the darkly colored solution into water (150 ml). The aqueous system was extracted with ether (2 × 100 ml) and the ether solution was washed with saturated aqueous sodium chloride solution and then dried over anhydrous magnesium sulfate. Triethylamine (10 g) was added to the ether filtrate, followed by benzoyl chloride (10 g, 0.07 mol). The reaction mixture was stirred for 3 hr at room temperature, washed with water, and distilled. After removal of ether at atmospheric pressure, the residue was distilled under vacuum yielding ethyl benzoate, bp 45° (0.05 Torr), followed by **24**, bp 80° (0.03 Torr). The distillate quickly solidified, mp 79–80° (4.5 g, 44% yield). Compound **25**, bp 85–87° (0.05 Torr), was similarly prepared in 65% yield from *trans*-*N*-carbethoxy-2-isopropyl-3-methylaziridine. Compounds **26** (30% yield) and **27** [bp 83–85° (17 Torr)] were prepared similarly, substituting pivaloyl chloride for benzoyl chloride in the acylation step.

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Hydrogen Bonding by Protic Solvents to Nitro Oxygens. Effects on Electronic Spectra of Nitroaniline Derivatives

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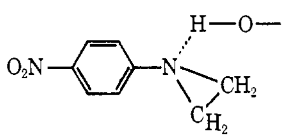
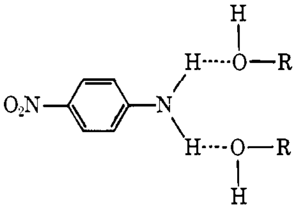
Abstract: Positions of uv maxima for *N*,*N*-diethyl-4-nitroaniline (**4**) in nonprotic solvents show good linear correlation with corresponding ν_{max} values for 4-nitroanisole (**5**). In proton-donor solvents, however, $\nu(\mathbf{4})_{max}$ values are shifted to the red relative to positions predicted from this linear relationship. These longer wavelength displacements $[-\Delta\Delta\nu(\mathbf{4}-\mathbf{5})^{A}{}_{\rightarrow NO_2}]$ are considered to be measures of the bathochromic influence of enhanced type-A hydrogen bonding *by* the protic solvents *to* the nitro oxygens of **4** compared with **5**. Magnitudes of the solvatochromic effects are related to solvent structures and acidities.

Earlier papers in this series dealt with spectral effects of two types of specific solvation phenomena involving hydroxylic solvents and nitroaromatic amine substrates: type-A hydrogen bonding,



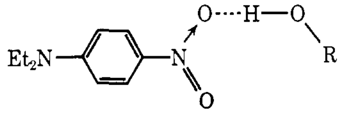
type-A hydrogen bonding *by* R-OH solvent *to* *N*-(4-nitrophenyl)aziridine (**1a**)



type-B hydrogen bonding *by* 4-nitroaniline (**2**) *to* R-OH solvent

wherein the solvent acts as proton donor and the amine nitrogen of the solute as acceptor (bonding *by* solvent *to* substrate); and type-B, wherein hydrogen bonding is *by* the amine protons of the solute *to* the solvent oxygen.[2–6] The effect of type-A solvation is to decrease ground state electron density on the amine nitrogen; hence it serves as a hypsochromic influence on the $[^{+}R_2N{=}C(1) \rightarrow C(4){=}NO_2^{-}]$ band in the uv spectrum.[7] Type-B hydrogen bonding has the converse effect; an increase in ground state charge density on the amine nitrogen results in a bathochromic displacement of the uv spectrum.[8,9]

In the present paper we will deal with the spectral consequences of still a third type of hydrogen-bonded complex formation which may occur in such systems. This again involves the solvent as proton donor, and thus represents another form of type-A bonding. Here, however, the oxygens of the nitro group are the proton acceptors. By decreasing ground state electron densities on the nitro oxygens (hence facilitating electronic transitions which feed charge into these sites), type-A hydrogen bonds to nitro would be expected to shift $[^{+}R_2N{=}C(1) \rightarrow C(4){=}NO_2^{-}]$ bands bathochromically.



type-A hydrogen bonding *by*R-OH solvent *to* nitro group oxygen of *N*,*N*-diethyl-4-nitroaniline (**4**)

Hammond and Modic[10] have postulated that such solvent-to-nitro bonding accounts for longer wavelength displacements in the spectrum of nitrobenzene on going from water to progressively stronger sulfuric

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[1] (a) Naval Ordnance Laboratory; (b) Engineer Topographic Laboratory.

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

[3] M. J. Kamlet, R. R. Minesinger, E. G. Kayser, M. H. Aldridge, and J. W. Eastes, *ibid.*, **36**, 3852 (1971).

[4] M. J. Kamlet, R. R. Minesinger, and W. H. Gilligan, *J. Amer. Chem. Soc.*, **94**, 4744 (1972).

[5] J. W. Eastes, M. H. Aldridge, and M. J. Kamlet, *J. Chem. Soc. B*, 922 (1969).

[6] M. J. Kamlet, *Isr. J. Chem.*, **1**, 428 (1963).

[7] J. C. Deardon and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).

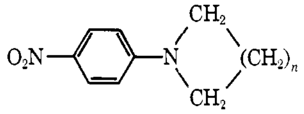
[8] J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963).

[9] B. D. Pearson, *Proc. Chem. Soc., London*, 78 (1962).

[10] G. S. Hammond and F. J. Modic, *J. Amer. Chem. Soc.*, **75**, 1385 (1953).

acid solutions. More recently, Taft and coworkers' pK_{HB} studies[11,12] have provided evidence that even relatively weakly acidic proton donors form hydrogen-bonded complexes with aromatic nitro compounds, and that bond strengths are greater and formation constants significantly higher than might be expected from simple pK_a comparisons.[13]

We demonstrated type-A bonding to amine nitrogen by comparing spectra of the *N*-(4-nitrophenyl)-polymethylenimines, **1a–d**, in a variety of solvents.[3]



1a, $n = 0$; $pK_a = ca.\ 1.1$
b, $n = 1$; $pK_a = 0.34$
c, $n = 2$; $pK_a = -0.42$
d, $n = 3$; $pK_a = 2.46$

In the cases of *N*-(4-nitrophenyl)azetidine (**1b**), -pyrrolidine (**1c**), and -piperidine (**1d**), all of which are near-sp^2 hybridized on the amine nitrogens, but which differ by 2.9 p*K* units in basicity,[14] excellent linear correlations between corresponding ν_{max} values were found for spectra in both hydroxylic and nonhydroxylic solvents.[15] This indicated that there were no *differential* solvent association effects involving the proton-donor solvents and the more basic substrates.

With *N*-(4-nitrophenyl)aziridine (**1a**), which is of intermediate basicity but is near-sp^3 hybridized on the amine nitrogen, good linear correlation with corresponding ν_{max} values for **1c** was again obtained for the spectra in the nonhydroxylic solvents. Here, however, spectra in the R–OH solvents did not conform with the linear relationship; ν_{max} values for **1a** were appreciably higher than required by the ν(**1a**) *vs.* ν(**1c**) correlation. Deviations from the correlation equation, $\Delta\Delta\nu(\mathbf{1a{-}1c})^{A}{}_{\rightarrow NR_2}$,[16] were greatest for water and the more acidic alcohols, and were taken as measures of the hypsochromic effect of type-A hydrogen bonding *by* the proton-donor solvents *to* the amine nitrogen of **1a**.[17]

Effects of type-B hydrogen bonding, which is reduced on N-alkylation and excluded on N,N-dialkylation, were evaluated as follows:[2] 4-nitroaniline (**2**), *N*-ethyl-4-nitroaniline (**3**), and *N*,*N*-diethyl-4-nitroaniline (**4**) show comparable red shifts ($-\Delta\nu$) on going from cyclohexane to CCl_4, $ClCH_2CH_2Cl$, or other more polar non-hydrogen-bond-acceptor solvents, indicating that the bathochromic influences of increasing solvent polarity or polarizability are similar for the three compounds. It follows that significantly enhanced longer wavelength shifts for **2** relative to **4** [$-\Delta\Delta\nu(\mathbf{2{-}4})$] or for **3** relative to **4** [$-\Delta\Delta\nu(\mathbf{3{-}4})$] on going to hydrogen-bond-acceptor solvents should be a consequence primarily of the bathochromic influence of type-B solvation. Values of $-\Delta\Delta\nu(\mathbf{2{-}4})^{B}{}_{\leftarrow H_2N}$ and $-\Delta\Delta\nu(\mathbf{3{-}4})^{B}{}_{\leftarrow HNR}$[16] were determined for a series of R–OH solvents and were found to arrange water and the alcohols in the "theoretical" basicity order. Indeed, good linear correlations were obtained between the $-\Delta\nu$'s and Taft σ^* values of R in R–OH.[2] More recently,[4] we also showed that $-\Delta\Delta\nu(\mathbf{2{-}4})^{B}{}_{\leftarrow H_2N}$ values for a variety of non-self-associating solvent types show remarkably good linear correlation with corresponding pK_{HB} and Δ values (logarithms of formation constants and limiting F-nmr shifts) for hydrogen-bonded complexes between the same bases and 4-fluorophenol as reported by Taft and coworkers.[11,12,18–20]

Results and Discussion

Our evidence for type-A hydrogen bonding to nitro oxygens will take the same form as was used to document solvent bonding *to* aziridine nitrogen. First a linear interrelationship with a high correlation coefficient will be shown to exist between corresponding ν_{max} values for two related substrates in a large number of aprotic solvents. Then ν_{max} values in a number of protic solvents will be shown to deviate from the correlation equation by statistically significant amounts. Finally, the relative magnitudes of the deviations will be shown to bear meaningful relationships with chemical structures and other independently established properties of the hydrogen-bond-donor solvents.

The linear interrelationship in the non-hydrogen-bond-donor solvents is between ν_{max} values for the corresponding electronic transitions[21] of *N*,*N*-diethyl-4-nitroaniline (**4**) and 4-nitroanisole (**5**). Data are assembled in Table I and plotted in Figure 1 (open circles) for spectra in 20 solvents; λ_{max} values cover a 46.5-nm range (3.10 kK) for **4** and a 22.5-nm range (2.43 kK) in the case of **5**, and the precision of the determinations is ± *ca.* 0.5 nm.

Least-squares treatment of the 20 data sets yields the correlation equation

$$\nu(\mathbf{4})_{max} = 1.278\nu(\mathbf{5})_{max} - 16.23 \text{ kK} \qquad (1)$$

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[11] R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *J. Amer. Chem. Soc.*, **91**, 4801 (1969).

[12] D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969).

[13] We have found Taft's pK_{HB} scale[11] extremely valuable in providing a quantitative context for the effects to be described here. The nitro oxygens of nitrobenzene ($pK_{HB} = 0.73$) have hydrogen bonding basicity comparable to dioxane ($pK_{HB} = 0.71$). Judging from other substituent effects reported by Taft,[11] the 4-diethylamino derivative **4** should show hydrogen-bond-acceptor properties on oxygen comparable to tetrahydrofuran (*i.e.*, $pK_{HB} = ca.\ 1.3$).

[14] J. W. Eastes, M. H. Aldridge, R. R. Minesinger, and M. J. Kamlet, *J. Org. Chem.*, **36**, 3847 (1971).

[15] Spectra of **1c**, the least basic of the polymethylenimines, were taken as the references against which other spectral displacements were compared. Excellent linear correlations were also obtained between corresponding ν_{max} values for *N*,*N*-dimethyl-4-nitroaniline and **1c**.

[16] The nomenclature used in our earlier papers becomes confusing and cumbersome when several types of hydrogen bonding with concomitant effects occur simultaneously. Hence, it appears to be appropriate at this point to introduce a new nomenclature system 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 (**1a–1c**) indicate that the reduced or enhanced effect is for compound **1a** relative to **1c**; the superscript A indicates that the effect is attributed to type-A hydrogen bonding; and the subscript $\rightarrow NR_2$ indicates that bonding is *by* solvent *to* amine nitrogen. Alternative subscripts in this nomenclature system are $\rightarrow O_2N$, indicating bonding *by* solvent *to* nitro oxygen, and $\leftarrow H_2N$, indicating bonding *by* amine protons *to* solvent.

[17] It was concluded that type-A solvation of aromatic amines depends primarily on the nature of the hybridization on nitrogen. Bonding is apt to occur where hybridization is near-sp^3, but not where near-sp^2 even under circumstances where the latter type compound might prove to be more basic toward complete proton transfer (*e.g.*, **1d** has a higher pK_a than **1a** in water, but **1a** is by far the better H-bond acceptor).

[18] L. Joris, J. Mitsky, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 3438 (1972).

[19] J. Mitsky, L. Joris, and R. W. Taft, *ibid.*, **94**, 3442 (1972).

[20] In both instances[2,4] good linear correlations were also obtained using sets of $-\Delta\Delta\nu^{B}{}_{\leftarrow HO}$ values, derived by comparing solvatochromic shifts for 4-nitrophenol and 4-nitroanisole.

[21] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapter 12.

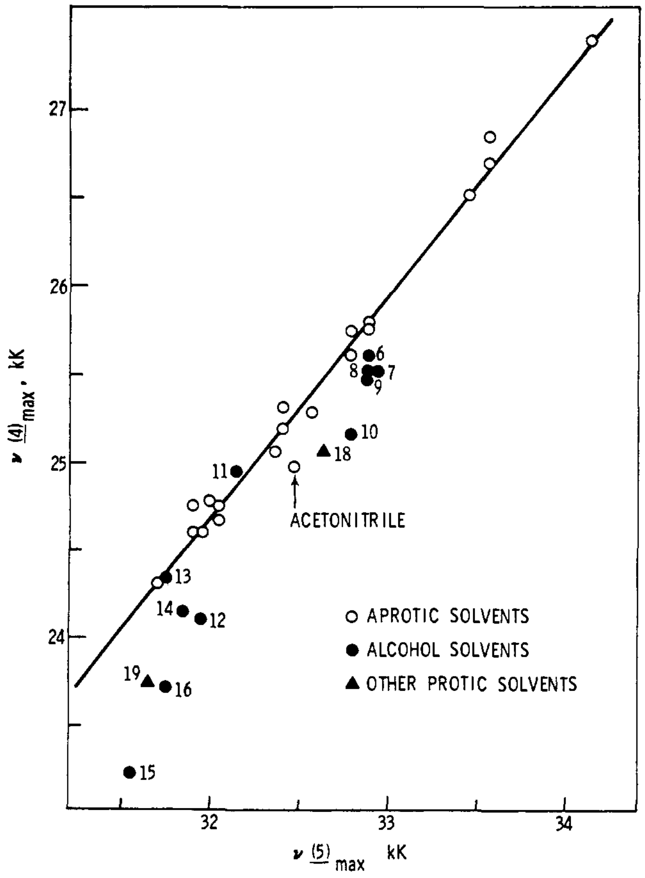

Figure 1. Positions of uv maxima for *N*,*N*-diethyl-4-nitroaniline (**4**) in nonprotic and protic solvents plotted against corresponding $\nu_{\max}$ values for 4-nitroanisole (**5**).

Table I. Absorption Spectra of 4-Nitroanisole (**5**) and *N*,*N*-Diethyl-4-nitroaniline (**4**) in Aprotic Solvents

Solvent	$\lambda(\mathbf{5})_{\max}$, nm	$\nu(\mathbf{5})_{\max}$, kK	$\lambda(\mathbf{4})_{\max}$, nm	$\nu(\mathbf{4})_{\max}$, kK
Cyclohexane	293	34.13	365	27.40
Carbon tetrachloride	298	33.56	374.5	26.70
1,2-Dichloroethane	309	32.36	399	25.06
Hexamethyl-phosphoramide	313.5	31.90	404	24.75
Triethyl phosphate	308.5	32.41	397	25.19
Dimethyl sulfoxide	315.5	31.70	411.5	24.30
N,*N*-Dimethylacetamide	312	32.05	404	24.75
N-Methylpyrrolidone	313.5	31.90	406.5	24.60
Dimethylformamide	312	32.05	405.5	24.66
Pyridine	312.5	32.00	403.5	24.78
Butyrolactone	313	31.95	406.5	24.60
Tetrahydrofuran	305	32.79	390.5	25.61
Tetrahydropyran	304	32.89	388.5	25.74
Ethyl acetate	305	32.79	388.5	25.74
Acetonitrile	308	32.47	400.5	24.97
Dibutyl ether	298	33.56	372.5	26.85
Diethyl ether	299	33.45	377	26.52
Dioxane	304	32.89	388	25.77
Ethyl chloroacetate	307	32.57	395.5	25.28
Anisole	308.5	32.41	395	25.31

with r (the correlation coefficient) $= 0.992$, Sd (the standard deviation) $= 0.11$ kK, and only the single data set for acetonitrile deviating from correlation by more than 2 standard deviations.[22] If the acetonitrile results are excluded from the least-squares treatment, the equation becomes

$$\nu(\mathbf{4})_{\max} = 1.273\nu(\mathbf{5})_{\max} - 16.02 \text{ kK} \qquad (2)$$

with $r = 0.994$ and Sd $= 0.09$ kK. Both pairs of r and Sd values correspond to excellent linear correlation.

Positions of the maxima in the protic solvents are assembled in Table II and plotted as filled data points in Figure 1. Also listed in the table is a set of $\nu(\mathbf{4})_{\mathrm{eq}\ 2}{}^{\mathrm{calcd}}$ values derived from the corresponding data for 4-nitroanisole and the correlation equation for the nonprotic solvents, as well as the term, $-\Delta\Delta\nu(\mathbf{4}\text{–}\mathbf{5})^{\mathrm{A}}{}_{\rightarrow\mathrm{O_2N}}$, representing differences between $\nu(\mathbf{4})_{\max}{}^{\mathrm{obsd}}$ and $\nu(\mathbf{4})_{\mathrm{eq}\ 2}{}^{\mathrm{calcd}}$.

It is seen that, with the exception of 2-phenylethanol (**11**) and benzyl alcohol (**13**), which fit eq 2 quite well, there is a consistent trend in the hydroxylic solvents toward lower $\nu_{\max}$ values for *N*,*N*-diethyl-4-nitroaniline than would be predicted if effects involving the solvent as proton donor were excluded. Magnitudes of the $-\Delta\Delta\nu(\mathbf{4}\text{–}\mathbf{5})^{\mathrm{A}}{}_{\rightarrow\mathrm{O_2N}}$ term amount to between 2 and 4 standard deviations of eq 2 in two cases, and more than 4 Sd's in all other instances, and appear to be greatest with the more acidic alcohols and water. Hence, the nonconformance of the spectra in the protic solvents with eq 2 must be taken to be statistically significant and attributable to a specific solvent association effect (providing, of course, that we can offer a satisfactory rationale for the differing behavior of **11** and **13** from the other R–OH solvents).

We believe that the observed noncolinearity of the protic with the aprotic solvent data arises from bathochromic displacements of the spectra of **4** relative to predictions from eq 2, with the effect attributable to enhanced type-A hydrogen bonding *by* the protic solvents *to* the nitro group oxygens of **4** compared with **5** [as is succinctly stated in our new nomenclature[16] by $-\Delta\Delta\nu(\mathbf{4}\text{–}\mathbf{5})^{\mathrm{A}}{}_{\rightarrow\mathrm{O_2N}}$]. It is necessary, however, to exclude an alternative possibility which could also account for the observed results. This second possibility involves a hypsochromic displacement of the spectra of **5** relative to predictions from eq 2, with the latter effect arising from enhanced type-A hydrogen bonding *by* protic solvents *to* the methoxyl oxygen of **5** as compared with the amine nitrogen of **4**, *i.e.*,[16] $\Delta\Delta\nu(\mathbf{5}\text{–}\mathbf{4})^{\mathrm{A}}{}_{\rightarrow\mathrm{OCH_3}}$.[23]

Fortunately, the data of Taft, *et al.*,[11] allow a clear

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(22) Our experience has been that acetonitrile falls out-of-line in a number of correlations involving solvent effects on the spectra of nitro compounds; see, for example, footnote 4 of ref 4. Also, excellent linear correlations exist between $\nu_{\max}$ values for **4** and **5** in the nonprotic solvents and Dimroth's corresponding E_{T} values for betaine charge transfer complexes [K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); see also F. W. Fowler and A. R. Katritzky, *J. Chem. Soc. B*, 460 (1971); we are grateful to a referee for pointing this out, and will comment on this in greater detail in a subsequent paper], but again the acetonitrile data fall seriously out-of-line in both correlations.

(23) This second possibility would appear to go against conventional thinking in that it would involve an OCH_3 group in **5** which is seemingly more basic than the $N(C_2H_5)_2$ group in **4**. However, as we have already mentioned,[17] near-sp^2 hybridized amine nitrogens like that in **4** do not appear to participate in spectroscopically measurable type-A hydrogen bonds,[3] and it is not unreasonable that hybridization on the methoxyl oxygen of **5** might be more favorable toward such complexing. Further, Taft and coworkers[11,12] have shown that basicities of different classes of compounds toward H-bond formation ($\mathrm{p}K_{\mathrm{HB}}$'s) do not necessarily parallel basicities toward complete proton transfer. Thus, for example, acetone and diethyl ether have higher $\mathrm{p}K_{\mathrm{HB}}$'s than dimethylaniline,[12] and neat *tert*-butyl alcohol is a stronger hydrogen bond base than *n*-butylamine (unpublished information; to be reported in a subsequent paper of this series). Hence, to whatever slight extent type-A solvent association occurs in either instance, it is not unreasonable that the OCH_3 group in **5** would be a better acceptor than the $N(C_2H_5)_2$ group in **4**.

Table II. Absorption Spectra of 4-Nitroanisole (**5**) and *N*,*N*-Diethyl-4-nitroaniline (**4**) in Protic Solvents

No.	Solvent	$\lambda(\mathbf{5})_{max}$, nm	$\nu(\mathbf{5})_{max}$, kK	$\lambda(\mathbf{4})_{max}$, nm	$\nu(\mathbf{4})_{max}{}^{obsd}$, kK	$\nu(\mathbf{4})_{eq\ 2}{}^{calcd}$, kK	$-\Delta\Delta\nu$-$(\mathbf{4}-\mathbf{5})^{A}{}_{\rightarrow O_2N}$, kK
6	*tert*-Butyl alcohol	304	32.89	390.5	25.61	25.85	0.24
7	Isopropyl alcohol	303.5	32.94	392	25.51	25.92	0.41
8	*n*-Butyl alcohol	304	32.89	392	25.51	25.85	0.34
9	Ethanol	304	32.89	392.5	25.48	25.85	0.37
10	Methanol	305	32.79	397.5	25.16	25.73	0.57
11	Phenylethanol	311	32.15	401	24.94	24.91	Nil[a]
12	Ethylene glycol	313	31.95	415	24.10	24.65	0.55
13	Benzyl alcohol	315	31.75	411	24.33	24.39	Nil[a]
14	Chloroethanol	314	31.85	414	24.15	24.52	0.37
15	Water	317	31.55	430.5	23.23	24.13	0.90
16	Trifluoroethanol	315	31.75	421.5	23.72	24.39	0.67
18	Acetic acid	306.5	32.63	399	25.06	25.52	0.46
19	Formamide	316	31.65	421.5	23.72	24.26	0.54

[a] Within precision of the measurements.

choice between the $-\Delta\Delta\nu(\mathbf{4}-\mathbf{5})^{A}{}_{\rightarrow O_2N}$ and $\Delta\Delta\nu$-$(\mathbf{5}-\mathbf{4})^{A}{}_{\rightarrow OCH_3}$ possibilities. The equilibrium constant for hydrogen-bonded complex formation with 4-fluorophenol is five times greater for nitrobenzene ($pK_{HB} = 0.73$) than for anisole ($pK_{HB} = 0.02$).[24] Further, judging from pK_{HB} values for nitro, methoxy, and dimethylamino derivatives of benzaldehyde and benzonitrile,[11] the K_f values should be higher by factors of 3–5 for bonding to the nitro oxygens of **4** and **5** as compared with nitrobenzene, and lower by a factor of 5–10 for bonding to the methoxyl oxygen of **5** as compared with anisole. Thus, while both of the above types of complex formation are possible, type-A bonding *by* protic solvents *to* nitro groups of **4** and **5** should dominate over bonding *to* methoxyl or amine groups of these same molecules by factors of several hundred to one.[25]

Many of the same alcohol solvents which demonstrate the bathochromic effect of solvent bonding to nitro in the present work had been used in our earlier studies to show the hyposchromic effect of type-A hydrogen bonding to *N*-(4-nitrophenyl)aziridine (**1a**) [compared with *N*-(4-nitrophenyl)pyrrolidine (**1c**)].[3] Since the magnitudes of both effects would be expected to reflect relative hydrogen-bond-donor abilities of the solvents, it is of interest to compare the $-\Delta\Delta\nu(\mathbf{4}-\mathbf{5})^{A}{}_{\rightarrow O_2N}$ and $\Delta\Delta\nu(\mathbf{1a}-\mathbf{1c})^{A}{}_{\rightarrow NR_2}$ values in the various media.[26] The data are tabulated in Table III, together with σ^* values of R in R–OH. For reasons which will be detailed in a subsequent paper (wherein we will suggest methods of unravelling multiple solvatochromic effects when solvation occurs simultaneously at several sites), the $\Delta\Delta\nu(\mathbf{1a}-\mathbf{1c})^{A}{}_{\rightarrow NR_2}$ values have been amended somewhat from results reported in ref 3.

Table III. Solvatochromic Shifts Attributable to Hydrogen Bonding by Protic Solvents

No.	Solvent, R–OH, R =	σ^* of R	$-\Delta\Delta\nu$-$(\mathbf{4}-\mathbf{5})^{A}{}_{\rightarrow O_2N}$, kK	$\Delta\Delta\nu$-$(\mathbf{1a}-\mathbf{1c})^{A}{}_{\rightarrow NR_2}$, kK[a]
6	$(CH_3)_3C$	−0.30	0.24	0.60 (0.79)
7	$(CH_3)_2CH$	−0.19	0.41	0.34 (0.65)
8	n-C_4H_9	−0.13	0.34	
9	C_2H_5	−0.10	0.37	0.34 (0.62)
10	CH_3	0.00	0.57	0.36 (0.80)
11	$C_6H_5CH_2CH_2$	+0.08	Nil	0.66 (0.66)
12	$HOCH_2CH_2$	+0.20	0.55	0.57 (1.02)
13	$C_6H_5CH_2$	+0.22	Nil	0.84 (0.84)
14	$ClCH_2CH_2$	+0.38	0.37	
15	H	+0.49	0.90	1.33 (2.17)
16	CF_3CH_2	+0.92	0.67	2.49 (3.21)

[a] Modified somewhat from values cited in ref 3 (which are given in parentheses). See text.

It is evident from Table III that the solvatochromic effects do not follow any quantitative Taft-type ρ–σ^* relationship in either case (possibly because of steric factors and varying sizes of the solvating clusters), but that both trends appear to be toward larger effects (stronger solvation) the more acidic the R–OH solvents, with the influence of acidity more pronounced for the $\Delta\Delta\nu(\mathbf{1a}-\mathbf{1c})^{A}{}_{\rightarrow NR_2}$ solvatochromic shift.

The differing relative effects of water and trifluoroethanol with the two types of hydrogen-bond-acceptor substrates are of particular interest. As expected, trifluoroethanol is a significantly better proton donor than water toward the aziridine nitrogen of **1a**. In marked contradistinction, however, the hydrogen bond *to* the nitro group of **4** appears to be stronger with water than with trifluoroethanol. We believe that these contrasting results may be explained on the basis of a stable cyclic doubly bonded complex between a water cluster and **4** (*e.g.*, **17a**), where the corresponding doubly bonded complex with trifluoroethanol clusters (**17b**) would be sterically less favorable.

Also to be noted in Table III is the differing behavior of the two aralkyl R–OH solvents, 2-phenylethanol (**11**) and benzyl alcohol (**13**), toward the two types of hydrogen-bond-acceptor substrates. Both show normal effects, commensurate with their σ^* values, in hydrogen-bond donation to the aziridine nitrogen of **1a**, but neither appears to form spectroscopically measurable hydrogen bonds to the nitro oxygens of **4**.

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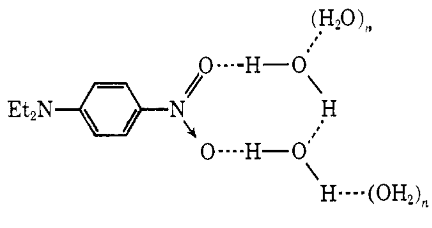
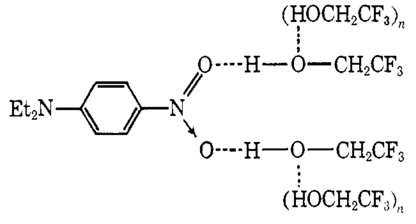
(24) Taft, *et al.*,[11] have also shown that equilibrium constants for H-bonding involving the aliphatic alcohols (methanol, ethanol, trifluoroethanol) as proton donors parallel those with 4-fluorophenol.

(25) Like 4-dimethylaminobenzaldehyde and 4-dimethylaminobenzonitrile, discussed by Taft, *et al.*,[11] **4** and **5** appear to be examples of compounds with multiple sites for protonation, more basic at the one site toward partial proton transfer and at the other site toward complete proton transfer. In a similar vein, it has been suggested that stabilization of nitroaniline nitroanion by solvation *at nitro* accounts for increases in acidity of nitroaniline indicators relative to hydrocarbon indicators with increasing water concentrations in aqueous DMSO solutions: E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, **89**, 2751 (1967).

(26) It should be kept in mind that the $\Delta\Delta\nu(\mathbf{1a}-\mathbf{1c})^{A}{}_{\rightarrow NR_2}$ data represent a total effect (*i.e.*, bonding to **1c** is *nil*), but that the $-\Delta\Delta\nu(\mathbf{4}-\mathbf{5})^{A}{}_{\rightarrow O_2N}$ values represent an effect which is enhanced in **4** relative to **5**, but which is probably still quite significant in **5**.



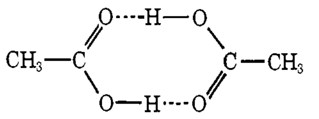
17a



17b

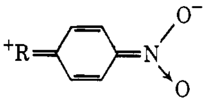
We consider that the conformance of **11** and **13** with eq 2 (behaving, in effect, like aprotic solvents) arises from preferential hydrogen bonding *by* these alcohols *to* the π-electron systems of their own benzene rings.[27] Although Taft and coworkers' pK_{HB} results for nitrobenzene and anisole,[11,12] cited above, would appear to indicate that a nitro group should normally be a stronger hydrogen-bond acceptor than an aromatic π system, self-association is probably favored in **11** and **13** on the basis of its being intramolecular. Reasonably strong internal hydrogen bonds to their own π-electron systems have been demonstrated (*via* infrared spectroscopy) for benzyl alcohol derivatives by Oki and Iwamura[28] and for 2-phenylethanols by Goldman and Crisler.[29] If this rationale is correct, the results for **11** and **13** in Table III provide the following information regarding the relative strengths of the hydrogen bonds under discussion: type-A bonding to aziridine nitrogen > intramolecular bonding to own π-electron system > type-A bonding to nitro.[30]

Also included in Table II as representative of other types of hydrogen-bond-donor solvents are $-\Delta\Delta\nu$-$(4\text{-}5)^{A}{}_{\rightarrow O_2N}$ results for acetic acid (**18**) and acetamide (**19**). A stable cyclic dimeric doubly bonded self-associating donor-acceptor system (**18a**) is the probable reason that **18** is not a better hydrogen-bond donor than the aliphatic alcohols or **19**. In a future paper we shall show that the lower-than-expected proton-donor ability of **18** toward $-\Delta\Delta\nu(4\text{-}5)^{A}{}_{\rightarrow O_2N}$ hydrogen bonding is accompanied by a greater-than-expected proton-acceptor ability toward $-\Delta\Delta\nu(2\text{-}4)^{B}{}_{\leftarrow H_2N}$ solvation (*e.g.*, the apparent pK_{HB} is higher for neat **18** than for dioxane).



18a

In conclusion, it remains only to suggest an explicit reason why solvent bonding *to* nitro should be stronger for *N*,*N*-diethyl-4-nitroaniline (**4**) than for 4-nitroanisole (**5**). Conventional resonance theory provides a completely adequate rationale in this regard. Bonding is stronger because ground state electron densities on the nitro oxygens are higher in **4** than in **5** which results, in turn, from the fact that the diethylamine group is a more effective mesomeric electron donor than methoxyl. Using Ingold's notation,[31] the +M effect is stronger for $(C_2H_5)_2N$ than for CH_3O, with the consequence that canonical structure **20a** is a more important ground state resonance contributor than **20b**.



20a, R = $(C_2H_5)_2N$
b, R = CH_3O

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[27] For a discussion of hydrogen-bond acceptor properties of the benzene π system, see G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, pp 22-24.

[28] M. Oki and H. Iwamura, *Bull. Chem. Soc. Jap.*, **32**, 955 (1959); **35**, 1552 (1962).

[29] I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958). Also of interest is intramolecular hydrogen bonding in the 1,2-diphenylethanol system: M. P. Servé and A. W. Bryant, *ibid.*, **36**, 3236 (1971).

[30] In this and earlier papers,[2-6] we have used solvatochromic shifts for the same electronic transition in different solvents as measures of relative hydrogen bond strengths *to* and *by* those solvents. This does not allow us to conclude, however, that hydrogen bonds *to* nitro oxygens and *to* aziridine nitrogens are of comparable strengths because the $-\Delta\Delta\nu(4\text{-}5)^{A}{}_{\rightarrow O_2N}$ and $\Delta\Delta(1a\text{-}1c)^{A}{}_{\rightarrow NR_2}$ values in Table III are of comparable absolute magnitudes. Such a conclusion would fail to take into account the markedly differing sensitivities of the $[{}^{+}R_2N{=}C(1) \rightarrow C(4){=}NO_2{}^{-}]$ electronic transition energies to changes in ground state electron densities at the different molecular sites.

[31] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Section II-7.