in 4 is similar to the 97.9-ppm C(2) resonance of vincorine,[4] the 3-ppm lower field value in the latter reflecting N_a-CH_3 substitution. Partial structure iii also is supported by the aromatic resonances of C(8')–C(13') observed in 4 which, with account taken for the C(11') substitution in 4, are in good agreement with the resonances of 10-methoxyindoline moieties.[3] We attribute the observed high-resolution mass spectral parent ion to 4, presumably a minor impurity in 1.

The two remaining methines which suffer minimal perturbation between 1 and 4 must belong to the A ring of the rauflexine residue. One of these shifts, 94.4 ppm, is diagnostic for a C(11) oxygen substituent[3] and establishes C(10) as the linkage site in this base. This is confirmed by the field position of the remaining aromatic methine, 124.1 ppm, which cannot be situated ortho to the oxygen-bearing carbon.

From these data, we conclude that the structure of flexicorine is as represented in formula 1 and that of its borohydride-reduced derivative is as shown in 4. To our knowledge, flexicorine is the first 10'-hydroxy-N_a'-unsubstituted indoline which preferentially exists in the oxidized iminoquinone form.

Experimental Section

^{13}C NMR spectra were recorded on a Varian XL-100-15 spectrometer operating at a ^{13}C radio frequency of 25.2 MHz in the Fourier transform mode. Deuteriochloroform or deuteriomethanol solutions of the substrates (0.005–0.2 M) were spun in 12-mm-o.d. tubes at 30 °C. The σ values of all compounds are referenced to the Me_4Si scale.

The preparation of 4 from flexicorine (1) was accomplished as follows. To 50 mg of 1 in CD_3OD contained in an NMR tube under an argon atmosphere was added excess $NaBH_4$ (15 mg) at 0 °C. The solution was warmed to room temperature and allowed to stand for 2 h. Two drops of concentrated HCl were added to complete the decomposition of excess $NaBH_4$. The argon-purged tube was capped, and the ^{13}C NMR spectra of 4 was recorded immediately. When the tube was opened 4 was converted to 5 rapidly.

Registry No. 1, 80765-85-1; 2, 70522-05-3; 3, 61091-18-7; 4, 80780-62-7; 5, 80765-86-2.

Linear Solvation Energy Relationships. 20. Intra- vs. Intermolecular Hydrogen Bonding by Some 2-Nitroaniline and 2-Nitrophenol Derivatives

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Received November 27, 1981

The solvatochromic comparison method is used to unravel and quantify effects of solvent dipolarity/polarizability and intra- and intermolecular hydrogen bonding on the electronic absorption spectra of 2-nitro-*p*-toluidine (1), *N*-methyl-2-nitro-*p*-toluidine (2), and 2-nitrophenol (3). Evidence is presented which indicates that 2 remains intramolecularly hydrogen bonded in solvents as strongly basic as *N*-methylpyrrolidone, whereas 3 breaks its *intra*molecular hydrogen bond to nitro to form an *inter*molecular hydrogen bond in even so weakly basic a solvent as anisole.

In earlier reports we have shown that when hydrogen-bonding effects are excluded, as when neither solutes nor solvents are *inter*molecular hydrogen-bond donors, solvent effects on p→π* and π→π* electronic spectral transitions are well described by the solvatochromic equation:

$$\nu(i)_{max} = \nu(i)_0 + s\pi^* \quad (1)$$

where π^* is a measure of solvent dipolarity/polarizability[1] (on a scale which ranges from −0.08 for *n*-hexane and 0.00 for cyclohexane to 1.00 for Me_2SO).[2-4] When the spectra are also influenced by solute to solvent (type B)[5] hydrogen-bonding effects, the form of the solvatochromic equation becomes:

$$\nu(i)_{max} = \nu(i)_0 + s\pi^* + b\beta \quad (2)$$

where β is a measure of solvent HBA (hydrogen-bond acceptor) basicity (on a scale ranging from 0.00 for non-HBA solvents to 1.05 for hexamethylphosphoramide).[2,6,7]

In part 2 of this series,[7] we used the solvatochromic comparison method and eq 1 and 2 to unravel and evaluate the effects of solvent dipolarity/polarizability[1] and type-B hydrogen bonding[5] on the UV–visible spectra of some 3- and 4-substituted and 3,5-disubstituted aniline derivatives. In the present paper we carry out a similar analysis of solvatochromic shift data for 2-nitro-*p*-toluidine (1), *N*-methyl-2-nitro-*p*-toluidine (2), and 2-nitrophenol (3). We offer evidence that the amine proton of 2 remains *intra*molecularly hydrogen bonded to the neighboring nitro oxygen in even such strong HBA base solvents as *N*-methylpyrrolidone (β = 0.77),[2] whereas 3 breaks its *intra*molecular hydroxyl to nitro hydrogen bond to form *inter*molecular type-B hydrogen bonds[5] to even such weak HBA base solvents as anisole (β = 0.22).[2] Spectral data

(1) The term solvent dipolarity is intended as a more specific description than the often misused solvent polarity, which has frequently included as well the effects of hydrogen-bonding interactions in varying combinations with the dipole/dipole effects.

(2) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

(3) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(4) Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

(5) 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.

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

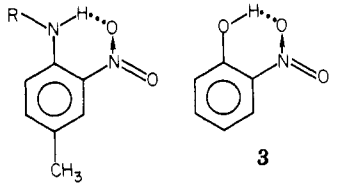
(7) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

Table I. Solvatochromic Shifts for Some Nitro Compounds

no.[a]	solvent[d]	π*	β	$\nu(1)_{max}$,[b] $cm^{-1} \times 10^3$	$\Delta\Delta\nu(1\text{-}\pi^*)$, $cm^{-1} \times 10^3$	$\nu(2)_{max}$,[b] $cm^{-1} \times 10^3$	$\nu(3)_{max}$, $cm^{-1} \times 10^3$	$\Delta\Delta\nu(3\text{-}\pi^*)$,[c] $cm^{-1} \times 10^3$
				Non-Hydrogen-Bonding Solvents				
1.	*n*-hexane	−0.08	nil	25.91		23.95	28.90	
2.	cyclohexane	0.00	nil	25.84		23.81	28.88	
6.	carbon tetrachloride	0.29	nil	25.19		23.34	28.69	
10.	trichloroethylene	0.53	nil	24.94			28.43	
12.	1,1,1-trichloroethane	0.49	nil				28.26	
20.	1,2-dichloroethane	0.81	nil	24.45		22.55	28.15	
				Hydrogen Bond Acceptor Solvents				
8.	toluene	0.54	0.11	24.81	−0.08	22.98		
9.	dioxan	0.55	0.37	24.43	−0.44	22.94		
11.	ethyl acetate	0.55	0.45	24.45	−0.42	22.99		
13.	tetrahydrofuran	0.58	0.55	24.21	−0.61	22.88		
14.	benzene	0.59	0.10	24.75	−0.05	22.91	28.37	+0.05
17.	anisole	0.73	0.22				28.47	+0.27
18.	acetone	0.71	0.48				28.88	+0.66
19.	triethyl phosphate	0.72	0.77	23.83	−0.76	22.66	29.63	+1.42
23.	*N,N*-dimethylacetamide	0.88	0.76				29.55	+1.49
25.	*N,N*-dimethylformamide	0.88	0.69	23.53	−0.79	22.37	29.28	+1.22
26.	hexamethylphosphoramide	0.87	1.05				29.58	+1.51
28.	*N*-methylpyrrolidone	0.92	0.77	23.47	−0.79	22.35		
29.	dimethyl sulfoxide	1.00	0.76	23.36	−0.77	22.20	29.32	+1.37
33.	bromobenzene	0.79	0.06				28.37	+0.23
39.	ethyl chloroacetate	0.70	0.35				28.74	+0.51
41.	cyclohexanone	0.76	0.53				28.88	+0.71

[a] Solvent numbering is the same in all papers of this series. [b] Reported earlier by Yokoyama, T; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1976**, *98*, 3233. [c] Determined at NSWC on a Cary Model 14 spectrophotometer. [d] The highest grade commercially obtainable solvents were used without further purification. We have found that in the absence of strong interactions involving the solute as hydrogen bond acceptor, where minor amounts of protonic impurities in nonprotonic solvents can have major effects, small amounts of impurities cause minimal shifts in positions of absorption maxima.

for 1–3 are given in Table I, together with solvent π* and β values.



1, R = H
2, R = CH_3

3

In unravelling and documenting solvent dipolarity/polarizability and hydrogen-bonding effects by the solvatochromic comparison method, it is necessary that three important conditions be fulfilled: (a) a plot of the property (ν_{max} in this case) against solvent π* values for a series of solvents of varying dipolarity, but wherein hydrogen bonding is excluded, should show linear regression with a statistically acceptable correlation coefficient ($r > 0.90$); (b) data points representing solvents in which hydrogen bonding occurs should be displaced from the regression line, all in the same direction and by statistically significant amounts; (c) the direction of the displacements should be consistent with the chemistry involved, and the relative magnitudes should reflect a reasonable order of solvent hydrogen bond donor strengths in the case of solvent to solute (type A) bonding, or solvent hydrogen bond acceptor strengths where the effects derive from solute to solvent (type B) hydrogen bonds.

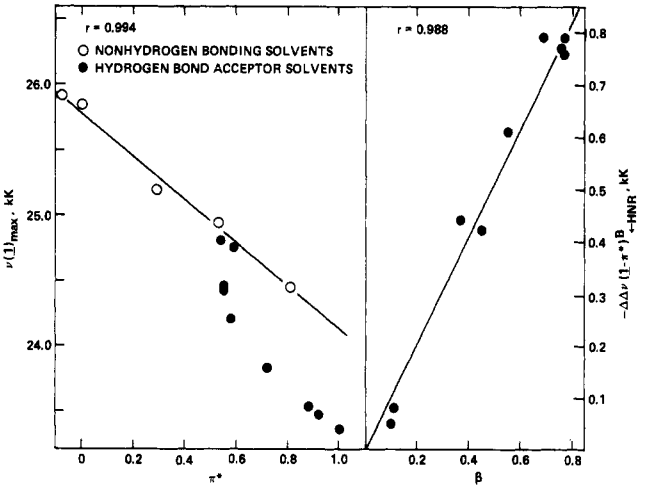


Figure 1. (a) $\nu(1)_{max}$ plotted against solvent π* values, (b) $-\Delta\Delta\nu(1\text{-}\pi^*)$ plotted against solvent β values.

If we consider first the results for 2-nitro-*p*-toluidine (1), the plot of $\nu(1)_{max}$ vs. solvent π* values is shown in Figure 1a, wherein it may be seen that the first condition is fully satisfied; $\nu(1)_{max}$ values for the non-HBA solvents (hexane, cyclohexane, CCl_4, trichloroethylene, and 1,2-dichloroethane) are nicely linear with corresponding π* values. The correlation equation, represented by the regression line in Figure 1a, is as shown in eq 3, with *r* (the correlation coefficient) = 0.994, and σ (the standard deviation) = 0.08 × 10^3 cm^{-1}.

$$\nu(1)_{max} = 25.78 - 1.65\pi^* \quad (10^3\ cm^{-1}) \qquad (3)$$

That condition b is satisfied is also seen in Figure 1a. Data points for HBA solvents which participate in >N–H···HBA hydrogen bonding are displaced from the regression line, all in the same direction and by amounts which range from 0.5 to 10 standard deviations of eq 3. Values of $-\Delta\Delta\nu(1\text{-}\pi^*)^{B}_{\leftarrow HN}$, corresponding to vertical displacements of the HBA solvent data points from the non-HBA solvent regression line and calculated from eq 4, are also assembled in Table I.

$$\Delta\Delta\nu(1\text{-}\pi^*)^{B}_{\leftarrow HN} = \nu(1)_{max}(obsd) - \nu(1)_{eq3}(calcd) \qquad (4)$$

That condition c for solvatochromic comparison is fulfilled is seen in Figure 1b. $\Delta\Delta\nu$ terms attributable to hydrogen bonding by 1 to HBA solvents are nicely linear with the solvent β values. The correlation line, force fitted through the origin to reflect direct proportionality, is described by eq 5, with $n = 9$, $r = 0.988$, and $\sigma = 0.04 \times 10^3$ cm^{-1}.

$$-\Delta\Delta\nu(1\text{-}\pi^*)^{B}_{\leftarrow HN} = 1.03\beta \quad (10^3\ cm^{-1}) \qquad (5)$$

Further, the direction of the $\Delta\Delta\nu(1\text{-}\pi^*)$ effect is bathochromic, which is consistent with the >N–H···HBA hydrogen bond stabilizing the excited state of the [^+H_2N=C(1) → C(2)=NO_2^-] electronic transition relative to the ground state. Hence, insofar as the directions of the solvent dipolarity/polarizability and type-B hydrogen-bonding effects are concerned, the solvatochromic behavior of the 2-nitroaniline derivative parallels the behavior reported earlier for 3-nitro-, 4-nitro-, and 3,5-dinitroaniline.[6]

Total Solvatochromic Equation for 1. The intercept and slope in eq 3 correspond to the $\nu(i)_0$ and s terms in eq 2, and the proportionality constant in eq 5 corresponds to the a coefficient. Combining the appropriate terms from eq 2 and 5, we therefore obtain the total solvatochromic equation for $\nu(1)_{max}$ (eq 6a, $n = 14$, $r = 0.997$).

$$\nu(1)_{max} = 25.78 - 1.65\pi^* - 1.03\beta \quad (10^3\ cm^{-1}) \qquad (6a)$$

An alternative route to the total solvatochromic equation is by the method of multiple-parameter least-squares correlation (multiple linear regression analysis), which has become quite convenient with the recent accessibility of inexpensive programmable computors. In this single-step procedure, correlation of $\nu(1)_{max}$ with solvent π^* and β values leads directly to eq 6b, with $n = 14$ and $s = 0.998$.

$$\nu(1)_{max} = 25.78 - 1.64\pi^* - 1.07\beta \quad (10^3\ cm^{-1}) \qquad (6b)$$

If we consider that nine solvent π^* values which served as input to eq 6b did not contribute to the determination of s in eq 6a, the fact that the agreement between the two equations is well within the precision of individual $\nu(1)_{max}$ determinations must be regarded as highly satisfactory.

The b value of −1.07 in eq 6b compares with $b = -1.14$ for *N*-ethyl-4-nitroaniline[7], which forms a single hydrogen bond to HBA solvents. Since solvatochromic effects of other N-monosubstitution are also similar in the 2- and 4-nitroaniline series (as is discussed below), and in the light of the results reported below for **2**, it is reasonable to conclude that the amine protons of **1** form one *intra*molecular hydrogen bond to nitro oxygen, and one *inter*molecular hydrogen bond to HBA solvents.

***N*-Methyl-2-nitro-*p*-toluidine (2).** With the above to serve as an example of the normal solvatochromic behavior of HBD (hydrogen-bond donor) indicators in HBA solvents, we now consider the contrasting behavior of *N*-methyl-2-nitro-*p*-toluidine (**2**) and 2-nitrophenol (**3**).

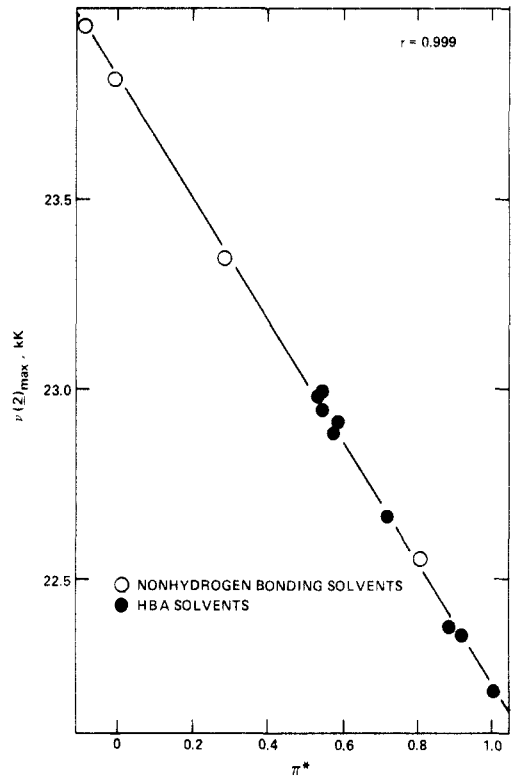


Figure 2. $\nu(2)_{max}$ plotted against solvent π^* values.

Values of $\nu(2)_{max}$ in 13 non-hydrogen bonding and HBA solvents (Table I) are plotted against solvent π^* values in Figure 2. It is seen that all data points conform closely to the regression line, the equation for which is as follows (with $r = 0.999$ and $\sigma = 0.03 \times 10^3$ cm^{-1}:

$$\nu(2)_{max} = 23.81 - 1.61\pi^* \quad (10^3\ cm^{-1}) \qquad (7)$$

That excellent correlation is obtained without invoking a dependence on solvent HBA basicity serves as strong evidence for the absence of type-B *inter*molecular hydrogen bonding by **2**. This is confirmed by the negligible term in β in the multiple linear regression equation (eq 8, $r = 0.999$).

$$\nu(2)_{max} = 23.82 - 1.57\pi^* - 0.05\beta \quad (10^3\ cm^{-1}) \qquad (8)$$

Hence we conclude that **2** behaves in effect as a nonprotic indicator and that the intramolecular hydrogen bond remains unbroken in even the stronger HBA solvents. It is also of interest that the s value of −1.61 for **2** compares with $s = -1.64$ for **1**; i.e., the *inter*molecular hydrogen bonding by **1** does not influence the dependence on solvent dipolarity/polarizability.

2-Nitrophenol (3). Compared with those for **1** and **2**, the solvatochromic correlations for **3**, although statistically still quite acceptable, are considerably less precise than in the earlier instances. Values of $\nu(3)_{max}$ in six non-hydrogen bonding and 11 HBA solvents (data in Table I) are plotted against solvent π^* values in Figure 3a. The correlation equation for the results in the non-HBA solvents, represented by the regression line in the figure, is given by eq 9 (with $r = 0.962$ and $\sigma = 0.10 \times 10^3$ cm^{-1}).

$$\nu(3)_{max} = 28.86 - 0.91\pi^* \quad (10^3\ cm^{-1}) \qquad (9)$$

It is seen in the figure that, as with **1**, the HBA solvent data points show statistically significant displacements from the regression line; the $\Delta\Delta\nu(3\text{-}\pi^*)^{B}_{\leftarrow HO}$ terms,[8] cor-

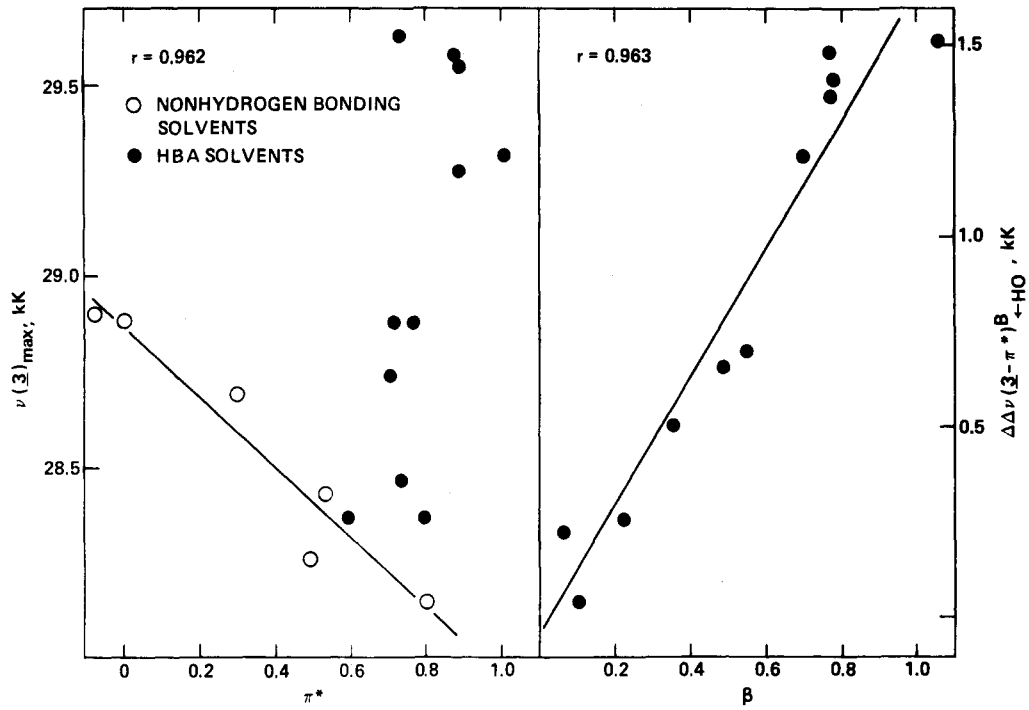


Figure 3. (a) $\nu(3)_{max}$ plotted against solvent π^* values, (b) $\Delta\Delta\nu(3\text{-}\pi^*)$ plotted against solvent β values.

responding to the differences between $\nu(3)_{max}$(obsd) and $\nu(3)_{eq\ 9}$(calcd), amount to 0.5–15 standard deviations of eq 9. Unlike $\Delta\Delta\nu(1\text{-}\pi^*)$, however, the $\Delta\Delta\nu(3\text{-}\pi^*)$ terms are *positive* in sign, indicating that the results of type-B hydrogen bonding by **3** to HBA solvents are *hypsochromic*.

The regression of the $\Delta\Delta\nu(3\text{-}\pi^*)$ terms with β is again reasonably linear as is shown by Figure 3b and eq 10 (r = 0.962, $\sigma = 0.16 \times 10^3$ cm^{-1}. As before, the s and b terms

$$\Delta\Delta\nu(3\text{-}\pi^*)^{B}_{\leftarrow HO} = -0.03 + 1.70\beta \quad (10^3\ \text{cm}^{-1}) \quad (10)$$

in the multiple linear regression equation (eq 11, n = 17, r = 0.963) agree well with the coefficients of π^* and β in the single regressions. From the above, it seems fair to

$$\nu(3)_{max} = 28.83 - 0.64\pi^* + 1.64\beta \quad (10^3\ \text{cm}^{-1}) \quad (11)$$

conclude that there are, indeed, specific solute/solvent interactions involving 2-nitrophenol and HBA solvents, whose effects are well beyond the uncertainties of the correlations or the precision of the measurements with anisole (β = 0.22) and the stronger HBA bases.

There remains the question of why type-B hydrogen bonding by **3** to HBA solvents should have a hypsochromic result, which is in marked contrast to the bathochromic effects of type-B bonding by other nitrophenol and nitroaniline indicators to HBA solvents. The answer almost certainly lies in the fact that the solute to solvent hydrogen bond which is formed has a smaller bathochromic effect than the *intra*molecular O–H···O=N hydrogen bond in **3** which is broken, so that the net result is hypsochromic.

We can estimate the relative magnitudes of the bathochromic effects of the *intra*- and *inter*molecular hydrogen bonds of **3** by considering the parallel effects of alkylation and hydrogen bonding on some 2- and 4-substituted nitrophenol and nitroaniline derivatives. We have mentioned that in eq 2, b = −1.14 for *N*-ethyl-4-nitroaniline, which forms a single hydrogen bond to HBA solvents, compared with b = −1.07 for **1**; i.e., single hydrogen bonds to HBA solvents have similar bathochromic effects for 2- and 4-nitroaniline derivatives. Effects of N-monoalkylation are also similar, as is seen from the following comparisons in cyclohexane solvent: 2-nitro-*p*-toluidine, $\nu_{max} = 25.84 \times 10^3$ cm^{-1}; *N*-methyl-2-nitro-*p*-toluidine, $\nu_{max} = 23.95 \times 10^3$ cm^{-1}, $\Delta\nu_{max} = -1.89 \times 10^3$ cm^{-1}; 4-nitroaniline, $\nu_{max} = 31.10 \times 10^3$ cm^{-1}; *N*-methyl-4-nitroaniline, $\nu_{max} = 29.37 \times 10^3$ cm^{-1}, $\Delta\nu_{max} = -1.73 \times 10^3$ cm^{-1}. We can estimate ν_{max} of a hypothetical noninternally hydrogen bonded 2-nitrophenol (**3′**) by analogy from the following: 4-nitroanisole, $\nu_{max} = 34.13 \times 10^3$ cm^{-1}; 4-nitrophenol, $\nu_{max} = 35.08 \times 10^3$ cm^{-1}, $\Delta\nu_{max} = +0.95 \times 10^3$ cm^{-1}; 2-nitroanisole, $\nu_{max} = 32.89 \times 10^3$ cm^{-1}. Using the same $\Delta\nu_{max}$ to estimate ν_{max} for the hypothetical **3′**, we obtain $\nu(3')_{max} = 33.84 \times 10^3$ cm^{-1}. From this result and $\nu(3)_{max} = 28.90 \times 10^3$ cm^{-1}, the bathochromic effect of the intramolecular hydrogen bond is ca. 4.9×10^3 cm^{-1}. This is quite a bit larger than the 2.2×10^3 cm^{-1} bathochromic effect of type-B hydrogen bonding by 4-nitrophenol (and 2-nitrophenol by analogy) to hexamethylphosphoramide, the strongest HBA base studied.

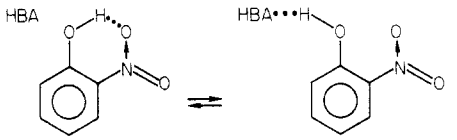
It is reasonable that the *intra*molecular hydrogen bond should lower the [$^+$HO=C(1) → C(2)=NO$_2^-$] electronic transition energy to a greater extent than the type-B hydrogen bond. This is because the internal hydrogen bond by OH to NO$_2$ has the effect of both increasing the ground-state electron density on the hydroxy group and decreasing the ground-state electron density on nitro; both factors lead to lower transition energies.[9] Intermolecualr type-B hydrogen bonding by the OH to HBA solvents has only the first effect, and hence the smaller $-\Delta\nu_{max}$.

One further point deserves comment. If the 2-nitrophenol were 100% hydrogen bonded to the solvents, we would expect the greatest $+\Delta\Delta\nu(3\text{-}\pi^*)$ term for the weakest

(8) The negative sign indicates a bathochromic effect; the 1-π^* 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, the subscript ←HN indicates that the bonding is by the amine proton of the solute. See earlier papers of this series for additional examples of this nomenclature system, which makes the description of the phenomenology much less confusing and cumbersome when several types of hydrogen bonding occur simultaneously.

(9) Kamlet, M. J.; Kayser, E. G.; Eastes, J. W.; Taft, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5210.

HBA base solvent (constant hypsochromic effect of breaking the internal H bond, smallest bathochromic effect of forming the H bond to solvent) and smaller $\Delta\Delta\nu$ terms for the stronger HBA solvents. As is seen in Table I and Figure 3, however, the converse order is observed. We can rationalize the results in terms of a **3a** ⇄ **3b** equilibrium, with the 2-nitrophenol spectrum a composite of bands arising from *intra*- and *inter*molecularly hydrogen bonded species [the separations between $\nu(\mathbf{3a})_{max}$ and $\nu(\mathbf{3b})_{max}$ are not sufficiently great for the spectrum to show resolution into two bands but lead rather to band broadening]. The



3a 3b

equilibrium is only slightly to the right in the weak HBA base solvent, anisole, and much farther to the right in hexamethylphosphoramide. The farther to the right the equilibrium, the greater is the contribution of **3b** to the composite spectrum and the greater is the hypsochromic shift.

Concluding Remarks. Steric and electronic factors undoubtedly play major roles in the differing hydrogen bonding behavior of **2** and **3**. Formation of a type-B hydrogen bond to HBA solvents would require that either the CH_3NH or NO_2 group of **2** be twisted from planarity, with a consequent decrease in amine → ring → nitro mesomeric interaction, and a significant loss in delocalization energy. The greater HBD acidity of **3** compared with that of **2** may also play a part.

Finally, the relationship between our findings and some interesting observations by Dyall and Kemp[10] deserve mention. These workers found that in weakly basic solvents *N*-methyl-2-nitroaniline (**4**) showed only a single NH stretching peak in the IR, which they attributed to the internally hydrogen bonded species. In the stronger HBA solvents, however, there appeared a low-frequency shoulder, which shifted to increasingly lower frequencies with increasing solvent HBA basicity (and which they resolved graphically into two peaks). In Me_2SO solvent, the lower frequency band was actually the stronger of the two peaks.

They did not conclude from this that the intermolecular hydrogen bond was broken but rather that the single amino hydrogen of **4** *simultaneously* formed an *intra*molelar hydrogen bond to NO_2 and an *inter*molecular hydrogen bond to the solvent, i.e., a *bifurcated* hydrogen bond. To accomplish this, they suggested that the CH_3NH group of **4** twists slightly from planarity.

The findings from the UV-visible and IR spectral studies are not necessarily mutually inconsistent. Dyall and Kemp's picture would be consistent with the present findings if the bathochromic effect of the *inter*molecular portion of the bifurcated hydrogen bond were offset by a slight decrease in the bathochromic effect of the (probably slightly weaker) internal hydrogen bond, and/or by a possible hypsochromic effect of twisting the CH_3NH group slightly from planarity.

Acknowledgment. The work by R.W.T. was supported in part by a grant from the Public Health Service. The work by M.J.K. was done under Naval Surface Weapons Center Independent Research Task IR-210.

Registry No. 1, 89-62-3; 2, 4600-08-2; 3, 88-75-5.

(10) Dyall, L. K.; Kemp. J. E. *Spectrochim. Acta* **1966**, *22*, 467.

Effect of α-Amino Substituents on Rates of Formation of sp^2-Hybridized Carbanions[1]

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Received October 6, 1981

Kinetics of the sodium methoxide catalyzed deuterium exchange of the methyl esters of *N,N*-dimethylglycine, *N*-methylproline, isovaleric acid, and *cis*- and *trans*-2-methylcyclopentanecarboxylic acid have been studied in methanol-*O*-*d* at 35 °C. The results are taken as additional evidence for destabilizing repulsions between unshared electron pairs as an important factor in decreasing reactivity in carbanion formation. Such repulsions can be minimized by rotation around the bond between the substituent and the carbanion center.

The effect of α-fluoro and α-alkoxy substituents on rates of formation of sp^2-hybridized carbanions has been studied previously by this research group. Rates of sodium methoxide catalyzed deuterium exchange in methanol-*O*-*d* were determined for methyl esters of fluoroacetic, methoxyacetic, tetrahydrofuran-2-carboxylic, 1,3-dioxolane-2-carboxylic, and several reference acids.[2,3] The results were discussed in terms of repulsions between unshared pairs of electrons and the electronegativities of fluorine and oxygen as well as simple steric and polar effects. Amino substituents differ from fluoro and alkoxy substituents in that they have only one unshared pair of electrons. Hence an α-amino substituent on a carbanion can orient itself (if rotation around the bond joining it to the carbanion system is feasible) so that all its unshared electrons are in an

(1) (a) Supported in part by Grant CHE 79 26319 from the National Science Foundation. Part 23 in the series "Structural Effects on Rates and Equilibria". (b) For part 22, see Hine, J.; Linden, S.-M. *J. Org. Chem.* **1981**, *46*, 1635-8.

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0022-3263/82/1947-1738$01.25/0