

COMPETITION BETWEEN INTER- AND INTRAMOLECULAR HYDROGEN BONDING IN MOLECULES WITH DONOR AND ACCEPTOR GROUPS. SOLVATOCHROMIC AND THERMOCHROMIC EVIDENCE IN *N*-(NITROPHENYL)ALKYLENEDIAMINES

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Solvent effects on the absorption spectra of *N*-(*p*-nitrophenyl)dimethylenediamine (Ia), *N*-(*p*-nitrophenyl)trimethylenediamine (Ib), *N*-(*p*-nitrophenyl)tetramethylenediamine (Ic), *N*-methyl-*N*-(*p*-nitrophenyl)tetramethylenediamine (II), *N*-butyl-*p*-nitroaniline (III) and *N*-(*o*-nitrophenyl)trimethylenediamine (IV) were studied at different temperatures. Whereas II, III and IV do not show any variation in their spectra characteristics with changes in temperature, I shows a hypsochromic shift with a hypochromic effect when the temperature is increased. The Kamlet and Taft solvatochromic comparison method was applied. A strong effect of the β parameter on I and III was interpreted as being due to the hydrogen bond donor ability of the H atom in the aromatic amino groups. In I, the β influence increases with increase in temperature. These facts are explained by proposing the formation of intramolecular hydrogen bonds between amine groups in all compounds I, besides the intermolecular interactions between compounds I and the solvent. On the other hand, the values of ρ_o , s and b for Ib are smaller than the corresponding values for Ia and Ic. Since in Ib a six-membered ring may be formed, a more stable bond is expected. Comparative ^1H NMR of the aniline hydrogen for I and IV (in non-hydrogen bond acceptor solvents) shows a particular downfield chemical shift for I which suggests hydrogen bond formation. Since this effect is independent of concentration, the hydrogen bond is assumed to be intramolecular, in agreement with solvatochromic and thermochemical studies. These conclusions were corroborated by IR spectroscopy in the solid state and in chloroform solutions.

INTRODUCTION

The knowledge of geometrical structures and the formulation of the fundamental relationships between structures and properties was essentially stimulated by advances in all spectroscopic techniques.¹ When absorption spectra are obtained in solvents of different polarity, it is found that the position, intensity and shape of the absorption bands are usually modified by these solvents. These changes are the result of physical intermolecular solute-solvent interactions, which can be classified into non-specific and specific. Although it

has been recognized that when specific interactions are present they tend to dominate the total effect,² the greatest difficulty is usually to determine which is the predominating solvent effect.

To unravel this problem, empirical parameters are commonly used.^{2,3} One of the most successful approaches is the solvatochromic comparison method (SCM) of Kamlet and Taft.⁴ This method allows specific interactions to be quantified and separated from polarity-polarizability effects. The usefulness of the empirical parameters π^* (dipolarity-polarizability), α (hydrogen bonding acidity) and β (hydrogen bonding basicity) for the quantitative analysis of solvent effects on chemical reactivity, solubility, spectroscopic proper-

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ties, chromatographic data and biological properties⁵ is widely recognized.

These solvatochromic parameters are used in linear solvation energy relationships⁴ of the general form

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

where XYZ is the property to be correlated and s , a and b measure the relative susceptibilities of XYZ to the indicated solvent property scales.

The hydrogen bond is one of the most interesting specific intermolecular interactions. Owing to its strong orientation and to a binding energy which may be of a magnitude comparable to that of covalent bonds, it often confers unusual properties on the chemical system in which it occurs.⁶

The donor-acceptor properties of hydrogen-bonded molecules are determined by their electronic structure. The formation of complexes is accompanied by the rearrangement of electron density not only in the region of the active group within the hydrogen bond but also in the other groups of molecules as well.⁷

The intramolecular hydrogen bond has been observed to have an influence on the extent and effects of intermolecular interactions.⁸⁻¹² A set of hydrogen bond rules from crystal chemistry and crystallographic data have recently been developed for organic compounds. This is valid for solids and solutions.¹³ However, it is emphasized that the expected or typical hydrogen bonds may not occur for several reasons, including the presence of multiple competitive hydrogen bond sites, steric overcrowding or competing bipolar or ionic forces.

On the other hand, it is known that solute-solvent interactions lead to either modified substituent interactions or modified transmission of the substituent effect, or both.^{14,15} In recent studies we have shown a symmetrical dependence of the alkyl substituent and solvent effects on the shifts of the absorption spectra of *N*-alkyl-*o*-nitroanilines.¹⁶

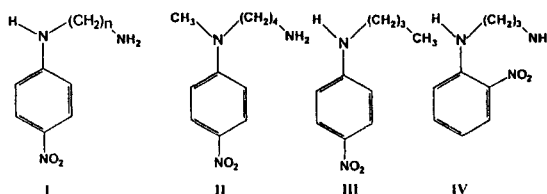
There are also a number of compounds which undergo a noticeable change in shape or intensity of their absorption spectrum over a small temperature range.¹⁷ This process, called thermochromism, is usually based on changes in the positions of equilibria.¹⁸

On the other hand, thermochromic shifts can be induced by temperature-dependent solvent polarity functions, such as $\{f(D) - f(n^2)\}$ and $f(n^2)$, where $f(D) = (D - 1)/(D - 2)$, which is a measure of solvent polarity, and $f(n^2) = (n^2 - 1)/(2n^2 + 1)$, which represents solvent polarizability,¹⁹ thus inducing changes in the solvation of the ground and excited states.^{20,21} This phenomenon is known as thermosolvatochromism.²¹

For *o*-nitroaniline and *N*-alkyl-*o*-nitroanilines, it has been shown, by UV-visible spectrophotometry,^{16,22} that the intramolecular hydrogen bond does not break

to form intermolecular hydrogen bonds even in solvents as basic as *N*-methylpyrrolidin-2-one. From NMR and IR studies,²³ it has been inferred that *m*- and *p*-nitroanilines form dimers in carbon tetrachloride and chloroform by hydrogen bonding between the hydrogen of one molecule of amine and the nitro group of the other. This is not observed for *o*-nitroaniline, where the intramolecular hydrogen bond reduces the possibility of intermolecular interaction. The intermolecular interaction in *p*-nitroaniline was not detected by UV-visible spectrophotometry.^{22,24}

In this paper, we report solvatochromic and thermochromic studies on *N*-(*p*-nitrophenyl)alkylenediamines (**I**), *N*-methyl-*N*-(*p*-nitrophenyl)tetramethylenediamine (**II**) *N*-butyl-*p*-nitroaniline (**III**) and *N*-(*o*-nitrophenyl)trimethylenediamine (**IV**). A comparative study of these compounds was performed to confirm the structural properties of compounds of type I.



Ia: $n = 2$; Ib: $n = 3$; Ic: $n = 4$

In addition to solute-solvent interactions, there are several possibilities of intra- or intermolecular solute-solute interactions for compounds I. Thus, the interaction can be (a) intramolecular $n-\pi$ -type charge transfer between the n electrons of the aliphatic amine nitrogen and the aromatic ring, as was detected for 1-(*p*-nitrophenyl)alkanes bearing a dimethylamino group on the last carbon;²⁵ (b) intramolecular hydrogen bonding between the hydrogen of the aniline and the nitrogen of the aliphatic amine; (c) intermolecular hydrogen bonding between the hydrogen of the aniline of one molecule and the nitro group of the other; (d) intermolecular hydrogen bonding between the hydrogen of the aniline of one molecule and the nitrogen of the aliphatic amine of the other molecule.

None of these types of interactions is possible for **II** and **III**. Compound **IV** can form an intramolecular hydrogen bond between the hydrogen of the aniline group and the oxygen of the nitro group, in addition to the interactions described.

These studies were aimed, through the analysis of solute-solvent interactions, at yielding further insight into the structure of those compounds which, having inherently large second-order polarizabilities, are good candidates for nonlinear optical materials owing to the strong intramolecular charge transfer present in their excited states.²⁶

EXPERIMENTAL

Compounds **I** were synthesized and purified following the method already reported: **Ia**, ^{27a} m.p. = 142 °C; **Ib**, ^{27b} m.p. = 111 °C; and **Ic**, ^{27c} m.p. = 106 °C.

Compound **II** was prepared from **Ic** as reported elsewhere.²⁸ The purity was determined by thin-layer chromatography (TLC) [silica gel F₂₅₄ with methanol–chloroform (2:1)].

Compound **III** was synthesized from *p*-dinitrobenzene by a similar method to that reported previously for the preparation of *o*-nitroalkylanilines;^{29,30} m.p. 145 °C.

Compound **IV** was obtained from its chloro hydrate (synthesized as reported elsewhere^{27b}) by treatment with 50% sodium hydroxide solution and then extracted with diethyl ether. Compound **IV** is an orange oil; its purity was determined by TLC [silica gel F₂₅₄ with toluene–light petroleum (3:7)].

The solvents used were hexane (Hx), benzene (Bz), toluene (Tl), dichloromethane (DCM), dichloroethane (DCE), chloroform (Chl), dimethylformamide (DMF), acetone (Ac), acetonitrile (ACN), ethyl acetate (EtAc), diethyl ether (EE), methanol (MeOH), ethanol (EtOH) and propan-2-ol (2-PrOH). They were purified to spectroscopic quality by standard methods.³¹ The UV cut-off point against air in a 10 mm UV cell was used as a purity criterion.

Spectroscopic measurements were performed using a Cary 17 spectrophotometer. Concentrations were about 10⁻⁵ M.

The value of ν_{\max} was measured by taking the midpoint between the two positions of the spectrum where the absorbance is equal to 0.09 A_{\max} .^{3a} Hence the uncertainties in ν_{\max} are ca 100 cm⁻¹.

¹H NMR spectra were determined on a Bruker AM-400 spectrometer using TMS as a reference standard. IR spectra were determined on a Bruker IFS 25 Fourier transform IR spectrometer.

RESULTS AND DISCUSSION

UV–visible spectrophotometric studies

The behaviours of **I–IV** were compared by measuring the position of the maximum of the longest wavelength absorption band in several pure solvents at two temperatures, $T_1 = 19.0 \pm 0.1$ °C and $T_2 = 41.0 \pm 0.1$ °C. This band, corresponding to a transition polarized along the *z*-axis, has a strong charge-transfer character and, consequently, it is greatly influenced by polar solvents.^{32,33} The results are given on Table 1.

Whereas **II–IV** do not show variations in their spectral characteristics with changes in temperature, **I** shows a hypsochromic shift with a hypochromic effect when the temperature is increased.

Spectra obtained for **Ib** in DCE at four different temperatures are shown in Figure 1. The lack of an isoabsorption point may indicate that the observed temperature dependence is not due to solute–solvent or solute–solute intermolecular interactions.^{20,34} A similar behaviour has been observed for several systems where intramolecular equilibrium was detected.^{20,35}

The correlations obtained by Kamlet and Taft's SCM [equation (1)] are given in Table 2.

The temperature dependence of the spectral properties for compounds **I** (not observed for the other compounds) and the trends in regression coefficients in Table 2 can be understood by considering that com-

Table 1. Maximum of the longest wavelength absorption bands ν_{\max} in kK for compounds **I–IV**^a

Solvent	Ia		Ib		Ic		II ^b	III ^b	IV ^b
	T_1	T_2	T_1	T_2	T_1	T_2			
Hx	29.32	29.47	28.38	28.80	28.73	28.94	27.67	31.52	24.39
Tl	27.35	27.63	26.83	27.25	26.96	27.25		23.54	
Bz			26.74	26.93				29.03	23.46
DCE	26.47	26.69	26.16	26.64	26.47	27.03	25.65		23.29
DCM	26.53	26.67	26.11	26.54	26.22	26.62	25.04	28.47	23.15
Chl								28.67	
EE								28.40	
EtAc	26.77	26.92	26.83	26.73	26.69	26.88	26.32		26.60
Ac	26.03	26.51	25.98	26.23	26.05	26.24	25.28	27.30	23.29
DMF									26.33
2-PrOH	26.18	26.28	26.03	26.11	25.95	26.11	25.54	26.49	23.60
EtOH	26.22	26.32	26.25	26.46	25.75	26.26	25.50		23.64
MeOH	26.72	26.50	25.91	26.27	26.20	26.22	25.67	27.06	23.68
ACN	26.14	26.27	25.93	25.93	26.10	26.22	25.41	27.56	23.21

^a $T_1 = 19.0 \pm 0.1$ °C; $T_2 = 41.0 \pm 0.1$ °C.

^bIdentical values of ν_{\max} at T_1 and T_2 .

Table 2. Terms of the solvatochromic comparison method⁴ for compounds I–IV^{a,b}

Compound	Temperature	ν_0	$-s$	$-b$	$-a$	r	n
Ia	T_1	29.11 ± 0.11	3.19 ± 0.16	1.53 ± 0.12	0	0.9948	10
Ia	T_2	29.27 ± 0.13	3.06 ± 0.17	1.57 ± 0.14	0	0.9926	10
Ib	T_1	28.23 ± 0.09	2.53 ± 0.13	1.00 ± 0.10	0	0.9915	11
Ib	T_2	28.66 ± 0.09	2.52 ± 0.14	1.31 ± 0.11	0	0.9928	11
Ic	T_1	28.53 ± 0.09	2.66 ± 0.15	1.21 ± 0.11	0	0.9927	10
Ic	T_2	28.77 ± 0.10	2.52 ± 0.16	1.52 ± 0.12	0	0.9917	10
II	T_1 or T_2	27.50 ± 0.17	2.54 ± 0.26	0	0.72 ± 0.20	0.9878	10
III	T_1 or T_2	30.98 ± 0.21	3.17 ± 0.33	3.09 ± 0.28	0	0.9877	10
IV	T_1 or T_2	24.30 ± 0.08	1.28 ± 0.13	0	0	0.9878	10

^a Confidence level of every correlation was greater than 99.99%, according to the *t*-test.

^b $T_1 = 19.0 \pm 0.1$ °C; $T_2 = 41.0 \pm 0.1$ °C.

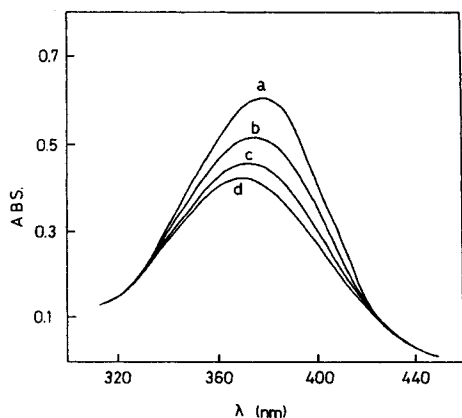
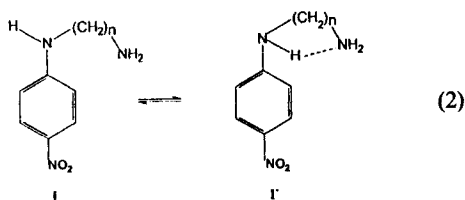


Figure 1. Absorption spectra of **Ib** in DCE (2.87×10^{-5} M). Temperature: (a) 18.0 ± 0.1 ; (b) 25.0 ± 0.1 ; (c) 37.0 ± 0.1 ; (d) 45.0 ± 0.1 °C

pounds of type **I** may establish an equilibrium as given in equation (2).



Then, the absorption band obtained for compounds **I** results from the sum of the spectra of both compounds. The relative populations of the two conformations, one involving an intramolecular hydrogen bond and the other, capable of forming an intermolecular hydrogen bond with hydrogen bond acceptor solvents, is temperature dependent.

As can be observed from the b values in Table 2, there is a strong effect of the β parameter on **I** and **III**. This effect can be interpreted as being due to the hydrogen bond donor ability of the H in the aromatic amino group, which seems to be large for **III**. In **I**, the sensitivity to the β parameter is temperature dependent. The higher the temperature, the larger is the sensitivity, thus implying a greater availability of aniline hydrogen at higher temperatures.

In contrast, there is no effect of β on **IV**. The values of b are lower than their standard deviation, with a significance level of about 50%, according to Student's *t*-test. This indicates that the H of the aromatic amino group is engaged with the *o*-nitro group in an intramolecular hydrogen bond. This bond is fairly stable, as observed in several *N*-alkyl-*o*-nitroanilines.¹⁶ As expected, no effect of β was found in **II**.

The values of s are high and negative, as expected, considering the important increase in the dipole moment on excitation for these solutes.³⁶ Compounds **I** show practically no variation of s when the temperature is changed.

On the other hand, the values of ν_0 for **I** increase with increase in temperature, which may indicate an excited-state stabilization at lower temperatures. In addition, the values of ν_0 , s and b for **Ib** (Table 2) are lower than the corresponding values for **Ia** and **Ic**, which may indicate a more negative value of ΔH for the equilibria of **Ib**. This seems to be reasonable, considering that the intramolecular hydrogen bond in **Ib'** involves a six-membered ring.¹³ The intramolecular hydrogen bond stabilizes the excited state owing to the dispersion of positive charge of the aniline nitrogen; then, a smaller value of ν_0 is observed. The lower value of s can also be explained by the stabilization of the excited state of this solute making it less sensitive to the solvent polarity.¹⁶ The lower value of b is due to the fact the aniline hydrogen is less available than the corresponding values for **Ia** or **Ic**.

¹H NMR studies

Proton chemical shifts are extremely sensitive to hydrogen bonding. In almost all cases, formation of a hydrogen bond causes the resonance of the bonded proton to move downfield. When the hydrogen bonding is intermolecular, the chemical shifts vary with concentration. Increasing dilution in inert solvents normally produces shifts to high field as the proportion of free monomer increases. When intramolecular hydrogen bonding occurs, the concentration dependence of chemical shifts is, of course, reduced, as the hydrogen bonding persists in dilute solution.³⁷

In general, there is a rough correlation between the NMR shift, and the strength of the bond as measured by the enthalpy of its formation.³⁷

In carbon tetrachloride as solvent, the chemical shift δ of the amine hydrogen for *p*-nitroaniline is 3.53 ppm³⁸ and for *o*-nitroaniline, where the formation of a very stable intramolecular hydrogen bond is known,^{16,22,23} the chemical shift δ is 6 ppm.³⁸

The chemical shifts of the aniline hydrogen measured for compounds type **I** and **III** are reported in Table 3. The downfield chemical shifts for **I** suggest intramolecular hydrogen bond formation.

The ¹H NMR spectra for **Ic** in chloroform-*d* (non-hydrogen bond acceptor solvent) at different concentrations are given in Table 3. It can be observed there is no change in the chemical shift for the aniline

hydrogen, indicating that the hydrogen bond is intramolecular. On the other hand, the chemical shift for **Ib** is at a lower field than that corresponding to **Ia** and **Ic** (Table 3).

The observed chemical shift, δ for compounds of type **I** is given by³⁹

$$\delta = p_1\delta_1 + p_2\delta_2 \quad (3)$$

where p_1 and p_2 are the fractional populations for **I'** and **I** [equation (2)], respectively, and δ_1 and δ_2 are their respective chemical shifts. If we assume that δ_1 and δ_2 are similar for the three compounds **I**, then $p_1:p_2$ is higher for **Ib** than for **Ia** or **Ic**. These findings seem to offer strong corroborative evidence for the conclusions drawn from the UV-visible studies.

IR studies

Primary and secondary amines can be identified in the infrared spectrum by the vibrations of NH₂ and NH groups. In the NH stretching region (3050–3500 cm⁻¹), primary amines show two bands (symmetric and asymmetric) whereas secondary amines show a single band.⁴⁰

Intermolecular and/or intramolecular hydrogen bonding effects are shown by most amines under suitable conditions. In the condensed phase, hydrogen bonding occurs with amines and causes a small decrease in the absorption frequency, which is usually less than 100 cm⁻¹.⁴¹

The intramolecular hydrogen bond between adjacent NH₂ and NO₂ groups in nitronaphthylamine results in characteristic frequency shifts compared with 1-naphthylamine or 2-nitro-8-aminonaphthalene.⁴² Similar results have been observed for *o*- and *p*-nitroanilines.⁴³

The infrared frequencies of the aliphatic ν_{NH} and aromatic $\nu_{(\text{Ar})\text{NH}}$ stretching band for **I–IV** in chloroform solution are given in Table 4. Comparing the values of $\nu_{(\text{Ar})\text{NH}}$, compounds **I** and **IV** appear at lower frequencies, as expected from the ability of these compound to form intramolecular hydrogen bonds. On

Table 3. ¹H NMR spectral data

Compound	Concentration (10 ⁻³ M)	δ^a
Ia	1	5.05
Ib	1	5.68
Ic	1	5.04
Ic	8	5.04
Ic	50	5.04
III	1	3.53

^aChemical shifts for the NH protons in chloroform-*d* in ppm from TMS as internal standard.

Table 4. Infrared frequencies (cm⁻¹) of the aliphatic ν_{NH} (symmetric and asymmetric) and aromatic $\nu_{(\text{Ar})\text{NH}}$ stretching bands for compounds **I–IV** in 6 × 10⁻³ M chloroform solution

Compound	ν_{AR}	$\nu_{\text{NH}}(\text{asym})$	$\nu_{\text{NH}}(\text{sym})$	$\Delta\nu^a$
Ia	3390	3444	3420	24
Ib	3266	3434	3390	44
Ic	3386	3440	3400	40
II	—	3504	3472	32
III	3436	—	—	—
IV	3384	3504	3472	32

^a $\nu_{\text{NH}}(\text{asym}) - \nu_{\text{NH}}(\text{sym})$.

Table 5. Infrared frequencies (cm^{-1}) of the aromatic $\nu_{(\text{Ar})\text{NH}}$ stretching bands for compounds **I** in the solid state

Compound	$\nu_{(\text{Ar})\text{NH}}$	$\Delta\nu_{(\text{Ar})\text{NH}}^a$
Ia	3229	161
Ib	3238	28
Ic	3294	92

^a $\nu_{(\text{Ar})\text{NH}}(\text{solution}) - \nu_{(\text{Ar})\text{NH}}(\text{solid state})$.

comparing the $\nu_{(\text{Ar})\text{NH}}$ values among compounds **I**, **Ib** appears at a lower frequency, with the highest proportion of intramolecular hydrogen bonding.

In the same way, compounds **I** show values of ν_{NH} lower than the corresponding values for **II** and **IV** in which the aliphatic NH_2 has no possibility of forming a hydrogen bond.

When the values of $(\Delta\nu)_{\text{NH}} = \nu_{\text{asym}} - \nu_{\text{sym}}$ are compared, the corresponding value for **Ib** is the highest. This indicates a stronger intramolecular hydrogen bond. For example, it is known⁴³ that the $(\Delta\nu)_{\text{NH}}$ value of *o*-nitroaniline (125 cm^{-1}) is larger than that for *p*-nitroaniline (98 cm^{-1}), both in carbon tetrachloride, indicating the presence of a sufficiently strong intramolecular hydrogen bond in *o*-nitroaniline.

Table 5 gives the infrared frequencies of the NH stretching band of compounds **I** in the solid state.

With the frequency values determined in the solid state it is not possible to predict intramolecular hydrogen bonds because nitroanilines in the solid state form polar hydrogen-bonded chain structures,^{13,26a} and both inter- and intramolecular hydrogen bonds showed lower ν_{NH} values.

The comparison of frequencies in the solid state with those in solution $\Delta\nu(\text{solution} - \text{solid})$, shows some shifts due to solid-state hydrogen bond interactions.^{26a} The $\Delta\nu_{(\text{Ar})\text{NH}}$ values (solution-solid) are depicted in Table 5.

The lowest value of $\Delta\nu_{(\text{Ar})\text{NH}}(\text{solution} - \text{solid})$ for **Ib** may be due to its higher proportion of the structure **Ib'**, which decreases the possibilities of forming an intermolecular hydrogen bond.

In summary, we have shown by different spectroscopic techniques (UV-visible, ¹H NMR and IR) that *N*-(*p*-nitrophenyl)alkylenediamines (compounds type **I**) form intramolecular hydrogen bonds between the H of the aromatic amino group and the N of the aliphatic amino group. Although the bond energy of these hydrogen bonds could not be determined, the variation of the UV-visible spectra with temperature indicates that they are weaker than the intramolecular hydrogen bond between the nitro group and hydrogen of the aromatic amine group in the *ortho* isomer (**IV**). Hence no intramolecular hydrogen bond between amine groups has been detected in **IV**. The strength of the bond depends on the number of methylene groups which sep-

arate them. The optimum number is three (**Ib**), since in this case a more stable six-membered ring is formed.

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