Intramolecular Hydrogen Bonding in Monoanions and Solvation of Dianions of Aromatic Dicarboxylic Acids in Acetonitrile and Dimethyl Sulfoxide

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Abstract: Dissociation constants in acetonitrile (AN), dimethyl sulfoxide (DMSO), and methanol (M) of o-. m-, p-phthalic, 2,2'-diphenic, and 1,8-naphthalic acids, their monomethyl esters, some homoconjugation constants, intramolecular hydrogen bond constants (K') of monoanions, transfer activity coefficients of diprotic acids, their mono- and dianions, and methanolation and some hydration constants of mono- and dianions in AN have been determined. In AN and DMSO values of K' of biphthalate, 3-methyl biphthalate, and diphenate are large. The methyl group in 3-methyl biphthalate markedly decreases K', which is of the order of 200 times smaller than K' of biphthalate. Intramolecular hydrogen bonding is virtually absent in the monoanions of m- and p-phthalic and 1,8-naphthalic acids. Values of transfer activity coefficients between AN or DMSO and water or methanol of monoanions support the interpretations presented in the text. Evidence is given that in the dianion of diphenic acid in AN and DMSO the two carboxylate groups are at a maximum distance while in the monoanion the carboxyl and carboxylate are in close vicinity and are strongly intramolecularly hydrogen bonded. Methanolation constants of dianions in AN decrease in the order phthalate > m-phthalate, diphenate. The methanolation of the o-phthalate ion resembles in this respect that of the succinate ion.

In previous publications the intramolecular hydrogen bonding in the monoanions of the homologous series of oxalic acid in acetonitrile (AN)[1] and in dimethyl sulfoxide (DMSO)[2] has been determined and its effect on titration curves of these acids in the dipolar aprotic solvents has been discussed. In a subsequent paper[3] the intramolecular hydrogen bonding between hydroxyl groups and carboxylate ions in mono- and dianions of some aliphatic acids in AN and DMSO has been studied. In the present paper we have investigated the intramolecular hydrogen bonding in monoanions of the aromatic acids phthalic, m-phthalic, 3-methylphthalic, p-phthalic, 2,2'-diphenic, and 1,8-naphthalic acids in AN and DMSO. As in previous work, the constant $K' = [\overline{HA^-}]/[HA^-]$, $\overline{HA^-}$ representing the intramolecularly hydrogen bonded monoanions, was calculated by using eq 1

$$\log (K' + 1) = pK[HE] - pK_1 - \log 2 \qquad (1)$$

originating with Westheimer and Benfy.[4] This equation is based on the reasonable assumption that when no intramolecular hydrogen bonding occurs in HA⁻, the constant $K_1 = a[H^+] a[HA^-]/a[H_2A] = 2K[HE]$, HE being the monoester of H₂A. Evidence derived from a comparison of the transfer activity coefficients $\gamma^{W,M}(AN)$ and $\gamma^{W,M}(DMSO)$ of monoanions in which intramolecular hydrogen bonding occurs (e.g., biphthalate) with those in which intramolecular hydrogen bonding is absent (e.g., m-biphthalate) is presented in support of the above assumption. The magnitude of the constants of solvation in AN of some dianions with methanol and water is correlated with values of $p\gamma^{W,M}(AN)[A^{2-}]$.

Experimental Section

Solvents. Acetonitrile,[1] dimethyl sulfoxide,[1] and methanol[1] have been purified as described previously. Dimethyl-d_6 sulfoxide was a Baker Co. product.

Diacids, Monoesters, and Salts. Eastman Kodak White Label m-phthalic and p-phthalic acids were used as received. Assay by alkalimetric titration in 1-propanol was 99.7 and 98.5%, respectively. 2,2'-Diphenic acid was an Aldrich Co. product, recrystallized from water, mp 230 °C (lit. mp 229 °C), assay 99.4%. 3-Methylphthalic acid was obtained by dissolving Aldrich 3-methylphthalic anhydride in boiling water and taking to dryness carefully. The diacid was recrystallized from benzene, mp 155 °C (lit. mp 157 °C), assay 97.0%. 1,8-Naphthalic acid was prepared from the anhydride (Aldrich Co.) by dissolving it in hot 1 M aqueous sodium hydroxide solution, cooling in an ice bath, and precipitating the acid with cold aqueous hydrochloric acid.[5] The acid was dried for 5 h at room temperature under a slow stream of dry nitrogen. Assay of the naphthalic acid was 105.3%.

Monoesters. Mono-n-butyl p-phthalate (Eastman Kodak) was used without further purification, mp 135–6 °C, assay by direct alkalimetric titration 99.8%. Monomethyl phthalate was used previously.[1] The monomethyl esters of 3-methylphthalic and diphenic acids were prepared by treating the corresponding anhydrides with boiling methanol. The diphenate ester was recrystallized from a methanol–water mixture, mp 111 °C (lit. mp 110 °C). The 3-methylphthalate ester was not recrystallized. The dimethyl ester of m-phthalic acid was prepared by direct esterification of the diacid in boiling methanol in the presence of a few drops of sulfuric acid as catalyst, mp 72–4 °C (lit. mp 67–8 °C). Assay by saponification was 95.2% Me₂A and 2.8% H₂A. The monomethyl ester of m-phthalic acid was prepared by reacting the diester with potassium hydroxide in a 1:1 mol ratio in boiling methanol for 3 h. The methanol solution was cooled in an ice bath and

Table I. Molar Solubility of Diprotic Acids in Various Solvents

Acid	W $c(H_2A)$	[H₂A]	M $c(H_2A)$	AN $c(H_2A)$	DMSO $c(H_2A)$
Phthalic		0.037^a	1.15^a	0.0245^a	3.77^a
3-Methylphthalic	0.295	0.280	3.28	0.181	
m-Phthalic	9.55×10^{-4}	5.44×10^{-4}	0.107	1.66×10^{-3}	2.77
p-Phthalic			5.2×10^{-3}		1.16
1,8-Naphthalic			0.198	5.19×10^{-3}	1.46
2,2′-Diphenic	3.17×10^{-3}	2.34×10^{-3}	1.26	0.064	2.46

^{a} Reference 2.

Table II. Dissociation Constants of Aromatic Dicarboxylic Acids and Their Monoesters in AN, DMSO, W, and M

	AN pK_1 or pK(HA)	pK_2	K_{homo}	pK(HE)	$\log K'$	DMSO pK_1 or pK(HA)	pK_2	pK(HE)	$\log K'$
Benzoic	20.7		4×10^3			11.1			
Phthalic	14.2^e	29.8^e	$0.9 \times 10^{2\ e}$	$19.4_7^g\ 20.0^e$	$5.0^g\ 5.5^e$	$5.7^a\ 6.2^b$	$16.0^a\ 16.0^b$	9.9_3^e	$3.9^a\ 3.4^{b,g}$
3-Methylphthalic	17.0^g	25.6^g	$3 \times 10^{2\ g}$	20.1^g	2.8^g	9.1_8^g	15.1_6^g	10.4_0^g	0.8_6
m-Phthalic	19.3_4^g	23.0^g		20.0_3^g	$\sim 0.2^g$	9.8_0^g	$12.3_8\ 12.2^a$		
p-Phthalic				19.7^g		9.8^g	$12.1_0^g\ 11.9^a$	10.1^f	$K' \sim 0$
1,8-Naphthalic	21.8^g	24.9_5^g				11.0^g	15.0^g		
2,2′-Diphenic	15.7_3^g	26.1^g		20.8_5^g	4.8^g	7.7^g	13.9_3^g	11.4_6^g	3.4^g

	W^d pK_1 or pK(HA)	pK_2		pK(HE)	$\log K'$	MeOH pK_1 or pK(HA)	pK_2	pK(HE)	$\log K'$
Benzoic	4.2_1					9.4			
Phthalic	3.0_0	5.40		3.18	$K' \sim 0$	$7.3_7^g\ 7.2_8^c$	$12.1_8\ 9.8^c$	8.5_7^e	0.9
3-Methylphthalic	3.1_6^g	5.20^g				8.4_3^g	11.7_6^g	8.7_8^g	$K' \sim 0$
m-Phthalic	3.54	4.62		3.89	$K' \sim 0$	8.6_5^g	10.6_1^g	8.9_1^g	$K' \sim 0$
p-Phthalic	3.54	4.46			$K' \sim 0$	8.4_9^g	10.3_0^g	8.8_2^f	$K' \sim 0$
1,8-Naphthalic						9.0_5^g	12.6_9^g		
2,2′-Diphenic	3.53^g	5.42^g		3.96^g	(-0.5)	7.7_5^g	12.7_9^g	9.5_8^g	1.5

^{a} Reference 21. ^{b} J. Courtot-Coupez and M. Le Démézet, *Bull. Soc. Chim. Fr.*, 1033 (1969). ^{c} C. Liteanu and A. Blazek-Bodò, *Rev. Roum. Chim.*, **17**, 1465 (1972). ^{d} Average of pK values from various sources, i.e., J. Walker, *J. Chem. Soc.*, **61**, 696 (1892); G. Dahlgren and F. A. Long, *J. Am. Chem. Soc.*, **82**, 1303 (1960); G. Körtum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, Washington, D.C., 1961. ^{e} Reference 2. ^{f} *n*-Butyl ester. ^{g} This work.

concentrated sulfuric acid added in a ½:1 mol ratio. The potassium *normal* sulfate which precipitated was filtered and the clear filtrate was taken almost to dryness in vacuo at room temperature. crystals of the monoester which separated were collected, mp 191–2 °C (lit. mp 193 °C). The monoesters were assayed (a) by direct alkalimetric titration in 1-propanol or (b) by saponification in an excess of aqueous sodium hydroxide followed by back-titration with standard hydrochloric acid. These two methods yielded the following results: *m*-phthalate 100.4, 99.6%; 3-methylphthalate 100.0% (direct titration), and diphenate 99.4, 95.3% (method b). The monotetraethylammonium salts of 3-phthalic and 3-methylphthalic acids were prepared as previously described for the monotetraethylammonium salts of aliphatic dicarboxylic acids.[1] Tetraethylammonium hydroxide solutions in methanol and in water (0.6 to 1.1 M) were prepared as described elsewhere[1] and used soon after preparation.

Techniques. Methods used for estimation of solubilities of diprotic acids, paH measurements in various acid–salt mixtures, have previously been described.[2,6] Ir spectra were run on a Perkin-Elmer 257 ir spectrometer using Irtran-2 cells with spacers of 100 and 200 μm path length.

Results

Solubility of Diacids. Solubilities of the various diacids in W, M, AN, and DMSO are listed in Table I. Correction for dissociation in water has been applied using the dissociation constants in Table II.

Values of pK_1, pK_2, and pK(HE) of Diacids and Monoesters in W, M, AN, and DMSO. Values of pK_1, pK_2, and pK(HE)

were estimated from the paH in equimolar mixtures of H_2A and HA^-, HA^-, and A^{2-}, or HE and E^- as described previously.[1] At the concentrations used the tetraethylammonium salts were completely dissociated into the ions.[1] In the organic solvents 0.9 M tetraethylammonium hydroxide in methanol was added to a solution of the diacid or monoester. The effect of methanol on paH was taken into consideration. In the study of the effect of water in AN as solvent on paH of mixtures of H_2A-HA^- and HA^--A^{2-} the base used in preparation of the mixtures was aqueous 0.65 M tetraethylammonium hydroxide. In water as solvent 0.10 M aqueous sodium hydroxide served as base. Correction for overlapping of the first and second steps in the dissociation of H_2A in water and the organic solvents was not necessary as $pK_2 - pK_1 \geq 2$. Values of pK_1, pK_2, pK(HE), and $\log K' = \log ([\overline{HA}^-]/[HA^-])$ are listed in Table II. In addition, the overall homoconjugation constant, K_{homo}, of 3-methylphthalic acid, and $K^f(HE_2^-)$ of the monoester of *m*-phthalic acid were estimated in AN from paH in mixtures of excess acid over salt, the concentration of the latter being fixed. For 3-methylphthalic acid $c(HA^-) = 1.46 \times 10^{-3}$ M, $c(H_2A) = 0.419 \times 10^{-2}$, 1.78×10^{-2}, 3.90×10^{-2}, 7.82×10^{-2}, and 0.139 M, paH = 16.19, 15.15, 14.47, 13.76, and 12.95, respectively, yielding $K_{homo} = 2.7 \times 10^2$; while for monomethyl *m*-phthalate $c(E^-) = 2.85 \times 10^{-3}$, $c(HE) = 2.85 \times 10^{-3}$, 2.14×10^{-2}, 4.39×10^{-2} M, paH = 19.88, 17.16, and 16.36, respectively, yielding $K^f(HE_2^-) = 5 \times 10^3$. As expected,

this value of $K^f(HE_2^-)$ is close to that of benzoic acid, 4.0×10^3,[7] while K_{homo} of 3-methylphthalic acid is much smaller as a result of intramolecular hydrogen bonding in the monoanion.[1] Unfortunately, solubility limitations precluded estimation of K_{homo} of m-phthalic acid, which should be close to twice that of benzoic acid, as intramolecular hydrogen bonding is practically negligible in the monoanion. No evidence of higher homoconjugates was found in this study.

Infrared Spectra. Ir spectra have been run of solutions of 0.13 M tetraethylammonium biphthalate and 3-methylbiphthalate in CH_3CN using a 200 μm cell. Ir spectra in $(CD_3)_2SO$ of 0.23 M solutions of these salts and in addition that of m-biphthalate were recorded in a 100 μm cell. Spectra of o- and m-phthalic acids (0.25 M) in $(CD_3)_2SO$ furnished information regarding the nonintramolecularly hydrogen bonded COOH group (see Discussion). From the fact that no doublet was observed at 1845 and 1775 cm^{-1}, as found for phthalic anhydride in KBr wafer,[8] it is concluded that anhydride formation does not occur in solutions of the diacids in DMSO.

Discussion

Dissociation Constants of Monoesters of Phthalic Acids. The difference in values of $pK(HE)$ of the monoesters of phthalic, 3-methylphthalic, m-phthalic, p-phthalic, and 2,2'-diphenic acids between the aprotic solvents AN and DMSO is 9.6 ± 0.1, which is within the experimental error equal to 9.7 found previously[9] for substituted benzoic acids. Furthermore, values of $pK(HE)$ of monoesters of m- and p-phthalic acids lie on plots of $(pK(HA))_{AN}$ vs. $(pK(HA))_{W,M}$ of substituted benzoic acids[10] as shown in Figure 1. From this the following Hammett σ values of the $COOCH_3$ group are obtained, meta $+0.32 \pm 0.04$, and para $+0.42 \pm 0.01$, as compared with literature values reported in water of $+0.3_7$ and $+0.4_5 \pm 0.1$, respectively, for the $COOC_2H_5$ group.[11] The monomethyl esters of phthalic, 3-methylphthalic, and 2,2'-diphenic acids do not fit the plot of $(pK(HA))_{AN}$ vs. $(pK(HA))_W$ in Figure 1. They are apparently stronger acids in water than expected from the above plot. The same situation was found for o-nitro- and o-chlorobenzoic acids[9] and has been attributed to much stronger solvation of the ortho-substituted anions in water than those of meta- or para-substituted anions. From our data a value of $+0.47 \pm 0.03$ is obtained for σ (o-COOCH$_3$). The similarity in σ values of the o- and p-COOCH$_3$ groups suggests that steric inhibition by resonance in the monomethyl ester of phthalic acid is practically absent. This requires that the $COOCH_3$ group be rotated considerably out of the plane of the ring. The resolution of acid strength between water and the aprotic solvents AN and DMSO for the ortho-substituted esters is 2.4, the same as for benzoic acids.[9]

Intramolecular Hydrogen Bonding in Monoanions. McCoy[12] studied the relation between stability of the intramolecular hydrogen bond in monoanions of 1,2-cycloalkene dicarboxylic acids and the O⋯O distance of the carboxylic groups in water. He found an optimum distance of 2.4_5 Å and pointed out that such spacing of the COOH and COO$^-$ groups does not in itself assure a stable intramolecular hydrogen bond but that it is also necessary that this hydrogen bond be essentially linear and the resulting skeletal structure be strain free. All the diacids in Table II except diphenic have rigid skeletal structures. As expected, values of K' of m- and p-biphthalates are close or equal to zero in the solvents studied, in marked contrast to those of o-biphthalate and 3-methylbiphthalate.

When the COOH and COO$^-$ groups in the monoanion of an aromatic or a cycloaliphatic dicarboxylic acid are close together, but both are out of the plane of the ring(s), only a weak intramolecular hydrogen bond may be formed. In 1,8-naphthalic acid monoanion, the oxygens of the COOH and
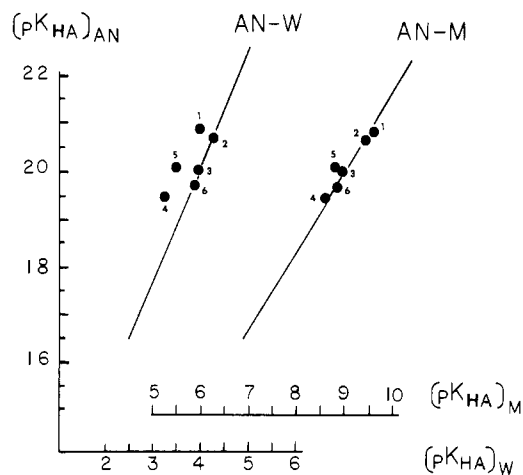

Figure 1. Plots of $pK(HA)_{AN}$ vs. $pK(HA)_M$ or $pK(HA)_W$ of monomethyl esters of phthalic acids: (1) diphenic; (2) benzoic acid; (3) m-phthalic; (4) phthalic; (5) 3-methylphthalic; (6) mono-n-butyl p-phthalate. Straight lines are plots of $pK(HA)$ values of a series of substituted benzoic acids from ref 10. Slopes are 2.4 and 1.7 for AN–W and AN–M, respectively. Value of $pK(HE)$ of ester 5 in water calculated from pK_1 of the corresponding diacid, taking $K' = 0$.

COO$^-$ groups would practically overlap if both groups were coplanar to the rings. On the other hand, if both groups are perpendicular to the rings, the O⋯O distance would be 2.5_0 Å, close to the optimal value. However, the O⋯H⋯O intramolecular hydrogen bond would be considerably bent. From the small values of $pK_2 - pK_1$ of naphthalic acid in the three organic solvents it appears that intramolecular hydrogen bonding is weak or absent in the naphthalate monoanion. The log K' values in AN and DMSO of 3-methylbiphthalate are some 2.0 to 2.5 units smaller than those of biphthalate. This is ascribed to rotation to a considerable extent of the COOH group out of the plane of the ring, in addition to that of the COO$^-$ group. The biphthalate ion, having a strong intramolecular hydrogen bond, must achieve a strain-free condition contrary to the conclusion by Eberson[13] on the basis of K' being zero in water. In methanol, on the other hand, we find a value of K' of the order of 10. Forsen[14] observed a large downfield ^{1}H NMR chemical shift in solutions of biphthalate in DMSO, which is to be expected on the basis of the large K' value in this solvent. Ir spectra of biphthalate and 3-methylbiphthalate in CH_3CN and $(CD_3)_2SO$[15] confirm strong intramolecular hydrogen bonding as was observed previously from ir spectra of biglutarate and bisuccinate in these solvents.[2] The biphthalate salt exhibits strong absorption from 2150 to 800 cm^{-1} in CH_3CN and $\sim$1950–1000 cm^{-1} in $(CD_3)_2SO$, the carbonyl band being absent. Spectra of the 3-methylbiphthalate salt are similar, but a carbonyl band occurs at 1694 and $\sim$1700 in CH_3CN and $(CD_3)_2SO$, respectively. These characteristics are accounted for by the smaller value of K' of 3-methylbiphthalate than of biphthalate.

In the crystal state potassium biphthalate appears not to be *intra*- but strongly *inter*molecularly hydrogen bonded by a COOH group of one molecule with a COO$^-$ of a neighboring one, as deduced from ir spectra by Davison[16] and x-ray diffraction data by Okaya.[17] There is no indication that dimers of biphthalate are present in aqueous or nonaqueous solution. In the 2,2'-bidiphenate ion the two rings are certainly not in the same plane. In fact, in 2,2'-dimethyl- or -diethylbiphenyl the planes are inclined 70° with respect to each other.[18] A similar orientation of the rings in 2,2'-bidiphenate allows formation of a stable intramolecular hydrogen bond between the COOH and COO$^-$ groups. The presence or absence of intramolecular hydrogen bonding in the monoanion of 8,8'-

Table III. Transfer Activity Coefficients of Diprotic Acid Species

	$p\gamma^W(AN)$ (H_2A)	$p\gamma^M(AN)$ (H_2A)	$p\gamma^{DMSO}(AN)$ (H_2A)	$p\gamma^W(AN)$ (n)	$p\gamma^M(AN)$ (n)	$p\gamma^{DMSO}(AN)$ (n)	$p\gamma^W(AN)$ (ΣHA^-)	$p\gamma^M(AN)$ (ΣHA^-)	$p\gamma^{DMSO}(AN)$ (ΣHA^-)
Benzoic	-1.4_8	$+0.6$		-2.3	-0.9		$+6.9^a$	$+5.7^a$	
Phthalic	$+0.2$	$+1.7$	$(+2.2)$	-1.4	-1.3	(-1.6)	$+3.4$	$+2.5$	(-1.2)
3-Methyl-phthalic	$+0.2$	$+1.2_6$		-1.4	-1.7		$+5.9$	$+3.7$	
m-Phthalic	-0.5	$+1.8$	$+3.2$	-2.1	-1.2	-0.6	$+7.2$	$+6.3$	$+1.3$
1,8-Naph-thalic		$+1.6$	$+2.4_5$		-1.4	-1.3		$+8.1$	$+1.9$
2,2'-Di-phenic	-1.4_3	$+1.3$	$+1.6$	-3.0	-1.7	-2.2	$+2.7$	$+3.0$	-1.8

	$p\gamma^W(AN)$ $(HA^-)_{el}$	$p\gamma^M(AN)$ $(HA^-)_{el}$	$p\gamma^{DMSO}(AN)$ $(HA^-)_{el}$	$p\gamma^W(AN)$ (A^{2-})	$p\gamma^M(AN)$ (A^{2-})	$p\gamma^{DMSO}(AN)$ (A^{2-})	$p\gamma^W(AN)$ $(A^{2-})_{el}$	$p\gamma^M(AN)$ $(A^{2-})_{el}$	$p\gamma^{DMSO}(AN)$ $(A^{2-})_{el}$
Benzoic	$+9.2^a$	$+6.6^a$							
Phthalic	$+9.0$	$+6.3$	$(+0.1)$	$+19.7$	$+14.0$	$(+1.2)$	$+21.1$	$+15.3$	$+2.2$
3-Methyl-phthalic	$+9.3$	$+6.7$		$+18.2$	$+11.3$		$+19.6$	$+13.0$	
m-Phthalic	$+8.9$	$+6.4$	$+0.4$	$+17.5$	$+12.5$	$+0.6$	$+19.6$	$+13.7$	$+1.2$
1,8-Naph-thalic	$+8.0$	$+1.3$		$+14.2$	$+0.5$		$+15.6$	$+1.8$	
2,2'-Di-phenic	$+9.7$	$+6.5$	-0.2	$+15.3$	$+10.1$	-1.0	$+18.3$	$+11.8$	$+1.2$

[a] Refers to simple benzoate ion.

dicarboxyl-1,1'-dinaphthyl could be deduced from potentiometric titration in aprotic solvents and should be useful in characterization of the diastereoisomers of this and related compounds.

Transfer Activity Coefficients. The transfer activity coefficients of a species i between AN and S (AN being the reference solvent) is defined as $-\Delta G°_{tr} = 2.303RTp\gamma^S(AN)(i)$, where $\Delta G°$ denotes the free energy of transfer. A positive value of $p\gamma^S(AN)(i)$ indicates greater solvation of i in S. In this and previous papers $\gamma^S(AN)$ of ions was evaluated using the extrathermodynamic tetraphenylborate assumption. Transfer activity coefficients of mono- and dianions were calculated from values of pK_1 and pK_2 using the following relationships:

$$(pK_1)AN - (pK_1)S = p\gamma^S(AN)(H^+)$$
$$+ p\gamma^S(AN)(\Sigma HA^-) - p\gamma^S(AN)(H_2A) \quad (2)$$

$$(pK_2)AN - (pK_2)S = p\gamma^S(AN)(H^+)$$
$$+ p\gamma^S(AN)(A^{2-}) - p\gamma^S(AN)(\Sigma HA^-) \quad (3)$$

Values of the transfer activity coefficients of uncharged diprotic acids, their monoanions, and dianions are entered in Table III. The transfer activity coefficients of H_2A are equal to $p\gamma^S(AN)(n) + 2p\gamma^S(AN)(H_a)$ in which $p\gamma(n)$ is the contribution of the neutral nonhydrogen bonded part and $p\gamma(H_a)$ that of the intermolecular hydrogen bond between the COOH group and the solvents AN and S. Previously[10] values of $p\gamma^W(AN)(H_a)$, $p\gamma^M(AN)(H_a)$, and $p\gamma^{DMSO}(AN)(H_a)$ were reported to be $+0.8$, $+1.5$, and $+1.9$, respectively. It is of interest to mention that $p\gamma^S(AN)(n)$ is positive for all the diprotic acids in Table III, S being W, M, or DMSO. This means that the non-hydrogen-bonding contribution to solvation of H_2A is greater in AN than in the other solvents. The dependence of $p\gamma^S(AN)(n)$ of substituted benzoic acids on substituent must involve changes in the π electron system in the ring. The effect of a second benzene ring on $p\gamma^{W,DMSO}(AN)(n)$ is clearly observed in diphenic acid. From the fact that K' values of the monoanions of phthalic and diphenic acids in aprotic solvents are virtually the same, and large, it has been concluded that the monoanions are strongly stabilized by intramolecular hydrogen bonding. Values of

$\gamma^{W,M}(AN)(\Sigma HA^-)$ of these ions are 2×10^3 to 3×10^4 times smaller than that of m-biphthalate. The value of the latter is close to that of unsubstituted benzoate. The decrease of log K' of 3-methylbiphthalate as compared to that of biphthalate in AN is virtually the same as the increase of $p\gamma^W(AN)(\Sigma HA^-)$ between the two solvents. The close relation between $\gamma^{W,M}(AN)(HA^-)$ and K' values lends strong support to the validity of eq 1. From the relations

$$p\gamma^S(AN)(\Sigma HA^-) = p\gamma^S(AN)(HA^-)$$
$$- \log (K' + 1)_{AN} + \log (K' + 1)_S \quad (4)$$

and

$$p\gamma^S(AN)(HA^-) = p\gamma^S(AN)(n)$$
$$+ p\gamma^S(AN)(H_a) + p\gamma^S(AN)(HA^-)_{el} \quad (5)$$

$p\gamma^S(AN)(HA^-)_{el}$, the electrostatic contribution of $p\gamma^S(AN)(HA^-)$, i.e., of the nonintramolecularly hydrogen bonded form of the monoanion, is calculated. Considering the diverse structures of the diprotic acids taken, it is gratifying that values of $p\gamma^S(AN)(HA^-)_{el}$ in Table III are of the same order of magnitude as that of $p\gamma^S(AN)(benzoate)_{el}$. From the fact that the inductive effect of the $COOCH_3$ group on $pK(HE)$ of the monoester has been found to be small (Table II) it is to be expected and found that the inductive effect of the COOH group in HA^- on $p\gamma^S(AN)(HA^-)_{el}$ also is small. Values of $p\gamma^S(AN)(A^{2-})_{el}$ of dianions, equal to $p\gamma^S(AN) \cdot (A^{2-}) - p\gamma^S(AN)(n)$, are close to twice that of benzoate (18.4 when $S = W$ and 13.3 when $S = M$). This is not the situation with the divalent phthalate and naphthalate ions. The close proximity of the two COO^- groups in the latter two anions favors abnormally strong solvation in W and M. This abnormality disappears when a methyl group is situated next to the COO^- groups in 3-methylphthalate. Values of $p\gamma^S(AN)$ $(A^{2-})_{el}$ of diphenate indicate that in this dianion the rings can rotate in such a way that the two COO^- groups are at a maximum distance, due to electrostatic repulsion. The above interpretation is substantiated in the next section in which the hydration and methanolation of some mono- and dianions are discussed.

Alcoholation and Hydration of Dianions in Acetonitrile. The expression for the overall solvation of a dianion, A^{2-}, in which
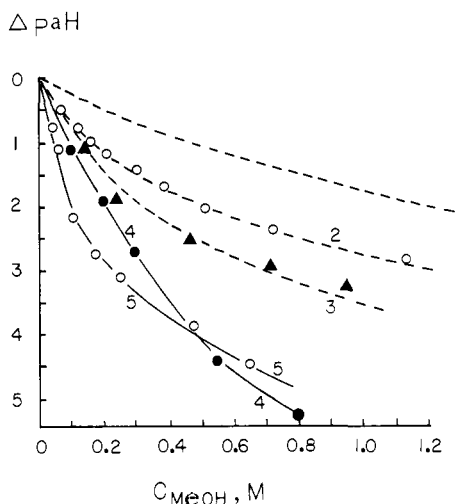
Figure 2. Effect of methanol on paH of mixtures of mono- and di-tetraethylammonium phthalates and diphenate in AN: (1) equimolar benzoic acid–benzoate mixture, $paH_0 = 20.7$; (2) m-phthalate, $c(HA^-)$ $= 0.25 \times 10^{-3}$, $c(A^{2-}) = 1.12 \times 10^{-3}$ M, $paH_0 = 23.45$; (3) diphenate, $c(HA^-) = c(A^{2-}) = 0.69 \times 10^{-3}M$, $paH = 25.9$; (4) phthalate, $c(HA^-)$ $= 2.42 \times 10^{-3}$, $c(A^{2-}) = 2.04 \times 10^{-3}$ M, $paH_0 = 29.4$; (5) succinate, $c(HA^-) = 1.29 \times 10^{-3}$, $c(A^{2-}) = 0.755 \times 10^{-3}$ M (1. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem.*, **47**, 1921 (1975)).

Table IV. Alcoholation and Hydration Constants of Monoanions in Acetonitrile

Acid system[a]	B→	W	M	n-BuOH
Benzoic[b]	$K(B\cdot A^-)$	(2.3)	8.5	5.7
	$K(2B\cdot A^-)$	1.5×10^1	2.3×10^1	6.0
	$K(3B\cdot A^-)$	1.0×10^1	0	0
m-Phthalic[c]	$K(B\cdot HA^-)$	4.7	2.4	0.6
	$K(2B\cdot HA^-)$	7.1	2.2	0
Diphenic[c]	$K(B\cdot\Sigma HA^-)$	0.8^d	0.8	

[a] Alcoholation or hydration of H_2A or HA negligible. [b] Reference 19. [c] This work. [d] Hydration constant assumed same as methanolation constant.

both charged groups are the same, in an aprotic solvent by a hydrogen bond donor B is derived in terms of the solvation constants of the monoanion prototype, A^-, possessing one such group. It is stipulated that (a) the two groups in A^{2-} are solvated independently, (b) the solvation constants of A^- are the same as those used in eq 6 to evaluate the overall solvation of A^{2-}, and (c) both groups in A^{2-} cannot simultaneously associate with additive to form a higher solvate from a lower one. The resulting expression for the overall solvation of A^{2-} by the hydrogen bond donor B is of the sixth degree in [B]:

$$\frac{v-1}{2} = K_B[B] + (K_B^2 + K_{2B})[B]^2$$
$$+ (4K_BK_{2B} + 3K_{3B})[B]^3 + (6K_BK_{3B} + 5K_{2B}^2)[B]^4$$
$$+ 24K_{2B}K_{3B}[B]^5 + 33K_{3B}^2[B]^6 \quad (6)$$

In eq 4, K_B and $K_{2B}\cdot K_{3B}$ denote the solvation constant of the monoanion prototype, A^-, by 1, 2, or 3 molecules of B. As an example of the derivation of eq 6 we consider the term in $[B]^2$. When two molecules of B associate with A^{2-}, $(OOC-R-COO\cdot B)^{2-} + B \rightleftarrows (B\cdot OOC-R-COO\cdot B)^{2-}$, the contribution to $(v-1)/2$ in eq 6 being $K_BK_B[B]^2$, since $(OOC-R-COO)^{2-}$ $+ B \rightleftarrows (OOC-R-COO\cdot B)^{2-}$, $(B\cdot OOC-R-COO)^{2-}$, the contribution being $K_B[B]$. In addition, $(OOC-R-COO)^{2-} + 2B \rightleftarrows (OOC-R-COO\cdot 2B)^{2-}$, $(2B\cdot OOC-R\cdot COO)^{2-}$, the contribution being $K_{2B}[B]^2$. The effect of B on paH of mixtures of HA^- and A^{2-} is $paH = paH_0 - \log (v/V)^1$ where v
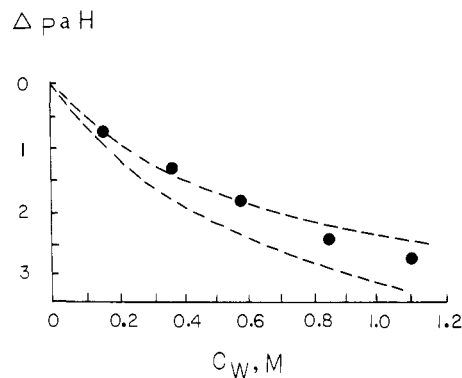

Figure 3. Effect of water on paH of a mixture of mono- and ditetraethylammonium m-phthalate in AN. $c(Et_4NHA) = 0.22 \times 10^{-3}$, $c(Et_4N)_2A$ $= 0.90 \times 10^{-3}$ M, $paH_0 = 23.3$. Upper dashed curves, calculated regarding benzoate as mono- and dihydrated; lower dashed curves, calculated regarding benzoate as mono-, di-, and trihydrated. Points are experimental values.

$\equiv 1 + K(B\cdot A^{2-})[B] + K(2B\cdot A^{2-})[B]^2 \ldots$ and $V \equiv 1 + K(HA^-\cdot B)[B] + \ldots$, $K(HA^-\cdot B)$, etc., being the solvation constants of the monoanion HA^-.

In the present work methanolation and hydration of diphenate and m-phthalate ions in AN are considered taking unsubstituted benzoate as the monoanion prototype. Condition (b) requires that the inductive effect of one COO^- group in A^{2-} on the solvation constants of the other COO^- group be negligible. A detailed study of inductive effects on hydration and methanolation of substituted benzoates is beyond the scope of this paper. Previously,[19] benzoate has been shown to become mono-, di-, and trihydrated and mono- and dimethanolated in AN; the constants are listed in Table IV. Also in Table IV are hydration and methanolation constants of m-biphthalate and bidiphenate ions, derived from the effects of water and methanol on paH in mixtures of H_2A and HA^-. In Figure 2, curves 1, 2, and 3, the calculated effects of methanol on paH of equimolar mixtures of benzoic acid–benzoate, m-biphthalate-m-phthalate, and bidiphenate-diphenate, respectively, have been plotted (dashed lines). Curves 4 and 5 are based on experimental data, as the calculations become very involved. All symbols refer to experimental values. A similar plot with water as additive in the m-biphthalate-m-phthalate system is presented in Figure 3. Omitted are similar results of the effect of water on paH in the bidiphenate-diphenate system. The observed effect of methanol to at least 1 M in Figure 2 is in good agreement with the calculated effect (eq 6), being about twice that of unsubstituted benzoate. With water as additive fairly good agreement in the above mixtures is found to about 0.7 M water, regarding each of the COO^- groups to be mono- and dihydrated (upper dashed line in Figure 3). In the m-phthalate and diphenate systems the presence of H_2A arising from the first dissociation step of H_2A can be neglected, even at the highest concentration of B. It should be noted that small uncertainties in the values of K_{2B} and particularly of K_{3B} are magnified in the calculation of the overall solvation of A^{2-}, especially at higher concentrations of B. The effect of methanol on paH in the biphthalate-phthalate mixture (Figure 2, curve 4) is attributed to clustering of alcohol molecules in the vicinity of the COO^- groups in phthalate.

Ionization of Aromatic Tricarboxylic Acids. On the basis of the results and their interpretation in this paper, pK values of benzenetri- and -tetracarboxylic acids can be predicted. In 1,2,3-benzenetricarboxylic acid the COOH group in the 1 (or 3) position ionizes first, the resulting COO^- group hydrogen bonding intramolecularly with the 2-COOH group, thus making it a very weak acid. Therefore, pK_1 should be close to

pK_1 of phthalic acid. Next, the COOH group in the 3 position ionizes, pK_2 approximating that of benzoic acid. Finally, the 2-COOH group ionizes, pK_3 being close to that of pK_2 of phthalic acid.[20] Martin[21] titrated a number of aliphatic and aromatic tri- and tetracarboxylic acids in DMSO with an aqueous solution of tetrabutylammonium hydroxide and has reported half neutralization potentials. Applying our pK scale (in anhydrous DMSO) to his data, Martin found for 1,2,3-benzenetricarboxylic acid $pK_1 = 7.0$ (which appears to be 1 or 2 units too large), $pK_2 = 11.2$ (pK of benzoic acid is 11.1), and $pK_3 = 16.2$ and for 1,2,4-benzenetricarboxylic acid 5.2, 11.4, and 15.8, respectively.

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# 1-Methylcyclopropylcarbinyl Cations[1]

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Abstract: A series of 1-methylcyclopropylcarbinyl cations have been prepared and their proton and ^{13}C NMR spectra investigated under stable ion conditions. The parent ion was found to be best represented in terms of a dynamic equilibrium involving significant contributions from both the 1-methylcyclobutyl cation and the set of three equivalent δ-delocalized 1-methylcyclopropylcarbinyl cations. Such a conclusion is supported by ab initio molecular orbital calculations at the split-valence-shell 4-31G level. Tertiary ions studied are static carbenium species and adopt the bisected geometry characteristic of cyclopropylcarbinyl cations. Destabilization of the bisected geometry due to eclipse of the C_1 methyl and one of the groups attached to C_α is undetectably small and, in fact, the 1-methylcyclopropyl group is slightly more effective than a cyclopropyl group with respect to charge delocalization.

Numerous studies of the solvolysis of cyclopropylcarbinyl derivatives[7,8] and direct observation of cyclopropylcarbinyl cations under stable ion conditions[9-11] have demonstrated the remarkable ability of a three-membered ring to stabilize an electron-deficient center to which it is attached. Indeed, in the gas phase, the cyclopropyl group has been shown to be even slightly more effective than a phenyl ring in stabilizing a tertiary (dimethyl substituted) carbocation center.[12] This stabilization arises primarily from the ability of the C_1–C_2 and C_1–C_3 linkages of the cyclopropyl group to donate electron density onto an atom to which it is attached. In the language of molecular orbital theory, what we are seeing is the interaction between the antisymmetric member of the degenerate set of "Walsh" orbitals on cyclopropane[13] and an empty p function at the formal center of positive charge. The transfer of electrons which results—from cyclopropane to C^+—results not only in a considerable shrinkage of the connecting linkage (i.e., the formation of a partial double bond), but also to sizable distortions within the small ring itself.[14] In particular, two of cyclopropane's carbon–carbon linkages have elongated, while the third has shortened. The previously reported theoretical geometrical structure for the parent cyclopropylcarbinyl cation
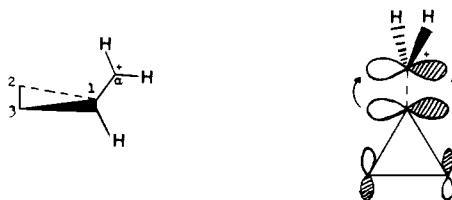
fully substantiates these contentions.[15] In simple valence bond terms, what such geometry suggests is the significant contri-

1.50 Å in cyclopropane
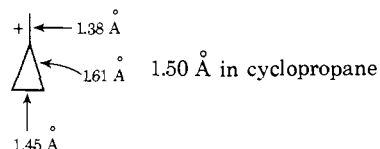
bution of resonance structures of the form (i.e. vinylated ethylene) shown in (1). It should be emphasized that although the

   (1)

picture of the primary cyclopropylcarbinyl cation which arises