

Protonation of 1,8-Bis(Dimethylamino)naphthalene by N-H Proton Donors in Acetonitrile

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FTIR studies were carried out on a number of systems composed of 1,8-bis(dimethylamino)-naphthalene (DMAN) and various N-H proton donors in acetonitrile. The degree of protonation was estimated based on the intensity of the Bohlmann bands. As in the case of systems containing OH acids homoconjugated anions play an important role in ionic equilibria. In the case of moderately strong proton donors the species present in solution are protonated DMAN, free DMAN, NHN^- homoconjugated anions and more complicated self-solvated species. The homoconjugated NHN^- anions are characterized by a broad doublet with submaxima at *ca.* 1950 and 2500 cm^{-1} .

It has previously been shown¹⁻⁹ that the protonation of 1,8-bis(dimethylamino)naphthalene (DMAN) by moderately strong acids such as phenols and benzoic acids occurs mainly with the participation of two proton donor molecules, AH. The AHA^- homoconjugated anions play an important role in that process. Simultaneously it was shown¹ that the formation constants of the 1:1 complexes of DMAN with phenols in weakly polar solvents are very low, *ca.* one order of magnitude lower than that for 2:1 complexes, $(\text{AH})_2\text{B}$. DMAN appeared to be the weakly active partner in the hydrogen-bond formation although both the $\text{p}K_a$ and proton affinity (PA) indicate very strong basicity. On the other hand, protonated DMAN is very stable in ionizing media. In a non-active medium the self-solvation of anions plays an ionizing role, leading in the simplest case, to the formation of AHA^- species.

It seemed to be justified to extend the studies on protonation of DMAN by means of N-H acids. In this case we have to expect the formation of homoconjugated NHN^- anions which are currently very little known.^{4,5}

Experimental

The compounds listed in Table 1 were of commercial origin. The systems with DMAN were prepared by mixing with the N-H acids in the desired stoichiometry. The 1:1 complexes with 2,4-dinitroimidazole, 4,5-dinitroimidazole and tetrazole (monohydrate) can be obtained in a crystalline form.

The IR spectra were recorded in acetonitrile solution (0.1 mol dm^{-3}) using a FTIR Bruker IFS 113v spectrophotometer. The solvent was purified using the usual procedure and dried over 3 Å molecular sieve. A cell with Si windows and wedge-shaped layer was used to avoid interferences (mean layer thickness 0.4 mm).

Results and Discussion

The N-H acids studied in this work form $\text{N-H}\cdots\text{N}\equiv\text{C}-\text{CH}_3$ hydrogen bonded complexes in acetonitrile, revealed in the band shapes of $\nu(\text{NH})$ stretching vibrations. The stronger the N-H acid the broader and more shifted to lower frequencies is the $\nu(\text{NH})$ band, as shown in Fig. 1.

In the case of the strongest acid studied, *i.e.* 2,4-dinitroimidazole a very broad low frequency wing extending up to *ca.* 2000 cm^{-1} is observed. No broad absorption in the fingerprint region is visible, so that the 'continua' below 2000 cm^{-1} can be entirely ascribed to AHA^+ and AHA^- species.

Table 1 Degree of protonation (%) of 1,8-bis(dimethylamino)naphthalene (DMAN) by N-H acids in acetonitrile

Compound	$\text{p}K_a$	Ratio of DMAN to acid	
		1:1	1:2
2,4-Dinitroimidazole (1)	2.85 ^a	96	100
4,5-Dinitroimidazole (2)	3.32 ^a	94	100
2-Methyl-4,5-dinitroimidazole (3)	4.14 ^a	96	100
3-Nitro-1,2,4-triazole (4)	6.05 ^b	70	98
Tetrazole (5)	4.89 ^c	60	90
4,5-Dichloroimidazole (6)	—	20	35
Benzotriazole (7)	8.57 ^c	3	—
Phthalimide (8)	—	2	—

^a Ref. 6. ^b Ref. 7. ^c Ref. 8.

As previously indicated, the analysis of the intensity of the Bohlmann bands⁹ located below 2950 cm^{-1} was used for the estimation of the degree of protonation of DMAN. For one of the strongest proton donors, *i.e.* 2-methyl-4,5-dinitroimidazole, an almost complete disappearance of those bands is observed for both 1:1 and 2:1 composition. The change of the composition does not cause a change of intensity of the broad absorption in the fingerprint region, as shown in Fig. 2.

On the other hand a substantial increase of intensity of the broad absorption is visible in the region above 1700 cm^{-1} . This additional broad absorption is characterized by a doublet structure with maxima centred at *ca.* 1950 and 2500 cm^{-1} . In the case of NHN^- bridges formed by aliphatic amines only one broad band in this region was observed.⁴ The shape of the band ascribed to protonic $\nu_s(\text{NHN}^-)$ vibrations is well seen in the difference spectra for three different salts shown in Fig. 3.

This band is very similar to those usually observed for moderately strong NHN^+ bridges, which have been studied many times.¹⁰ Let us remember that the doublet character of this band is most probably due to Fermi resonance with overtones of the $\delta(\text{NHN})$ deformation modes¹¹ when an aromatic amine is involved. In the case of very strong NHN^+ hydrogen bonds in homoconjugated cations the broad absorption is extended over the fingerprint region. Such a typical situation was found for the 4-aminopyridine hemiperchlorate single crystal.¹² In the case of protonated DMAN we also observe such broad absorption in acetonitrile solution. For weaker NHN^+ bridges, such as those formed in solid pyrazine

perchlorate, the absorption is limited to the high frequency region above 1700 cm^{-1} .¹³

For the 1:1 4,5-dinitroimidazole-DMAN system no complete disappearance of the Bohlmann bands takes place. The contribution of the non-protonated DMAN is only 6%. The excess of the acid (at composition 2:1) causes complete ion-

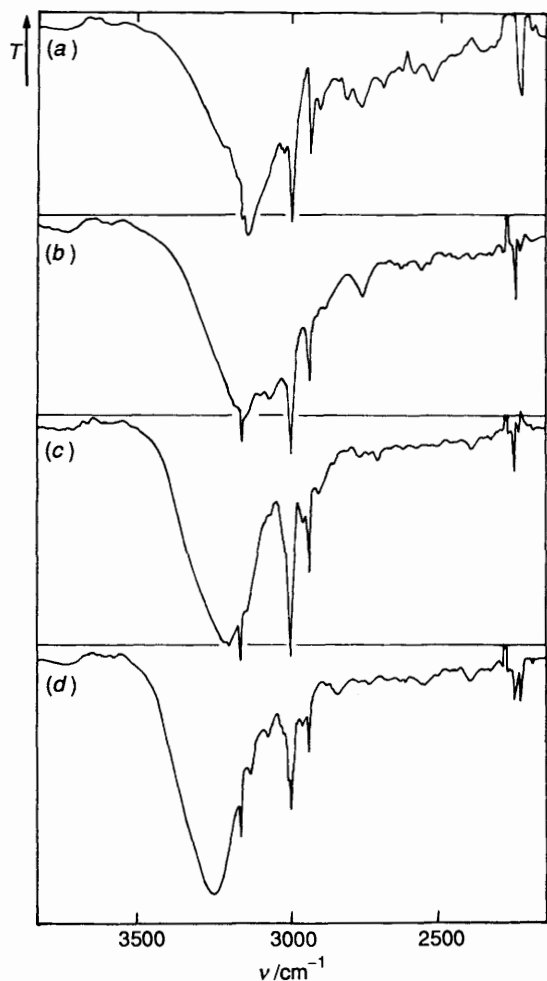


Fig. 1 $\nu(\text{NH})$ absorption bands of N-H acids: (a) 2,4-dinitroimidazole; (b) 2-methyl-4,5-dinitroimidazole; (c) 3-nitro-1,2,4-triazole; (d) 4,5-dichloroimidazole

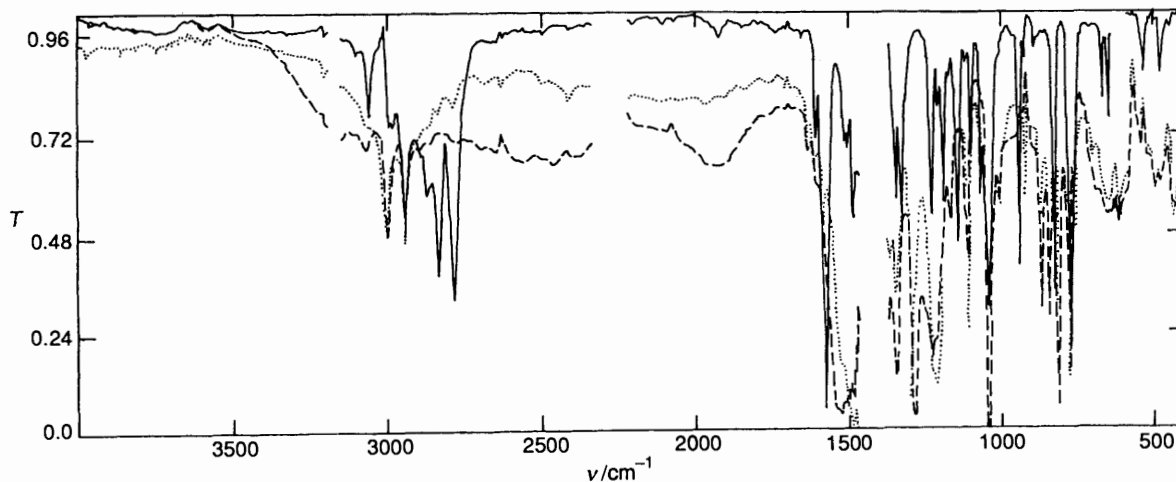
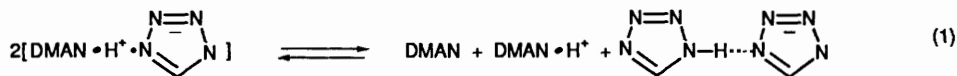
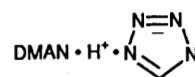


Fig. 2 IR spectra of DMAN-2-methyl-4,5-dinitroimidazole in acetonitrile: solid line, DMAN; dotted, 1:1 system; dashed, 1:2 system

ization of DMAN and bonding of dinitroimidazole anion to a NHN^- homoconjugated anion. In addition to a considerable increase of intensity above 1700 cm^{-1} a slight increase of absorption in the fingerprint region takes place (see Fig. 4).

An interesting group of N-H proton donors (compounds 4-6 in Table 1) show only limited protonation of DMAN. Let us consider in more detail the situation in the system DMAN-tetrazole. Both X-ray diffraction¹⁴ and NMR studies¹⁵ show that in the solid state (monohydrate) the 1:1 complex is completely ionized as shown. In acetonitrile solution some decomposition takes place according to eqn. (1).



Based on the spectra shown in Fig. 5, and particularly on the intensity of the Bohlmann bands, we conclude that at 1:1 composition *ca.* 60% of DMAN is protonated, while at the 1:2 composition the degree of protonation reaches 90%. 3-Nitro-1,2,4-triazole behaves similarly although the degree of protonation in this case is a little higher. The weakest proton donor from this group is 4,5-dichloroimidazole. Simultaneously one should notice some contribution to the high frequency wing of broad absorption due to noncomplexed N-H acids. This contribution is noticeable for the weakest acids.

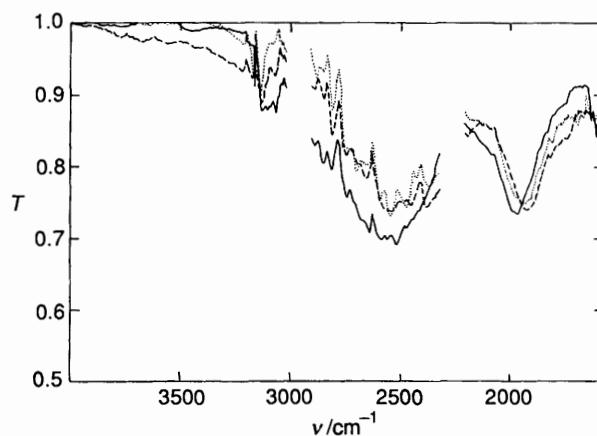


Fig. 3 Difference IR spectra of homoconjugated NHN^- anions: solid line, 3-nitrotriazole; dotted, 2,4-dinitroimidazole; dashed, 4,5-dinitroimidazole

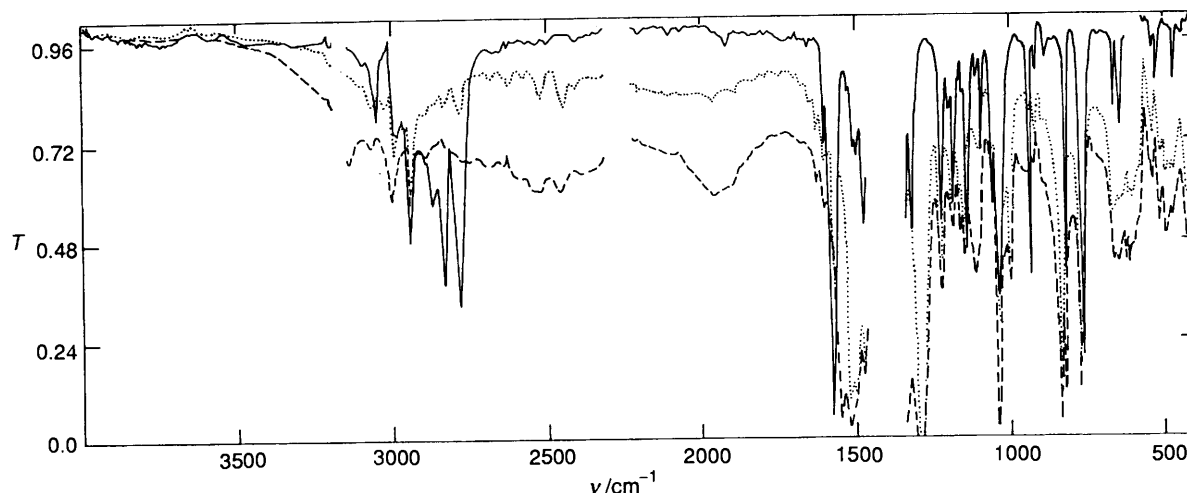


Fig. 4 IR spectra of DMAN-2,4-dinitroimidazole in acetonitrile: solid line, DMAN; dotted, 1:1 system; dashed, 1:2 system

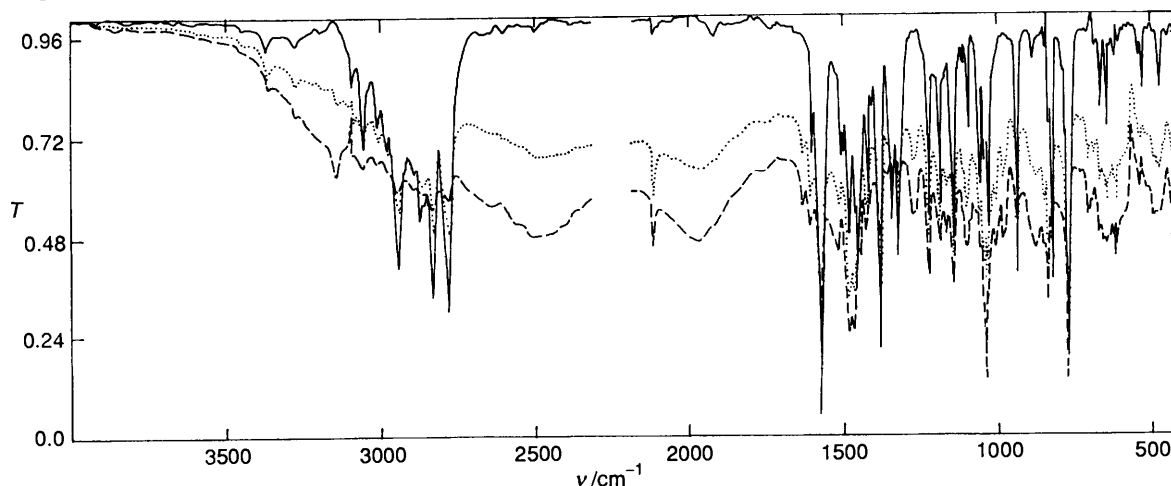


Fig. 5 IR spectra of DMAN-tetrazole in acetonitrile: solid line, DMAN; dotted, 1:1 system; dashed, 1:2 system

Comparison of the results obtained in this work with those reported previously^{2,3} for OH acids indicates that the tendency of an N-H acid to form the homoconjugated anions is similar to that observed for phenols. The pK_a value corresponding to half-protonated DMAN for phenols and N-H heterocyclic acids equals *ca.* 5. For benzoic acids it is markedly lower. In the case of benzotriazole and phthalimide only a negligible amount of ionized species was detected. Such weak N-H acids as 2-ethylimidazole, 1,2,4-triazole, 2-methylbenzimidazole, urea and uracil do not show any protonation of DMAN.

The following conclusions can be drawn from the results obtained. Firstly, the IR spectroscopic behaviour of homoconjugated NHN^- anions is to a large extent analogous to that of relatively weak homoconjugated NHN^+ cations. In both cases a broad doublet in the region $1600\text{--}3000\text{ cm}^{-1}$ of protonic $\nu_s(\text{NHN})$ vibrations is visible. There is a lack of broad absorption in the fingerprint region. Such behaviour is quite different to that of OHO^- homoconjugated anions under the same conditions. The OHO^- bridges show intense background absorption at low frequencies, which is characteristic of very strong hydrogen bonds. Secondly, the comparison of the IR spectroscopic behaviour of symmetric OHO and NHN systems is consistent with *ab initio* calculations¹⁶ which show that OHO bridges should be stronger than NHN ones.

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