The Solvatochromic Comparison Method. I. The β-Scale of Solvent Hydrogen-Bond Acceptor (HBA) Basicities[1]

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Abstract: The solvatochromic comparison method is outlined. Magnitudes of enhanced solvatochromic shifts in HBA (hydrogen-bond acceptor) solvents are determined for 4-nitroaniline (**1**) relative to *N,N*-diethyl-4-nitroaniline (**2**) $[-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}}]$ and for 4-nitrophenol (**3**) relative to 4-nitroanisole (**4**) $[-\Delta\Delta\nu(\mathbf{3}-\mathbf{4})^{\mathrm{B}}{}_{\leftarrow\mathrm{HO}}]$. The $-\Delta\Delta\nu$ values for the HBD (hydrogen-bond donor) substrates **1** and **3** in corresponding HBA solvents are shown to be proportional to one another, proportional to limiting ^{19}F NMR shifts of hydrogen-bonded complexes of 4-fluorophenol with the same HBA's, and linear with log association constants of hydrogen-bonded complexes between 4-fluorophenol ($\mathrm{p}K_{\mathrm{HB}}$) and phenol and the same HBA molecules. The LFE relationships are used to establish a β-scale of solvent HBA basicities.

Although frequency differences between free and bonded X-H stretching vibrations in the infrared are more frequently used as measures of hydrogen-bond strengths, solvatochromic comparisons of uv-visible spectral data can provide equally useful information in this regard. In this paper we will use the *solvatochromic comparison method* to construct a β-scale of solvent hydrogen-bond acceptor ability ($\beta \sim$ HBA basicity),[3] and in a subsequent paper, we will construct an α-scale of solvent hydrogen-bond donor ability ($\alpha \sim$ HBD acidity).[3]

Documentation of solvent-substrate hydrogen-bonding interactions by the solvatochromic comparison method requires that three important conditions be fulfilled: (a) first a plot of corresponding $\nu_{\max}$ values (or other appropriate spectroscopic or free energy parameters) for two substrates 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)[3] strengths in the case of solvent to substrate (type-A)[5] bonding, or solvent hydrogen-bond acceptor (HBA)[3] strengths where the effects derive from substrate to solvent (type-B)[5] hydrogen bonds. The present paper deals with type-B hydrogen-bonding phenomena[5] and the β-scale.

In our first example, $\nu_{\max}$ values for the $[>\mathrm{N^+{=}C(1)} \rightarrow \mathrm{C(4){=}NO_2^-}]$ electronic transition of 4-nitroaniline (**1**) are compared with results in corresponding solvents for *N,N*-diethyl-4-nitroaniline (**2**) (Figure 1 and Table I). Both **1** and **2** are capable of acting as HBA substrates (at the nitro oxygens)[6] in HBD solvents, but only **1** can act as a HBD substrate in HBA solvents. The solvents are of three types: 9 which are considered to be neither HBA nor HBD's (their $\mathrm{p}K_{\mathrm{HB}}$'s would be anticipated to be lower than -0.5)[7] are represented by open circles in Figure 1; 25 HBD solvents ($\mathrm{p}K_{\mathrm{HB}} > -0.2$)[7] are represented by squares; and 10 amphiprotic R-OH solvents (capable of acting as either HBA's or HBD's) are represented by triangles.

It is seen in Figure 1 that the results satisfy the first requirement for solvatochromic comparison in that the data points representing the nonhydrogen-bonding solvents exhibit good linear regression. The regression equation is

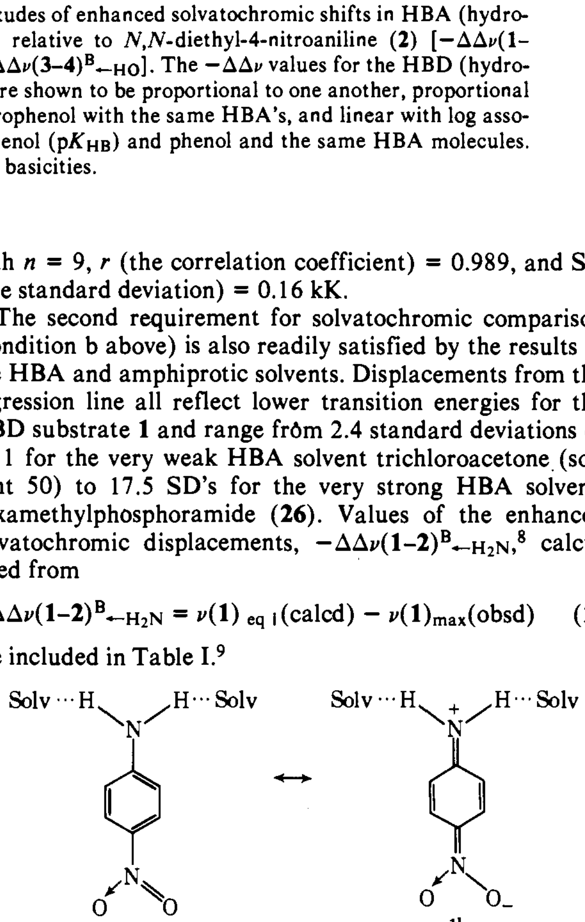
$$\nu(\mathbf{1})_{\max} = 1.035\nu(\mathbf{2})_{\max} + 2.64 \text{ kK} \qquad (1)$$

with $n = 9$, r (the correlation coefficient) $= 0.989$, and SD (the standard deviation) $= 0.16$ kK.

The second requirement for solvatochromic comparison (condition b above) is also readily satisfied by the results in the HBA and amphiprotic solvents. Displacements from the regression line all reflect lower transition energies for the HBD substrate **1** and range from 2.4 standard deviations of eq 1 for the very weak HBA solvent trichloroacetone (solvent 50) to 17.5 SD's for the very strong HBA solvent, hexamethylphosphoramide (**26**). Values of the enhanced solvatochromic displacements, $-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}}$,[8] calculated from

$$-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}} = \nu(\mathbf{1})_{\mathrm{eq\,1}}(\mathrm{calcd}) - \nu(\mathbf{1})_{\max}(\mathrm{obsd}) \qquad (2)$$

are included in Table I.[9]



1a **1b**

An electronic transition from a type-B hydrogen-bonded ground state resembling **1a** to an excited state more like **1b** would lead to hydrogen-bond strengthening in the electronic excitation, with a corresponding lowering in electronic transition energy. Hence the bathochromic effect of hydrogen bonding by **1** to solvent is as anticipated, as are the greater magnitudes of the $-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}}$ values in the more strongly basic solvents.

Exactly parallel effects to the above are seen in the solvatochromic comparison of uv spectral data for 4-nitrophenol (**3**) and 4-nitroanisole (**4**) (Figure 2 and Table I). The linear regression equation for the data points in the nonhydrogen-bonding solvents is

$$\nu(\mathbf{3})_{\max} = 0.901\nu(\mathbf{4})_{\max} + 4.16 \text{ kK} \qquad (3)$$

with $n = 6$, $r = 0.997$, and SD $= 0.06$ kK.

As before, displacements of the data points representing the HBA and amphiprotic solvents are in the direction which indicates that hydrogen bonding produces an enhanced bathochromic effect for the HBD relative to the nonprotic substrate. Also as before, magnitudes of the vertical displacements from the regression line, represented by the $-\Delta\Delta\nu(\mathbf{3}-\mathbf{4})^{\mathrm{B}}{}_{\leftarrow\mathrm{HO}}$ values in Table I,[8,9] increase with in-

Table I. Spectral Data (in kK) for 4-Nitroaniline (1), *N*,*N*-Diethyl-4-nitroaniline (2), 4-Nitrophenol (3), and 4-Nitroanisole (4)

Solvent	$\nu(2)_{max}$	$\nu(1)_{max}$		$-\Delta\Delta\nu$-$(1-2)^{B}_{\leftarrow H_2N}$	$\nu(4)_{max}$	$\nu(3)_{max}$		$-\Delta\Delta\nu$-$(3-4)^{B}_{\leftarrow HO}$
		Obsd	Eq 1			Obsd	Eq 3	
Nonhydrogen-bonding								
1. Hexane, heptane	27.71	31.30			34.31	35.08		
2. Cyclohexane	27.40	31.01			34.13	34.97		
6. CCl_4	26.70	30.30			33.56	34.42		
8. Toluene	25.87	29.41						
10. $Cl_2C{=}CHCl$	25.76	29.63						
14. Benzene	25.60	29.07			32.84	33.73		
15. Chlorobenzene	25.38	28.82						
20. $ClCH_2CH_2Cl$	25.06	28.37			32.36	33.27		
21. CH_2Cl_2	24.96	28.65			32.25	33.33		
Hydrogen-bond acceptors								
17. Anisole	25.31	28.17	28.83	0.67	32.41	32.73	33.36	0.63
39. Ethyl chloroacetate	25.28	27.89	28.80	0.91	32.57	32.68	33.50	0.82
9. Dioxane	25.77	28.25	29.31	1.06	32.89	32.89	33.79	0.90
46. Dibenzyl ether	25.09	27.47	28.61	1.14				
47. Ethyl benzoate	25.31	27.66	28.84	1.22				
7. Ethyl ether	26.52	28.65	30.09	1.44	33.45	33.11	34.30	1.19
5. Butyl ether	26.85	29.03	30.43	1.40	33.56	33.17	34.40	1.23
11. Ethyl acetate	25.74	27.93	29.28	1.35	32.79	32.57	33.70	1.13
18. Acetone	25.22	27.32	28.74	1.42				
16. 2-Butanone	25.28	27.38	28.80	1.44				
40. Tetrahydropyran	25.74	27.82	29.28	1.46				
13. Tetrahydrofuran	25.61	27.59	29.14	1.55	32.79	32.47	33.70	1.23
27. Butyrolactone	24.60	26.81	28.10	1.29	31.95	31.85	32.94	1.09
48. Tri-*n*-butylamine	27.14	28.86	30.72	1.87				
49. Dimethylbenzylamine	26.04	27.93	29.59	1.66				
24. Pyridine	24.78	26.42	28.29	1.87	32.00	31.44	32.97	1.55
3. Triethylamine	27.14	28.77	30.73	1.96				
25. Dimethylformamide	24.66	26.18	28.16	1.98	32.05	31.35	33.03	1.68
29. Dimethyl sulfoxide	24.30	25.71	27.79	2.08	31.70	31.06	32.72	1.66
19. Triethyl phosphate	25.19	26.49	28.71	2.22	32.41	31.70	33.36	1.66
26. Hexamethylphosphoramide	24.75	25.45	28.25	2.80	31.90	30.67	32.90	2.23
23. Dimethylacetamide	24.75	26.21	28.26	2.05	32.05	31.30	33.03	1.73
28. *N*-Methylpyrrolidone	24.60	26.01	28.10	2.09	31.90	31.25	32.90	1.65
50. Trichloroacetone	25.31	28.45	28.83	0.38				
51. Cyclopentanone	25.09	27.10	28.61	1.51				
Amphiprotic solvents								
101. *tert*-Butyl alcohol	25.61	26.49	29.15	2.66	32.94	31.74	33.84	2.10
102. Isopropyl alcohol	25.51	26.46	29.04	2.58	32.94	32.00	33.84	1.84
103. *n*-Butyl alcohol	25.51	26.67	29.04	2.37	32.89	31.95	33.79	1.84
104. Ethanol	25.48	26.85	29.01	2.16	32.89	32.10	33.79	1.69
105. Methanol	25.16	26.95	28.68	1.73	32.79	32.10	33.70	1.60
106. Phenylethanol	24.94	26.67	28.45	1.78	32.15	31.50	33.12	1.62
107. Ethylene glycol	24.10	26.14	27.58	1.44	31.95	31.55	32.94	1.39
109. Benzyl alcohol	24.33	26.25	27.82	1.57				
110. Chloroethanol	24.15	26.77	27.63	0.87	31.87	31.60	32.87	1.23
111. Water	23.23	26.28	26.68	0.40	31.55	31.50	32.58	1.08

creasing HBA ability of the solvents [and range from 10.5 SD's of eq 3 for anisole (solvent **17**) to 37.2 SD's for hexamethylphosphoramide (**26**)].[11]

The next step is to compare magnitudes of the enhanced bathochromic displacements attributable to hydrogen bonding by 4-nitroaniline (**1**) and by 4-nitrophenol (**3**) to the same acceptors, i.e., plot $-\Delta\Delta\nu(\mathbf{1\text{-}2})^{B}{}_{\leftarrow H_2N}$ against corresponding $-\Delta\Delta\nu(\mathbf{3\text{-}4})^{B}{}_{\leftarrow HO}$ values. Such a plot, involving 15 HBA solvents is shown in Figure 3. For reasons which will be discussed later, the $-\Delta\Delta\nu$ results for the amphiprotic solvents must be treated separately.

The excellent linear correlation shown in the plot in Figure 3 lends confidence that the $-\Delta\Delta\nu$ values being compared do indeed reflect real and intrinsic properties of the solvents. The least-squares regression equation (solid line) is

$$-\Delta\Delta\nu(\mathbf{3\text{-}4})^{B}{}_{\leftarrow HO} = 0.740[-\Delta\Delta\nu(\mathbf{1\text{-}2})^{B}{}_{\leftarrow H_2N}] + 0.14 \text{ kK} \qquad (4)$$

with $n = 15$, $r = 0.993$, and SD = 0.05 kK. Considering that the two sets of $-\Delta\Delta\nu$'s represent *differences* between experimental results and values calculated from eq 1 and 3, it deserves particular comment that the standard deviation of eq 4 is lower than the SD of either of the antecedent equations, and no greater than the probable experimental errors in the measurements.

The relatively small value of the intercept in eq 4 (0.14 kK, compared with 0.16 kK SD of eq 1) is also important in that it suggests the likelihood that the quantities being compared are directly proportional to one another. Such would be required if the $-\Delta\Delta\nu$ values were independently proportional to the same intrinsic properties of the solvents, as is the basic tenet leading to our use of solvatochromic comparison data to construct the β-scale of solvent HBA basicities. Imposing direct proportionality on the correlation in a regression line force-fitted through the origin (dashed line in Figure 3) gives

$$-\Delta\Delta\nu(\mathbf{3\text{-}4})^{B}{}_{\leftarrow HO} = 0.825[-\Delta\Delta\nu(\mathbf{1\text{-}2})^{B}{}_{\leftarrow H_2N}] \pm 0.05 \text{ kK} \qquad (5)$$

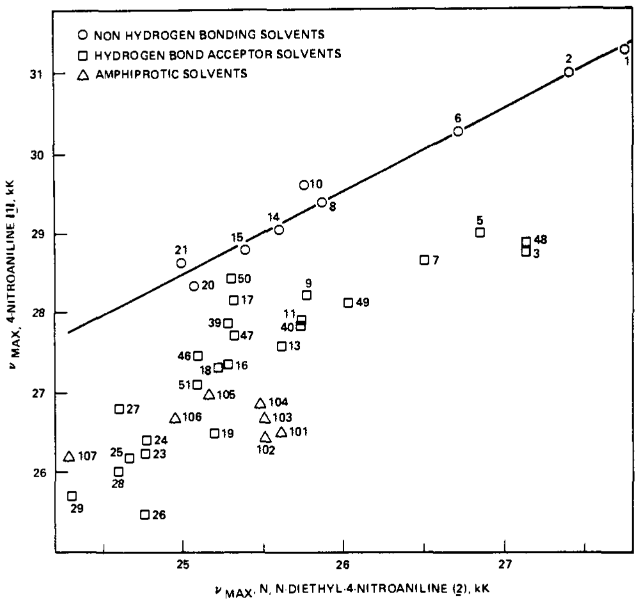


Figure 1. Solvatochromic comparison of 4-nitroaniline (1) and *N,N*-diethyl-4-nitroaniline (2) uv spectral data.

Relationship between $-\Delta\Delta\nu$ and pK_{HB} Values. The correlation described above suggested to us that magnitudes of enhanced solvatochromic shifts resulting from hydrogen bonding by HBD substrates to HBA solvents depend on some intrinsic measure of ability of these solvents to act as hydrogen-bond bases. Fortunately, independently derived information was available to test this possibility.

Using 0.01 *M* *p*-fluoroanisole as an internal reference standard in CCl_4, Gurka and Taft[12] have quantitatively evaluated the shielding effects of hydrogen bonded complex formation by 0.01 *M* *p*-fluorophenol. They determined formation constants, K_f, and limiting ^{19}F NMR shifts, Δ, for the 1:1 hydrogen-bonded complexes of this reference acid with a large number of bases of widely differing structures in CCl_4 at 25°C. Logarithms of these formation constants served as the basis for a pK_{HB} scale of HBA basicity.[7]

Linear free energy relationships with the pK_{HB} scale have been demonstrated for formation constants and other properties of additional OH and NH reference acids and have included HBA's of many and varying types.[7,13] Most importantly also, it has been abundantly documented that these hydrogen-bonding phenomena involving partial proton transfer (estimated at ca. 10–30%) had little or nothing in common with pK_a's (proton transfer measures) when acceptors with different functional groups were compared.[7,13]

Figure 4 shows how the enhanced bathochromic shifts for 4-nitroaniline relative to *N,N*-diethyl-4-nitroaniline in 24 HBA solvents relate to Taft and co-workers' measure of hydrogen-bond basicity of those solvents. It is seen that correlation between the $-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{2})^{B}{}_{\leftarrow H_2N}$ and pK_{HB} values is quite good. The linear regression equation is

$$pK_{HB} = 1.571[-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{2})^{B}{}_{\leftarrow H_2N}] - 1.00 \qquad (6)$$

with $r = 0.979$ and SD = 0.18 log units.

Correlation is, of course, comparable in a plot of 4-nitrophenol $-\Delta\Delta\nu$'s against corresponding pK_{HB}'s (Figure 4, data in Tables I and III). The regression equation is

$$pK_{HB} = 2.179[-\Delta\Delta\nu(\mathbf{3}\text{-}\mathbf{4})^{B}{}_{\leftarrow HO}] - 1.32 \qquad (7)$$

with $n = 15$, $r = 0.972$, and SD = 0.23 log units.

Effectively, eq 6 and 7 (and the $-\Delta\Delta\nu$ vs. ^{19}F NMR Δ correlations which will be discussed next) serve as further confirmation that LFER concepts are applicable to the wide range of phenomena and properties which derive from relatively weak molecular complexation interactions. Here, uv spectral displacements resulting from hydrogen bonding by two HBD indicator substrates to a wide variety of HBA molecules are linear with NMR spectral shifts and with free energies of formation of hydrogen-bonded complexes between still a third HBD substrate and the same HBA molecules. Further, the solvatochromic effects involve the acceptors as pure solvents, while the NMR results and equilibri-

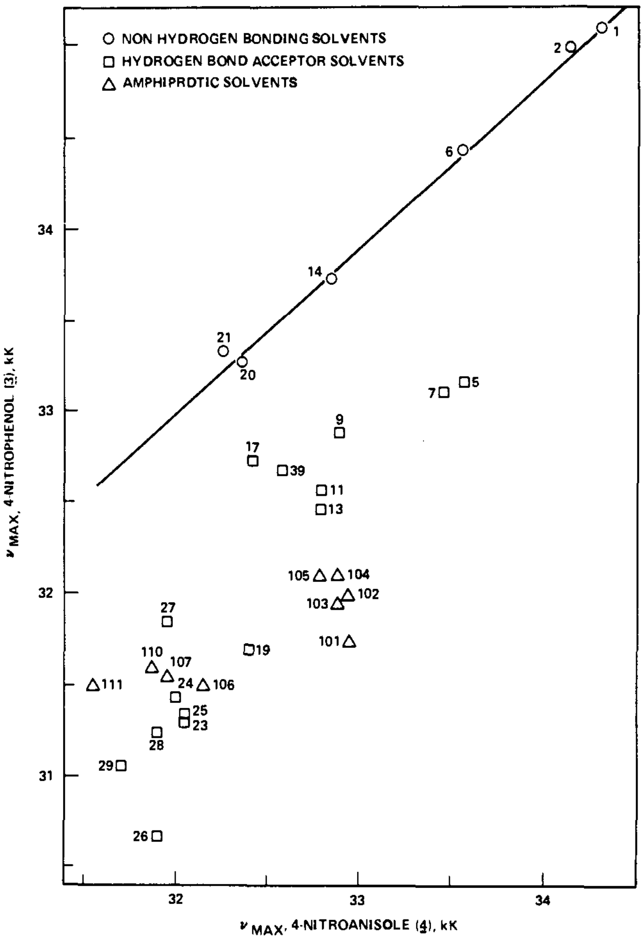


Figure 2. Solvatochromic comparison of 4-nitrophenol (3) and 4-nitroanisole (4) uv spectral data.

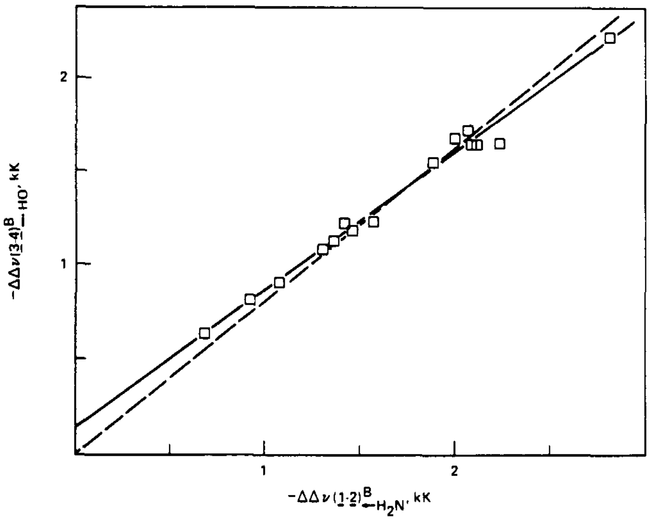


Figure 3. Enhanced bathochromic shifts for 4-nitroaniline (1) in HBA solvents plotted against enhanced bathochromic shifts for 4-nitrophenol (3).

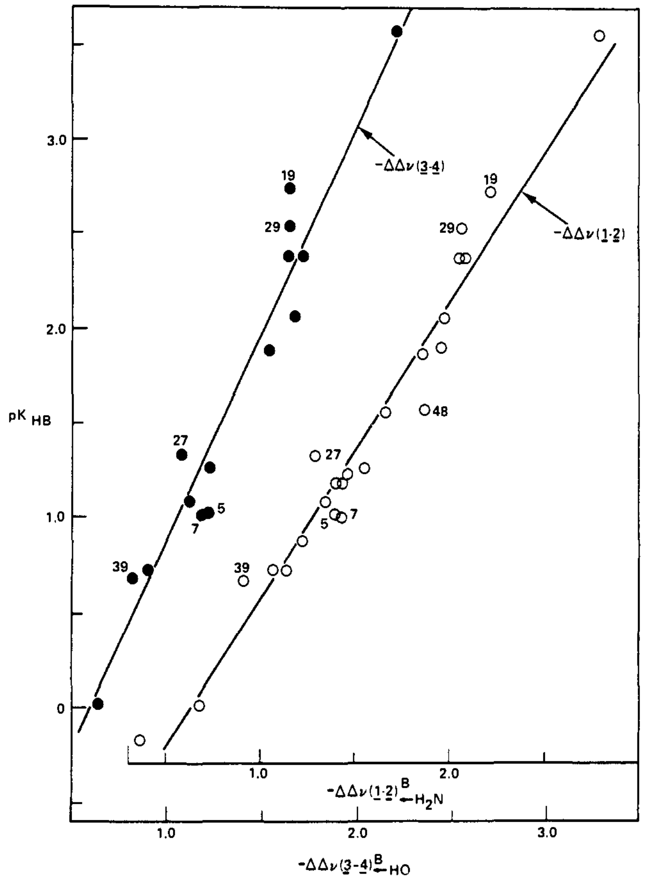


Figure 4. pK_{HB} values for HBA bases plotted against enhanced bathochromic shifts for 4-nitroaniline (1) and 4-nitrophenol (3).

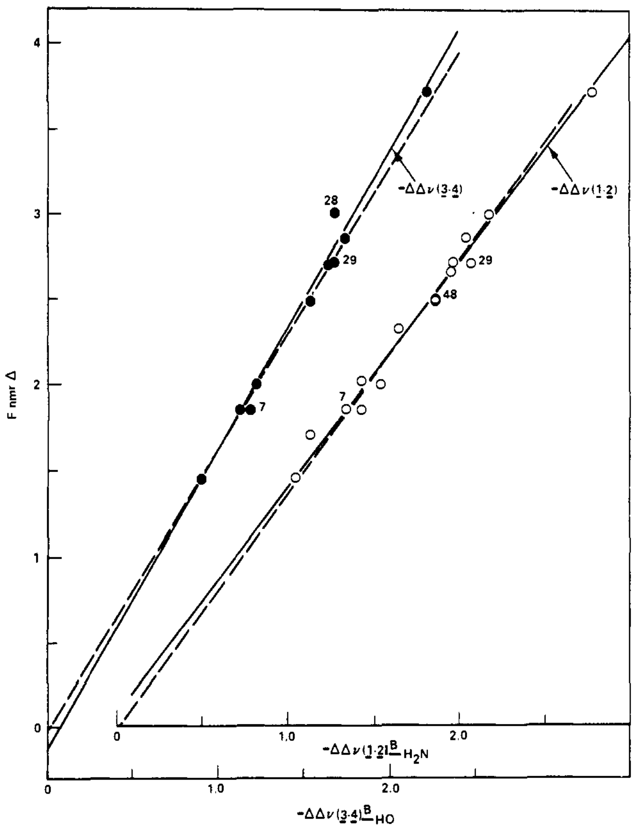


Figure 5. Limiting F NMR shifts for hydrogen bonded complexes of 4-fluorophenol with HBA bases plotted against enhanced bathochromic shifts for 4-nitroaniline (1) and 4-nitrophenol (3).

um constants are determined in dilute solutions in CCl_4 (which accords well with the striking finding by Arnett et al. that enthalpies of hydrogen-bonded complex formation are very nearly the same in dilute CCl_4 solutions as in the pure bases).[14]

Relationship between $-\Delta\Delta\nu$ and ^{19}F NMR Δ Values. Equations 6 and 7 indicate that the $-\Delta\Delta\nu$ values fall to zero as pK_{HB} goes to −1.00 in the case of 4-nitroaniline, −1.32 in the 4-nitrophenol case (the difference in intercepts is comfortably within the combined precision limits of the equations). These intercepts are of interest in that they accord with an important earlier finding, and one may see a pattern beginning to emerge. In a LFE relationship between the 4-fluorophenol ^{19}F NMR Δ terms and pK_{HB}'s reported by Gurka and Taft,[12] Δ went to zero as pK_{HB} went to ca. −1.25. The almost equal intercepts for the two $-\Delta\Delta\nu$'s and the ^{19}F NMR Δ terms in their plots against pK_{HB} indicate that the proportionality between the $-\Delta\Delta\nu$ terms extends also to the ^{19}F NMR Δ terms. The finding that independently determined properties with different indicator acids vary proportionally with one another and go to zero as the equilibrium constant for hydrogen-bonded complex formation with 4-fluorophenol goes to $0.5-1.0 \times 10^{-1}$ is most important. It allows us to construct a β-scale based on averaged proportionality constants relative to some standard HBA as determined through the various correlation equations.

The relationship between the ^{19}F NMR Δ values and the $-\Delta\Delta\nu$'s is shown in Figure 5. The least-squares correlation equations are

$$\Delta = 1.307[-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})^{B}{}_{\leftarrow H_2N}] + 0.09 \text{ ppm} \qquad (8)$$

with $n = 15$, $r = 0.989$, and SD = 0.09 ppm, and

$$\Delta = 1.737[-\Delta\Delta\nu(\mathbf{3}-\mathbf{4})^{B}{}_{\leftarrow HO}] - 0.13 \text{ ppm} \qquad (9)$$

with $n = 10$, $r = 0.989$, and SD = 0.11 ppm.

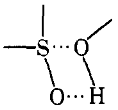
The relatively low values of the intercepts in eq 8 and 9 again lend confidence that we do the data no injustice in force-fitting the plots in Figure 5 through the origins (dashed lines). Hence, to reflect direct proportionality, the correlation equations become:

$$\Delta = 1.365[-\Delta\Delta\nu(\mathbf{1}-\mathbf{2})^{B}{}_{\leftarrow H_2N}] \pm 0.07 \text{ ppm} \qquad (10)$$

and

$$\Delta = 1.642[-\Delta\Delta\nu(\mathbf{3}-\mathbf{4})^{B}{}_{\leftarrow HO}] \pm 0.06 \text{ ppm} \qquad (11)$$

The significantly higher r values for eq 8 and 9 compared with those for eq 6 and 7 are of interest in the light of some earlier observations by Gurka and Taft.[12] In their correlation of limiting ^{19}F NMR shifts with pK_{HB}'s, these workers found that deviations for bases of large steric requirements were all in the direction which indicated that the ^{19}F NMR shift has a smaller dependence on steric requirements than does the standard free energy of complex formation. They also found a smaller than expected Δ value for Me_2SO (possibly reflecting some



interaction in the complex). The same tendencies can be seen in the $-\Delta\Delta\nu$ vs. pK_{HB} plots in Figure 4, i.e., $-\Delta\Delta\nu$ values smaller than predicted for Me_2SO (solvent **29**) and larger than predicted for tri-*n*-butylamine (**48**), dibutyl ether (**5**), and diethyl ether (**7**). In the $-\Delta\Delta\nu$ vs. ^{19}F NMR

Δ plots in Figure 5, however, these points fall directly on the regression line, indicating that steric effects and other secondary interaction phenomena have correspondingly small influences on the solvatochromic and NMR results.

Another comparison involving the ^{19}F NMR Δ and $-\Delta\Delta\nu$ results is worth mentioning. By comparing the Δ value for complete ionization of 4-fluorophenol in Me_2SO with the limiting ^{19}F NMR values for hydrogen-bonded complex formation, Taft and co-workers[15] have estimated that the latter process involves a 10–25% extent of proton transfer. The $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})^{B}{}_{\leftarrow HO}$ values in Table I, compared with a value of 7.7 kK for "complete" ionization [a 6.62 kK difference in $\nu_{max}(H_2O)$ between 4-nitrophenoxide and 4-nitrophenol added to the 1.08 kK $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})$ value for water (Table I)], lead to similar estimates for extents of proton transfer in hydrogen-bonded complexes with **3**.

Comparison of $-\Delta\Delta\nu$ Values with Phenol Association Constants. Another test of the precision of the solvatochromic comparison method is available in a series of papers by Gramstad and co-workers,[16] wherein accurate association constants in CCl_4 are reported for hydrogen-bonded complexes of phenol. Taft and co-workers[7] have already commented on the excellent correlation between pK_{HB} and phenol log $K_{assn}(20°)$; indeed, Gramstad's results were cited as the basis for a number of secondary pK_{HB} values. Hence, good correlation between the $-\Delta\Delta\nu$'s and the log $K_{assn}(20°)$ values comes as no surprise. However, since assembling the β-scale will involve an averaging process, as will be discussed next, and since the phenol association constants were determined by independent investigators and by a different experimental method (spectroscopic measurements in the near-ir), it is appropriate to include the correlation here.

The phenol log $K_{assn}(20°)$ values are plotted against corresponding $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})^{B}{}_{\leftarrow H_2N}$ results in Figure 6 (data in Tables I and III). The same tendencies for individual solvents can be seen as in Figure 4, e.g., the data points for solvents **19**, **27**, **29**, and **39** displaced toward lower $-\Delta\Delta\nu$ values than called for by the correlation equation, and sterically hindered solvents **5** and **7** tending toward higher $-\Delta\Delta\nu$ values. The regression equation is

$$\log K_{assn}(20°) = 1.54[-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})^{B}{}_{\leftarrow H_2N}] - 1.05 \quad (12)$$

with $n = 18$, $r = 0.982$, and SD = 0.16 log unit. The roughly equal slopes and intercepts in eq 6 and 12 suggest a relatively low ρ value for the HBD acidities of substituted phenols.

The β-Scale of Hydrogen-Bond Basicities. In subsequent papers, the β-scale of solvent HBA basicities, together with an α-scale of HBD acidities, will be shown to be 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 β-scale, some definitions and a fixed point of reference are in order. We take the $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ value of 2.80 kK for hexamethylphosphoramide (solvent **26**) as the single fixed reference point and set the β-value corresponding to this datum as equal to unity by definition; i.e., $\beta_1(\mathbf{26}) = 1.000$. In the term $\beta_1(\mathbf{26})$, the number in parentheses indicates that we are dealing with solvent **26** (solvents numbered in Tables I and III), and the subscript indicates that we are dealing with property or reaction series 1 (see below). The β term represents the proportional *experimental* value for that property (XYZ) in that solvent relative to the *calculated* value for XYZ in hexamethylphosphoramide, where the calculated value is determined through the equation correlating XYZ with $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$. If the correlation equation (in series 4, for example) involves direct proportionality, i.e., XYZ = $A[-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})]$, then the β-value for solvent **23** is given by $\beta_4(\mathbf{23}) = \text{XYZ}(\mathbf{23})/2.80(A)$. If the correlation equation involves linearity, but not direct proportionality, i.e., XYZ = $A[-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})] + B$, the β value is given by $\beta_4(\mathbf{23}) = (\text{XYZ}(\mathbf{23}) - B)/2.80(A)$. Finally, the term $\beta_{1\text{–}5}(\mathbf{23})$ represents the average of the β values for solvent **23** in series 1 through 5.

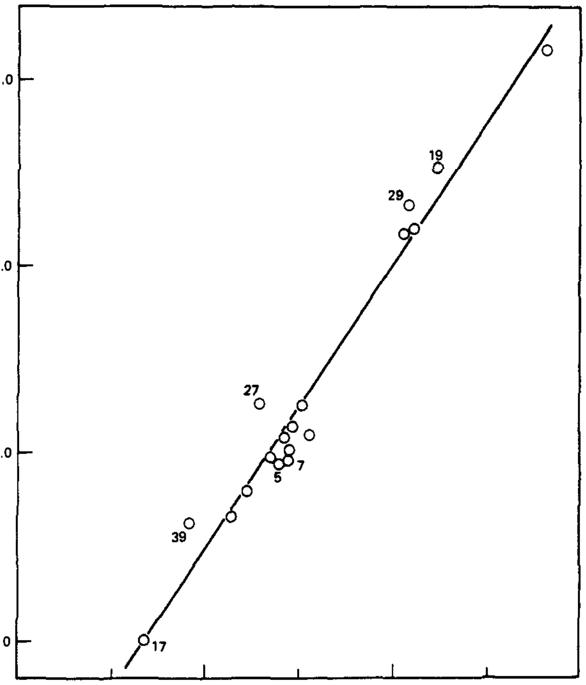
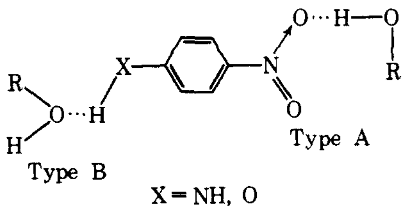


Figure 6. Log formation constants for hydrogen bonded complexes of phenol with HBA bases plotted against enhanced bathochromic shifts for 4-nitroaniline (**1**).

The properties discussed thus far provide the information for five series of β values as shown in Table II. The individual β values and the data used in their calculation are assembled in Table III, together with the average $\beta_{1\text{–}5}$ results. The table includes results for some solvents for which solvatochromic data were not available and where $\beta_{1\text{–}5}$ values were determined from literature data in combination with eq 15–17.

Solvatochromic Effects in Amphiprotic Solvents. The results in the amphiprotic alcohol solvents require separate treatment in the $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ vs. $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})$ comparison. This is because multiple effects may result from simultaneous type-B bonding by nitrophenol or nitroaniline hydrogens to solvent oxygens and type-A bonding by solvent hydrogens to substrate nitro oxygens. Both types of hydrogen bonds lead to lowered $[X^{+}{=}C(1) \rightarrow C(4){=}NO_2^{-}]$ electronic transition energies.



That effects of type-A hydrogen bonding by alcohol solvents to nitro oxygens are spectroscopically discernible has been shown in a solvatochromic comparison of *N*,*N*-diethyl-4-nitroaniline with 4-nitroanisole.[6] There is no ques-

Table II

Property	Correlation eq	Eq for β	
Series 1.			
Enhanced solvatochromic shift for 4-nitroaniline relative to *N,N*-diethyl-4-nitroaniline	1	$\beta_1 = \dfrac{-\Delta\Delta\nu(1\text{–}2)}{2.80}$	(13)
Series 2.			
Enhanced solvatochromic shift for 4-nitrophenol relative to 4-nitroanisole	5	$\beta_2 = \dfrac{-\Delta\Delta\nu(3\text{–}4)}{(2.80)(0.825)}$	(14)
Series 3.			
Log formation constant for hydrogen-bonded complex with 4-fluorophenol	6	$\beta_3 = \dfrac{\text{p}K_{\text{HB}} + 1.00}{(2.80)(1.571)}$	(15)
Series 4.			
Limiting ^{19}F NMR shift, Δ, for hydrogen-bonded complex with 4-fluorophenol	10	$\beta_4 = \dfrac{^{19}\text{F NMR}\Delta}{(2.80)(1.365)}$	(16)
Series 5.			
Log formation constant for hydrogen-bonded complex with phenol	12	$\beta_5 = \dfrac{\log K + 1.05}{(2.80)(1.54)}$	(17)

tion, however, as to which is the dominant solvatochromic effect in the present instances. Values of $-\Delta\Delta\nu$ in Table I, increasing in the order: methanol (solvent **105**) < ethanol (**104**) < *n*-butyl alcohol (**103**) < isopropyl alcohol (**102**) < *tert*-butyl alcohol (**101**), are characteristic of type-B hydrogen-bonding effects wherein the alcohols serve as HBA bases. Where type-A effects, involving the alcohols as hydrogen-bond donors, dominate, the order of enhanced bathochromic displacements is almost invariably **101** < **102** < **103** < **104** < **105** (as will be shown in subsequent papers).

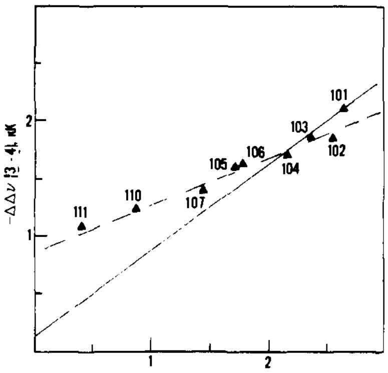


Figure 7. Enhanced bathochromic shifts for 4-nitroaniline (1) in amphiprotic solvents plotted against enhanced bathochromic shifts for 4-nitrophenol (3).

Values of $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})$ are plotted against $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ results in corresponding amphiprotic solvents in Figure 7. It is seen that these data, taken alone, show good linear regression, but that the least-squares correlation equation (represented by the dashed line in Figure 7) differs significantly from the correlation equation for the nonprotic HBA solvents (solid line, eq 4). The regression equation in this instance is

$$-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4}) = 0.406[-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})] + 0.88\ \text{kK} \quad (18)$$

with $n = 9$, $r = 0.976$, and SD = 0.07 kK. The differences between eq 4 and 18 are well beyond experimental or statistical error.

The differences between eq 4 and 18 probably arise from either or both of two possibilities wherein hydrogen bonding to and by the amphiprotic solvents occurs at more than one site: (a) as a consequence of stronger type-A hydrogen bonding by the HBD solvents to nitro oxygens of **2** relative to **1**, the bathochromic shift of $\nu_{\max}$ for **1** relative to **2** is

Table III. The β-Scale of Solvent HBA Basicities

Solvent	Series 1	Series 2	Series 3		Series 4		Series 5			
	β_1	β_2	pK_{HB}	β_3	Δ, ppm	β_4	log *K*	β_5	β_{1-5}	(*n*)
17. Anisole	0.239	0.272	0.02	0.233			0.004	0.244	0.247 ± 0.013	(4)
54. Diethyl sulfide			0.11	0.252	1.10	0.288			0.270 ± 0.018	(2)
39. Ethyl chloroacetate	0.325	0.354	0.69	0.384			0.635	0.390	0.363 ± 0.024	(4)
9. Dioxane	0.379	0.390	0.73	0.393	1.45	0.380			0.386 ± 0.006	(4)
31. Nitrobenzene			0.73	0.393					0.393	(1)
37. Benzonitrile			0.79	0.406	1.71	0.477	0.568	0.375	0.409 ± 0.025	(3)
46. Dibenzyl ether	0.407		0.72	0.391	1.70	0.445	0.664	0.397	0.410 ± 0.018	(4)
47. Ethyl benzoate	0.436		0.88	0.427			0.810	0.430	0.431 ± 0.004	(3)
52. Methyl acetate			1.00	0.454			0.925	0.458	0.456 ± 0.002	(2)
11. Ethyl acetate	0.482	0.489	1.09	0.475	1.85	0.484	0.992	0.473	0.481 ± 0.005	(5)
7. Diethyl ether	0.514	0.515	1.01	0.456	1.85	0.484	0.983	0.470	0.488 ± 0.021	(5)
5. Di-*n*-butyl ether	0.500	0.532	1.02	0.459			0.974	0.468	0.490 ± 0.026	(4)
27. Butyrolactone	0.461	0.471	1.33	0.530			1.228	0.527	0.497 ± 0.031	(4)
18. Acetone	0.507		1.18	0.495			1.090	0.495	0.499 ± 0.005	(3)
16. 2-Butanone	0.514		1.19	0.498	2.02	0.528	1.013	0.477	0.504 ± 0.017	(4)
40. Tetrahydropyran	0.521		1.23	0.507			1.140	0.507	0.512 ± 0.006	(3)
13. Tetrahydrofuran	0.553	0.523	1.26	0.514	2.00	0.524	1.110	0.500	0.523 ± 0.013	(5)
41. Cyclohexanone			1.30	0.522	2.12	0.554	1.226	0.527	0.534 ± 0.013	(3)
51. Cyclopentanone	0.539						1.258	0.534	0.537 ± 0.002	(2)
49. Dimethylbenzylamine	0.593		1.56	0.582	2.33	0.610			0.595 ± 0.010	(3)
48. Tri-*n*-butylamine	0.668		1.57	0.584	2.50	0.654			0.635 ± 0.034	(3)
24. Pyridine	0.668	0.670	1.88	0.655	2.49	0.652			0.661 ± 0.008	(4)
3. Triethylamine	0.700		1.91	0.661	2.66	0.696			0.686 ± 0.016	(3)
25. Dimethylformamide	0.707	0.727	2.06	0.695	2.72	0.712			0.710 ± 0.009	(4)
23. Dimethylacetamide	0.732	0.748	2.38	0.768	2.86	0.749	2.182	0.748	0.749 ± 0.008	(5)
28. *N*-Methylpyrrolidone	0.746	0.714	2.38	0.768	3.00	0.785	2.212	0.756	0.754 ± 0.019	(5)
29. Dimethyl sulfoxide	0.743	0.718	2.53	0.802	2.71	0.790	2.362	0.790	0.752 ± 0.035	(5)
19. Triethyl phosphate	0.792	0.718	2.73	0.847			2.545	0.832	0.797 ± 0.042	(4)
26. Hexamethylphosphoramide	1.000	0.965	3.56	1.036	3.71	0.971	3.176	0.979	0.990 ± 0.024	(5)

Table IV. HBA Basicities (β Values) of R–OH Solvents

Solvent	β_1	$(\beta_2)^a$
101. *tert*-Butyl alcohol	0.95	(0.91)
102. Isopropyl alcohol	0.92	(0.80)
103. *n*-Butyl alcohol	0.85	(0.80)
104. Ethanol	0.77	(0.73)
105. Methanol	0.62	(0.70)
106. Phenylethanol	0.64	
107. Ethylene glycol	0.51	(0.60)
109. Benzyl alcohol	0.56	
110. Chloroethanol	0.31	(0.53)
111. Water	0.14	(0.47)

[a] Values in parentheses are alternative set determined from $-\Delta\Delta\nu(3-4)$ results and eq 14.

smaller than would be called for if the solvents had acted only as HBA bases; or (b) type-A bonding by HBD solvents to nitro is stronger with **3** than with **4**, leading to a greater bathochromic displacement (larger $-\Delta\Delta\nu$) than would arise from a pure type-B effect. In our new notational system,[8] these possibilities are represented by:

$$\text{(a)}\ -\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})_{\text{total}} = [-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})^{\text{B}}{}_{\leftarrow \text{H}_2\text{N}}] - [-\Delta\Delta\nu(\mathbf{2}\text{–}\mathbf{1})^{\text{A}}{}_{\rightarrow \text{O}_2\text{N}}] \quad (19)$$

and

$$\text{(b)}\ -\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})_{\text{total}} = [-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})^{\text{B}}{}_{\leftarrow \text{HO}}] + [-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})^{\text{A}}{}_{\rightarrow \text{O}_2\text{N}}] \quad (20)$$

We prefer possibility b on the basis that independent evidence (to be discussed in a subsequent paper) indicates that type-A hydrogen bonding to the nitro of 4-nitroanisole is so weak as to be spectroscopically not discernible.[17] Also, we would expect that a through-conjugated molecule like 4-nitrophenol (or 4-nitroaniline), acting at one resonance terminus as a HBD acid, would have increased ground-state electron density at the other resonance terminus and, hence, become a stronger HBA base than its *O*-alkyl (or *N,N*-dialkyl) derivative. On this assumption, which will be tested in subsequent papers, the preferred set of β values for the alcohols (assembled in Table IV) was determined from the $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ results and eq 13. An alternative set, determined from the $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})$ results and eq 14, is given in parentheses.

The absolute magnitudes of the $-\Delta\Delta\nu$'s in the alcohol solvents were initially somewhat surprising to us in that, by the criteria discussed in this paper, *tert*-butyl alcohol, isopropyl alcohol, and *n*-butyl alcohol appeared to be stronger HBA's than pyridine, triethylamine, or the alkyl ethers (Table III). It should be recalled, however, that in the neat solvents we are dealing with alcohol polymers and that, in common with water, as recently demonstrated by Gordon,[18] self-associated alcohols[19] are probably significantly more basic than alcohol monomers. In a future paper, we shall show that dilution effects on hydrogen bonded complexes between HBD's and self-associated HBA solvents differ markedly from dilution effects on complexes involving non-self-associated HBA's, and that alcohol monomer HBA basicities are of the same order as that for ethers and esters.

Conclusion

In future papers we shall expand the data base for the β-scale by relating $\beta_{1\text{-}5}$ values to additional $\Delta\Delta\nu$ results, equilibrium constants for hydrogen-bonded complex formation, proton and ^{19}F NMR shifts, and HBA "catalytic" rate constants for a variety of reactions. One result, which we will later discuss in detail, deserves preliminary mention at this time.

We have found that K_f values reported by Gilkerson and Aitkin[20] for hydrogen-bonded complexes of a variety of HBA's with tri-*n*-butylammonium ion show good correlation with our $\beta_{1\text{-}5}$ values. The correlation equation is

$$\log K_f = 9.79\beta_{1\text{-}5} - 3.14 \quad (21)$$

with $n = 9$, $r = 0.973$, and SD = 0.43 log unit. This appears to confirm that hydrogen-bonding effects by neutral and charged proton donors follow similar patterns. Also, as might be expected, the slope of the correlation equation with Bu_3NH^+ as the hydrogen-bond donor is very much greater (about sixfold) than that with phenol or 4-fluorophenol (slopes ca. 1.5).

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References and Notes

(1) Preliminary communication: M. J. Kamlet, R. R. Minesinger, and W. H. Gilligan, *J. Am. Chem. Soc.*, **94**, 4744 (1972).

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

(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.[4] In the present paper, HBD (hydrogen-bond donor) and HBA (hydrogen-bond acceptor) refer to donation and acceptance of the proton.

(4) Gutmann, for example, uses the term *donicity* as a measure of ability to donate the electron pair: V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, New York, N.Y., 1968, Chapter 2.

(5) M. J. Kamlet, E. G. Kayser, R. R. Minesinger, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36**, 3852 (1971).

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

(8) Earlier nomenclature becomes confusing and cumbersome when several types of hydrogen bonding with concomitant spectral effects occur simultaneously. For this reason, we recently introduced a new nomenclature system[6] as follows: $\Delta\Delta\nu$ denotes a hypsochromic effect or a reduced bathochromic shift; $-\Delta\Delta\nu$ denotes an enhanced bathochromic shift or effect; the numbers in parentheses (**1**–**2**) indicate that the reduced or enhanced effect is for compound **1** relative to compound **2**; the superscript B indicates that the effect is attributed to type-B hydrogen bonding;[5] and the subscript $\leftarrow H_2N$ indicates that bonding is by amine protons to solvent. Alternative subscripts in this nomenclature system are $\rightarrow O_2N$, indicating bonding by solvent to nitro oxygen, and $\rightarrow NR_2$, indicating bonding by solvent to amine nitrogen.

(9) In the preliminary communication[1] and other earlier studies,[10] we determined shifts ($-\Delta\nu$ values) from cyclohexane to each solvent for **1**, **2**, **3**, and **4**. The $-\Delta\Delta\nu$ values were simply the differences ($[-\Delta\nu(\mathbf{1})] - [-\Delta\nu(\mathbf{2})]$ and $[-\Delta\nu(\mathbf{3})] - [-\Delta\nu(\mathbf{4})]$). The earlier method was satisfactory where solvent polarity effects were comparable for the substrates being compared but breaks down where the slopes in the regression equations for the nonhydrogen-bonding solvents differ significantly from unity.

(10) R. R. Minesinger, E. G. Kayser, and M. J. Kamlet, *J. Org. Chem.*, **36**, 1342 (1971).

(11) 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.

(12) D. Gurka and R. W. Taft, *J. Am. Chem. Soc.*, **91**, 4794 (1969).

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(17) The 4-nitroanisole uv spectrum was taken as the reference property in many of the solvatochromic comparisons which we will report later because, of over 50 spectra considered, it appeared to be least influenced by hydrogen bonding effects while still showing a reasonable response to changing solvent polarity.

(18) J. E. Gordon, *J. Am. Chem. Soc.*, **94**, 650 (1972).

(19) C. Dubuq, *Spectrochim. Acta*, **30**, 431 (1974).

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