The Solvatochromic Comparison Method. 5. Spectral Effects and Relative Strengths of the First and Second Hydrogen Bonds by 4-Nitroaniline to Hydrogen Bond Acceptor Solvents[1]

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The enhanced bathochromic shifts attributable to type B hydrogen bonding by 4-nitroaniline (**1**) to HBA (hydrogen bond acceptor) solvents are more than twice as large as comparable solvatochromic displacements for *N*-methyl-, *N*-ethyl-, and *N*-isopropyl-4-nitroaniline (**2a–c**). Solvatochromic dilution experiments show the VF_{50} values in Me_2SO/CCl_4 (volume fractions of HBA solvent at which the hydrogen bonded complex is half dissociated) to be 0.0057 for **2b** and 0.0063 for **1**. It is concluded that the ratio of the spectral effects of the first and second hydrogen bonds of **1** is 1/(0.93 ± 0.13), whereas hydrogen bond strengths are in a ratio of about 1.5:1.

In part 1 of this series,[3] we reported the solvatochromic comparison of UV-visible spectral data for 4-nitroaniline (**1**) with results in corresponding non-hydrogen-bonding, hydrogen bond acceptor, and amphiprotic solvents for *N*,*N*-diethyl-4-nitroaniline (**3**). The work was an extension and refinement of an earlier study,[4] in which spectral data for **1** and its *N*-ethyl and *N*,*N*-diethyl derivatives, in alcohol solvents only, had been correlated through a preliminary, cruder version of the solvatochromic comparison method.[5] In the present paper we extend our investigations to *N*-methyl- (**2a**), *N*-ethyl- (**2b**), and *N*-isopropyl-4-nitroaniline (**2c**), and consider how the enhanced solvatochromic shifts attributable to type B hydrogen bonding[6] by these solutes to HBA (hydrogen bond acceptor) solvents,[7] $-\Delta\Delta\nu(\mathbf{2a,b,c}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN}$,[8] relate to corresponding $-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})^{B}{}_{\leftarrow H_2N}$ displacements determined earlier.[3] We also employ the solvatochromic dilution procedure, described in part 4,[1] to determine relative HBD (hydrogen bond donor)[7] acidities of these indicator solutes.

The purposes of this exercise are to compare the strengths and spectral effects of one hydrogen bond each by the amine protons of **2a–c** to HBA solvents with the strengths and effects of two such hydrogen bonds (presumed) in the case of **1**. The investigation was prompted by findings from the initial study,[4] which appeared to indicate that two type B hydrogen bonds by the amine protons of **1** to alcohol solvents produce more than twice as large an enhanced bathochromic effect as the single type B hydrogen bond formed by **2b**. We considered that this result required corroboration, since a logical (but difficult to accept) corollary seemed to be that the second hydrogen bond by **1** to HBA solvents is as strong as (or stronger than) the first.

In HBD solvents, **3** has been shown to behave as a weak type A hydrogen bond[6] acceptor at the nitro oxygens;[9] **1** and **2a–c** most likely behave similarly, and spectral effects of type A bonding to nitro are assumed to cancel out in the solvatochromic correlation equations.[10] In HBA solvents **1** and **2a–c**, but not **3**, can act as type B hydrogen bond donors at the amine substituents; hence, the differential solvatochromic shifts between **1**, **2a–c**, and **3** are considered to reflect the spectral effects of hydrogen bonding by the amine protons. Since such type B bonding leads to greater stabilization (hydrogen bond strengthening) in electronic excited states relative to ground states of $[RHN^{+}{=}C(1) \rightarrow C(4){=}NO_2^{-}]$ electronic transitions, spectral displacements due to such solvent association are bathochromic, with the effects increasing with increasing β values (indicators of HBA basicity)[3] of the solvents.

In the documentation of solvent hydrogen bonding effects on electronic spectra by the solvatochromic comparison method, the first step involves the determination of relative solvent polarity effects by linear correlation of positions of absorption maxima of the HBD indicator solute (**2a–c** in the present instance) with those of the non-HBD reference solute (**3**) in a series of non-HBA solvents. Spectral data required for these correlations are assembled in Table I, and $\nu(\mathbf{2b})_{max}$ values are plotted against corresponding $\nu(\mathbf{3})_{max}$ values in Figure 1.

It is seen in the plot, and confirmed by least-squares regression analyses, that the linear correlations of the data in the non-HBA solvents (the first nine solvents in Table I) are excellent. The regression equations are

$$\nu(\mathbf{2a})_{max} = 1.1031\ \nu(\mathbf{3})_{max} - 0.943\ \text{kK} \qquad (1a)$$

with *r* (the correlation coefficient) = 0.996 and SD (the standard deviation) = 0.11 kK,

$$\nu(\mathbf{2b})_{max} = 1.0834\ \nu(\mathbf{3})_{max} - 0.589\ \text{kK} \qquad (1b)$$

with *r* = 0.997 and SD = 0.10 kK, and

$$\nu(\mathbf{2c})_{max} = 1.0460\ \nu(\mathbf{3})_{max} + 0.232\ \text{kK} \qquad (1c)$$

with *r* = 0.997 and SD = 0.09 kK. These standard deviation values represent about the best precision which might be expected in the light of the band overlap and band dissymmetry effects which are usually encountered in electronic spectra of this type, coupled with the experimental uncertainties in picking the exact positions of maxima of relatively broad bands.[11]

As the next step in the solvatochromic comparisons, the enhanced bathochromic shifts resulting from type B hydrogen bonding by the HBD solutes are evaluated by substracting observed ν_{max} values for **2a–c** in HBA and amphiprotic solvents from values calculated through eq 1a–c and the corresponding $\nu(\mathbf{3})_{max}$ results.

$$-\Delta\Delta\nu(\mathbf{2a,b,c}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = \nu(\mathbf{2a,b,c})^{calcd}_{eq\ 1a\text{-}c} - \nu(\mathbf{2a,b,c})^{obsd}_{max} \qquad (2)$$

Equation 2 cancels out solvent polarity effects as well as effects deriving from type A bonding[6] by the amphiprotic solvents to nitro oxygens (assumed to be similar for **2a–c** and **3**). Values of $\nu(\mathbf{2a,b,c})^{calcd}_{eq\ 1a\text{-}c}$ and $-\Delta\Delta\nu(\mathbf{2a,b,c}\text{-}\mathbf{3})$, as well as averaged $-\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{3})$ values are included in Table I, together with $-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})^{B}{}_{\leftarrow H_2N}$ terms reported earlier.[3] It is seen that for most solvents considered the $-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})$ terms are more than twice as large as the corresponding $-\Delta\Delta\nu(\mathbf{2}\text{-}\mathbf{3})$ terms. Also, for solvents with major steric requirements about the HBA site (e.g., **46, 48, 49, 101**) there does seem to be steric weakening of the hydrogen bonding effect, particularly in the case of the *N*-isopropyl indicator compound.

To complete these solvatochromic comparisons, it remains to be shown that the enhanced solvatochromic shifts are

Table I. Solvatochromic Comparison of Spectral Data for *N*-Methyl- (2a), *N*-Ethyl- (2b), and *N*-Isopropyl-4-nitroaniline (2c) with Results in Corresponding Solvents for *N*,*N*-Diethyl-4-nitroaniline (3)

Solvent[c]	β_{1-8}[a]	$\nu(3)$	ν(2a)		$-\Delta\Delta\nu$	ν(2b)		$-\Delta\Delta\nu$	ν(2c)		$-\Delta\Delta\nu$	$-\Delta\Delta\nu$ (2–3)	$-\Delta\Delta\nu$
			Obsd	Calcd	(2a–3)	Obsd	Calcd	(2b–3)	Obsd	Calcd	(2c–3)	av	(1–3)
1. Hexane		27.71	29.50			29.33			29.15				
2. Cyclohexane		27.40	29.37			29.15			28.90				
6. CCl_4		26.70	28.57			28.37			28.17				
8. Toluene		25.87	27.55			27.47			27.36				
10. $Cl_2C{=}CCl_2$		25.76	27.59			27.40			27.25				
14. Benzene		25.60	27.36			27.25			27.14				
15. Chlorobenzene		25.38	26.92			26.77			26.67				
20. Ethylene dichloride		25.06	26.60			26.46			26.32				
21. Methylene chloride		24.96	26.67			26.49			26.35				
17. Anisole	0.247	25.31	26.67	26.97	0.30	26.56	26.83	0.27	26.46	26.71	0.25	0.27	0.67
39. Ethyl chloroacetate	0.363	25.28	26.39	26.94	0.55	26.28	26.80	0.52	26.18	26.67	0.49	0.52	0.91
9. Dioxane	0.379	25.77	26.92	27.48	0.56	26.77	27.33	0.56	26.56	27.19	0.63	0.58	1.06
46. Dibenzyl ether[b]	0.410	25.09	26.35	26.73	0.38	26.18	26.59	0.41	26.28	26.48	0.20	0.39	1.14
47. Ethyl benzoate	0.431	25.31	26.39	26.97	0.58				26.14	26.71	0.57	0.58	1.22
7. Ethyl ether	0.488	26.52	27.66	28.31	0.65	27.55	28.14	0.59	27.36	27.97	0.61	0.62	1.44
5. Butyl ether	0.490	26.85	27.82	28.68	0.86	27.78	28.50	0.72	27.59	28.32	0.73	0.77	1.40
11. Ethyl acetate	0.474	25.74	26.81	27.45	0.64	26.77	27.30	0.53	26.60	27.16	0.56	0.58	1.35
18. Acetone	0.499	25.22	26.28	26.88	0.60	26.18	26.73	0.55	26.01	26.61	0.60	0.58	1.42
16. 2-Butanone	0.504	25.28	26.32	26.94	0.62	26.18	26.80	0.62	26.08	26.67	0.59	0.61	1.44
40. Tetrahydropyran	0.512	25.74	26.77	27.45	0.68	26.67	27.30	0.53	26.53	27.16	0.63	0.61	1.46
13. Tetrahydrofuran	0.556	25.61	26.60	27.31	0.71	26.46	27.16	0.70	26.35	27.02	0.67	0.69	1.55
27. Butyrolactone	0.497	24.60	25.64	26.19	0.55	25.54	27.06	0.52	25.45	25.96	0.51	0.53	1.29
48. Tri-*n*-butylamine	0.635	27.14	28.05	29.00	0.95	28.09	28.81	0.72	28.05	28.62	0.57[b]	0.84	1.87
49. Dimethylbenzylamine	0.595	26.04	26.74	27.78	1.04	26.70	27.62	0.92	26.70	27.47	0.77	0.91	1.66
24. Pyridine	0.661	24.78	25.48	26.39	0.91	25.38	26.26	0.88	25.35	26.15	0.80	0.86	1.87
25. Dimethylformamide	0.690	24.66	25.45	26.26	0.81	25.35	26.13	0.78	25.19	26.03	0.84	0.81	1.98
29. Dimethyl sulfoxide	0.749	24.30	25.06	25.86	0.80	24.91	25.74	0.83	24.81	25.65	0.84	0.82	2.08
19. Triethyl phosphate	0.772	25.19	25.87	26.84	0.97	25.77	26.70	0.93	25.61	26.58	0.97	0.96	2.22
26. Hexamethylphosphoramide	0.990	24.75	25.25	26.36	1.11	25.06	26.22	1.18	25.06	26.12	1.06	1.12	2.80
23. Dimethylacetamide	0.749	24.75	25.45	26.36	0.91	25.35	26.22	0.87	25.25	26.12	0.87	0.88	2.05
28. *N*-Methylpyrrolidone	0.741	24.60	25.32	26.19	0.87	25.22	26.06	0.84	25.09	25.96	0.87	0.86	2.09
51. Cyclopentanone	0.537	25.09	26.11	26.73	0.62	25.97	26.59	0.62	25.84	26.48	0.64	0.63	1.51
101. *tert*-Butyl alcohol	1.014	25.61	25.81	27.32	1.50	25.77	27.17	1.40	25.84	27.02	1.16	1.35	2.66
102. 2-Propanol	0.949	25.51	25.94	27.20	1.26	25.84	27.05	1.21	25.64	26.91	1.27	1.25	2.58
103. 1-Butanol	0.884	25.51	25.87	27.20	1.33	25.87	27.05	1.18	25.71	26.91	1.20	1.24	2.37
112. 1-Propanol	0.746	25.35	25.91	27.02	1.11	25.81	26.87	1.06	25.64	26.75	1.09	1.09	2.10
104. Ethanol	0.773	25.48	26.11	27.16	1.05	25.94	27.02	1.08	25.77	26.88	1.11	1.08	2.16
105. Methanol	0.615	25.16	26.08	26.81	0.73	25.87	26.67	0.80	25.71	26.55	0.84	0.79	1.73
106. 2-Phenylethanol	0.640	24.94	25.67	26.57	0.90	25.45	26.43	0.98	25.25	26.32	1.07	0.98	1.78
107. Ethylene glycol	0.522	24.10	25.13	25.64	0.51	25.09	25.52	0.43	24.97	25.44	0.47	0.47	1.44
109. Benzyl alcohol	0.498	24.33	25.25	25.90	0.65	25.19	27.77	0.58	25.13	25.68	0.55	0.59	1.57
111. Water	0.181	23.23	24.60	24.68	0.08	24.45	24.58	0.13	24.33	24.53	0.20	0.14	0.40
113. Trifluoroethanol	Nil	23.70	25.19	25.20	0.01	25.06	25.07	0.01	24.91	25.02	0.11	0.05	Nil

[a] Reference 3. [b] Large steric effect; excluded from correlation. [c] Solvent numbering is the same in all papers of this series.

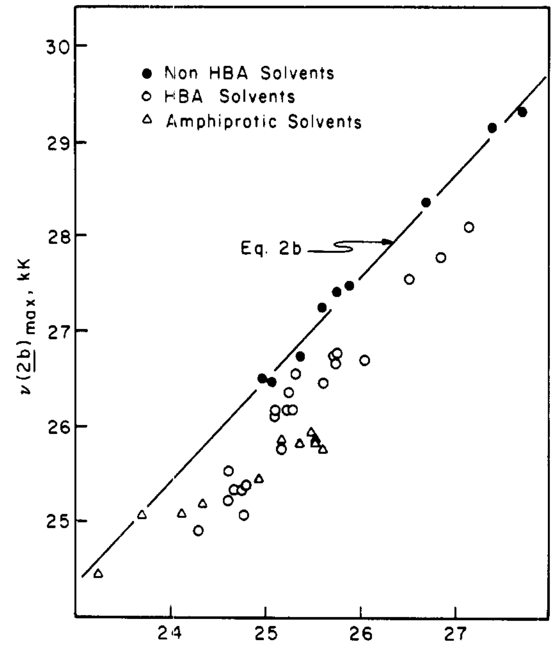


Figure 1. Plot of ν_{max} values for *N*-ethyl-4-nitroaniline (**2b**) against results in corresponding solvents for *N*,*N*-diethyl-4-nitroaniline (**3**).

consistent with the chemistry involved and (in the present case of type B hydrogen bonding) reflect a reasonable order of solvent HBA strengths. This is demonstrated by good linear plots of $-\Delta\Delta\nu$(**2a,b,c-3**) terms vs. solvent β_{1-8} values,[3,12] and by statistically satisfactory least-squares correlations. The plots are shown in Figure 2; the regression equations are

$$-\Delta\Delta\nu(\mathbf{2a}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.350\beta_{1-8} - 0.023 \text{ kK} \quad (3a)$$

with $n = 33$ (22 HBA, 11 amphiprotic solvents), $r = 0.937$, and SD = 0.11 kK,

$$-\Delta\Delta\nu(\mathbf{2b}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.327\beta_{1-8} - 0.050 \text{ kK} \quad (3b)$$

with $n = 32$, $r = 0.954$, and SD = 0.10 kK,

$$-\Delta\Delta\nu(\mathbf{2c}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.208\beta_{1-8} + 0.033 \text{ kK} \quad (3c)$$

with $n = 32$, $r = 0.938$, and SD = 0.09 kK, and

$$-\Delta\Delta\nu(\mathbf{2}_{av}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.281\beta_{1-8} - 0.007 \text{ kK} \quad (3d)$$

with $n = 33$, $r = 0.952$, and SD = 0.09 kK. For comparison, the corresponding regression equation for 4-nitroaniline is

$$-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})^{B}{}_{\leftarrow H_2N} = 2.755\beta_{1-8} + 0.026 \text{ kK} \quad (4)$$

with $r = 0.994$ and SD = 0.07 kK.[13]

Particularly to be noted in eq 3a-d are the low values of the intercepts compared with the SD's, as well as the fact that the latter are not larger than the SD's of antecedent eq 1a-c. These results lend confidence that the correlations do indeed reflect direct proportionality of the $-\Delta\Delta\nu$ with the β_{1-8} terms, and that we do no violence to the data in force-fitting the regression lines through the origins. On this basis, the correlation equations become

$$-\Delta\Delta\nu(\mathbf{2a}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.312\beta_{1-8} \pm 0.085 \text{ kK} \quad (5a)$$

$$-\Delta\Delta\nu(\mathbf{2b}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.240\beta_{1-8} \pm 0.088 \text{ kK} \quad (5b)$$

$$-\Delta\Delta\nu(\mathbf{2c}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.260\beta_{1-8} \pm 0.093 \text{ kK} \quad (5c)$$

$$-\Delta\Delta\nu(\mathbf{2}_{av}\text{-}\mathbf{3})^{B}{}_{\leftarrow HRN} = 1.281\beta_{1-8} \pm 0.090 \text{ kK} \quad (5d)$$

and, for comparison,

$$-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})^{B}{}_{\leftarrow H_2N} = 2.793\beta_{1-8} \pm 0.051 \text{ kK} \quad (6)$$

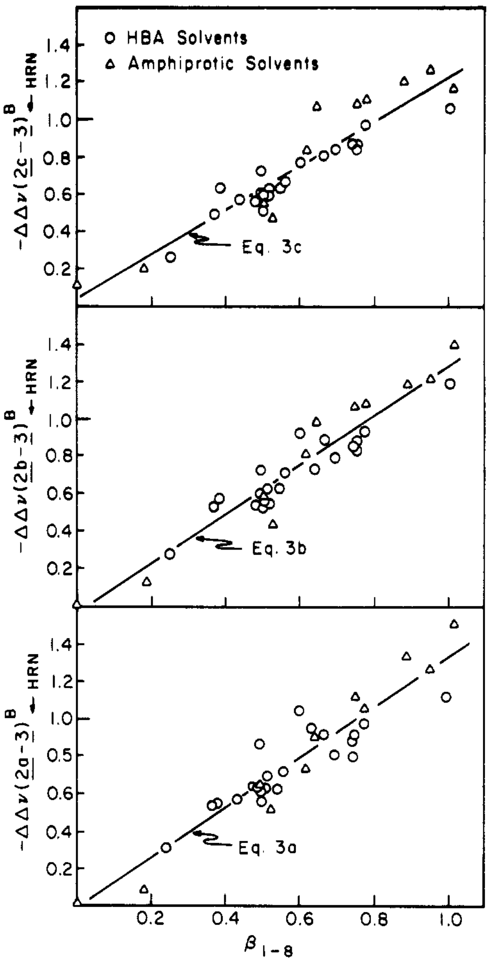


Figure 2. Enhanced bathochromic shifts attributable to hydrogen bonding by *N*-methyl-, *N*-ethyl-, and *N*-isopropyl-4-nitroaniline (**2a-c**) to HBA solvents plotted against solvent β values.

The proportionality constants in eq 5a-d and 6, which we shall refer to as *b* values,[14] can now serve us as average relative measures of the bathochromic effects of type B hydrogen bonding on electronic spectra of **1** and **2a-c**. Plots of $-\Delta\Delta\nu(\mathbf{2}_{av}\text{-}\mathbf{3})$ and $-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})$ vs. β_{1-8}, with the regression lines force-fitted through the origins (slopes = *b*), are compared in Figure 3.

Solvatochromic Comparisons of Spectra for 3-Methyl-4-nitroaniline Derivatives. Although the $-\Delta\Delta\nu$ and *b* values for **2a-c** seemed straightforward, unambiguous, and mutually supporting,[15] we were uncomfortable that the $-\Delta\Delta\nu$(**1-3**) values with which they were compared involved only single HBD and non-HBD indicator solutes. It seemed desirable to narrow the possibility that the more than doubled *b* value for **1** relative to **2a-c** might derive from some unconsidered obscure effect, specific to either **1** or **3**. Toward this end, we include here the results of exactly analogous solvatochromic comparisons of spectral data for 3-methyl-4-nitroaniline (**4**) and *N*-ethyl-3-methyl-4-nitroaniline (**5**), with the reference indicator *N*,*N*-diethyl-3-methyl-4-nitroaniline (**6**).[16] Spectral data and derived $-\Delta\Delta\nu$ values are assembled in Table II.

As before, the results in the non-hydrogen-bonding solvents are nicely linear with one another. The regression equations are

$$\nu(\mathbf{4})_{max} = 1.1163\nu(\mathbf{6})_{max} + 0.539 \text{ kK} \quad (7)$$

with $n = 9$, $r = 0.998$, and SD = 0.09 kK, and

$$\nu(\mathbf{5})_{max} = 1.1054\nu(\mathbf{6})_{max} - 1.209 \text{ kK} \quad (8)$$

Table II. Solvatochromic Comparison of Spectral Data for 3-Methyl-4-nitroaniline (4) and *N*-Ethyl-3-methyl-4-nitroaniline (5) with Results in Corresponding Solvents for *N,N*-Diethyl-3-methyl-4-nitroaniline (6)

Solvent	$\nu(6)$	$\nu(4)$ Obsd	$\nu(4)$ Calcd	$-\Delta\Delta\nu$ (4–6)	$\nu(5)$ Obsd	$\nu(5)$ Calcd	$-\Delta\Delta\nu$ (5–6)
1. Heptane	27.78	31.55			29.50		
2. Cyclohexane	27.62	31.35			29.28		
43. $Cl_2C{=}CCl_2$	26.88	30.53			28.53		
6. CCl_4	26.85	30.58			28.53		
12. 1,1,1-Trichloroethane	26.11				27.62		
10. $Cl_2C{=}CHCl$	26.01	29.54			27.55		
30. Chloroform	25.22	28.82			26.74		
20. $ClCH_2CH_2Cl$	25.25	28.57			26.63		
21. Methylene chloride	25.19	28.74			26.67		
22. $ClCH_2CHCl_2$	25.19	28.61			26.60		
17. Anisole	25.61	28.49	29.13	0.64	26.77	27.10	0.33
39. Ethyl chloroacetate	25.38	27.82	28.87	1.05	26.42	26.86	0.43
9. Dioxane	25.94	28.37	29.50	1.13	27.03	27.47	0.44
46. Dibenzyl ether	25.41	28.01	28.90	0.89	26.49	26.88	0.39
47. Ethyl benzoate	25.48	27.89	28.98	1.09	26.56	26.96	0.40
11. Ethyl acetate	26.01	28.13	29.67	1.54	26.92	27.54	0.62
7. Ethyl ether	26.70	28.78	30.34	1.56	27.62	28.31	0.69
5. Butyl ether	27.03	29.15	30.71	1.56	27.97	28.67	0.70
27. Butyrolactone	24.84	27.03	28.27	1.24	25.81	26.25	0.44
18. Acetone	24.41	27.47	28.90	1.43	26.32	28.88	0.56
16. 2-Butanone	25.54	27.59	29.05	1.46	26.46	27.02	0.56
40. Tetrahydropyran	26.08	27.97	29.65	1.68	26.85	27.62	0.77
51. Cyclopentanone	25.38	27.40	28.87	1.47	26.28	26.85	0.57
13. Tetrahydrofuran	25.91	27.86	29.46	1.60	26.74	27.43	0.69
49. Dimethylbenzylamine	26.32	28.13	29.92	1.79	27.03	27.89	0.86
48. Tri-*n*-butylamine	27.32	29.50	31.04	1.54	28.25	28.99	0.74
24. Pyridine	24.97	26.74	28.41	1.67	25.64	26.39	0.75
25. Dimethylformamide	24.91	26.46	28.35	1.89	25.58	26.33	0.75
28. *N*-Methylpyrrolidone	24.81	26.18	28.23	2.05	25.45	26.22	0.77
29. Dimethyl sulfoxide	24.60	26.04	28.00	1.96	25.25	25.98	0.73
23. Dimethylacetamide	24.97	26.32	28.41	2.09	25.58	26.39	0.81
19. Triethyl phosphate	25.38	26.67	28.87	2.20	25.97	26.85	0.88
26. Hexamethylphosphoramide	25.00	25.67	28.45	2.78	25.28	26.43	1.15
101. *tert*-Butyl alcohol	25.74	26.60	29.27	2.67	25.94	27.24	1.30
102. 2-Propanol	25.54	26.63	29.05	2.42	25.87	27.02	1.15
103. 1-Butanol	25.41	26.70	28.90	2.20	25.87	26.88	1.01
112. 1-Propanol	25.41	26.63	28.90	2.27	25.81	26.88	1.07
104. Ethanol	25.51	26.88	29.02	2.14	26.04	26.99	0.95
105. Methanol	25.22	26.95	28.69	1.74	25.91	26.67	0.76
107. Ethylene glycol	24.51	26.35	27.90	1.55	25.03	25.88	0.85
109. Benzyl alcohol	24.57	26.63	27.97	1.34	25.28	25.95	0.67
106. 2-Phenylethanol	24.84	26.74	28.27	1.53	25.58	26.25	0.67
111. Water	23.59	26.52	26.87	0.35	24.75	24.86	0.11
113. Trifluoroethanol	23.87	27.28	27.19	−0.09	25.19	25.18	−0.01

with $n = 10$, $r = 0.999$, and SD = 0.05 kK. Also as before, the $-\Delta\Delta\nu$ terms, arrived at by subtracting observed values of $\nu(4)_{max}$ and $\nu(5)_{max}$ from values calculated through eq 7 and 8, are nicely linear with β_{1-8} values. These correlation equations are

$$-\Delta\Delta\nu(4\text{–}6)^{B\leftarrow H_2N} = 2.667\beta_{1-8} + 0.043 \text{ kK} \tag{9}$$

with $n = 34$ (23 HBA, 11 amphiprotic solvents), $r = 0.971$, and SD = 0.15 kK, and

$$-\Delta\Delta\nu(5\text{–}6)^{B\leftarrow HRN} = 1.200\beta_{1-8} - 0.005 \text{ kK} \tag{10}$$

with $n = 34$, $r = 0.938$, and SD = 0.10 kK. Again the relatively small values of the intercepts compared with the SD's in eq 9 and 10 warrant force-fitting and regression lines through the origins, whereupon we arrive at the proportionalities with β_{1-8},

$$-\Delta\Delta\nu(4\text{–}6)^{B\leftarrow H_2N} = 2.740\beta_{1-8} \pm 0.115 \text{ kK} \tag{11}$$

$$-\Delta\Delta\nu(5\text{–}6)^{B\leftarrow HRN} = 1.191\beta_{1-8} \pm 0.085 \text{ kK} \tag{12}$$

Thus, the enhanced solvatochromic effects of hydrogen bonding by the double hydrogen bond donor are again more than twice as large as those for the closely related donor of a single hydrogen bond.

Estimation of Relative HBD Acidities of 1 and 2b by the Solvatochromic Dilution Method. The b values for the indicators, $4\text{-}NO_2C_6H_4N(H)R$, vary with substituent σ^* values as follows: R = CH_3, $\sigma^* = 0.00$, $b = 1.312$; R = CH_3CH_2, $\sigma^* = -0.10$, $b = 1.240$; R = $(CH_3)_2CH$, $\sigma^* = -0.19$, $b = 1.260$. We have arrived at a b value for the first hydrogen bond of **1** by estimating that this progression, in its extension to R = H, $\sigma^* = +0.49$, gives a likeliest value in the range $b = 1.45 \pm 0.10$. Taken with $b = 2.79$ for the combined effects of both hydrogen bonds, it follows that the spectral effect of the second hydrogen bond is between 0.80 and 1.07 times as great as that of the first.

Is it a necessary corollary of the above that the second hydrogen bond by **1** to HBA solvents is about *as strong* as the first? To answer this question, we have used the solvatochromic dilution procedure, described in part 4,[1] to assess relative HBD acidities of **1** and **2b**. This procedure involves determining how $-\Delta\Delta\nu$ values for the complex between the HBD indicator solutes and an HBA solvent vary as the HBA solvent is progressively diluted into a non-HBA cosolvent.

Table III. Solvatochromic Comparison of Spectral Data for 4-Nitroaniline (1) and *N*-Ethyl-4-nitroaniline (2b) with Results for *N,N*-Diethyl-4-nitroaniline (3) in Mixed Dimethyl Sulfoxide–Carbon Tetrachloride Solvents[a]

Vol fraction Me_2SO	$\nu(3)_{max}^{obsd}$	$\nu(1)$		$-\Delta\Delta\nu$ (1–3)	$\nu(2b)$		$-\Delta\Delta\nu$ (2b–3)
		Obsd	Calcd		Obsd	Calcd	
1.000	24.27	25.74	27.76	2.02	24.88	25.71	0.83
0.800	24.39	25.81	27.88	2.07	24.94	25.84	0.90
0.600	24.60	25.87	28.10	2.23	25.06	26.06	1.00
0.400	24.84	26.08	28.35	2.27	25.25	26.32	1.07
0.200	25.19	26.25	28.71	2.46	25.51	26.70	1.19
0.100	25.58	26.56	29.11	2.55	25.74	27.12	1.38
0.080	25.67	26.70	29.21	2.51	25.88	27.22	1.34
0.060	25.84	26.95	29.38	2.43	25.97	27.41	1.44
0.040	26.04	27.21	29.59	2.38	26.21	27.62	1.41
0.020	26.32	27.86	29.88	2.02	26.60	27.93	1.33
0.010	26.46	28.37	30.02	1.65	27.14	28.08	0.94
0.008	26.49	28.57	30.10	1.57	27.21	28.11	0.90
0.006	26.56	28.94	30.13	1.19	27.40	28.19	0.79
0.005	26.56	29.07	30.13	1.06	27.62	28.19	0.57
0.004	26.60	29.24	30.17	0.93	27.78	28.23	0.45
0.003	26.63	29.41	30.20	0.79	27.89	28.27	0.36
0.002	26.67	29.67	30.24	0.57	27.97	28.31	0.34
0.001	26.67	29.94	30.24	0.30	28.15	28.31	0.16
0.000	26.70	30.33	30.27	−0.06	28.37	28.34	−0.03

[a] Data for 1 and 3 differ slightly from results for the same materials reported in part 4.[1] The data were obtained in separate experimental studies on different spectrophotometers. Comparison of the two sets of data allows evaluation of representative experimental precision to be expected in solvatochromic comparisons.

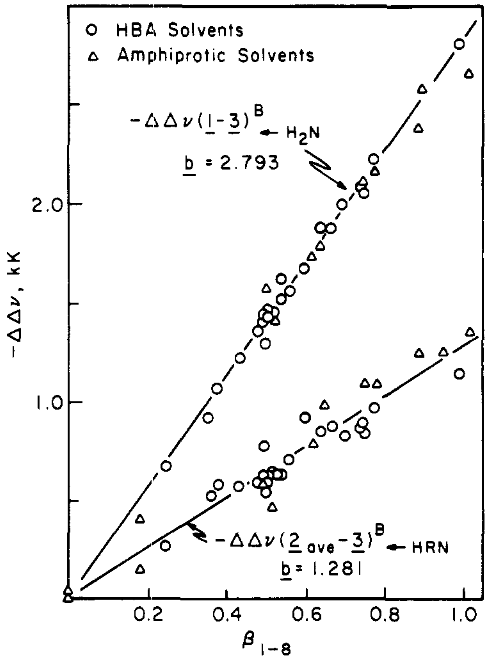


Figure 3. Enhanced bathochromic shifts for 4-nitroaniline and average shifts for the *N*-alkyl-4-nitroanilines plotted against solvent β values.

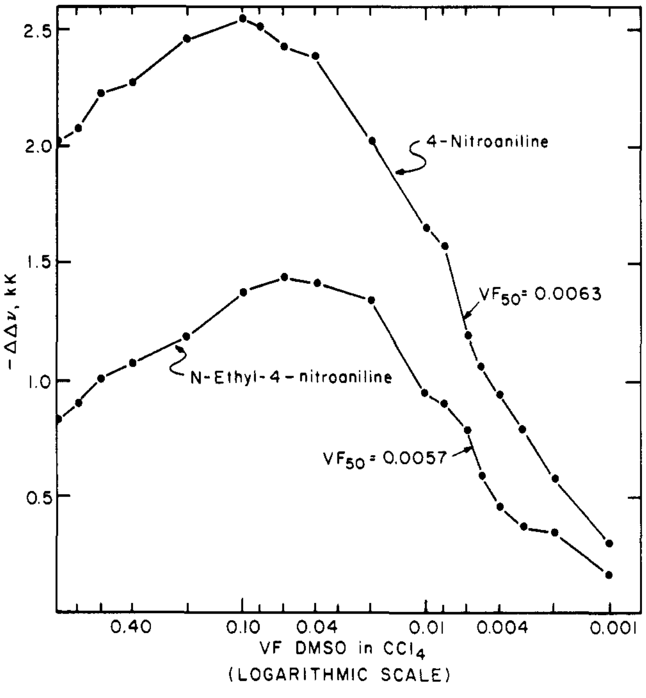


Figure 4. Solvatochromic dilution plots for 4-nitroaniline and *N*-ethyl-4-nitroaniline; HBA solvent, Me_2SO; non-HBA cosolvent, CCl_4; reference indicator, *N,N*-diethyl-4-nitroaniline.

VF_{50} values, the volume fractions (HBA solvent in non-HBA cosolvent) at which the HBD:HBA complex is half dissociated,[17] can be used to arrive at rough estimates of the formation constants.

In the present dilution study, **1** and **2b** are the HBD indicator solutes, **3** the non-HBD reference solute, dimethyl sulfoxide the HBA solvent, and carbon tetrachloride the non-HBA cosolvent. Values of ν_{max} in the mixed solvents, together with the $-\Delta\Delta\nu$ terms (obtained, as before, by subtracting ν_{max}^{obsd} values from values calculated through eq 1b and 2), are assembled in Table III, and $-\Delta\Delta\nu$(**1**–**3**) and $-\Delta\Delta\nu$(**2b**–**3**) terms are plotted against volume fraction (VF) Me_2SO/CCl_4 (the latter on a logarithmic scale) in Figure 4.

It may be seen in the plot that the solvatochromic dilution of **2b** follows the same pattern shown earlier for **1** and other HBD indicator solutes.[1] As the Me_2SO grows progressively more dilute in CCl_4, the $-\Delta\Delta\nu$(**2b**–**3**) term first rises to a maximum because of a polarity augmentation effect in the cybotactic region (see discussion in part 4),[1] then falls off as the **2b**:Me_2SO complex begins to dissociate. The volume fraction at which the **2b**:Me_2SO complex is half dissociated,

VF_{50} = 0.0057, corresponding to 0.081 M Me_2SO in CCl_4. This compares with VF_{50} = 0.0063 (0.0062),[18] corresponding to 0.081 M Me_2SO in CCl_4 for the complex with 1.

These Me_2SO molarities at half-dissociation allow rough estimates of formation constants, and hence relative hydrogen bond strengths. For the half-dissociated **2b**:Me_2SO complex

$$K_f^{2b} = \frac{(\mathbf{2b}:Me_2SO)}{(\mathbf{2b})\ (Me_2SO)} = 1/(Me_2SO) = 12.5\ \mathrm{L\ mol^{-1}}$$

For the singly hydrogen bonded Me_2SO complex with 1

$$K_1 = \frac{(1:Me_2SO)}{(1)\ (Me_2SO)}$$

and for the doubly hydrogen bonded complex

$$K_2 = \frac{(Me_2SO:1:Me_2SO)}{(1:Me_2SO)\ (Me_2SO)}$$

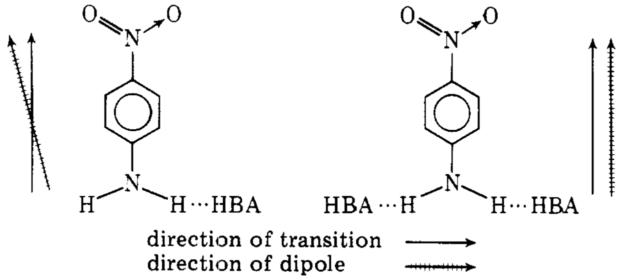
$$K_1K_2 = \frac{(Me_2SO:1:Me_2SO)}{(1)\ (Me_2SO)^2}$$

Since, at half-dissociation, (1) = (Me_2SO:1:Me_2SO)

$$K_1K_2 = 1/(Me_2SO)^2 = 126.2\ \mathrm{L^2\ mol^{-2}}$$

If we estimate that the first hydrogen bond by 1 to Me_2SO is about 1.1 times as strong as the **2b**:Me_2SO hydrogen bond, and take into account the statistical factor for the two protons, we arrive at a value of 27.5 L mol^{-1} for K_1 and 4.6 L mol^{-1} for K_2. Again taking into account the statistical factor, it follows that the bond strengths of the first and second type B hydrogen bonds by 4-nitroaniline to HBA solvents are in a ratio of about 13.75/9.2, or about 1.5:1. Thus, the spectral effect of the second compared with the first solvent associated proton is somewhat greater than the relative hydrogen bond strengths would indicate.

We have no easy rationale for this phenomenon. One possible line of reasoning is that optimal solvent stabilization of the excited state of an electronic transition occurs when the direction of that transition corresponds exactly with the direction of the molecule's ground state dipole (a solvent shell best oriented to stabilize the ground state is also optimally oriented for excited state stabilization). Such a situation obtains with uncomplexed 1 and with doubly complexed 1, but with singly complexed 1 the ground state dipole is rotated slightly. Hence, in going from 1 to 1:HBA, we have the bathochromic effect of the hydrogen bonding minus a small Δ term due to noncorrespondence of transition and dipole directions, while on going from 1:HBA to HBA:1:HBA, we have the hydrogen bonding effect *plus* the same small Δ term as the transition and dipole are brought back into line.



The findings reported here are completely consistent with results which we will report in a future paper, wherein substituent, solvent polarity, and solvent hydrogen bonding effects on spectra of 2-, 3-, and 4-nitroanilines will be compared. We will demonstrate that spectral effects and HBD acidities of 3-nitroaniline and *N*-ethyl-3-nitroaniline show about the same relationships to one another as reported here for the 4-nitro derivatives; i.e., for 3-nitroaniline, *b* = 2.738, VF_{50} (Me_2SO/CCl_4) = 0.0105; for *N*-ethyl-3-nitroaniline, *b* = 1.485, VF_{50} = 0.0101.

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Registry No.—**1,** 100-01-6; **2a,** 100-15-2; **2b,** 3665-80-3; **2c,** 25186-43-0; **3,** 2216-15-1; **4,** 611-05-2; **5,** 52177-09-0; **6,** 52177-26-1.

References and Notes

(1) Part 4: J. W. Eastes, E. G. Kayser, M. E. Jones, R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, submitted for publication.

(2) (a) Naval Surface Weapons Center; (b) University of California; (c) deceased; (d) Visiting Scientist, UCI, 1976–1977.

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

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

(5) In the earlier study,[4] we determined shifts ($-\Delta\nu$ values) from cyclohexane to each solvent for **1**, **2b**, and **3**. The $-\Delta\Delta\nu$ values were simply the differences $[-\Delta\nu(\mathbf{1})] - [-\Delta\nu(\mathbf{3})]$ and $[-\Delta\nu(\mathbf{2b})] - [-\Delta\nu(\mathbf{3})]$. The earlier method is satisfactory where solvent polarity effects are comparable for the indicators being compared, but breaks down where the slopes of the regression lines for the non-hydrogen-bonding solvents differ significantly from unity.

(6) M. J. Kamlet, E. G. Kayser, R. R. Minesinger, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36,** 3852 (1971). In type A hydrogen bonding the solvent acts as proton donor and the solute as proton acceptor; the converse applies in type B bonding.

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

(8) The notation $-\Delta\Delta\nu(\mathbf{2a}\text{-}\mathbf{3})^{B}{}_{\leftarrow HNR}$ signifies an enhanced bathochromic (or reduced hypsochromic) displacement for **2a** relative to **3**, caused by type B hydrogen bonding by an amine proton to the solvent. See footnote 8 of part 1[3] 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.

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

(10) The possibility of the alcohols acting as hydrogen bond donors and the nitroanilines as hydrogen bond acceptors at the amine nitrogens has been essentially eliminated in the case of sp^2 hybridized 4-nitroaniline derivatives.[6]

(11) To minimize band asymmetry complications (differing band shapes for the same solute in different solvents), we determine ν_{max} by taking the midpoint between the two positions on the spectrum where OD (optical density) = 0.90 OD_{max}.

(12) T. Yokoyama, R. W. Taft, and M. J. Kamlet, *J. Am. Chem. Soc.*, **98,** 3233 (1976). The subscript indicates that data from eight sets of properties were averaged to obtain the β values. As the β scale is used to rationalize hydrogen bonding effects on additional rate constants, equilibrium constants, and spectral and chemical properties, the new experimental information will be used reciprocally to refine and expand the β scale.

(13) No particular significance should be attributed to the very high *r* value and the low SD for eq 4, since the $-\Delta\Delta\nu(\mathbf{1}\text{-}\mathbf{3})$ terms were among the properties used in constructing the β scale.

(14) The proportionality constants are the same *b* terms which we will use in future papers in a generalized equation describing solvent effects on many types of free energy related properties, $XYZ = XYZ_0 + s\pi + a\alpha + b\beta$.

(15) We consider that the difference in *b* values for **2b** and **2c** is within the range of probable experimental error.

(16) Spectral data for these compounds, as well as for the corresponding 3,5-dimethyl derivatives, were determined as part of a study of the effects of steric inhibition of resonance on type B hydrogen bonding effects. The results of that study will be published in a future paper.

(17) VF_{50} is the volume fraction of HBA solvent in non-HBA cosolvent at which the $-\Delta\Delta\nu$ term is half of the maximum observed value, the latter being equal to the $-\Delta\Delta\nu$ value in the neat HBA solvent plus the cybotactic polarity increment; see part 4.[1]

(18) $-\Delta\Delta\nu$ values and the VF_{50} value differ slightly from those reported earlier, which were determined on a different spectrophotometer. Comparing the data in Table III with results for the same system in Table I of part 4[1] provides a measure of typical experimental reproducibility in solvatochromic dilution studies.