Linear Solvation Energy Relationships. Part 2.† Correlations of Electronic Spectral Data for Aniline Indicators with Solvent π^* and β Values

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The solvatochromic comparison method is employed with electronic spectral data to unravel solvent polarity and hydrogen bonding effects on the $p\rightarrow\pi^*$ transitions of ethyl 4-aminobenzoate, 4-aminobenzophenone, 3,5-dinitroaniline, 3-nitroaniline, and *N*-ethyl-3-nitroaniline. Values of *b* in the solvatochromic equation, $\nu(i)_{\max} = \nu_0 + s\pi^* + b\beta$ are rationalized in terms of indicator HBD (hydrogen bond donor) acidities and solvent-induced rehybridization effects.

IN earlier papers we described the formulation of a π^*-scale of solvent polarity–polarizabilities,[1] an α-scale of solvent HBD (hydrogen bond donor) acidities,[2] and a β-scale of solvent HBA (hydrogen bond acceptor) basicities.[3,4] These solvent property indexes were intended to serve, alone or in combination with one another, to unravel and correlate solvent effects on many chemical and spectroscopic properties and reactivity parameters. In the present paper, we use the solvatochromic comparison method with electronic spectral data for $p\rightarrow\pi^*$ transitions to rationalize and quantify hydrogen bonding interactions of five variously substituted aniline indicators.

Where effects of type-A or type-AB hydrogen bonding ‡ are excluded, as when correlations are limited to non-HBD solvents, total solvatochromic equations for electronic spectral transitions usually take the form,

$$\nu(i)_{\max.} = \nu_0 + s\pi^* + b\beta \qquad (1)$$

The *s* and *b* terms in equation (1) represent the responses of $\nu(i)_{\max.}$ to changing solvent polarity–polarizability and solvent HBA basicity.

The indicators whose solvatochromic behaviour we shall analyse in terms of equation (1) are: ethyl 4-aminobenzoate (1), 4-aminobenzophenone (2), 3,5-dinitroaniline (3), 3-nitroaniline (4), and *N*-ethyl-3-nitroaniline (5). Because these indicators form type-AB hydrogen bonds at their amine sites with amphiprotic solvents (rather than pure type-B bonds wherein the amine function serves only as proton donor, as was observed earlier with 2- and 4-nitroaniline),[3,4] we have limited the correlations to non-HBD solvents. We shall deal with the solvatochromic behaviour of (1)—(5) in amphiprotic solvents in a future paper devoted specifically to type-AB hydrogen bonding phenomenology.

RESULTS

Solvent effects on positions of band maxima for the $p\rightarrow\pi^*$ transitions of (1)—(5) are assembled in Table 1 together with solvent π^* and β-values. Total solvatochromic equations in the form of equation (1) have been determined for these indicators in two ways, (a) by stepwise solvatochromic comparisons with π^* and β, and (b) by multiple linear-regression analysis. We shall illustrate both versions of the solvatochromic comparison method for indicator (1), and summarize corresponding findings for (2)—(5) in Table 2.

In the stepwise method, we first evaluate solvent polarity–polarizability effects by correlating $\nu(1)_{\max.}$ results in non-hydrogen bonding solvents with solvent π^*-values. The least squares correlation equation, represented by the regression line in Figure 1a, is

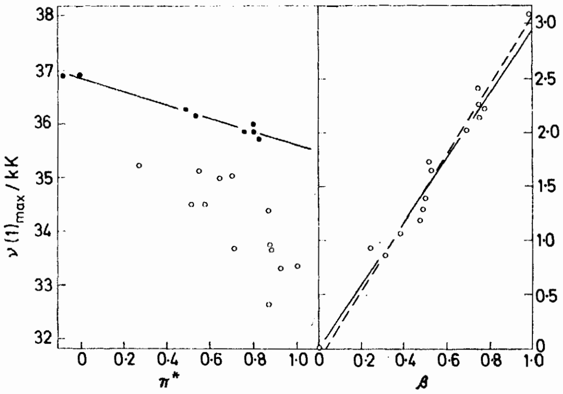

FIGURE 1 Solvatochromic comparison plots for ethyl 4-aminobenzoate. Sequential method. (a) $\nu(1)_{\max}$ *vs.* π^*. (b) $-\Delta\Delta\nu$ $(1-\pi^*)$ *vs.* β. ● = Non-hydrogen bonding solvents and ○ = HBA solvents

$$\nu(1)_{\max.} = -1.258\,\pi^* + 36.85\text{ kK} \qquad (2)$$
$$\text{kK} = 10^3\text{ cm}^{-1}$$

with $n = 8$, r (the correlation coefficient) $= 0.989$ and SD (the standard deviation) $= 0.075$ kK. Next, $-\Delta\Delta\nu$-$(1-\pi^*)^{B}_{\leftarrow H_2N}$ terms,§ representing enhanced bathochromic

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† Part 1, M. J. Kamlet and R. W. Taft, preceding paper.

‡ In type-A hydrogen bonding the solute acts as HBA base and the solvent as HBD acid. The converse applies in type-B hydrogen bonding. In type-AB hydrogen bonding, which we will document in detail in a future paper, the solute acts simultaneously as HBD acid and HBA base *at the same site*, associating with at least two molecules of amphiprotic HBA–HBD solvent in a probably cyclic complex. We have so far observed type-AB hydrogen bonding only with sp^3-hybridized aromatic amine indicators.

§ The negative sign indicates a bathochromic shift; the $(1-\pi^*)$ term indicates that the effect is for indicator (1) relative to a position predicted from a correlation with the π^*-scale; the superscript B indicates that the effect is due to type-B hydrogen bonding; and the subscript $\leftarrow H_2N$ indicates that bonding is by the amine protons of the indicator. See the earlier papers of this series [1-4] for additional examples of this nomenclature system, which makes descriptions of the phenomenology much less confusing and cumbersome when several types of hydrogen bonding with concomitant spectral effects occur simultaneously.

TABLE 1

Solvatochromic comparisons with the π^*-scale of solvent polarities and the β-scale of solvent HBD acidities. Electronic spectral data in kK [(1) ethyl 4-aminobenzoate; (2) 4-aminobenzophenone; (3) 3,5-dinitroaniline; (4) 3-nitro*aniline*; (5) *N*-ethyl-3-nitroaniline]

π^*	β	β corr.[a]	No.	Solvent	$\nu(1)$	$-\Delta\Delta\nu$ $(1\text{-}\pi^*)$	$\nu(2)$	$-\Delta\Delta\nu$ $(2\text{-}\pi^*)$	$\nu(3)$	$-\Delta\Delta\nu$ $(3\text{-}\pi^*)$	$\nu(4)$	$-\Delta\Delta\nu$ $(4\text{-}\pi^*)$	$\nu(5)$	$-\Delta\Delta$ $(5\text{-}\pi^*)$
−0.081	NHBA[b]		(1)	Hexane, Heptane	36.90		33.22		27.74		28.99		27.21	
0.000	NHBA		(2)	Cyclohexane	36.90		33.06		27.47		28.82		27.06	
0.277	NHBA		(43)	Tetrachloroethylene			32.57				28.41		26.53	
0.294	NHBA		(6)	Carbon Tetrachloride			32.52		27.32		28.49		26.63	
0.490	NHBA		(12)	1,1,1-Trichloroethane	36.23		32.52				27.93		25.97	
0.534	NHBA		(10)	Trichloroethylene	36.17		32.10		26.85		28.01		26.08	
0.760	NHBA		(30)	Chloroform[e]	35.84		31.70		26.60		27.70		25.57	
0.807	NHBA		(20)	1,2-Dichloroethane	35.84		31.70		26.32		27.43		25.41	
0.802	NHBA		(21)	Methylene chloride	35.97		31.80		26.49		27.62		25.57	
0.829	NHBA		(22)	1,1,2-Trichloroethane	35.71		31.70		26.39		27.43		25.41	
0.734	0.247	0.223	(17)	Anisole			31.45	0.40	25.91	0.65	27.10	0.55	25.34	0.28
0.704	0.363	0.348	(39)	Ethyl chloroacetate	35.03	0.93	31.15	0.75	25.64	0.96	26.77	0.93	25.22	0.46
0.553	0.379	0.369	(9)	Dioxan	35.09	1.06	31.30	0.85	25.67	1.14	26.99	0.96	25.51	0.47
0.739	0.434	0.412	(47)	Ethyl benzoate			30.96	0.88	25.32	1.23	26.70	0.94	25.06	0.55
0.545	0.474	0.446	(11)	Ethyl acetate	34.97	1.19	31.25	0.91	25.64	1.19	26.81	1.15	25.45	0.55
0.273	0.488	0.466	(7)	Ethyl ether	35.21	1.29	31.60	1.02	25.84	1.37	27.14	1.27	25.97	0.57
0.239	0.490	0.453	(5)	n-Butyl ether	(35.59)[c]		31.85	0.82	25.77	1.49	27.36	1.11	26.14	0.47
0.873	0.497	0.489	(27)	Butyrolactone	34.36	1.39	30.63	0.99	24.91	1.49	26.18	1.24	24.64	0.71
0.683	0.499	0.478	(18)	Acetone					25.28	1.35	26.49	1.24	25.06	0.66
0.674	0.504	0.481	(16)	Butan-2-one					25.25	1.39	26.66	1.09	25.06	0.68
0.513	0.512	0.544	(40)	Tetrahydropyran	34.48	1.72	31.01	1.20	25.22	1.65	26.53	1.48	25.32	0.74
0.756	0.537	0.524	(51)	Cyclopentanone					25.16	1.37	26.18	1.43	24.81	0.77
0.576	0.556	0.550	(13)	Tetrahydrofuran	34.48	1.65	30.96	1.15	25.25	1.53	26.42	1.49	25.19	0.75
0.494	0.595	0.570	(49)	*NN*-Dimethylbenzylamine			31.06	1.19	25.13	1.77	26.66	1.38	25.28	0.82
0.162	0.635	0.618	(48)	Tri-n-butylamine			(32.15)[c]		25.67	1.70	27.06	1.53	(26.15)[c]	
0.140	0.686	0.705	(3)	Triethylamine					*d*		26.74	1.89	25.74	1.06
0.867	0.661	0.642	(24)	Pyridine			30.21	1.42	24.69	1.68	25.83	1.60	24.39	0.97
0.875	0.690	0.689	(25)	Dimethylformamide	33.73	2.02	30.02	1.49	25.54	1.82	25.54	1.87	24.33	1.01
0.921	0.741	0.774	(28)	*N*-Methylpyrrolidone	33.28	2.41	29.81	1.73	24.15	2.14	25.09	2.25	24.03	1.22
1.000	0.749	0.764	(29)	Dimethyl sulphoxide	33.33	2.26	29.72	1.69	24.18	2.00	25.06	2.16	23.98	1.11
0.882	0.749	0.756	(23)	Dimethylacetamide	33.61	2.13	29.94	1.66	24.27	2.08	25.32	2.08	24.24	1.09
0.715	0.772	0.774	(19)	Triethyl phosphate	33.72	2.22	30.30	1.58	24.48	2.10	25.54	2.14	24.48	1.18
0.871	0.990	1.056	(26)	Hexamethylphosphoramide	32.62	3.12	29.20	2.42	23.45	2.91	24.27	3.15	23.75	1.60
0.535		0.112	(8)	Toluene			32.00	0.17	26.39	0.45	27.62	0.36	25.91	0.10
0.588		0.100	(14)	Benzene			31.90	0.19	26.42	0.35	27.66	0.23	25.77	0.14
0.703		0.071	(15)	Chlorobenzene			31.85	0.04	26.32	0.27	27.58	0.11	25.51	0.16
0.794		0.062	(33)	Bromobenzene					26.25	0.22	27.36	0.19	25.45	0.05
0.713		0.310	(50)	Acetonitrile[e]	35.09	0.86	31.20	0.68	25.74	0.84	26.92	0.76	25.16	0.50

[a] Amended β-values obtained by averaging the β_i-values back-calculated from the present correlation equations with β_i values determined earlier. [b] NHBA = non-hydrogen bond acceptor solvent. [c] Strong steric effects. Excluded from correlations. [d] Seems to react. [e] Weak HBD acids which seem to behave in effect as non-HBD solvents with these weak HBA base indicators.

shifts attributable to type-B hydrogen bonding by the amine protons of the HBD indicator (1) to HBA solvents (and corresponding to vertical displacements of the HBA solvent data points from the regression line in Figure 1a), are calculated through expression (3).

$$-\Delta\Delta\nu(1\text{-}\pi^*)^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}} = \nu(1)^{\mathrm{calc}}_{\mathrm{eqn.(2)}} - \nu(1)^{\mathrm{obs}}_{\mathrm{max}} \qquad (3)$$

When the enhanced solvatochromic shifts are next compared with solvent HBA basicities, it is seen in Figure 1b that the $-\Delta\Delta\nu$ terms are linear with and very nearly proportional to the solvent β-values (as is intrinsic in the Linear Solvation Energy Relationship concept). The least-squares regression equation for 14 data points (13 HBA solvents and one zero/zero point representing all non-HBA solvents), denoted by the broken line in Figure 1b, is

$$-\Delta\Delta\nu(1\text{-}\pi^*)^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}} = 3.167\,\beta - 0.12\ \mathrm{kK} \qquad (4)$$

with $r = 0.986$ and SD = 0.101 kK. Force-fitted through the origin to reflect the necessary direct proportionality, this becomes,

$$-\Delta\Delta\nu(1\text{-}\pi^*)^{\mathrm{B}}{}_{\leftarrow\mathrm{H_2N}} = 2.951\,\beta \pm 0.13\ \mathrm{kK} \qquad (5)$$

The relatively low values of the intercept and SD in equation (4), comparable in magnitude to the 0.10 kK precision of the spectral determinations, indicate that we do no violence to the data in force-fitting the correlation through the origin (represented by the solid regression line in Figure 1b).

The Total Solvatochromic Equations.—The slope and intercept in equation (2) correspond to the s and ν_0 terms in equation (1) and the proportionality constant in equation (5) corresponds to the b coefficient. Combining the appropriate terms from equations (2) and (5), we obtain the stepwise total solvatochromic equation (6) with $r = 0.996$ and SD = 0.113 kK (the latter terms being derived from a correlation of calculated with observed $\nu_{\mathrm{max.}}$ values).

$$\nu(1)_{\mathrm{max.}} = -1.258\,\pi^* - 2.951\,\beta + 36.85\ \mathrm{kK} \qquad (6)$$

The alternative route to the total solvatochromic equations is the method of multiple linear-regression analysis (multiple-parameter least-squares correlation) which has become quite convenient with the recent availability of

TABLE 2

Total solvatochromic equations in non-HBD solvents. Spectral data in kK

$$\nu(i)_{\mathrm{max.}} = \nu_0 + s\pi^* + b\beta$$

A = Stepwise, by successive single-parameter correlations.
B = By multiple linear regression analysis.

Equation	i	s	b	ν_0	r [a,c]	SD [a]	n
A-1	(1)	−1.258	−2.951	36.86	0.996 [b]	0.11	21
B-1		−1.297	−3.005	36.89	0.996	0.12	
A-2	(2)	−1.664	−2.139	33.07	0.995 [b]	0.10	28
B-2		−1.738	−2.207	33.14	0.995	0.11	
A-3	(3)	−1.420	−2.800	27.60	0.995 [b]	0.10	32
B-3		−1.357	−2.815	27.57	0.996	0.10	
A-4	(4)	−1.652	−2.642	28.86	0.991 [b]	0.14	33
B-4		−1.741	−2.700	38.96	0.991	0.15	
A-5	(5)	−1.986	−1.408	27.08	0.995 [b]	0.08	32
B-5		−2.031	−1.494	27.14	0.995	0.09	

[a] Values of r and SD determined by least-squares correlation of $\nu(i)_{\mathrm{calc.}}$ with $\nu(i)_{\mathrm{obs.}}$. [b] Correlation coefficients in the single parameter least-squares fits were: A-1, 0.989, 0.986; A-2, 0.983, 0.983; A-3, 0.985, 0.985; A-4, 0.990, 0.974; A-5, 0.993, 0.978. [c] For comparison, the r value for the correlation of π^* *versus* β for the solvents of Table 1 is 0.337.

inexpensive programmable computers. In this one-step procedure, correlation of $\nu(1)_{\text{max.}}$ results with the π^* and β terms leads directly to the desired equations. For (1), the relationship obtained by multiple linear-regression analysis is

$$\nu(1)_{\text{max.}} = -1.297\,\pi^* - 3.005\,\beta + 36.89\ \text{kK} \quad (7)$$

with $n = 22$, $r = 0.996$, and SD = 0.120 kK.

Considering that 13 solvent π^* values, which served as input to equation (7), did not contribute to the determination of s in equation (6), the fact that agreement between the two equations is well within the precision limits of the individual spectral determinations must be regarded as highly satisfactory. Values of $\nu(1)^{\text{obs.}}_{\text{max.}}$ are plotted against $\nu(1)^{\text{calc.}}_{\text{eqn.(7)}}$ in Figure 2.

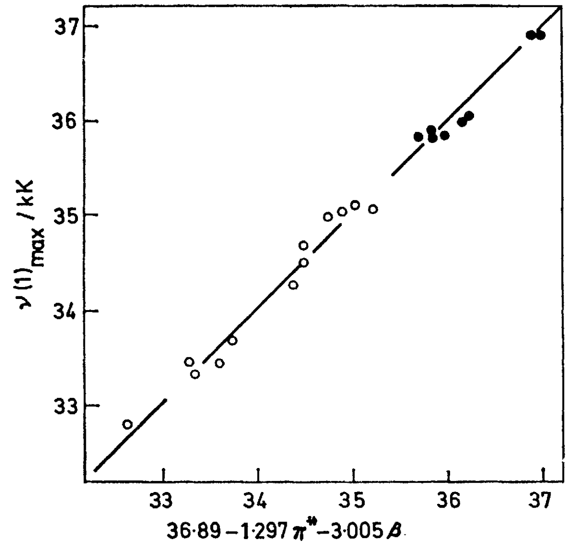
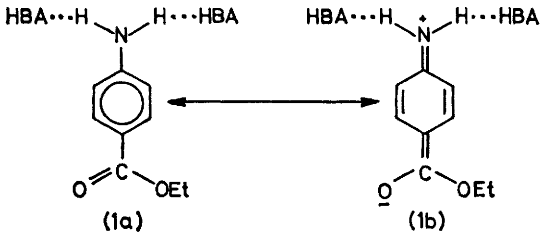


FIGURE 2 Solvatochromic comparison plot for ethyl 4-aminobenzoate; multiple linear-regression method. ● = Non-hydrogen bonding solvents and ○ = HBA solvents

Agreement between the two methods is equally good for the other four indicators. Values of ν_0, s, and b determined by the two versions of the solvatochromic comparison method are compared for (1)—(5) in Table 2.

In other studies we have sometimes had insufficient experimental data in non-hydrogen bonding solvents to determine solvatochromic equations by the stepwise method, so that it was necessary to use the method of multiple linear-regression analysis. In several such instances, we were faced by referees' assertions that with the greater number of parameters the correlations were statistically less rigorous. We therefore emphasize the excellent correspondence between the two methods (Table 2), since we believe that it is difficult to find statistical fault with the stepwise method, which involves successive single-parameter correlations, and wherein the goodness of the fit is confirmed at every stage.



(1a) (1b)

The negative signs of s and b in the total solvatochromic equations [$\nu(1)_{\text{max.}}$ shifted to the red by both increasing solvent polarity and solvent HBA basicity] are consistent with an electronic excited state resembling (1b), whose energy is lowered relative to a ground state more closely resembling (1a) by virtue of dielectric stabilization of charge separation and hydrogen bond strengthening in the electronic excitation.

DISCUSSION

Factors Influencing the Solvatochromic Coefficients.—Some very valuable information regarding the indicators may be adduced from the ν_0, s, and b terms in equation (1). These solvatochromic coefficients are assembled in Table 3 for (1)—(5), as well as for 4-nitro- (6) and *N*-ethyl-nitroaniline (7), whose solvatochromic behaviour has already been reported.[3,5,6] Also listed in the Table are values of VF_{50} (DMSO–CCl_4) and $+\Delta\Delta\nu(CF_3CH_2OH)$.

TABLE 3

Factors influencing the solvatochromic coefficients

Indicator aniline	ν_0	$-s$	$-b$	VF_{50} (DMSO–CCl_4) [c]	$+\Delta\Delta\nu$/kK (F_3CCH_2OH) [d]
4-Nitro-(6)	31.10	3.14 [b]	2.79 [a]	0.0063 [a]	Nil
N-Ethyl-4-nitro-(7)	29.17	3.32 [b]	1.14 [a]	0.0057 [a]	Nil
3,5-Dinitro-(3)	27.61	1.42	2.80	0.0026 [e]	0.47
3-Nitro-(4)	28.87	1.65	2.64	0.0105 [e]	2.26
N-Ethyl-3-nitro-(5)	27.10	1.98	1.41	0.0101 [e]	2.00
4-Benzoyl-(2)	33.09	1.66	2.14	0.0135 [e]	1.04
4-Ethoxy-carbonyl (1)	36.85	1.26	3.01		1.85

[a] Ref. 6. [b] Ref. 1. [c] Volume fraction of DMSO in CCl_4 at which the DMSO–HBD–DMSO or DMSO–HBD complex is approximately half dissociated; inverse measure of indicator HBD acidity. [d] *Hypsochromic* effect of type-AB hydrogen bonding to and by trifluoroethanol; increases as the hybridization on the amine nitrogen approaches sp^3; to be reported in a future paper. [e] Results of solvatochromic dilution studies to be reported in a future paper.

The VF_{50} (Me_2SO–CCl_4) terms, obtained by the solvatochromic dilution procedure as discussed in earlier papers,[5,6] are the volume fractions of DMSO in CCl_4 at which the 2 : 1 complexes of DMSO with compounds (2), (3), (4), and (6) and the 1 : 1 complexes with (5) and (7) are approximately half dissociated.† VF_{50}'s are inversely related to formation constants of the DMSO–Indicator–DMSO and DMSO–Indicator complexes, and are hence inverse measures of indicator hydrogen-bond strengths. It is seen in the Table that the order of HBD acidities is $3 > 7 \sim 6 > 5 \sim 4 > 2$, which reflects the $\Sigma\sigma$'s of the aniline substituents.

The $+\Delta\Delta\nu(CF_3CH_2OH)$ terms are the *hypsochromic* effects of type-AB hydrogen bonding by and to trifluoroethanol at the amine nitrogen sites of the indicators. Since we have not yet reported on the very characteristic phenomenology of type-AB hydrogen bonding, it suffices at this juncture to indicate that the $\Delta\Delta\nu$ result in tri-

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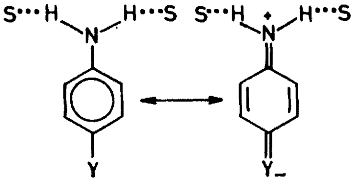
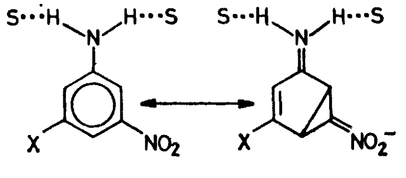
† Actually, the VF_{50} is the volume fraction at which the $-\Delta\Delta\nu$ value is half of the maximum value observed in the solvatochromic dilution plot.[5]

fluoroethanol is a sensitive measure of hybridization on aromatic amine nitrogens, *nil* for sp^2-hybridized anilines, and increasingly positive with increasing *p*-character of the hybridization.

As we have already reported,[1] substituent effects on ν_0 and *s* for $[^+X{=}C(1){\rightarrow}C(4){=}Y^-]$ electronic transitions are relatively straightforward, ν_0 values decreasing and *s* values increasing with increasing electron-donor ability of X and electron-acceptor ability of Y. Thus the descending ν_0's and ascending *s* values in the orders 1,2,6 and 6,7 and 4,5 reflect increasing stabilization of the charge-separated electronic-excited states relative to ground states by electron-acceptor ability: $NO_2 > C_6H_5CO > EtO_2C$; and electron donor ability: $EtNH > NH_2$.



(8a) Y = CO_2Et
COC_6H_5
NO_2
(8b)



(9a) X = H
NO_2
(9b)

Phenomenology Contributing to Hydrogen Bonding Effects.—Substituent effects on the phenomena influencing the susceptibility of $\nu(i)_{\text{max.}}$ to solvent HBA basicities are more complex and need to be unravelled. We consider that four main factors contribute to the *b*-coefficient: (a) the number of type-B hydrogen bonds by the amine protons of the indicator to the solvent; (b) the HBD acidity of the indicator and its influence on the strengths of the hydrogen bonds; (c) the effect on the electronic transition of the increase in ground-state electron density on the amine nitrogen which is caused by the hydrogen bonding; and (d) the strong bathochromic effects of changes in hybridization on the amine nitrogen induced by hydrogen bonding. It is useful to consider these factors in terms of contributions of solvated canonical structures (8a—b) and (9a—b) to ground and electronic-excited states.†

(a) By comparing 4-nitroaniline (6) with its *N*-alkyl derivatives, we showed in an earlier paper that (6) forms two hydrogen bonds to HBA solvents, that the first and second hydrogen bond strengths are in a ratio of *ca.* 1.5 to 1, and that their spectral effects are in a ratio of 1/(0.93 ± 0.13).[6] There are minor differences in the details of the comparison of *m*-nitroaniline (4) with its *N*-ethyl derivative (5), *e.g.* the *b*-value for (4) is somewhat less than double that for (5).‡ However, the general conclusion remains the same. *m*-Nitroaniline forms two hydrogen bonds to HBA solvents whose strengths and contributions to the *b*-coefficients are not markedly dissimilar.

(b) We have shown[1] that the *HBA basicity of the solvent* influences the $-\Delta\Delta\nu(i\text{-}\pi^*)^{B}{}_{\leftarrow H_2N}$ term through its effect on the hydrogen bond strength (the stronger hydrogen bonds stabilizing electronic excited states resembling (8b),(9b) to a greater extent than ground states resembling (8a),(9a), and it might be expected that *HBD acidity of the indicator solute* should have an exactly analogous effect. However, comparison of the *b* and VF_{50} values in Table 3 shows clearly that relative indicator HBD acid strengths are not the dominant factor influencing the *b*-terms.

(c) One way of looking at the mechanism by which the hydrogen-bond influences $\nu_{\text{max.}}$ is that it increases ground-state electron density on amine nitrogen, thereby making the nitrogen a better electron donor. We have mentioned that transition energies of $[^+X{=}C(1){\rightarrow}C(4){=}Y^-]$ electronic transitions decrease with increasing electron-donor ability of X, and it will be shown that similar effects apply with $[^+X{=}C(1){\rightarrow}C(3){=}Y^-]$ electronic transitions. We can then pose the question ' If isolable from other factors, what is the effect of a given increase in ground state electron density on the amine nitrogen on the transition energies of indicators (1)—(7)? ' The greater the effect, the greater should be the indicator β-value.

An alternative way of increasing ground-state electron density on amine nitrogens, which is less obscured by other contributing effects, is by alkylation, so that it is instructive to compare the effects of *NN*-dialkylation on ν_0 of compounds (1), (2), (4), and (6). Here we do see an order of effects which parallels the order of *b* values in Table 3: (1) > (6) > (4) > (2). The question of why type-B hydrogen bonding and *NN*-dialkylation should

	ν_0	$-\Delta\nu_0$
$4\text{-}NO_2C_6H_4\text{-}NH_2$ (6)	31.10	
$\text{-}NMe_2$	28.10	3.00
$\text{-}NEt_2$	27.52	3.58
$3\text{-}NO_2C_6H_4\text{-}NH_2$(4)	28.87	
$\text{-}NEt_2$	25.52	3.25
$4\text{-}PhCOC_6H_4\text{-}NH_2$ (2)	33.09	
$\text{-}NMe_2$	30.40	2.69
$4\text{-}EtO_2C_6H_4\text{-}NH_2$ (1)	36.85	
$\text{-}NMe_2$	33.31	3.54

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† Structure (9b) is a ' bond pusher's ' way of accommodating Murrell's suggestion that absorption bands near 400 nm for *o*-, *m*-, and *p*-nitroaniline derive from similarly founded electronic transitions.[7] We will deal with this matter further in a future paper on the nature of *meta*-interactions.

‡ The differences between the *b*(4)/*b*(5) and *b*(6)/*b*(7) ratios may derive from differing geometric relationships between the ground-state dipole directions and the directions of the electronic transitions; see discussion in ref. 6.

both cause greater bathochromic shifts with (1) than with (6) leads us to the next factor to be examined, effects of hydrogen bonding (and *NN*-dialkylation) on hybridization on amine nitrogens, and effect of changing hybridization on the solvatochromic coefficient, *b*.

(d) A wealth of evidence indicates that hybridization on aromatic amine nitrogens is intermediate between sp^2 and sp^3, approaching sp^2 with strong mesomeric electron-acceptor substituents X and Y in structures (8a) and (9a), and nearer sp^3 in unsubstituted aniline or $\text{YC}_6\text{H}_4\text{–NH}_2$, where Y is an electron-donor substituent.

Evidence is also available that replacing protons on amine nitrogens by alkyl groups [and by the analogy in (c), hydrogen bonding by amine protons] introduces a strong tendency in the direction of sp^2 hybridization. Finally, there seems no question that rehybridization toward sp^2 is strongly bathochromic. Information in support of these observations from the literature and from our own findings is as follows.

(1) Strametz and Schmitke [8] have calculated from u.v. spectra that for aniline, the inversion angle α [the angle between the C(1)–N bond and the bisector of the plane of the amine group] is 39°, compared with $\alpha = 0°$ for sp^2 and 54.74° for sp^3 hybridization.

(2) The one-bond $^{15}\text{N–}^1\text{H}$ coupling constant in aniline is found to be intermediate between those expected for tetrahedral and trigonal nitrogen, and electron-withdrawing groups cause an increase in $^1J(^{15}\text{N–}^1\text{H})$. These observations have been interpreted by Axenrod and his co-workers [9] in terms of a change in hybridization on nitrogen toward sp^2. These workers also report that *N*-methylation and ethylation of aniline also lead to increased $^1J(^{15}\text{N–}^1\text{H})$ values and, continuing the analogy between *N*-alkylation and hydrogen bonding, Paolillo and Becker have shown that the coupling constant in aniline increases similarly with increasing HBA basicity of the solvent.[10]

(3) In a similar vein, Wasylishen [11] has estimated hybridization on amine nitrogens from $^{15}\text{N–}^{13}\text{C}$ spin–spin coupling constants. He has estimated $J(^{15}\text{N–}^{13}\text{C})$ for sp^3 and sp^2 hybridization to be 8.1 and 15.7 Hz, respectively, and has reported $J(^{15}\text{N–}^{13}\text{C})$ values of 10.9—12.1 (solvent dependent, higher in HBA solvents) for aniline and 14.9—15.0 for 4-nitroaniline.

(4) Smith [12] has reported, and Cumper and Singleton [13] have confirmed from electric-dipole measurements that θ [the angle at which the dipole is inclined from the C(1)–N bond] (in benzene) is: for aniline, 48.5°; for *N*-methylaniline, 38.5°; for *NN*-dimethylaniline, 30°. Aroney and his co-workers [14] prefer Marsen and Sutton's [15] θ-estimate of 43° for aniline, and also indicate that hybridization is nearer sp^2 in dimethylaniline.

(5) By way of contrast, Aroney and his co-workers [16] conclude from molecular polarizability studies that θ is very near zero for 4-nitroaniline, and hybridization is very near sp^2.

(6) Total crystal structures have been reported by Mak and Trotter for *NN*-dimethyl-4-nitroaniline [17] and by Delugeard and Messager for *NN*-dimethyl-3-nitroaniline.[18] In both instances the three angles about the amine nitrogens totalled 360 ± 1.0°, *i.e.* very near sp^2 hybridization.

(7) In contrast with the $+\Delta\Delta\nu$ value of +2.26 kK (hypsochromic) for 3-nitroaniline (Table 3), the $\Delta\Delta\nu(i\text{-}\pi^*)$-($\text{CF}_3\text{CH}_2\text{OH}$) value for *NN*-dimethyl-3-nitroaniline is −0.13 kK, *i.e.* experimentally bathochromic, but probably *nil* within experimental error.[1] We interpret this to mean that hybridization is intermediate between sp^2 and sp^3 in (4), and very near sp^2 in the dimethyl derivative.

(8) The effect of rehybridization toward sp^2 is strongly bathochromic, as increasing p–π orbital overlap stabilizes excited states resembling (8b),(9b) to a far greater extent than ground states more closely resembling (8a),(9a). Compare, for example, the ν_0 values which we have reported for the *N*-(4-nitrophenyl)polymethyleneimines,[19] $4\text{-NO}_2\text{–C}_6\text{H}_4\text{–}\overline{\text{N–(C}}\text{H}_2)_n$ (n = 2—6). The enhanced red shifts for the azetidine, pyrrolidine, and piperidine in trifluoroethanol reflect the bathochromic effects of type-A hydrogen bonding by trifluoroethanol to the nitro oxygens,[20] *i.e.* $-\Delta\Delta\nu(i\text{-}\pi^*)^{\text{A}}{}_{\rightarrow\text{O}_2\text{N}}$. From the ν_0 results, we infer that the effect of rehybridization from $sp^{3.0}$ to $sp^{2.0}$ for a 4-nitroaniline derivative should be bathochromic by *ca.* 3—4 kK.

	ν_0/kK	$+\Delta\Delta\nu$/kK ($\text{F}_3\text{CCH}_2\text{OH}$)	Hybridization on nitrogen
N-(4-Nitrophenyl)-aziridine	32.11	+3.21	$sp > 3$
-azetidine	28.17	−0.41	near sp^2
-pyrrolidine	27.56	−0.53	near sp^2
-piperidine	27.93	−0.81	near sp^2

Rationalization of the Relative b-*Values*.—Bringing all the above observations together, we interpret the relative *b*-values in Table 3 as follows. Taking 4-nitroaniline (6) as the reference, we consider that the conformation about amine nitrogen is already very near trigonal in non-HBA solvents, so that there is very little effect of rehybridization in HBA solvents. The *b*-value of 2.79 derives from a reasonably strong HBD acidity coupled with a reasonably strong bathochromic effect of increasing electron density on nitrogen.

With ethyl 4-aminobenzoate (1) despite a probably relatively very much weaker HBD acidity, strong rehybridization toward sp^2 in HBA solvents leads to a higher *b* value of 3.01 (and a greater bathochromic effect of dimethylation) than with (6). With 4-aminobenzophenone (2), the *b*-value of 2.14 is probably a consequence of the *b*-lowering effect of the weaker hydrogen bonds to HBA solvents [compared with (6)] more than offsetting the *b*-hightening effect of rehybridization which is intermediate between (1) and (6).

Strengths of hydrogen bonds to HBA solvents and the amount of rehybridization are greater for 3,5-dinitroaniline (3) than for 4-nitroaniline (6), but the bathochromic effect of a given increase in amine electron-donor ability is probably very much lower for the $[^+\text{H}_2\text{N=C(1)}\rightarrow\text{C(3,5)=NO}_2{}^-]$ electronic transition than for the $[^+\text{H}_2\text{N=C(1)}\rightarrow\text{C(4)=NO}_2{}^-]$ transition. The latter effect is also strongly suggested by the lesser sensitivity to solvent polarity [the lower s value of 1.42 for (3) in Table 3, compared with 3.14 for (6)]. The first two effects and the third just about offset one another, with the result that the b-values are quite similar for (3) and (6). The slightly lower b-value for 3-nitroaniline (4) compared with (3) results from the weaker hydrogen-bond strengths more than offsetting the effect of the greater rehybridization in HBA solvents.

New and Amended β-*Values*. We have used the present correlations to determine β-values for several additional solvents and to amend the earlier values. The new values are included together with the old in Table 1. As might be expected, if the correlations are redone using these new and revised parameters, correlation coefficients and standard deviations are improved significantly over the already excellent results in Table 2.

The new results for the aromatic solvents are of particular interest. Although type-B hydrogen bonding to aromatic π-systems is well documented,[21,22] band-overlap problems had caused us to overlook weak HBA basicity effects of the aromatic solvents in previous solvatochromic comparisons,[3,4] wherein we had included toluene [solvent (8)], benzene (14), and chlorobenzene (15) among the non-hydrogen bond acceptors. However, the present results and findings to be reported in future papers have consistently indicated small but real $-\Delta\Delta\nu$ terms attributable to type-B hydrogen bonding by HBD indicators to (8), (14), (15), and bromobenzene (33), with the magnitudes of the effects often showing rough parallelisms with substituent σ_p values.

This trend is shown in Table 4 and Figure 3, with β and σ_p values also included for anisole (17) and NN-dimethylaniline. The latter β-value was estimated from $\mathrm{p}K_{\mathrm{HB}} = 0.45$,[23] and the correlation equation reported earlier,[3] $\beta = (\mathrm{p}K_{\mathrm{HB}} + 1.00)/4.44$.

TABLE 4

Variation of aromatic solvent β-values with σ_p.

Solvent C_6H_5X, X =	σ_p [a]	β
Br	0.232	0.062
Cl	0.227	0.071
H	0.000	0.100
Me	−0.170	0.112
CH_3O	−0.268	0.223
Me_2N	−0.83	(0.334) [b]

[a] A. J. Gordon and R. A. Ford, 'The Chemist's Companion,' Wiley, New York, 1972, p. 145. [b] Estimated from $\mathrm{p}K_{\mathrm{HB}} = 0.45$; see text.

Our initial impulse had been to cite the rough linear relationship between the six β and σ_p values ($r = 0.962$), represented by the dashed line in Figure 2 as an indication that type-B hydrogen bonding by HBD solutes to anisole and NN-dimethylaniline might be to their π-systems. However, Wayland and Drago [22] have presented convincing evidence from i.r. studies that anisole forms two distinct 1 : 1 hydrogen-bonded complexes with phenol. One of these involves π-electron donation by the ring (in a plot of phenol O–H $\Delta\nu$ vs acceptor σ_p, the data point for this complex is co-linear with data points for toluene, benzene, chlorobenzene, bromobenzene, and benzyl chloride), while the other involves n-electron donation by the methoxy-group. Further, they estimated that, of a total phenol : anisole formation constant of 1.2 l mol^{-1}, $ca.$ 0.2—0.3 l mol^{-1} could be attributed to the π-complex.

From the latter estimate, and from the regression equation between β and log K_f for complex formation between phenol and HBA solvents,[3] $\beta = \log K_f + 1.00)/4.31$, we arrive at a β estimate of 0.081—0.122 for hydrogen bonding to the anisole π-system (represented by the X in Figure 3). On this basis, the relationship between β and σ_p for the π-bases in Figure 3 must be as represented by the solid regression line.

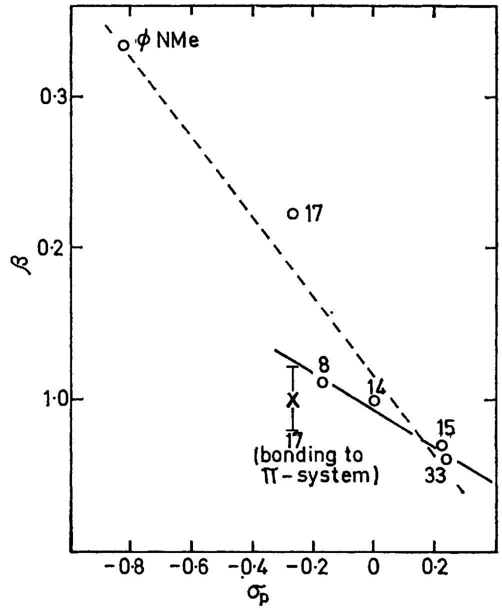

FIGURE 3 β-Values of C_6H_5X solvents plotted $vs.$ σ_p of X

EXPERIMENTAL

Indicators and solvents were commercially available and were purified by standard means to meet conventional spectrophotometric criteria of purity. Spectra were determined on a Cary model 14 spectrophotometer.

The effects of band overlap (usually with higher intensity higher energy bands), of hidden underlying lower-intensity bands, and of changing band shape with changing solvent, all of which we include in the term *spectral anomalies*, can cause shifts in $\nu_{\mathrm{max.}}$ of as much as 0.4—0.5 kK. We have attempted to minimize such complications by taking $\nu_{\mathrm{max.}}$ as the mid-point between the two positions on the spectral envelope where O.D. (optical density) = 0.9 O.D.$_{\mathrm{max.}}$. We consider that for 'well behaved' spectra, combined uncertainties due to *usual spectral anomalies* and experimental precision limits in measuring the spectra are $ca.$ 0.10 kK.

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