of individual pK^d_{HA} values, ±0.15 unit, resulting ρ_{HA} values are the same in the three aprotic solvents. Our average ρ_{HA} value of −2.4 is considerably less negative than those of Miron and Hercules in AN and DMF, and slightly less negative than Ritchie's in DMSO. The following substituents, the σ values of which are known to be solvent dependent,[30] *p*-methoxy, *p*-ethoxy, *p*-amino, and *p*-hydroxy, have been excluded from the present study. Miron and Hercules stated that deviation of *m*-aminobenzoic acid from the Hammett plots increases with decreasing dielectric constant of the solvent, owing to the presence of the zwitterion form of the acid. No such deviation of this acid in DMSO (dielectric constant 46) is apparent in Figure 4. In the present work, no appreciable deviation of 3,4-dimethylbenzoic acid from the Hammett plots in Figure 4 was observed, deviation of *p*-methylbenzoic acid in nitro solvents having been attributed by Miron and Hercules[25] to π-electron complexation of the acid and solvent.

Excluding ortho substitution (*vide infra*), we now consider solvent effects on the hydrogen-bond-accepting property of substituted benzoate ions, A^-, with reference to formation of the 1:1 heteroconjugate $HR \cdot A^-$, HR being *p*-bromophenol. In DMF and DMSO as in AN[3] the hydrogen-bond-accepting capacity of A^- with reference to HR increases with increasing basicity of A^-. Linear Hammett plots of log $K^f_{HR \cdot A^-}$, constructed from the data in Table II, were obtained in DMSO and DMF (Figure 5), as in AN.[3] Least-squares $\rho_{HR \cdot A^-}$ values and intercepts are −0.62, 3.53; −0.57, 2.37; and −0.65, 1.69 in AN, DMF, and DMSO, respectively. Within the experimental error of ±0.05 unit in log $K^f_{HR \cdot A^-}$, $\rho_{HR \cdot A^-}$ is identical in the three solvents and equal to 0.6. In the following section we consider the significance of the constancy of the ρ values in pK^d_{HA} and log $K^f_{HR \cdot A^-}$ *vs.* σ relations on the medium transfer coefficients of the species involved.

Medium Transfer Coefficients of HA, A^-, and $HR \cdot A^-$. A simple expression relates the medium transfer coefficient of the undissociated benzoic acids, ${}^2\gamma^1{}_{HA}$, their

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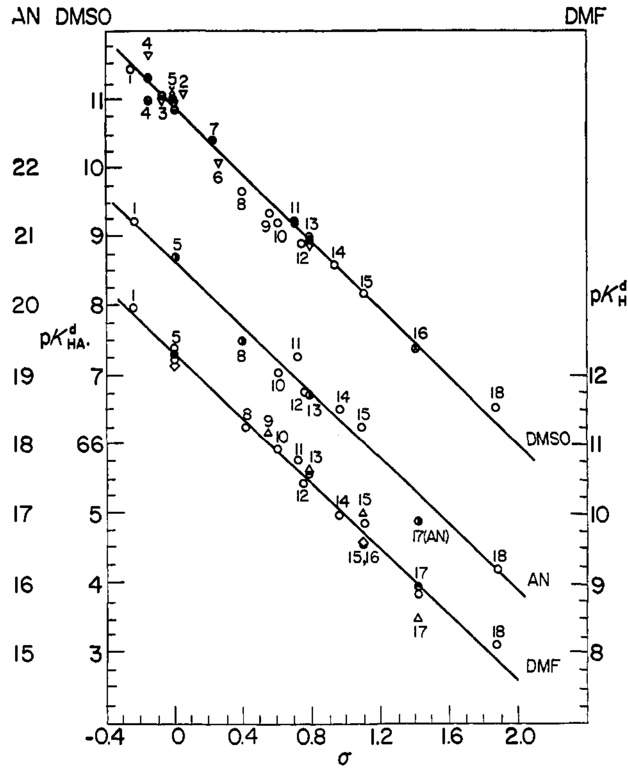

Figure 4. Plots of pK^d_{HA} of benzoic acids *vs.* Hammett σ values in AN, DMF, and DMSO. Numbers are the same as those in Table I. Intercepts and slopes are 20.65 and −2.41 in AN, 12.33 and −2.36 in DMF, and 10.92 and −2.4 in DMSO, respectively. Numbers refer to the letters of references cited in footnote in Table I as follows: *a*, ◒, *b*, △; *c*, ◇; *d*, ▽; *e*, +; *f*, ×; *g*, ◐; *h*, ●; *i*, ○; *j*, ◓; and *k*, ◑.

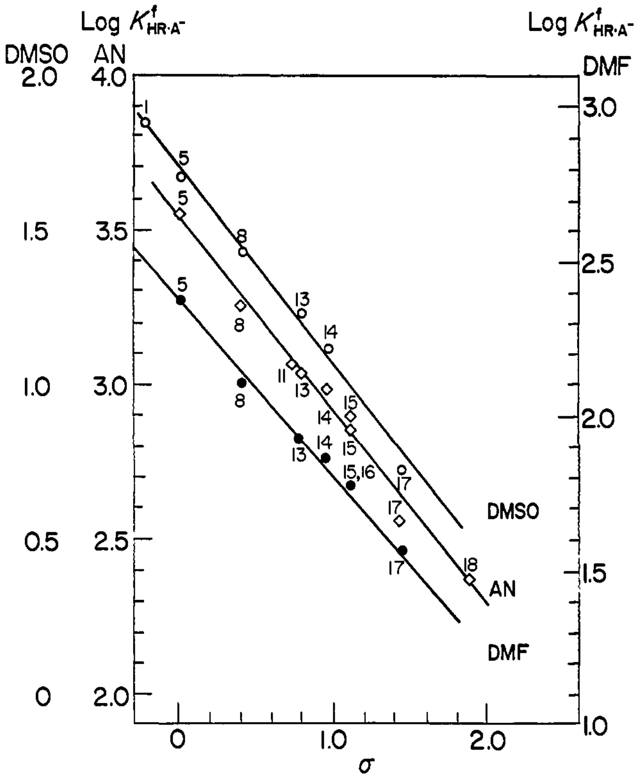

Figure 5. Plots of log $K^f_{HR\cdot A^-}$ of benzoates *vs.* Hammett σ values in AN, DMF, and DMSO. Numbers are same as those in Table I. Intercepts and slopes are 3.53 and −0.62 in AN, 2.37 and −0.57 in DMF, and 1.69 and −0.65 in DMSO.

anions, ${}^2\gamma^1_{A^-}$, and their dissociation constant, K^d_{HA}, between solvents 1 and 2.[31]

$$\Delta pK^d_{HA} = (pK^d_{HA})_1 - (pK^d_{HA})_2 = \log {}^2\gamma^1_{H^+} + \log {}^2\gamma^1_{A^-} - \log {}^2\gamma^1_{HA} \quad (1)$$

Since ΔpK^d_{HA} was found to be the same for any two substituted benzoic acids HA and HA′ between a given pair of the three aprotic solvents in Table I, it follows from eq 1 that $(\gamma_{A'^-}/\gamma_{A^-})_1{}^2 = (\gamma_{HA'}/\gamma_{HA})_1{}^2$, *i.e.*, $\Delta\Delta pK^d_{HA} = 0$. This implies that the electrical part of the free energy transfer of A^- from the isodielectric solvent 1 to 2 can be neglected as compared to the nonelectrical part. A similar situation holds for the heteroconjugation constants of substituted benzoates with *p*-bromophenol, HR.

$$\log (K^f_{HR\cdot A^-})_2 - \log (K^f_{HR\cdot A^-})_1 = \log {}^2\gamma^1_{HR\cdot A^-} - \log {}^2\gamma^1_{HR} - \log {}^2\gamma^1_{A^-} \quad (2)$$

Since $\Delta \log K^f_{HR\cdot A^-}$ has been found to be the same for any two substituted benzoates A'^- and A^- between a given pair of aprotic solvents (1 and 2) in Table II, $\Delta\Delta \log K^f_{HR\cdot A^-} = 0$ and $(\gamma_{HR\cdot A'^-}/\gamma_{HR\cdot A^-})_1{}^2 = (\gamma_{A'^-}/\gamma_{A^-})_1{}^2$. This relation states that the medium effect of the heteroconjugate $HR\cdot A^-$ parallels that of the simple anion A^-.

Ortho Substituents. It was shown in AN[3] that for ortho-substituted nitro- and chlorobenzoic acids and benzoates the substituent effect σ is essentially electrical in nature, steric effects being practically absent. Values of pK^d_{HA} and log $K^f_{HR\cdot A^-}$ in AN lie on the respective Hammett plots when $\sigma_{o\text{-}NO_2} = +1.10$ and $\sigma_{o\text{-}Cl} = +0.60$ (log $K^f_{HR\cdot A^-}$). The value of $\sigma_{o\text{-}NO_2} = +1.10$ also fits the Hammett plots of pK^d_{HA} in Figure 4 and log $K^f_{HR\cdot A^-}$ in Figure 5 in DMF and DMSO. The value of $\sigma_{o\text{-}Cl} = +0.55$ as compared to +0.50 reported by Traynham[32] fits the Hammett plots in Figure 4 in the three solvents and in Figure 5 in DMF and DMSO. It is evident that the substituent effects of the *o*-nitro and *o*-chloro groups are independent of the nature of any of the three aprotic solvents. Furthermore, Davis and Hetzer[33] obtained values of $\sigma_{o\text{-}NO_2} = +1.04$ and $\sigma_{o\text{-}Cl} = +0.38$ from the Hammett plot of the logarithm of the equilibrium constant corresponding to the reaction of substituted benzoic acids, HA, and diphenylguanidine, B, in benzene, *i.e.*, $HA + B \rightleftarrows BHA$. No data are available for corresponding σ values in other aromatic solvents, which may be quite different due to π bonding.

Intramolecular Hydrogen Bonding in *o*-Hydroxybenzoic Acids and Their Anions in AN, DMF, and DMSO. Although no quantitative information can be derived from the data in this study, it is possible to make some qualitative statements regarding the nature and the relative strengths of the intramolecular hydrogen bonding in salicylic and 2,6-dihydroxybenzoic acids and their anions in these solvents.

In the infrared spectra in Figure 2 the broad -OH stretching band of the carboxyl group in AN in benzoic acid occurs from 3400 down to at least 3050 cm^{-1} and is shifted to slightly lower frequencies (by ~40

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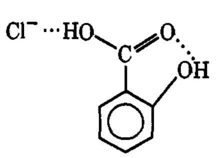
[31] I. M. Kolthoff, J. J. Lingane, and W. D. Larson, *J. Amer. Chem. Soc.*, 60, 2512 (1938).

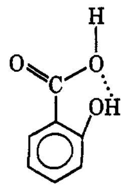
[32] M. Tribble and J. Traynham, *ibid.*, 91, 379 (1969).

[33] M. M. Davis and H. Hetzer, *J. Res. Nat. Bur. Stand.*, 60, 569 (1958).

cm^{-1}) in salicylic acid. Salicylic acid (as monomer) in carbon tetrachloride gives a narrower -OH stretching band around 3530 cm^{-1}.[34] The difference in frequency and breadth of this band of salicylic acid in the two solvents is attributed to appreciable intermolecular hydrogen bonding of the carboxyl -OH group to AN. The intramolecular hydrogen-bonded phenolic -OH stretching band in salicylic (~3200–2900 cm^{-1}) and 2,6-dihydroxybenzoic acids (~3200–2400 cm^{-1}), which is absent in benzoic acid in AN, apparently overlaps the methyl C–H stretching bands of the solvent (~3200–2800 cm^{-1}) as well as the carboxyl -OH stretch. The former band occurs around 3230 cm^{-1} in salicylic acid (monomer and dimer) in carbon tetrachloride.[34] In the presence of chloride the carboxyl -OH stretching band in all the acids is shifted to lower frequencies (2800 to at least 2300 cm^{-1}; Figure 2) owing to intermolecular hydrogen bonding with chloride (structure I for salicylic acid). Intermolecular hydrogen-bonded -OH stretching bands found in the spectrum of a mixture of *p*-bromophenol and chloride (Figure 2) occur between 3200 and 2500 cm^{-1}, but the extinction coefficient at 2750–2550 cm^{-1} is only about one-half that of the carboxyl -OH chloride band (4 and 9 in Figure 2). This difference permits us to make a distinction between intermolecular hydrogen bonding of chloride with phenolic -OH and with carboxyl -OH group(s). From comparison of spectra between 2750 and 2550 cm^{-1} mixtures of chloride with benzoic, 2,6-dihydroxybenzoic, and salicylic acids and *p*-bromophenol (Figure 2), it is concluded that salicylic and 2,6-dihydroxybenzoic acids are intermolecularly hydrogen bonded to chloride primarily through the carboxyl rather than the phenolic -OH groups(s). Apparently, chloride does not break the intramolecular hydrogen bond of these acids to an appreciable extent, which would be expected if salicylic acid had structure II.



I



II

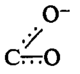
Presence of the intramolecularly hydrogen-bonded carbonyl oxygen of the carboxyl group in salicylic and 2,6-dihydroxybenzoic acids in AN is confirmed by comparison of the C=O stretching frequencies tabulated in Table III, but not drawn in Figure 2. The lower frequency of the C=O group band in salicylic acid as compared to that of benzoic acid (as monomer) in dioxane has been attributed to intramolecular hydrogen bonding in the former.[35] Addition of chloride also results in a shift to lower carbonyl frequencies in salicylic and benzoic acids in AN (Table III). For some unexplained reason this is not true for 2,6-dihydroxybenzoic acid. It is to be noted that resonance energy in the carboxyl group must be partially overcome in the complexation to chloride. As a result, it is possible that the intramolecular hydrogen bond in salicylic acid is actually somewhat strengthened owing to stabilization of structure I rather than weakened by conjugation of the carboxyl group to chloride. This situation may account for the fact that $K^{f}_{HA\cdot Cl^-}$ is 5×10^2 for salicylic acid as compared to only 1.6×10^2 for benzoic acid. The addition of two chloride ions, one to hydroxyl and one to carboxyl, in one salicylic acid molecule is more or less excluded on electrostatic grounds. Chloride ion appears to be a strong hydrogen-bond acceptor, as $(HSal)_2Cl^-$ is quite stable, $\beta_{HA\cdot Cl^-}$ being the same order of magnitude for both salicylic and benzoic acids (*cf.* ref 3).

Table III. Carbonyl Stretching Band Frequency (cm^{-1}) in Solutions of Substituted Benzoic Acids in AN in the Absence and Presence of Chloride

	Concentration of Et_4NCl added, *M*		
Benzoic acid[a]	0	0.23	0.73
Unsubstituted	1722 1720[b]	1700	1700
m-Hydroxybenzoic	1717	1709	
Salicyclic	1682 1680[b]	1652	1650
2,6-Dihydroxybenzoic	1685	1682	

[a] Concentration 0.18–0.23 *M* (see text). [b] In dioxane; ref 35.

The salicylate ion in AN is a fairly strong hydrogen-bond acceptor, log $K^{f}_{HR\cdot Sal^-}$ being 2.1 as compared to a value of 3.5 for log $K^{f}_{HR\cdot Bz^-}$. Infrared spectra in AN of salicylate and 2,6-dihydroxybenzoate indicate the presence of broad -OH stretching bands starting at 2800 cm^{-1} and extending to at least 1800 cm^{-1} and possibly beyond. These bands are attributed to intramolecular hydrogen bonding and are much broader and occur at much lower frequency in the anions than in the parent acids (see discussion of Figure 2). As expected, the intensity of the 2,6-dihydroxybenzoate -OH band(s) is about twice that of the salicylate from 2700 to 1800 cm^{-1}. No -OH stretching band was found in *m*-bromobenzoate. The antisymmetric



stretching band is found at 1610, 1578, and 1590 cm^{-1} in *m*-bromobenzoate, salicylate, and 2,6-dihydroxybenzoate, respectively.

No constant value of $\sigma_{o\text{-}OH}$ is found when values of K^{d}_{HSal}, $K^{f}_{HSal\cdot Cl^-}$, $K^{f}_{HR\cdot Sal^-}$, and $K^{f}_{HSal\cdot Sal^-}$ are introduced into the corresponding plots of the logarithms of these constants *vs.* σ. In the order mentioned, the following values of σ would be obtained: 1.7 (average value in AN, DMF, and DMSO), 1.1 (in AN), 2.3 (average value in AN, DMF, and DMSO), and -1.0 (in AN). For 2,6-dihydroxybenzoic acid in AN values of $\sigma_{o\text{-}OH} = 3.3/2$ (from pK^{d}_{HA}) and 3.7/2 (from log $K^{f}_{HR\cdot A^-}$) are found. Owing to intramolecular hydrogen bonding in AN these values of $\sigma_{o\text{-}OH}$ are much more positive (except from $K^{f}_{HA_2^-}$) than a value of -0.41 reported by Traynham[32] from nmr proton chemical shifts of phenols in hexamethylphosphoramide. In this rather strongly basic solvent, intramolecular hydrogen bonding is considered negligible. The steric interference with hydrogen bonding of one and even two *o*-hydroxyl groups in benzoates is likely to be small, the sum of the van der Waals radii of H and O being 2.72 as compared to 2.59 Å for the nitro group[36]

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[34] A. Martin, *Nature* (*London*), **166**, 474 (1950).

[35] M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).

[36] M. Charton, *J. Amer. Chem. Soc.*, **91**, 619 (1969).

($r_{V_{max}}$). The steric effect of the latter group on $pK^d{}_{HA}$ of benzoic acids in aprotic solvents was shown to be negligible.[3]

The small value of $pK^d{}_{HSal}$ of 16.7 as compared to $pK^d{}_{HBz}$ of 20.7 in AN is partly due to relatively weak intramolecular hydrogen bonding in the acid and a much stronger intramolecular hydrogen bond in the anion on the one hand and the electron-releasing inductive effect of the *o*-hydroxyl group on the other. A similar situation exists in DMSO and DMF.

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A Comparison of the CNDO and Mulliken Semiempirical Molecular Orbital Methods[1]

Raymond G. Jesaitis

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11790.

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Abstract: The CNDO/2 method is related to the Mulliken method. Application of similar parameter schemes in both approaches is discussed and applied to calculations of several simple organic molecules including acetylene, ethylene, ethane, and cyclobutane.

The primary goal for most *ab initio* quantum mechanical molecular calculations is the exact determination of whatever molecular property one is interested in by the use of as refined a mathematical approach as is necessary for the physical problem. Semiempirical calculations generally have a more limited and often more contradictory set of goals. The major consideration for them has been the gross simplification of *ab initio* methods in such a way as to reduce the time and effort necessary to obtain wanted results for large systems. A second consideration, perhaps more important in the future, has been the conceptual utility of methods which give insight into the important qualitative and semiquantitative propositions of chemistry rather than just a numerical solution as exact *ab initio* results are wont to be.

Semiempirical methods generally have attempted to solve the Hartree–Fock SCF equations by using various assumptions to reduce the volume of integral computations. In addition, parameters for these calculations have usually been based on experimentally observed quantities with the aim in mind of compensating for the electron correlation deficiencies of the Hartree–Fock method. Moreover, the methods were usually intended for a fairly limited set of applications such as dipole moments, geometries, reactivities, spectra, or thermodynamic stabilities and could not really be expected to be valid for all applications or even all cases within an application.[2a]

In this context it is important to evaluate parameter sets and methods with respect to each other so that their applicability and limitations become clearer, and so that the "chemical" consequences of the parametrization become more evident. A great deal of interest has been shown in semiempirical calculations performed by the CNDO/2 method, which was parametrized to make results agree with Hartree–Fock calculations.[2] Somewhat less interest has been shown in calculations performed by Mulliken-type methods both of the SCF and non-SCF type.[3] The severe approximations of the CNDO method and possible approximations for other semiempirical methods have been discussed by a number of workers.[4–6] However, results by Mulliken and CNDO methods have not in general been compared, although the use of Mulliken approximations to lesser or greater extents within various methods is extensive (*e.g.*, ref 2a and 3–6).

Both methods are correct only to the first order in overlap by the *S*-expansion technique.[5] The similarity of the two methods may be seen by the following treatment, where the CNDO method is shown to be related to the Mulliken method.

In the Mulliken method, the Hartree–Fock matrix[7]

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \qquad (1)$$

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu/\lambda\sigma) - {}^1\!/_2(\mu\sigma/\lambda\nu)] \qquad (2)$$

where

$$\mathbf{FC} = E\mathbf{SC} \qquad (3)$$

is approximated by

$$H_{\mu\nu} = {}^1\!/_2(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu} \qquad (4)$$

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(1) This research was supported in part by Grant No. 1425-G1 from the Petroleum Research Fund, administered by the American Chemical Society. Most of the calculations were run with time donated by the Computer Center of the State University of New York, Stony Brook.

(2) (a) See, for example "Sigma Molecular Orbital Theory," K. B. Wiberg and O. Sinanoğlu, Ed., Yale University Press, New Haven, Conn., 1970, for a compendium of calculations performed by various MO methods; (b) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(3) For example (a) R. S. Mulliken, *J. Chim. Phys. Physicochim. Biol.*, 46, 497, 675 (1949); (b) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2353 (1966); (c) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); (d) T. Yonezawa, K. Yamaguchi, and H. Kato, *Bull. Chem. Soc. Jap.*, **40**, 536 (1967).

(4) D. B. Cook, P. C. Hollis, and R. McWeeney, *Mol. Phys.*, **13**, 553 (1967).

(5) R. D. Brown and K. R. Roby, *Theor. Chim. Acta*, **16**, 175, 194, 278, 291 (1970).

(6) J. P. Dahl, *Acta Chem. Scand.*, **21**, 1244 (1967).

(7) The notation is similar as far as possible to that of ref 2b.