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SOLVENT EFFECT ON POLAR AND SPECTROSCOPIC PROPERTIES OF 2-*N*-METHYLAMINO-5-NITRO-6-METHYLPYRIDINE AND 2-*N*-METHYLAMINO-3-NITRO-6-METHYLPYRIDINE

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Dipole moments of 2-*N*-methylamino-5-nitro-6-methylpyridine (I) and 2-*N*-methylamino-3-nitro-6-methylpyridine (II) were determined in solvents of different polarity and basicity. The solvent effect is discussed in terms of the two-parameter (π^*–β) Kamlet–Taft expression. The solvent dependences of the energy of intramolecular charge-transfer transition and the frequency of the ν(NH) stretching vibration are in keeping with the dielectric results. It was found that the solvent-induced disturbance in the electronic structure of I is brought about by hydrogen bond interaction with the NH group. The strong intramolecular hydrogen bond in II is stable in weakly basic solvents and the electronic structure is insensitive to the environment. However, in more basic solvents the intramolecular hydrogen bond is partly broken and an N—H· · ·solvent hydrogen bond is formed, bringing about distinct changes in polarity and spectroscopic properties. © 1997 John Wiley & Sons, Ltd.

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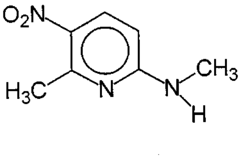
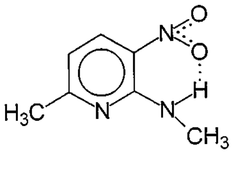
INTRODUCTION

The introduction of a strong electron-accepting nitro group into the 2-*N*-alkylaminopyridine system causes a clear modification of the electronic structure. In the 5-nitro derivative (**I**), strong conjugation between the NO_2 and NHR groups leads to intramolecular charge transfer. In a previous paper,[1] we reported a pronounced influence of nitrogen amino substitution on the charge-transfer effect in 2-amino-5-nitro-6-methylpyridines. The *N*-substituted 2-amino-5-nitropyridines have attracted considerable interest owing to their non-linear optical properties.[2–7] The large first-order hyperpolarizability β in these high push–pull chromophores is due to an intramolecular charge-transfer interaction between NO_2 and NR_2 groups. For such molecules, the electronic properties may exhibit a pronounced sensitivity to the environment. In fact, it has been pointed out earlier[8–10] that the solvent polarity exerts an important influence on β. In the 3-nitro derivative (**II**), an important structural element is the intramolecular hydrogen bond between the NO_2 and NHR groups. This intramolecular interaction reduces the tendency of the NH bond to form intermolecular HB with the solvent molecules. For 2-nitro-*N*-alkylanilines there is extensive IR,[11, 12] UV–VIS,[13, 14] NMR[15] and dipole moment[16] evidence for the persistence of the chelate structure **II** in a wide variety of solvents. There have been no such studies on 2-amino-3-nitropyridines.



I



II

The first step in our investigation of the influence of the solvent on charge distribution and intramolecular HB in aminonitropyridines was to examine **I** and **II** in solvents of low polarity and basicity (hydrogen-acceptor ability). In such media, dipole moment measurements, and spectroscopic methods (IR, UV–VIS), should reveal the sensitivity of the molecular electronic properties to the environment. Because the influence of the solvent on the electronic structure of the solute is brought about by electrostatic and specific solute–solvent interactions, we decided to describe this phenomenon using the Kamlet–Taft[17] solvatochromic parameters π^* (dipolarity/polarizability term) and β (hydrogen-bond acceptor ability) of the solvent.

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EXPERIMENTAL

Dielectric permittivities were measured on a Dipolmeter DM01 instrument which operates using the superheterodyne beat method at 2 MHz. The measuring condensers made it possible to determine the dielectric capacity with an accuracy $\Delta C/C \leq 1\times10^{-4}$. The density was determined pyknometrically with an accuracy $\pm10^{-4}$ g cm^{-3} and the refractive index for the D-line of sodium was measured using an Abbé refractometer to an accuracy $\pm5\times10^{-5}$. All the measurements were performed at 25±0·02 °C. The molar dipole polarization at infinite dilution was calculated from an expression[18] based on Onsager's local field:[19]

$$P_{\infty}^{\mathrm{dip}} = \frac{(\varepsilon_1 - n_1^2)(2\varepsilon_1 + n_1^2)\mathrm{M}_1}{\varepsilon_1(n_1^2+2)^2\mathrm{d}_1}$$

$$\left(\frac{\alpha\varepsilon_1 - \gamma n_1^2}{\varepsilon_1 - n_1^2} + \frac{2\alpha\varepsilon_1 + \gamma n_1^2}{2\varepsilon_1 + n_1^2} - \frac{2\gamma n_1^2}{n_1^2+2} - \alpha - \beta + \frac{M_2}{\mathrm{M}_1}\right) \qquad (1)$$

The coefficients α, β and γ are defined as follows:

$$\alpha\varepsilon_1 = \left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}x_2}\right)_{x_2\to0};\ \beta = \frac{1}{d_1}\left(\frac{\mathrm{d}d}{\mathrm{d}x_2}\right)_{x_2\to0};\ \gamma n_1^2 = \left(\frac{\mathrm{d}n^2}{\mathrm{d}x_2}\right)_{x_2\to0}$$

M, *ε*, *d*, *n* and *x* are molecular mass, dielectric permittivity, density, refractive index and mole fraction, respectively, and the subscripts 1 and 2 refer to solvent and solute, respectively. The dipole moment measurements were carried out in the range of mole fractions 8×10^{-3}–5×10^{-2} for pyridine and 1×10^{-3}–5×10^{-3} for **I** and **II**. In the above ranges no concentration dependences of the dielectric polarization were observed. The average of the absolute deviations of the dipole moments from their mean did not exceed 0·03 D. UV–VIS and IR spectra were recorded on Specord M40 and Nicolet 205 FT-IR spectrometers in quartz and KBr cuvettes of varying thicknesses. The accuracies of wavenumber readings were 50 and 1 cm^{-1}, respectively. The solvents and pyridine were purified by standard methods[20] and were dried over sodium or molecular sieves of type 4 Å. 2-*N*-Methylamino-5-nitro-6-methylpyridine (**I**) and 2-*N*-methylamino-3-nitro-6-methylpyridine (**II**) were synthesized as described previously,[21] recrystallized from benzene and stored over $CaCl_2$ in a vacuum desiccator. The melting points and other purity critera were given previously.[21]

RESULTS AND DISCUSSION

The influence of the solvent on the dipole moments of **I** and **II** is exerted by the electrostatic and specific (hydrogen-bond and charge-transfer) solute–solvent interactions. Both molecules contain nitro and *N*-methylamino groups in addition to the pyridine moiety, which are subject to solvation in different ways. For a thorough treatment of this problem, it is expedient to discuss first the influence of the solvent on the dipole moments of molecules which are polar fragments of **I** and **II**. As shown previously,[18] changes in the dipole moment of nitrobenzene in the solvents investigated in this work were only slight. The same seems to apply to pyridine, whose dipole moments in the solvents tested are given in Table 1.

The *N*-methylamino group can act as a hydrogen donor (N—H bond) and hydrogen acceptor (nitrogen atom). However, because of its strong conjugation, the basicity is considerably attenuated. The dipole moment of *N*,*N*-dimethylaniline in *n*-hexane, CCl_4, benzene and dioxane is constant and equal to 1·61±0·02 D.[22] The constancy of the dipole moments of molecules constituting polar, but basic (hydrogen-bond acceptor), fragments of compounds **I** and **II** is due to the absence in the solvents tested of specific hydrogen-bond interactions of the type B· · ·HR (B=NO_2 group or nitrogen atom, HR=hydrogen-bond donor solvent).

Table 2 gives the dipole moments of compounds **I** and **II**. Even a rough inspection indicates that the solvent dependences of the dipole moments of the two compounds are different. There is a considerable increase in μ(**I**) with increase in the polarity of the solvent. However, it is noteworthy that the dipole moment in *n*-chlorobutane (ε=7·05) is definitely lower than that not only in the isodielectric tetrahydrofuran (ε=7·46) but also in the non-polar dioxane and aromatic solvents. The enhancement of the effective dipole moment is due mainly to the specific hydrogen bond interaction N—H· · ·B (B=basic oxygen or π-electron system). It is not unlikely that in aromatic solvents also the π–π interaction is significant. The

Table 1. Dipole moment of pyridine in various solvents

Solvent	$\alpha\varepsilon_1$	β	γn_1^2	P (cm^3)	μ (D)
Tetrachloroethylene	7·097	−0·2171	0·2173	115·0	2·36
Mesitylene	4·316	0·0923	0·0840	98·3	2·18
Benzene	6·899	0·1212	0·1485	110·0	2·20
Dioxane	7·305	−0·0343	0·2764	108·0	2·28
Ethyl acetate	5·104	0·0899	0·3471	105·7	2·26
n-Chlorobutane	4·486	0·0808	0·2565	110·5	2·31
Tetrahydrofuran	6·071	0·1255	0·3494	113·4	2·34

Table 2. Dipole moments of 2-*N*-methylamino-5-nitro-6-methylpyridine (**I**) and 2-*N*-methylamino-3-nitro-6-methylpyridine (**II**) in various solvents

	I					**II**				
Solvent	$\alpha\varepsilon_1$	β	γn_1^2	P (cm^3)	μ (D)	$\alpha\varepsilon_1$	β	γn_1^2	P (cm^3)	μ (D)
Tetrachloroethylene	31·596	− 0·3197	0·5422	526·4	5·04	13·474	− 0·3182	0·5510	219·3	3·26
Benzene	42·001	0·6564	0·7972	607·4	5·42	16·461	0·6389	0·8071	231·1	3·34
Mesitylene	24·950	0·3983	0·3909	569·2	5·24(5)	10·123	0·3988	0·4471	224·4	3·29
Dioxane	47·589	0·3523	1·0877	701·5	5·82	16·109	0·2790	1·0543	229·4	3·33
Ethyl acetate	54·332	0·6176	1·3368	770·8	6·10	19·821	0·6087	1·1186	305·2	3·84
n-Chlorobutane	36·740	0·5573	0·9171	563·0	5·21	13·602	0·6811	1·1123	221·6	3·27
Tetrahydrofuran	71·503	0·7793	1·4442	806·4	6·24	34·873	0·9572	1·6350	395·1	4·37

consequence of specific N—H· · ·B interactions is an increase in intramolecular charge transfer. This in turn may raise the second-order molecular polarizability. It is worth mentioning that optically non-linear 2-*N*-substituted-5-nitropyridines in the crystalline state form intermolecular hydrogen bonds between the nitro oxygens and the NH groups which link the molecules into chains.[4–7]

For a quantitative description of the sollvent effect on μ we have proposed a two parameter Kamlet–Taft equation[17] of the form

$$\mu_s = \mu_o + s\pi^* + b\beta \qquad (2)$$

where π^* is the measure of solvent dipolarity/polarizability (electrostatic interaction) and β is the measure of the solvent hydrogen-bond acceptor ability (see Table 3 and 4). The equation obtained by the method of linear regression analysis is

$$\begin{aligned}\mu_s(\mathbf{I}) = \;& 4{\cdot}85 \quad + 0.67\pi^* + \; 1{\cdot}80\beta \\ & (\pm 0{\cdot}18) \; (\pm 0{\cdot}45) \; (\pm 0{\cdot}24) \end{aligned} \qquad (3)$$

$$(n = 7,\ r = 0{\cdot}988,\ \mathrm{SEE} = 0{\cdot}09)$$

where SEE is the standard error of the estimate. As can be seen, the parameters π^* and β describe the solvent dependence satisfactorily. The π^* coefficient and its standard deviation are comparable in magnitude, suggesting, that this term is not significant. In fact, the following single-parameter equation describes the solvent dependence very well:

$$\begin{aligned}\mu_s(\mathbf{I}) = \;& 5{\cdot}11 \quad + \; 2{\cdot}05\beta \quad (n = 7,\ r = 0{\cdot}981,\ \mathrm{SEE} = 0{\cdot}10) \\ & (\pm 0{\cdot}06) \; (\pm 0{\cdot}18) \end{aligned} \qquad (4)$$

Equation (4) indicates that a specific N—H· · ·B interaction is the decisive factor disturbing the electronic structure.

Now let us consider the solvent effect on the dipole moment of compound **II**. In contrast to **I**, the dipole moment μ(**II**) in C_2Cl_4, benzene, mesitylene, dioxane and *n*-chlorobutane is weakly differentiated and a good correlation is satisfied:

$$\begin{aligned}\mu_s(\mathbf{II}) = \;& 3{\cdot}18 \quad + 0{\cdot}26\pi^* + \; 0{\cdot}03\beta \\ & (\pm 0{\cdot}02) \; (\pm 0{\cdot}05) \; (\pm 0{\cdot}04) \end{aligned} \qquad (5)$$

$$(n = 5,\ r = 0{\cdot}980,\ \mathrm{SEE} = 0{\cdot}01)$$

As can be seen, the β term is not significant and can be dropped to give the following correlation with similar precision:

$$\begin{aligned}\mu_s(\mathbf{II}) = \;& 3{\cdot}17 \quad + 0{\cdot}28\pi^* \quad (n = 5,\ r = 0{\cdot}976,\ \mathrm{SEE} = 0{\cdot}01) \\ & (\pm 0{\cdot}02) \; (\pm 0{\cdot}04) \end{aligned} \qquad (6)$$

On this basis it may be supposed that the intramolecular hydrogen bond is not subject to cleavage. However, in ethyl acetate and tetrahydrofuran, a marked enhancement of μ is observed, while correlations (5) and (6) considering also these solvents are clearly not satisfied. This suggests that in both of these solvents there is an (at least partial) cleavage of intramolecular hydrogen bond and intermolecular N—H· · ·B bonds to the solvent molecules are formed. This effect may be accompanied by changes in conformation (e.g. partial loss of coplanarity and conjugation).

Further evidence for stability of intramolecular HB and the specific role of the N—H· · ·solvent interaction is given by spectroscopic data.

In Table 3 are given the positions of longwave $\pi \rightarrow \pi^*$ bands of the intramolecular charge-transfer type (IMCT) for both the compounds and in solvents of different polarity. The criterion for the selection of the solvents in this case was the lack of hydrogen-bond donor and hydrogen-bond acceptor abilities (Kamlet–Taft parameters α and β equal to zero). It is obvious that in non-interacting solvents the spectral shift is controlled by the dipolarity/polarizability term π^*.

The solvatochromic equations are as follows:

$$\begin{aligned}\tilde{\nu}_s(\mathbf{I}) = \;& 29{,}945 - 2620\pi^* \quad (n = 8,\ r = 0{\cdot}960,\ \mathrm{SEE} = 198) \\ & (\pm 150) \quad (\pm 310) \end{aligned} \qquad (7)$$

and

$$\tilde{\nu}_s(\mathbf{I}) = \underset{(\pm 60)}{25{,}095} - \underset{(\pm 125)}{1410}\pi^* \quad (n=8,\ r=0{\cdot}977,\ \mathrm{SEE}=79) \qquad (8)$$

According to expectation,[24] compound **II** with intramolecular HB manifests a clearly reduced solvent sensitivity as compared with **I**.

Table 4 shows the wavenumbers of IMCT transitions in **I** and **II** dissolved in basic solvents tested dielectrically; further discussion is based on the Kamlet–Taft[14] procedure and deviations from the dependence of ν versus π^* [equations (7) and (8)] were determined. Deviations $\delta\Delta E$, defined as the difference in the transition energies observed (ΔE_{obs}) and calculated according to equations (7) and (8) (ΔE_{calc}) are given in Table 4. The magnitude of $\delta\Delta E$ is attributable to the strength of N—H· · ·solvent interactions in excited and ground states. As can be seen, $\delta\Delta E(\mathbf{I})$ cover a wide range (2·0–7·3 kJ mol^{-1}) and become more negative (bathochromic shifts) with increasing hydrogen-bond acceptor properties of the solvent, e.g. increase in β. The deviation observed in benzene may be caused by charge-transfer solute–solvent interactions, which in the case of mesitylene is less important owing to steric hindrance. The $\delta\Delta$E(**I**) energies roughly correlate with the effective dipole moments:

$$\mu_s(\mathbf{I}) = \underset{(\pm 0{\cdot}13)}{5{\cdot}35} - \underset{(\pm 0{\cdot}05)}{0{\cdot}18}\,\delta\Delta E(\mathbf{I}) \quad (n=6,\ r=0{\cdot}878,\ \mathrm{SEE}=0{\cdot}27) \qquad (9)$$

The dipole moment $\mu_s(\mathbf{I}) = 5{\cdot}35 \pm 0{\cdot}13$ D obtained by extrapolation to $\delta\Delta E = 0$ is that in the absence of any specific solvent effects. This dipole moment is not compatible with that estimated from equation (3) [$\mu_s(\mathbf{I}) = 4{\cdot}85 \pm 0{\cdot}18$ D], which is related to non-polar solvents, e.g. aliphatic hydrocarbons. Hence it may be concluded that the dipole moment enhancement caused by pure electrostatic interactions in solvents of $\varepsilon < 8$ is not higher than 0.5 D.

Now let us consider the more interesting solvatochromic properties of **II**. Table 4 shows that in C_2Cl_4, benzene, mesitylene, dioxane and *n*-chlorobutane the $\delta\Delta E(\mathbf{II})$ values are small and the solvatochromic equation (8) is satisfied. It should be remembered that in this group of solvents the constancy of the dipole moment was also found (see Table 2). Hence the UV–VIS data confirm that even if the solvent interacts specifically with **II**, then this interaction does not lead to cleavage of intramolecular HB or any significant disturbances of the charge distribution. In more polar and at the same time basic solvents, such as ethyl acetate,

Table 3. Wavenumbers of the intramolecular charge-transfer bond in 2-*N*-methylamino-5-nitro-6-methylpyridine (**I**) and 2-*N*-methylamino-3-nitro-6-methylpyridine (**II**) in non-interacting solvents

Solvent	π^*	$\tilde{\nu}$(**I**) (cm^{-1})	$\tilde{\nu}$(**II**) (cm^{-1})
n-Hexane	−0·08	30,090	25,200
CCl_4	0·28	29,550	24,700
1,2-Dibromomethane	0·75	28,090	24,020
n-Bromobutane	0·47[a]	28,780	24.510
1,1,1-Trichloroethane	0·49	28,480	24,410
n-Chlorobutane	0·39	28,890	24,580
Bromoethane	0·53[a]	28,570	24,420
1,1-Dichloroethane	0·48[a]	28,430	24,260

[a] From Ref. 23.

Table 4. Wavenumbers of IMCT transitions $\tilde{\nu}_{\pi\to\pi^*}$ and of the ν(NH) vibrations in 2-*N*-methylamino-5-nitro-6-methylpyridine (**I**) and 2-*N*-methylamino-3-nitro-6-methylpyridine (**II**) in various solvents (top values for **I** and bottom values for **II**)

Solvent	π^* (Ref. 17)	β (Ref. 17)	($\tilde{\nu}_{\pi\to\pi^*}$) (cm^{-1})	$\delta\Delta$ (kJ mol^{-1})	ν (NH) (cm^{-1})
Tetrachloroethylene	0·28	0·00	29,380	2·0	3443
			24,710	0·1	3406
Mesitylene	0·41	0·13	28,800	−0·8	3417
			24,440	−0·9	3405
Benzene	0·59	0·10	28,570	2·0	3433
			24,280	0·2	3405
Dioxane	0·55	0·37	28,320	−2·2	3354
			24,310	−0·1	3402(sh)
Ethyl acetate	0·55	0·45	28,350	−1·9	3397
			24,520	2·4	3405(sh)
n-Chlorobutane	0·39	0·00	28,890	−0·4	3440
			24,580	0·4	3407
Tetrahydrofuran	0·58	0·55	27,970	−5·6	3331
			24,410	1·6	3407 (3380)
Acetone	0·71	0·48	27,700	−4·6	
			24,340	2·9(5)	
Dimethylacetamide	0·88	0·76	27,030	−7·3	
			24,050	2·3(5)	

tetrahydrofuran, acetone and dimethylacetamide, positive $\delta\Delta E$(**II**) values are observed. This result was not unexpected, as it has been reported previously[14, 25, 26] for some aromatic systems with intramolecular hydrogen bonds. Most probably, formation of an intermolecularly H-bonded form, even if accompanied by increased polarity of the system, cannot compensate for the effects connected with partial cleavage of the intramolecular hydrogen bond, e.g. loss of coplanarity and conjugation. Hence in this case a simple relationship between the effective dipole moment and ν (or $\delta\Delta E$) should not be expected.

Compounds **I** and **II**, compared with primary anilines, are simpler for testing the solvent effect on the hydrogen bond by IR spectroscopy. Disturbance of the spectra by the Fermi resonance between ν(NH) and the δ(NH) overtone can be avoided. The ν(NH) stretching vibration frequencies in compounds **I** and **II** are presented in Table 4. Here we shall discuss only the solvent shifts of that band. The band of the free NH group in **I** in C_2Cl_4 and *n*-chlorobutane occurs at about 3440 cm^{-1}. The ν(NH) (**I**) band in the other solvents is shifted to lower frequencies owing to the specific NH$\cdots$O or NH$\cdots\pi$ interactions. The poor correlation between ν(NH) (**I**) and μ(**I**) can be simply explained. The enhancement of the effective dipole moment arises largely from a change in intramolecular charge transfer, while the ν(NH)(**I**) shift is caused mainly by local environmental disturbances to the NH bond. Therefore, the position of the ν(NH) (**I**) band correlates well with the relative magnitude of the electron-donor ability of the solvent, defined as the difference between the position of the ν(OD) band of methanol-*d* solution in a given solvent and benzene as standard solvent, i.e. $\Delta\nu(\mathrm{OD}) = \nu(\mathrm{OD})\ (\mathrm{benzene}) - \nu(\mathrm{OD})\ (\mathrm{solvent})$.[27] The $\Delta\nu$(OD) frequencies in C_2Cl_4, *n*-chlorobutane and mesitylene determined by us are -24, -12 and 10 cm^{-1}, respectively. The relationship between ν(NH) (**1**) and $\Delta\nu$(OD) is given by the equation

$$\nu(\mathrm{NH})(\mathbf{I}) = 3427 - 0{\cdot}988\delta\Delta\nu \quad (\pm 3) \quad (\pm 0{\cdot}062) \qquad (10)$$

$$(n = 7,\ r = 0{\cdot}990,\ \mathrm{SEE} = 6{\cdot}674)$$

It has been found[11] that 2-nitro-*N*-methylaniline exists in the intramolecularly bonded form and partly as an HB complex in pyridine. The evidence for the intermolecular HB is the low-frequency shoulder on the sharp band at about 3390 cm^{-1}, ascribed to the form with the intramolecular HB. The same compound has been intensively investigated[12] in a wide range of solvents of various polarities and basicities. The low-frequency shoulder becomes more intense along with increasing hydrogen-bond acceptor properties of the solvent. In DMSO the frequency shift is 55 cm^{-1} and the lower component becomes more intense. However, on the basis of the Bellamy plot,[28] it is argued[12] that the N—H$\cdots$$NO_2$ bridge is not interrupted even in such basic solvents as diethyl ether, DMSO and pyridine. In the authors' opinion, a bifurcated hydrogen bond is formed, in which the NH group interacts simultaneously with the nitro group and the solvent molecule. The spectroscopic picture in the region of the ν(NH) vibrations observed for **II** is similar to that in 2-nitro-*N*-methylaniline (see Table 4). The position of the band at 3400 cm^{-1} is almost constant in all the solvents tested. The shoulder observed in dioxane is weak, whereas that in ethyl acetate is more intense. In tetrahydrofuran, the lower frequency band is well developed and is observed at 3380 cm^{-1}. Considering the IR picture together with the dielectric and UV–VIS data, we think that, at least in tetrahydrofuran, there is partial cleavage of the intramolecular HB and its replacement with an intermolecular N–H$\cdots$O bond. The frequencies of the ν(NH) vibration in N—H$\cdots$O are, however, not much lower than those in the intramolecular NH$\cdots$$NO_2$ bridge. On the other hand, the formation of bifurcated hydrogen bonds in weakly basic and polar solvents cannot be precluded. Anyhow, this kind of interaction does not lead to significant disturbances of the charge distribution in a molecule.

Summing up, it may be concluded that electronic structure **I** is very sensitive to the influence of the medium. In basic solvents the intramolecular charge-transfer effect is intensified by the hydrogen-bond interaction of the NH group with the solvent. Constancy of the dipole moment, the position of the ν(NH) band and the normal behaviour of the IMCT transition for **II** in weakly basic solvents confirm that the intramolecular bridge is stable. However, the dielectric and spectroscopic data concerning ethyl acetate and tetrahydrofuran suggest that the intramolecular hydrogen bond is partly interrupted and replaced by an intermolecular NH$\cdots$solvent bond.

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