9.5 ml (20–50-fold excess) of alcohol solution and thermostating for the period of time required for the disappearance of the yellow color of Cr(VI). Sodium hydroxide (100 ml, 2.5 M) was then added with cooling to the mixture to neutralize the acetic acid. Completeness of neutralization was monitored with pH paper. The resulting aqueous solution was twice extracted with 100 ml of ether, and the combined ether extracts were washed with water and dried ($MgSO_4$) and evaporated to a volume of ca. 0.5 ml. The mixture was then analyzed on a Hewlett-Packard Model 700 gas chromatograph equipped with dual flame ionization detectors. In each case, only the alcohol starting material and normal oxidation product were detected.

Determination of Activation Parameters. Once the rate constants at various temperatures had been determined, Arrhenius plots of the natural logarithm of the rate constant against the reciprocal of the absolute temperature were made. To aid in the accurate plotting of these data and their linear regression analysis, the University of Delaware Burroughs B-6700 computer was utilized. The appropriate program was written by Dr. John J. Stanulonis of these laboratories and made available to us. The program permitted the determination of the least-squares slope of the plot and its intercept, as well as statistical information which indicated the reliability of the data. The statistical equations were those suggested by Bauer.[35]

From the slope of the Arrhenius plot, the energy of activation may be determined, using the relationship

$$\ln k = \ln A - E_a/RT$$

Plotting $\ln k$ vs. $1/T$ resulted in a straight line whose slope is to be equated with $-E_a/R$.

The entropy of activation is calculated from the relationship[36]

$$\Delta S^{\ddagger} = R(\ln A - \ln T - 24.76)$$

where A is the Arrhenius intercept and T is the absolute temperature.

References and Notes

(1) K. B. Wiberg, "Oxidation in Organic Chemistry", Academic Press, New York, N.Y., 1965, p 142 ff.

(2) R. Stewart, "Oxidation Mechanisms", W. A. Benjamin, New York, N.Y., 1964.

(3) W. A. Waters, "Mechanisms of Oxidation of Organic Compounds", Wiley, New York, N.Y., 1964.

(4) H. Kwart and J. H. Nickle, *J. Am. Chem. Soc.*, **95**, 3394 (1973).

(5) (a) H. Kwart and J. H. Nickle, *J. Am. Chem. Soc.*, **96**, 7572 (1974). (b) Tables of these data [given in the Ph.D. dissertation of J. H. Nickle, University of Delaware, June 1975, pp 33–51] are available through *Dissertation Abstracts.*

(6) (a) H. Kwart and M. C. Latimore, *J. Am. Chem. Soc.*, **93**, 3770 (1971); (b) H. Kwart and J. Slutsky, *J. Chem. Soc., Chem. Commun.*, 1182 (1972); (c) H. Kwart, J. F. Sarner, and J. Slutsky, *J. Am. Chem. Soc.*, **95**, 5242 (1973).

(7) A most recent review is given in H. Taube, *Adv. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(8) See R. P. Bell, *Chem. Soc. Rev.*, **3**, 513 (1974), for a recent general review of this subject; see also, J. R. Hulett, *Q. Rev., Chem. Soc.*, **18**, 227 (1964), E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969), and M. D. Harmon, *Chem. Soc. Rev.*, **1** 211 (1972).

(9) E. F. Caldin and S. Mateo, *J. Chem. Soc., Chem. Commun.*, 854 (1973), and many earlier citations of the work of this group discussed in ref 8.

(10) R. G. Pearson, *Top. Curr. Chem.*, **41**, 75 (1973).

(11) J. Halpern, *Q. Rev., Chem. Soc.*, **15**, 207 (1961).

(12) R. W. Dodson and N. Davidson, *J. Phys. Chem.*, **56**, 866 (1952).

(13) (a) D. R. Stranks In "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960; (b) W. L. Reynolds and R. Lumry, *J. Chem. Phys.*, **23**, 2560 (1955); (c) R. A. Horne and E. W. Axelrod, *ibid.*, **40**, 1518 (1964); (d) I. M. Klotz, J. Ayers, Y. Y. C. Ho, M. G. Horowitz, and R. E. Heiney, *J. Am. Chem. Soc.*, **80**, 2132 (1958).

(14) (a) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961); (b) H. Taube, *ibid.*, **77**, 4481 (1955); (c) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964); **87**, 4730 (1965).

(15) F. S. Dainton and F. T. Jones, *Radiat. Res.*, **17**, 388 (1962).

(16) G. A. Rechnitz and H. A. Catherino, *Inorg. Chem.*, **4**, 112 (1965).

(17) R. Stewart and D. Lee, *Can. J. Chem.*, **42**, 439 (1964).

(18) (a) E. S. Lewes and L. Funderburk, *J. Am. Chem. Soc.*, **86**, 2531 (1964); **89**, 2322 (1967); (b) R. P. Bell and D. M. Goodall, *Proc. R. Soc. London*, **294**, 273 (1967).

(19) G. J. Karabatsos and N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965).

(20) (a) L. Kaplan, *J. Am. Chem. Soc.*, **77**, 5469 (1955); (b) D. Lee and R. Stewart, *J. Org. Chem.*, **32**, 2868 (1967).

(21) The subject of a forthcoming article from these laboratories.

(22) (a) J. Roček, F. H. Westheimer, A. Eschenmoser, L. Moldovanyi, and J. Schreiber, *Helv. Chim. Acta*, **45**, 2554 (1962); (b) E. J. Corey and L. D. Melvin, Jr., *Tetrahedron Lett.*, 929 (1975).

(23) In general, the methods used for the purification of the reagents are in accordance with those discussed in D. D. Perrin, W. L. Amerago, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, London, 1966.

(24) V. L. Hansley, U.S. Patent, 2 724 503 (1956).

(25) H. D. Hartzler, *J. Am. Chem. Soc.*, **93**, 4527 (1971).

(26) J. S. Cook and I. W. Reece, *Aust. J. Chem.*, **14**, 211 (1961).

(27) T. F. McGrath and R. Levine, *J. Am. Chem. Soc.*, **77**, 3656 (1955).

(28) B. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956).

(29) R. Stewart and R. Van der Linden, *Can. J. Chem.*, **38**, 399 (1960).

(30) P. Tarbell and M. C. Paulson, *J. Am. Chem. Soc.*, **64**, 2842 (1942).

(31) W. L. Truett and W. N. Moulton, *J. Am. Chem. Soc.*, **73**, 5913 (1951).

(32) "Durrum Operations Manual", Durrum Inst. Corp., Palo Alto, Calif., 1972.

(33) K. B. Wiberg and R. J. Evans, *J. Am. Chem. Soc.*, **80**, 3019 (1958).

(34) C. H. Rochester, "Acidity Functions", Academic Press, London, 1970.

(35) E. L. Bauer, "A Statistical Manual for Chemists", Academic Press, London, 1971.

(36) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941.

The Solvatochromic Comparison Method. 2. The α-Scale of Solvent Hydrogen-Bond Donor (HBD) Acidities

R. W. Taft*[1a] and Mortimer J. Kamlet*[1b]

Contribution from the Department of Chemistry, University of California, Irvine, California 92664, and the Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910.

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Abstract: The solvatochromic comparison method is used to evaluate hydrogen-bonding contributions in HBD (hydrogen-bond donor) solvents to several commonly used dye indicator solvent polarity scales (Dimroth's E_{T30}, Brooker's χ_R. Kosower's Z). Hydrogen-bonding effects on other spectral properties, equilibria, and reaction rates are determined. and the results are used to construct an α-scale of solvent HBD acidities.

In part I of this series,[2] information obtained through solvatochromic comparisons was used in constructing a β-scale of solvent hydrogen-bond acceptor (HBA)[3] basicities. This β-scale was to serve, together with an α-scale of solvent hydrogen-bond donor (HBD)[3] acidities, toward correlation of solvent effects on many reaction rates, equilibria, and spectroscopic properties, XYZ, through equations of the form

$$XYZ = XYZ_0 + \text{solvent polarity-polarizability effect} + a\alpha + b\beta \quad (1)$$

where a and b represent the susceptibilities of XYZ to changing solvent HBD[3] acidity and HBA basicity, respectively. In the present paper we shall use the same solvatochromic comparison method toward the formulation of the α-scale of solvent HBD

Table I. Solvatochromic Comparison of Spectral Data for Dimroth's Betaine (**2**) and Brooker's Merocyanine (**3**) and of Brownstein's *S* Values with Spectral Data for 4-Nitroanisole (**1**) in Corresponding Solvents

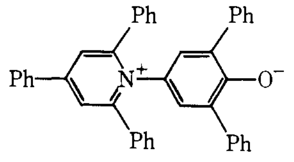
Solvents	$\nu(\mathbf{1})_{max}$, kK	$\nu(\mathbf{2})_{max}$, kK		$\Delta\Delta\nu$, kK	$\nu(\mathbf{3})_{max}$, kK		$-\Delta\Delta\nu$, kK	*S* Value		$\Delta\Delta S$
		Lit.[6]	Calcd		Lit.[14]	Calcd		Lit.[21]	Calcd	
Nonprotic solvents										
1. C_5H_{12}, C_6H_{14}, C_7H_{16}	34.31	10.80			17.79			−0.337		
2. Cyclohexane	34.13	10.91			17.48			−0.324		
5. Di-*n*-butyl ether	33.56	11.68			16.99			−0.286		
6. CCl_4	33.56	11.36			17.02			−0.245		
7. Diethyl ether	33.45	12.09			16.88			−0.277		
9. Dioxane	32.89	12.59			(16.92)[a]			−0.179		
11. Ethyl acetate	32.79	13.32			16.50			−0.210		
13. Tetrahydrofuran	32.79	13.08			16.29					
14. Benzene	32.84	12.06			16.40			−0.215		
17. Anisole	32.41	13.01						−0.214		
19. Triethyl phosphate	32.41	14.09								
20. $ClCH_2CH_2Cl$	32.36	14.65						−0.151		
23. Dimethylacetamide	32.05	15.28			15.03					
24. Pyridine	32.00	14.06			15.35					
25. Dimethylformamide	32.05	15.31			15.30			−0.142		
27. Butyrolactone	31.95				14.90					
29. Dimethyl sulfoxide	31.70	15.73			14.69					
Protic solvents										
101. *tert*-Butyl alcohol	32.94	15.34	12.88	2.46				−0.105	−0.219	0.114
102. Isopropyl alcohol	32.94	16.99	12.88	4.11	15.53	16.30	0.77	−0.041	−0.219	0.178
103. *n*-Butyl alcohol	32.89	17.55	12.98	4.57	15.53	16.25	0.72	−0.024	−0.215	0.191
112. *n*-Propyl alcohol	32.89	17.73	12.98	4.75	15.42	16.25	0.83	−0.016	−0.215	0.199
104. Ethanol	32.89	18.14	12.98	5.16	15.31	16.25	0.94	0.000	−0.215	0.215
105. Methanol	32.79	19.40	13.16	6.24	15.07	16.13	1.06	0.050	−0.206	0.256
107. Ethylene glycol	31.95	19.68	14.74	4.94	14.08	15.15	1.07	0.068	−0.135	0.203
109. Benzyl alcohol	31.75	17.76	15.11	2.65						
111. Water	31.55	22.06	15.49	6.57				0.154	−0.101	0.255
201. Acetic acid	32.63	17.86	13.46	4.40				0.005	−0.193	0.198
202. Formamide	31.65	19.80	15.30	4.50				0.046	−0.110	0.156
203. $CHCl_3$	32.47	13.69	13.76	(−0.09)[b]	15.45	15.76	0.31[c]	−0.200	−0.178	(−0.022)[d]
204. Acetonitrile	32.47	16.07	13.76	2.31	15.97	15.76	(−0.21)[c]	−0.104	−0.178	0.074

[a] Not included in correlation leading to eq 4. [b] Compare with 0.57 kK SD of eq 2. [c] Compare with 0.20 kK SD of eq 4. [d] Compare with 0.022 unit SD of eq 8.

acidities.[4]

Documentation of solute-solvent hydrogen-bonding interactions by the solvatochromic comparison method requires that three important conditions be satisfied: (a) first a plot of corresponding ν_{max} values (or other appropriate spectroscopic or free energy properties) for two solutes of differing hydrogen-bonding ability in a series of solvents of varying polarity, but wherein hydrogen bonding is excluded, should show a linear relationship with a statistically acceptable correlation coefficient; (b) next, data points representing solvents in which hydrogen bonding occurs should be displaced from the regression line (all in the same direction) by statistically significant amounts; (c) and finally, the direction of the displacements should be consistent with the chemistry involved and the relative magnitudes should reflect a reasonable order of solvent hydrogen-bond donor (HBD) strengths in the case of solvent to substrate (type-A)[5] bonding, or solvent hydrogen-bond acceptor (HBA) strengths where the effects derive from solute to solvent (type-B) hydrogen bonds. Part I dealt with type-B hydrogen-bonding phenomena;[2] we address ourselves in the present paper to type-A interactions.

Dimroth's Betaine. In our first example, ν_{max} values reported by Dimroth and co-workers[6] for the lowest energy band in the uv-visible spectrum of 4-(2,4,6-triphenylpyridinium) 2,6-diphenylphenoxide (**2**) are plotted against corresponding ν_{max} positions for 4-nitroanisole (**1**)[7] in 30 solvents (Table I, Figure 1). Displacements of this "solvachromiebande" of the betaine **2** serve as the basis for Dimroth's widely cited E_{T30} scale of solvent polarity.[6] Although the usual assumption has been that solvent polarity and polarizability were the dominant effects influencing E_{T30} values, it has been mentioned that for HBD solvents this scale also contained contributions from type-A hydrogen-bonding interactions.[6,8]



2

As is seen in Figure 1, the results satisfy the requirement that the data in media wherein hydrogen bonding is excluded should show statistically acceptable linear correlation. The regression equation for the results in the non-HBD solvents is

$$\nu(\mathbf{2})_{max} = -1.873\nu(\mathbf{1})_{max} + 74.58 \text{ kK} \qquad (2)$$

with $n = 17$, r (the correlation coefficient) = 0.938, and SD (the standard deviation) = 0.57 kK.

The further condition that ν_{max} values in the hydrogen-bonding solvents should deviate from the regression equation by statistically significant amounts is also fulfilled. Solvatochromic displacements attributable to enhanced hydrogen bonding by the HBD solvents to the strong HBA solute **2** (relative to the weak HBA solute **1**)[7] are calculated from the equation

$$\Delta\Delta\nu(\mathbf{2}-\mathbf{1})^{A}{}_{\to\text{-O-Ar}} = \nu(\mathbf{2})_{max}(\text{obsd}) - \nu(\mathbf{2})_{eq\,2}(\text{calcd}) \qquad (3)$$

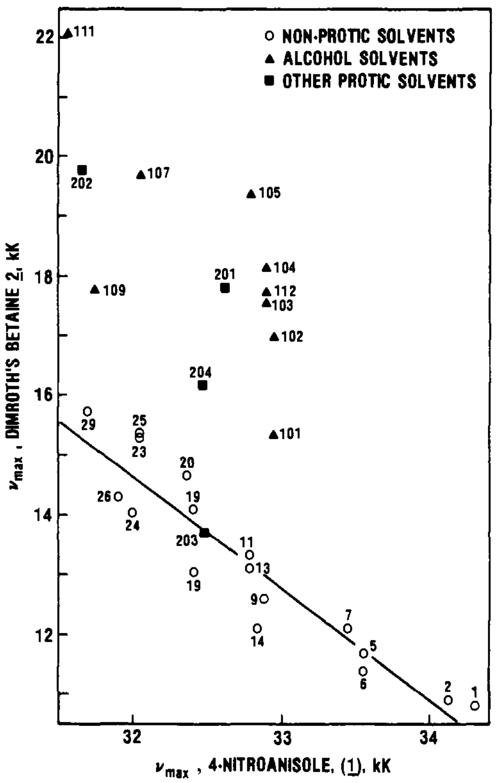
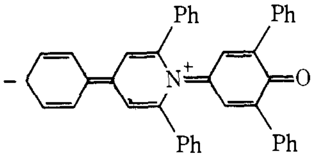


Figure 1. Spectral data for Dimroth's betaine, **2**, plotted against results in corresponding solvents for 4-nitroanisole (**1**).

and are included in Table I. The $\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{1})^{\mathrm{A}}{}_{\to\text{-O-Ar}}$ values[9] for the R-OH solvents range from 4.3 SD of eq 2 for *tert*-butyl alcohol (solvent **101**) to 11.5 SD for water (**111**).

Finally, the condition is met that the signs and relative magnitudes of the solvatochromic shifts be consistent with the chemistry involved. The electronic transition leading to the "solvatochromiebande" involves charge delocalization from the phenoxide oxygen into the pyridinium ring and the phenyl groups attached thereto (i.e., canonical resonance structures like **2a** contributing more to electronic excited than ground state). Hence, hydrogen bonding to phenoxide oxygen should stabilize the ground state relative to the electronic excited state, and the effect in HBD solvents should be hypsochromic as is observed.[10]



2a

Also, $\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{1})^{\mathrm{A}}{}_{\to\text{-O-Ar}}$ magnitudes should be expected to increase with increasing HBD ability of R-OH solvents, and such a trend is indeed clearly observed. Enhanced solvatochromic shifts (Table I) are in the order: *tert*-butyl alcohol (solvent **101**) < isopropyl alcohol (**102**) < *n*-butyl alcohol (**103**) < *n*-propyl alcohol (**112**) < ethylene glycol (**107**) < ethanol (**104**) < methanol (**105**) < water (**111**).[11] We shall see similar orderings in many of our solvatochromic comparisons involving type-A hydrogen-bonding effects.[12]

It is instructive to compare hydrogen bonding and polarity contributions to $E_{\mathrm{T}30}$ differences [$\Delta E_{\mathrm{T}30} = 2.86\ \Delta\nu(\mathbf{2})_{\mathrm{max}}$] between typical nonpolar and R-OH solvents, e.g., cyclohexane, $E_{\mathrm{T}30} = 31.2$, and **103**, $E_{T30} = 50.2$. Of the 19.0 kcal difference, the solvent polarity-polarizability component, calculated from eq 2, is ca. 6.0 kcal; the remainder, ca. 68% of the total effect, must be attributed to preferential stabilization of the ground state relative to the electronic excited state of **2** by a *specific solvent association effect.* Hence, insofar as it is applied to protic solvents, the $E_{\mathrm{T}30}$ scale is more a measure of solvent hydrogen-bonding ability than polarity. These findings support the conclusion by Figueras[13] that "solvent polarity rankings based on the behavior of a dye indicator—particularly in cases involving possible hydrogen bond formation—depend on the structure of the indicator, and may have no general significance".

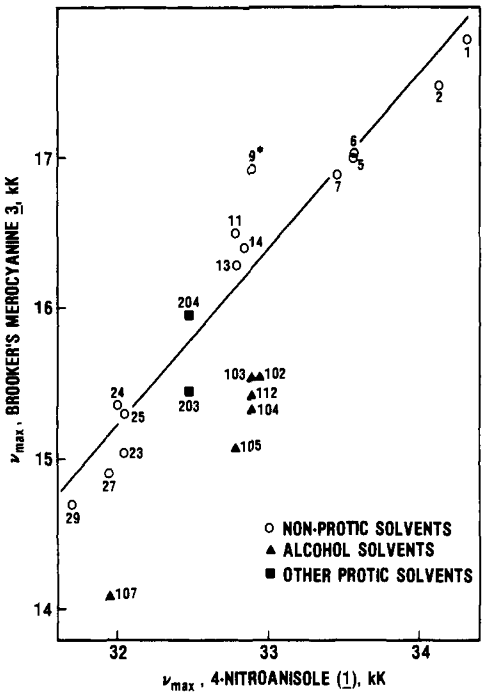
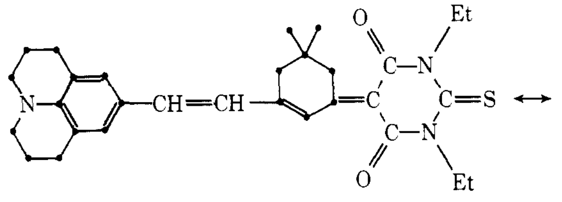
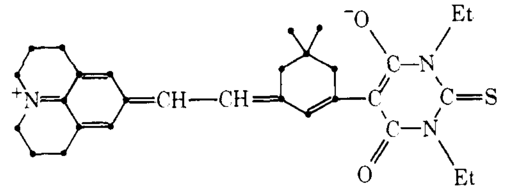


Figure 2. Spectral data for Brooker's merocyanine, **3**, plotted against results for 4-nitroanisole (**1**) in corresponding solvents.

Brooker's Merocyanine. The χ_{R} solvent polarity scale of Brooker et al.[14] represents a ranking based on transition energies for the longest wavelength band in the uv-visible spectrum of the merocyanine **3**, i.e., $\chi_{\mathrm{R}} = E_{\mathrm{T}}(\mathbf{3})$ in kcal = 2.86 $\nu(\mathbf{3})_{\mathrm{max}}$ in kK. The electronic transition for **3** involves more charge in the electronic excited state than in the ground state (excited state more like **3a**), so that, unlike **2**, increased solvent polarity leads to lower transition energy.



3



3a

Figure 2 shows a plot of Brooker and co-workers' $\nu(\mathbf{3})_{\mathrm{max}}$ results against corresponding $\nu(\mathbf{1})_{\mathrm{max}}$ values[7] in 23 solvents (data in Table I). As before, it is seen that the results satisfy the initial requirement for documentation of hydrogen-bonding effects by the solvatochromic comparison method in that the data in the non-hydrogen-bonding media (open circles) show statistically acceptable linear correlation. The regression equation is

$$\nu(\mathbf{3})_{\max} = 1.161\nu(\mathbf{1})_{\max} - 21.94 \text{ kK} \qquad (4)$$

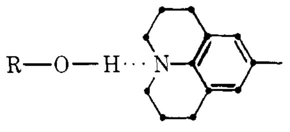
with $n = 13$,[15] $r = 0.983$, and SD = 0.20 kK.

The further condition is also fulfilled that $\nu_{\max}$ values in the HBD solvents (triangles) deviate from the regression equation by statistically significant amounts. Displacements attributable to hydrogen bonding, calculated from the equation

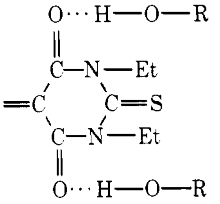
$$-\Delta\Delta\nu(\mathbf{3}\text{-}\mathbf{1})^{A}{}_{\rightarrow O=C} = \nu(\mathbf{3})_{\text{eq } 4}(\text{calcd}) - \nu(\mathbf{3})_{\max}(\text{obsd}) \qquad (5)$$

are included in Table I and, for the R-OH solvents, are all greater than 3.6 times the standard deviation for the non-HBD solvents.[16,17]

The final requirement for solvatochromic comparison, that the signs and relative magnitudes of the $\Delta\Delta\nu$ terms be consistent with the chemistry involved, merits some detailed discussion in this instance. There are two important sites where solvent association might influence the electronic transition energy of **3**.[18] A type-A hydrogen bond at the amine terminus of the extended chromophore (**3b**) would stabilize the ground state relative to the electronic excited state and should lead to a hypsochromic displacement. Conversely, type-A hydrogen bonds by HBD solvents to the two equivalent carbonyl termini (**3c**) should be strengthened in the **3**-**3a** electronic transition, and the spectral consequence of such solvent association would be bathochromic.



3b



3c

To assess the relative importance of **3b** vs. **3c** hydrogen bonding in the overall solvation picture, it is useful to compare **3b** with a typical aromatic amine (dimethylaniline, $pK_{HB} = 0.43$)[19] and **3c** with a typical carboxamide (dimethylbenzamide, $pK_{HB} = 2.22$).[19] The strong and extended through-conjugation between the +M site and the two equivalent −M sites (**3a**) should result in the ground state electron density on amine nitrogen being lower in **3** than in dimethylaniline (lower pK_{HB}, lower HBA strength) and the electron density on carboxamide oxygens being higher in **3** than in dimethylbenzamide (higher pK_{HB}, greater HBA strength). The consequence, then, would be that **3c**-type hydrogen bonding should dominate over **3b** by many orders of magnitude, and the anticipated solvatochromic displacements should be bathochromic, as is observed, with the effects being greater the greater the proton-donor ability of the solvent, as is observed.

Having confirmed that all conditions are met for assessment of hydrogen-bonding effects by the solvatochromic comparison method, it is again instructive to calculate the hydrogen-bonding contribution to the ca. 5.5 kcal χ_R difference between cyclohexane (solvent **2**) and *n*-butyl alcohol (**103**). From eq 4 and 5, the hydrogen-bonding component ($\Delta\Delta\chi_R = 2.86\ \Delta\Delta\nu$) is ca. 2.0 kcal or roughly 35% of the total solvatochromic shift.

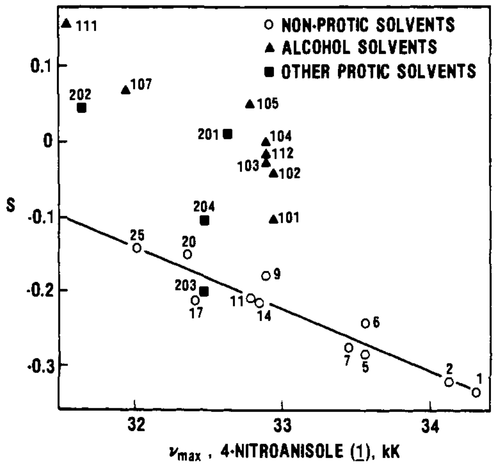


Figure 3. Values of Brownstein's S parameter plotted against spectral data for 4-nitroanisole (**1**) in corresponding solvents.

Kosower's Z and Brownstein's S Solvent Polarity Scales. Another widely used dye indicator polarity index is Kosower's Z-scale, based on transition energies for the charge transfer band of *N*-ethyl-4-carbethoxypyridinium iodide (**4**).[20] Solubility difficulties have limited the number of nonprotic solvents for which Z-values are available, so that direct solvatochromic comparison has not been feasible. However, Brownstein[21] has, in effect, extended Kosower's scale by assembling a number of reaction rates, equilibrium constants, and uv, ir, and NMR spectra which are (*or appear to be*) linear with Z and relating them to the Kosower parameter through the equation

$$\log (k_{\text{solv}}/k_{\text{EtOH}}) = (S)(R) \qquad (6)$$

R is a constant characteristic of the sensitivity of a given reaction to solvent effects and is chosen to be 1.000 for the shift of the absorption maximum of **4**. The S value, Brownstein's solvent polarity parameter, is taken as 0.000 for ethanol (solvent **104**) by definition. Since $Z(\mathbf{104}) = 79.6$, the two scales are related by

$$Z = 79.6(1 + S) \qquad (7a)$$

$$\Delta\Delta Z = 79.6\Delta\Delta S \qquad (7b)$$

$$\Delta\Delta\nu(\mathbf{4}\text{-}\mathbf{1}) = (79.6/2.86)\Delta\Delta S = 27.83\Delta\Delta S \qquad (7c)$$

S values for 23 solvents are plotted against corresponding $\nu_{\max}$ values in Figure 3 (data in Table I). Again, as required for solvatochromic comparison, the results in the non-hydrogen-bonding solvents show statistically acceptable linear correlation. The regression equation is

$$S = -0.0846\nu(1)_{\max} + 2.569 \qquad (8)$$

with $n = 11$, $r = 0.947$, and SD = 0.022. Deviations of the HBD solvent data points from the correlation line ($\Delta\Delta S$ values) are positive, corresponding to a hypsochromic effect of hydrogen bonding on $\nu(\mathbf{4})_{\max}$, and are relatively large (5.1 to 11.6 SD of eq 8).[17] Also, as was observed in the earlier examples, magnitudes of the $\Delta\Delta S$ values (assembled in Table I) are in the antiinductive order for the alkyl-OH solvents, increasing with decreasing $-\sigma^*$ of the alkyl group.

If the nature of the electronic transition for **4** is as proposed by Kosower,[20] a charge-transfer band with a ground state more like **4a** and an electronic excited state more like **4b–d**, the signs and relative magnitudes of the hydrogen-bonding effects are rationalized on the assumption that the spectroscopically important hydrogen bond is to iodide ion.

Finally, the $\Delta\Delta S$ value of 0.191 for *n*-butyl alcohol (Table I) represents 64% of the difference in S-values between *n*-butyl alcohol and cyclohexane. Thus, the S-scale of solvent polarities (and hence the Z-scale) appears to be twice as sensitive to hydrogen-bonding effects by HBD solvents as the χ_R-scale and only slightly less influenced by specific solvation than the E_{T30} scale. The similar relative contributions of polarity effects and hydrogen-bonding effects to the E_{T30} and Z-scales account for the very nice linear correlation of E_{T30} and Z values commented upon by Dimroth and co-workers.[6]

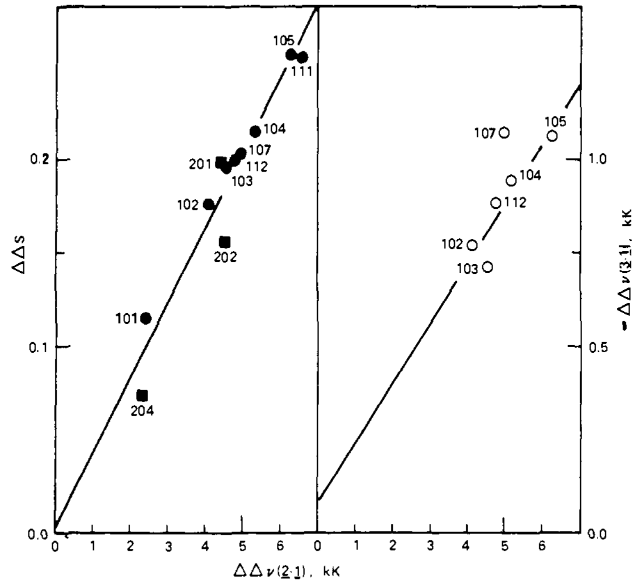


Figure 4. $\Delta\Delta S$ and $-\Delta\Delta\nu(\mathbf{3-1})$ values plotted against $\Delta\Delta\nu(\mathbf{2-1})$ values for corresponding solvents.

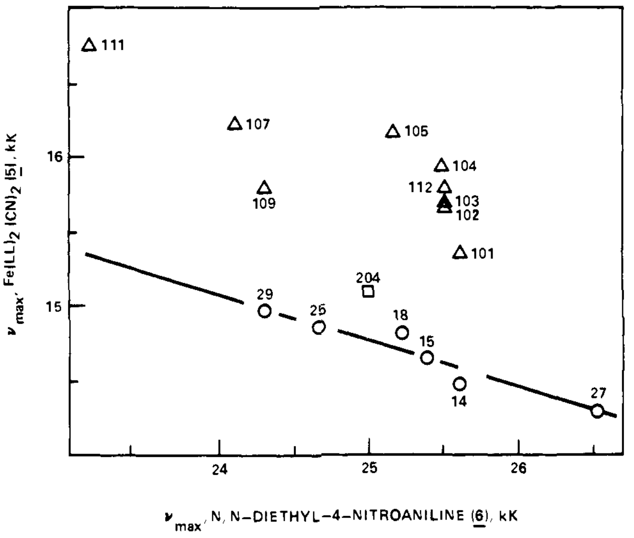
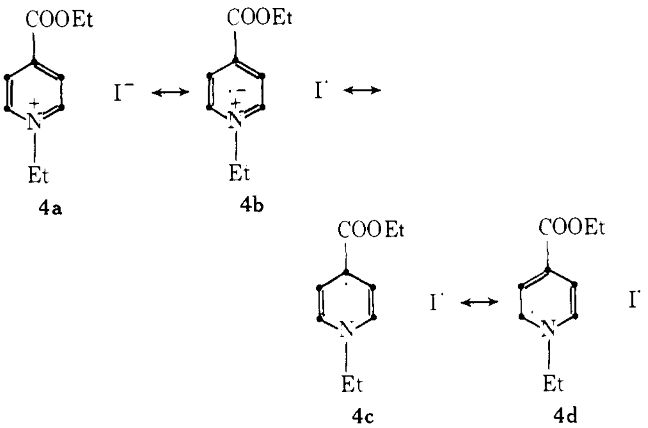


Figure 5. Spectral data for bis[α-(2-pyridylbenzylidene)·3,4-dimethylaniline]bis(cyano)iron(II)(**5**) plotted against results in corresponding solvents for *N,N*-diethyl-4-nitroaniline (**6**).



4a **4b** **4c** **4d**

Relationship between Enhanced Solvatochromic Shifts and Solvent HBD Strengths. Close inspection of Figures 1 and 3 shows remarkably similar orderings of the vertical displacements of the HBD solvent data points from the non-hydrogen-bonding solvent regression lines. This correspondance is better seen when $\Delta\Delta S$ values for the HBD solvents are plotted against corresponding $\Delta\Delta\nu(\mathbf{2-1})^{\mathrm{A}}$ results (left-hand plot, Figure 4).

The good linear correlation shown in the plot lends confidence that the $\Delta\Delta\nu$ values being compared do indeed reflect real and intrinsic properties of the HBD solvents. The least-squares regression equation is

$$\Delta\Delta S = 0.0403[\Delta\Delta\nu(\mathbf{2-1})^{\mathrm{A}}{}_{\rightarrow\text{-O-Ar}}] + 0.002 \qquad (9)$$

with $n = 11$, $r = 0.965$, and SD = 0.015. Considering that the two sets of ΔΔ's represent differences between reported results and values calculated from eq 2 and 8, it deserves particular comment that the standard deviation of eq 9 is lower than the SD of either of the antecedent equations and not much greater than representative experimental errors in the $\nu_{\max}$ measurements.

The very small value of the intercept in eq 9 is also important in that it strongly suggests that the quantities being compared are proportional to one another. Such would be the required relationship if the $\Delta\Delta S$ and $\Delta\Delta\nu(\mathbf{2-1})^{\mathrm{A}}{}_{\rightarrow\text{-O-Ar}}$ values were independently proportional to the same intrinsic properties of the solvents, as is the basic tenet leading to our use of solvatochromic comparison results to construct the α-scale of solvent HBD acidities.

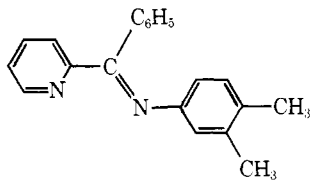
Correlation between the $\Delta\Delta\nu(\mathbf{2-1})^{\mathrm{A}}{}_{\rightarrow\text{-O-Ar}}$ and $-\Delta\Delta\nu(\mathbf{3-1})^{\mathrm{A}}{}_{\rightarrow\text{O=C}}$ results for the R-OH solvents (right-hand plot in Figure 4), although significantly poorer, is still statistically acceptable if the data point for ethylene glycol (**107**) is excluded. The regression equation is

$$-\Delta\Delta\nu(\mathbf{3-1})^{\mathrm{A}}{}_{\rightarrow\text{O=C}} = 0.1584[\Delta\Delta\nu(\mathbf{2-1})^{\mathrm{A}}{}_{\rightarrow\text{-O-Ar}}] + 0.08\ \text{kK} \qquad (10)$$

with $n = 5$, $r = 0.927$, and SD = 0.06 kK. Excluding the data point for **107** is not unreasonable on the basis that type-A hydrogen bonding at multiple sites of **3** (the two carbonyl groups or carbonyl and thiocarbonyl) by ethylene glycol or a self-associated ethylene glycol cluster could lead to a "tighter" and hence more stable hydrogen bonded complex than would be the case for the monohydric alcohols.

As before, the low value of the intercept in eq 10 (0.08 kK, compared with the 0.06 kK SD of eq 10 and the 0.20 kK SD of antecedent eq 4) suggests the likelihood that the $\Delta\Delta\nu$ values being compared are directly proportional to one another.

Burgess' Fe(LL)$_2$(CN)$_2$ Spectra. Burgess[22] has described medium effects on the metal to ligand charge-transfer bands in the uv-visible spectra of a number of metal clathrate complexes including bis[α-(2-pyridylbenzylidene)-3,4-dimethylaniline]bis(cyano)iron(II), Fe(LL)$_2$(CN)$_2$ (**5**). Solvent absorption obscures the spectrum of **1** in several of the solvents employed in Burgess' study, so solvatochromic comparison in this instance is between **5** and an alternative reference substrate, *N,N*-diethyl-4-nitroaniline (**6**).[23] The data for **5** are given in Table II, the corresponding results for **6** in Table I of part I.[2]



LL in **5**

Positions of maximal absorption of **5** in 16 solvents are plotted against corresponding $\nu(\mathbf{6})_{\max}$ values in Figure 5. Again it is seen that linear correlation in the non-HBD solvents is good. The regression equation is

Table II. Additional Data Used in the Solvatochromic Comparisons

	$Fe(LL)_2(CN)_2$ (**5**)			$Et_4N^+I^-$ (**7**)			t-C_4H_9Cl solvolysis		
	ν(**5**)$_{max}$, kK			$\Delta G_c{}^t$(**7**), kcal			Y', kcal		
Solvents	Lit.[22]	Calcd	$\Delta\Delta\nu$, kK	Lit.[25]	Calcd	$-\Delta\Delta G_c{}^t$, kcal	Lit.[27]	Calcd	$\Delta\Delta Y'$, kcal
			Nonprotic solvents						
1. C_5H_{12}, C_6H_{14}, C_7H_{16}				14			4.9		
2. Cyclohexane				13			6.1		
6. CCl_4				11					
7. Diethyl ether	14.29			8.9			8.1		
11. Ethyl acetate				5.3					
14. Benzene	14.47			6.9			8.8		
15. Chlorobenzene	14.64								
18. Acetone	14.81								
20. $ClCH_2CH_2Cl$				1.6					
24. Pyridine							11.5		
28. *N*-Methylpyrrolidone				1.0					
25. Dimethylformamide	14.86			0.9			13.4		
29. Dimethyl sulfoxide	14.97			0.5			14.8		
			Protic solvents						
101. *tert*-Butyl alcohol	15.34	14.57	0.77	3.8	6.4	2.6	12.9	9.61	3.29
102. Isopropyl alcohol	15.65	14.60	1.05	2.4	6.4	4.0	14.8	9.61	5.19
103. *n*-Butyl alcohol	15.67	14.60	1.07	2.1	6.2	4.1	15.2	9.78	5.42
112. *n*-Propyl alcohol	15.77	14.60	1.17	1.8	6.2	4.4	15.4	9.78	5.62
104. Ethanol	15.92	14.61	1.31	1.3	6.2	4.9	15.9	9.78	6.12
105. Methanol	16.16	14.71	1.45	0	5.6	5.6	17.4	10.21	7.27
107. Ethylene glycol	16.21	15.04	1.17						
109. Benzyl alcohol	15.80	14.97	0.83				15.9	13.68	2.22
111. Water	16.75	15.32	1.43	−0.4	−1.3	(−0.9)[a]	(24.1)	14.31	(9.79)
							22.2[b]		7.89[b]
201. Acetic acid							17.3	10.66	6.64
204. Acetonitrile	15.11	14.78	0.34	1.4	3.8	2.4	13.2	11.25	1.95

[a] Not included in correlation leading to eq 14. [b] Preferred alternative datum from ref 29; see text.

$$\nu(\mathbf{5})_{max} = -0.3196\nu(\mathbf{6})_{max} + 22.75 \text{ kK} \quad (11)$$

with $n = 6$, $r = 0.962$, and SD = 0.08 kK.

The effect of hydrogen bonding in the HBD solvents is hypsochromic, as appears to be characteristic of charge-transfer bands, and the magnitudes of the enhanced solvatochromic effects range from 4.5 to 18 SD's of eq 11.[17] Values of $\Delta\Delta\nu(\mathbf{5\text{-}6})^A$ are included in Table II. Although we are not now able to pinpoint where $Fe(LL)_2(CN)_2$ association with the HBD solvents takes place, there seems no question that we are dealing with type-A hydrogen-bonding phenomena.[5]

The comparison of $\Delta\Delta\nu(\mathbf{5\text{-}6})^A$ values with corresponding $\Delta\Delta\nu(\mathbf{2\text{-}1})^A{}_{\rightarrow\text{-O-Ar}}$ results is shown in Figure 6. Linear correlation in this instance is fair; the regression equation is

$$\Delta\Delta\nu(\mathbf{5\text{-}6})^A = 0.210[\Delta\Delta\nu(\mathbf{2\text{-}1})^A{}_{\rightarrow\text{-O-Ar}}] + 0.14 \text{ kK} \quad (12)$$

with $n = 10$, $r = 0.934$, and SD = 0.13 kK.[24]

Free Energies of Transfer of the $Et_4N^+I^-$ Ion Pair between Solvents. The solvatochromic comparisons in the previous examples were between sets of uv-visible spectral data or solvent polarity scales derived therefrom. According to LFER concepts, however, the general method should be applicable to many other types of free energy dependent properties and reaction parameters, and such is indeed the case. In our next solvatochromic comparison, free energies of transfer of the $Et_4N^+I^-$ ion pair (**7**) from methanol to a series of solvents, $\Delta G_c{}^t$ (**7**), reported by Abraham,[25] are compared with our 4-nitroanisole spectral data in corresponding solvents (data in Table II).

The plot of $\Delta G_c{}^t$ (**7**) against $\nu(\mathbf{1})_{max}$ is shown in Figure 7, and again we observe the same general pattern. The results in the non-hydrogen-bonding solvents show good linear regression: the correlation equation is

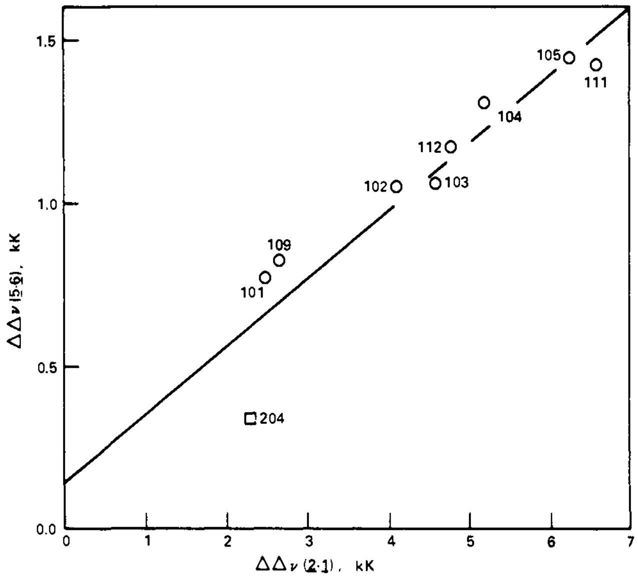


Figure 6. $\Delta\Delta\nu$(**5-6**) values plotted against $\Delta\Delta\nu$(**2-1**) values for corresponding solvents.

$$\Delta G_c{}^t(\mathbf{7}) = 5.59\nu(\mathbf{1})_{max} - 177.7 \text{ kcal/mol} \quad (13)$$

with $n = 10$, $r = 0.987$, and SD = 0.9 kcal/mol. The data points representing the HBD solvents (with only the exception of water)[26] fall off the regression line in the expected direction, i.e., type-A hydrogen bonding by the HBD solvents to iodide ion stabilizes the ion pair. Values of the vertical displacements

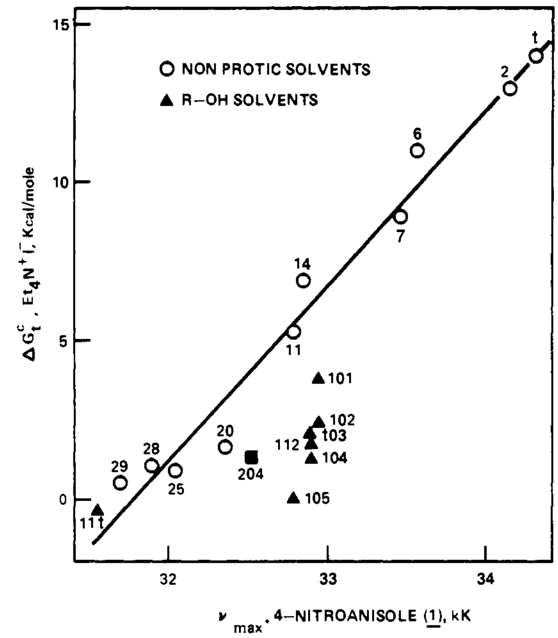


Figure 7. Free energies of transfer from methanol to a series of solvents for the $Et_rN^+I^-$ ion pair (**7**) plotted against spectral data for 4-nitroanisole (**1**) in corresponding solvents.

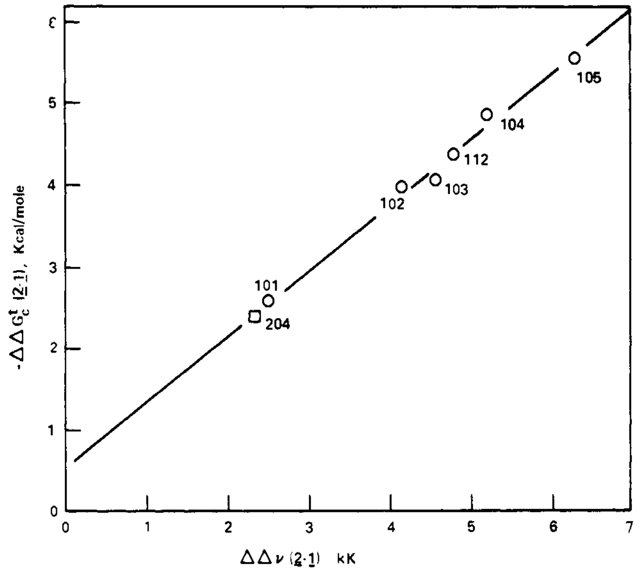


Figure 8. $-\Delta\Delta G_c{}^t(\mathbf{7}\text{-}\mathbf{1})^A{}_{\to I^-}$ results plotted against $\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{1})^A{}_{\to\text{-O-Ar}}$ values in corresponding solvents.

from the regression line, $-\Delta\Delta G_c{}^t(\mathbf{7}\text{-}\mathbf{1})^A{}_{\to I^-}$, amounting to 2.6 to 6.2 SD of eq 13,[17] are included in Table II.

The plot of $-\Delta\Delta G_c{}^t(\mathbf{7}\text{-}\mathbf{1})^A{}_{\to I^-}$ against corresponding $\Delta\Delta\nu(2\text{-}1)^A{}_{\to\text{-O-Ar}}$ results is shown in Figure 8. Correlation is excellent; the least-squares regression equation is

$$-\Delta\Delta G_c{}^t(\mathbf{7}\text{-}\mathbf{1})^A{}_{\to I^-} = 0.812[\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{1})^A{}_{\to\text{-O-Ar}}] + 0.6 \text{ kcal/mol} \quad (14)$$

with $n = 7$, $r = 0.996$, and SD = 0.11 kcal/mol. The 0.6 kcal/mol intercept in eq 14 is smaller than the 0.9 kcal/mol SD of eq 13, so that again the plots appear to confirm that the results reflect a direct proportionality between the ΔΔ quantities being compared.

Solvolysis of *tert*-Butyl Chloride. Koppel and Palm[27] have assembled 120 °C rate constants for the solvolysis of *tert*-butyl chloride (**8**) in a number of solvents in terms of Y' values, where

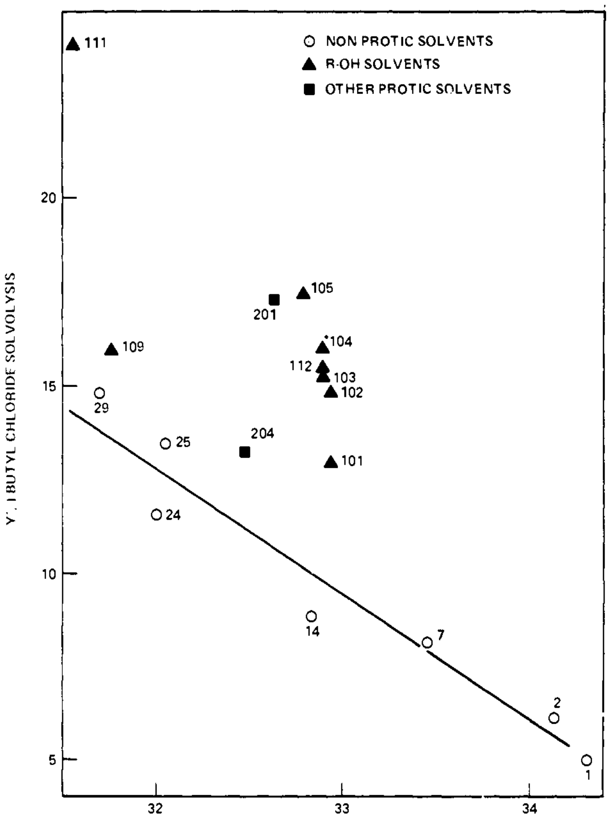


Figure 9. Y'-values for *tert*-butyl chloride solvolysis plotted against spectral data for 4-nitroanisole (**1**) in corresponding solvents.

$Y' = 1.800[\log k_{\text{solvent}}(120\ °\text{C}) - \log k_{\text{gas phase}}(120\ °\text{C})]$ kcal/mol. A plot of these Y' values against $\nu(\mathbf{1})_{max}$ positions in 17 corresponding solvents is shown in Figure 9 (data in Table II), where again the same familiar pattern emerges.

The data points representing the nonprotic solvents show good linear regression; the correlation equation is

$$Y' = -3.38\ \nu(\mathbf{1})_{max} + 121.0 \text{ kcal/mol} \quad (15)$$

with $n = 7$, $r = 0.970$, and SD = 1.0 kcal/mol. The data points for the HBD solvents are all displaced from the regression line by statistically significant amounts (2.2 to 7.9 SD of eq 15),[17] and the direction of the displacements indicates that type-A solvation by the HBD solvents, most probably at the leaving chlorine atom, has a significant accelerating effect on the rate of *tert*-butyl chloride solvolysis.

When $\Delta\Delta Y'(\mathbf{8}\text{-}\mathbf{1})^A{}_{\to\text{Cl-R}}$ results in the HBD solvents (Table II) are plotted against corresponding $\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{1})^A{}_{\to\text{-O-Ar}}$ values (Figure 10), correlation is again good. The regression equation is

$$\Delta\Delta Y'(\mathbf{8}\text{-}\mathbf{1})^A{}_{\to\text{Cl-R}} = 1.308[\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{1})^A{}_{\to\text{-O-Ar}}] - 0.49 \text{ kcal/mol} \quad (16)$$

with $n = 10$, $r = 0.953$, and SD = 0.66 kcal/mol. Again the intercept in eq 16 is smaller than the SD of antecedent eq 15, so that it is reasonable to conclude that the results reflect direct proportionality.

In this solvatochromic comparison, a problem arises regarding the important data point for water. If Koppel and Palm's Y' value of 24.1 kcal/mol is used,[27] the data point falls off the regression line in Figure 10 by about 2 kcal/mol. This Y' value corresponds to $\log k_{H_2O}(120\ °\text{C}) = 1.92$, obtained by Arrhenius extrapolation to 120 °C of near-ambient temperature rate constants, using an activation energy reported by

Table III

Property	Correlation eq	Eq for α	
Series 1. Enhanced solvatochromic shift for betaine **2** relative to 4-nitroanisole		$\alpha_1 = \Delta\Delta\nu(\mathbf{2\text{–}1})/6.24$	(17)
Series 2. Enhanced solvatochromic shift for merocyanine **3** relative to 4-nitroanisole	10	$\alpha_2 = \dfrac{-\Delta\Delta\nu(\mathbf{3\text{–}1}) - 0.08}{(0.1584)(6.24)}$	(18)
Series 3. Augmented value of S relative to solvatochromic shift for 4-nitroanisole	9	$\alpha_3 = \dfrac{\Delta\Delta S - 0.002}{(0.0403)(6.24)}$	(19)
Series 4. Enhanced solvatochromic shift for $\mathrm{Fe(LL)_2(CN)_2}$ relative to *N,N*-diethyl-4-nitroaniline	12	$\alpha_4 = \dfrac{\Delta\Delta\nu(\mathbf{5\text{–}6}) - 0.14}{(0.210)(6.24)}$	(20)
Series 5. Reduced free energy of transfer of $\mathrm{Et_4N^+I^-}$ relative to solvatochromic shift for 4-nitroanisole	14	$\alpha_5 = \dfrac{-\Delta\Delta G_c{}^{t}\,(\mathbf{7\text{–}1}) - 0.6}{(0.812)(6.24)}$	(21)
Series 6. Augmented Y' value for *tert*-butyl chloride solvolysis relative to solvatochromic shift for 4-nitroanisole	16	$\alpha_6 = \dfrac{\Delta\Delta Y'\,(\mathbf{8\text{–}1}) + 0.49}{(1.308)(6.24)}$	(22)

Moelwyn-Hughes and co-workers.[28] However, a table in an earlier paper by Koppel and Palm[29] contained, in addition to the log $k_{\mathrm{H_2O}}$(120 °C) value of 1.92, a second value of 0.83 resulting from an alternative activation energy reported earlier by Moelwyn-Hughes.[30] The log $k_{\mathrm{H_2O}}$(120 °C) value of 0.83 corresponds to $Y' = 22.2$, which, as shown in Figure 10, falls almost directly on the correlation line. Since there appears to be equal justification in using either of Moelwyn-Hughes activation energies for the extrapolation to 120 °C, we have used $Y' = 22.2$ in the correlation leading to eq 16 and in calculating the α-value for water.

In view of the very large amount of attention devoted to *tert*-butyl chloride solvolysis in ethanol–water mixtures, it is interesting to note that 1.77 kcal (28%) of the 6.3 kcal/mol difference in Y' values between pure ethanol and pure water derives from differential hydrogen bonding effects, with the remaining 72% attributable to the change in solvent polarity. That both isocomposition and isodielectric activation energies for this reaction in ethanol–water mixtures are strongly temperature dependent may result from changing HBD strength with changing temperature.

The α-Scale of Solvent Hydrogen-Bond Donor Acidities. In future papers, the α-scale of solvent HBD acidities, together with the β-scale of solvent HBA basicities reported in part I,[2] and an index (or indexes)[4] of solvent polarity-polarizability will be shown applicable to a generalized quantitative treatment of pure solvent effects on many reaction rates, equilibria, and spectroscopic properties.

As a point of departure in constructing the α-scale, some definitions and a fixed point of reference are in order. We take the $\Delta\Delta(\mathbf{2\text{–}1})$ value of 6.24 kK for methanol (solvent **105**) as the single fixed reference point and set the α-value corresponding to this datum as equal to unity by definition, i.e., $\alpha_1{}^{105} = 1.000$. In the term $\alpha_1{}^{105}$, the superscript indicates that we are dealing with solvent **105** and the subscript denotes that we are dealing with property or reaction series 1 (see below). The α term represents the ratio between the regression from the intercept of the *experimental* value for that solvatochromic effect ($\Delta\Delta XYZ$) and the *calculated* regression from the intercept for $\Delta\Delta XYZ$ in methanol, where the intercept and the calculated regression value are obtained through the correlation equation relating $\Delta\Delta XYZ$ to $\Delta\Delta\nu(\mathbf{2\text{–}1})$. Since the correlation equations in the present paper are all of the form, $\Delta\Delta XYZ = A[\Delta\Delta\nu(\mathbf{2\text{–}1})] + B$, the α value (for solvent **103** in series 5, for example) is given by $\alpha_5{}^{103} = (\Delta\Delta XYZ^{103} - B)/(6.24)(A)$. Finally, the term $\alpha_{1\text{–}6}{}^{103}$ represents the average of the α values for solvent **103** in the first six series correlated.

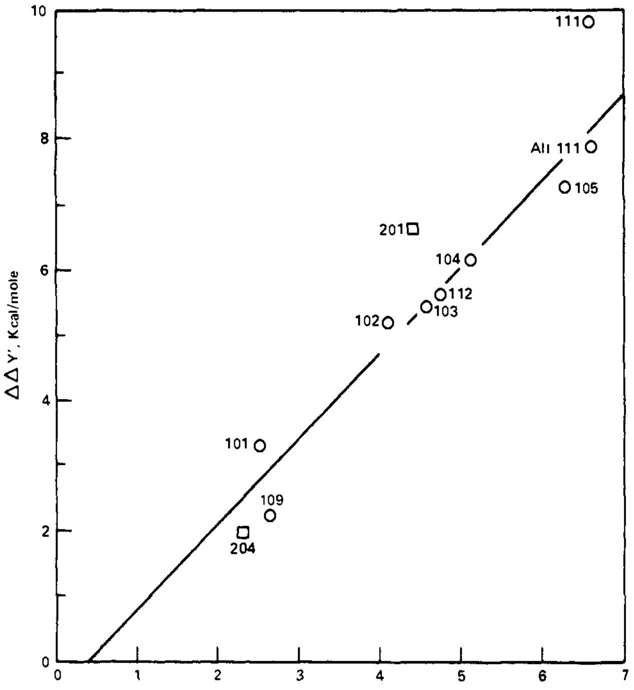


Figure 10. $\Delta\Delta Y'(\mathbf{8\text{–}1})^{\mathrm{A}}{}_{\rightarrow\mathrm{Cl\text{-}R}}$ values plotted against $\Delta\Delta\nu(\mathbf{2\text{–}1})^{\mathrm{A}}{}_{\rightarrow\mathrm{-O\text{-}Ar}}$ values for corresponding solvents.

The properties discussed so far in this paper and the $\Delta\Delta XYZ$ values in Tables I and II provide the information for six sets of α values as shown in Table III. The individual α values are assembled in Table IV, together with the averaged $\alpha_{1\text{–}6}$ results.

We will have ample opportunity in subsequent papers to discuss individual α values for the HBD solvents and to expand the data base. It suffices at this point to make the following pertinent observations: (a) The aliphatic alcohols **101–105** and **112** show decreasing HBD acidity with increasing electron-donating ability of R in R–OH, the effect being closely proportional to σ^* values of the alkyl groups. (b) However, electron-withdrawing groups like R = $\mathrm{C_6H_5CH_2}$ and $\mathrm{HOCH_2CH_2}$ *do not* increase acidity relative to R = $\mathrm{CH_3}$, and R = H increases acidity only marginally. (c) The range of variation of

Table IV. The α-Scale of Solvent HBD Acidities

Solvent	α_1	α_2	α_3	α_4	α_5	α_6	Average α_{1-6}	(n)
101. *tert*-Butyl alcohol	0.394		0.445	0.481	0.401	0.463	0.436 ± 0.031	(5)
102. Isopropyl Alcohol	0.659	0.698	0.700	0.694	0.677	0.695	0.687 ± 0.013	(6)
103. *n*-Butyl alcohol	0.732	0.647	0.752	0.710	0.697	0.724	0.710 ± 0.026	(6)
112. *n*-Propyl alcohol	0.761	0.759	0.783	0.786	0.756	0.749	0.766 ± 0.013	(6)
104. Ethanol	0.827	0.870	0.847	0.893	0.855	0.810	0.850 ± 0.022	(6)
105. Methanol	1.000	0.991	1.010	1.000	0.993	0.951	0.990 ± 0.014	(6)
107. Ethylene glycol	0.792	(0.985)[a]	0.799	0.786			0.792 ± 0.004	(3)
109. Benzyl alcohol	0.424			0.527		0.332	0.43 ± 0.07[b]	(3)
111. Water	1.053		1.006	0.984		1.027	1.017 ± 0.023[b]	(4)
201. Acetic acid	0.705		0.779			0.874	0.79 ± 0.06[a]	(3)
202. Formamide	0.721		0.612				*c*	
203. $CHCl_3$	(nil)	0.233[d]	(nil)				*c*, probably nil	
204. Acetonitrile	0.370	(nil)[a]	0.286	0.153	0.361	0.299	0.29 ± 0.06[e]	(5)

[a] Not included in average; see text. [b] Based on preferred alternative Y′ value; see text. [c] Insufficient data for meaningful average. [d] Possibly attributable to 0.5% ethanol stabilizer in most commercial chloroform. [e] Less reliable values are given to two significant figures.

the individual α values is relatively small (<0.10 unit) for the alkanols, ethylene glycol, and water, and the α_{1-6} values for these solvents are therefore considered to be the most reliable. (d) Somewhat greater variations of the individual α values (ca. 0.2 unit) for benzyl alcohol, acetic acid, acetonitrile, and chloroform impel us to assign a lower reliability to these α_{1-6} values. The possibility of competitive intramolecular hydrogen bonding to its own π-electron system by benzyl alcohol has been commented on,[31] and the hydrogen-bond donor strength of chloroform is probably near or below the bottom end of the range discernible by solvatochromic comparison methods.

It should be kept in mind also that the α values compiled here are intended to represent the HBD strengths of the neat, strongly self-associated solvents. It is quite possible that R–OH monomers, such as would be encountered in dilute solutions in CCl_4, might show markedly different orderings of HBD strengths.

The relative α_{1-6} values for the alkanols, water, and acetic acid are also of some interest. They confirm that, as has been abundantly documented for HBA bases,[19,32] hydrogen-bonding phenomena involving partial proton transfer (estimated at ca. 10–30%)[33] have little in common with pK_a's (proton-transfer measures) when substrates with different functional groups are compared.

Acknowledgment. The work by M.J.K. was done under Navsurfwpncen Foundational Research Task IR-44. We are indebted to Dr. W. H. Gilligan, Dr. R. R. Minesinger, Dr. J. W. Eastes, Dr. H. G. Adolph, and Miss E. Kayser for assistance.

References and Notes

(1) (a) University of California; (b) Naval Surface Weapons Center.

(2) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).

(3) There has been some confusion in the hydrogen-bonding literature as to whether the terms donor and acceptor refer to the proton or the electron pair. In the present series of papers, HBD (hydrogen-bond donor) and HBA (hydrogen-bond acceptor) refer to donation and acceptance of the proton.

(4) We are currently investigating whether a single scale adequately represents the solvent polarity–polarizability effect or whether separate indexes are required to reflect the polarity and polarizability contributions. The results will be reported in a future paper.

(5) M. J. Kamlet, E. G. Kayser, R. R. Minesinger, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36**, 3853 (1971).

(6) K. Dimroth, C. Reichardt, T. Seipmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); C. Reichardt, *ibid.*, **752**, 64 (1971); C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(7) The 4-nitroanisole uv spectrum is taken as the reference property in most of our solvatochromic comparisons because, of over 50 spectra considered, it appears to be the least influenced by hydrogen-bonding effects while still showing a reasonable response to changing solvent polarity.

(8) F. W. Fowler, A. R. Katritzky, and R. J. D. Rutherford, *J. Chem. Soc. B*, 460 (1971).

(9) The notation $\Delta\Delta(\mathbf{2-1})^{A}{}_{\rightarrow\text{-O-Ar}}$ signifies a hypsochromic displacement for **2** relative to **1** caused by type-A hydrogen bonding by a protic solvent *to* the charged aryloxy oxygen. See footnote **8** of part I for an outline of this system, which makes nomenclature much less confusing and cumbersome when several types of hydrogen bonding with concomitant spectral effects occur simultaneously.[2]

(10) Charge delocalization in the electronic excitation also accounts for the blue shift in the aprotic solvents with increasing solvent polarity.

(11) Solvent numbering is the same in all papers of this series.

(12) The R–OH solvents are, of course, amphiprotic. In part I,[2] we showed that when enhanced solvatochromic shifts in alcohol solvents resulted from type-B hydrogen bonding by HBD solutes to the alcohols acting as HBA's, the magnitudes of the effects were in the exactly converse order, i.e., 105 < 104 < 103 < 112 < 102 < 101.

(13) J. Figueras, *J. Am. Chem. Soc.*, **93**, 3255 (1971).

(14) L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.*, 87, 2443 (1965).

(15) The single data point for dioxane (solvent **9**) was excluded from the correlation.

(16) The notation $-\Delta\Delta\nu(\mathbf{3-1})^{A}{}_{\rightarrow O=C}$ signifies a bathochromic displacement for **3** relative to **1** caused by type-A hydrogen bonding *by* an HBD solvent *to* the carbonyl oxygen.

(17) We continue to express the $\Delta\Delta\nu$ values in terms of standard deviations of the correlation equation to emphasize that requirement b for solvatochromic comparison (statistical significance) must be and has been satisfied.

(18) Strong hydrogen bonding would also be anticipated at the C=S site, but the effect on $\nu(\mathbf{3})_{max}$ would be relatively small.

(19) D. Gurka and R. W. Taft, *J. Am. Chem. Soc.*, **91**, **4974** (1969); R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, **4801** (1969).

(20) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

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

(22) J. Burgess, *Spectrochim. Acta, Part A*, **26**, 1957 (1970).

(23) Although **6** has been shown to be an HBA (at the nitro oxygens),[31] the important criterion for solvatochromic comparison is that the substrates being compared *differ* in their HBA ability. The spectral effects of hydrogen bonding by HBD solvents to **6**, though greater than with **1**,[7] are still relatively minor compared with **5**.

(24) If the data point for acetonitrile (**204**) is excluded, the correlation equation becomes: $\Delta\Delta\nu(\mathbf{5-6}) = 0.172[\Delta\Delta\nu(\mathbf{2-1})] + 0.34$ with $n = 9$, $r = 0.981$, and SD = 0.05 kK. It may be that the too low $\Delta\Delta\nu(\mathbf{5-6})$ value for solvent **204** is not because of too weak hydrogen bonding to **5**, but rather because of anomalously strong hydrogen bonding to the nitro oxygens of the reference substrate **6**; see footnote 22 of ref 31.

(25) M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1343 (1972).

(26) We cannot explain the anomalous result for H_2O. We would have expected a value like −7 kcal/mol for the $\Delta G_c{}^t$ into water.

(27) I. A. Koppel and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, **6**, 504 (1969).

(28) E. A. Moelwyn-Hughes, R. E. Robertson, and S. Sugamori, *J. Chem. Soc.*, 1965 (1965).

(29) I. A. Koppel and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, **4**, 862 (1967).

(30) E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1517 (1961).

(31) M. J. Kamlet, E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).

(32) J. Mitsky, L. Joris, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 3442 (1972); E. M. Arnett, E. Mitchell, and T. S. S. R. Murty, *ibid.*, **96**, 3875 (1974).

(33) D. Gurka, R. W. Taft, L. Joris, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **89**, 5957 (1967).