SHORT PAPER

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Synthesis and infrared spectroscopic investigation of hydrogen-bonded complexes between 1,8-bis(dimethylamino)naphthalene and 2,6-dihydroxynaphthalene in 2:1 and 1:2 ratios in the crystalline forms and in acetonitrile[†]

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Two hydrogen bonded complexes between 1,8- bis(dimethylamino) naphthalene (DMAN) and 2,6-dihydroxynaphthalene (DHN) in 2:1 and 1:2 ratios were synthesised and studied using FTIR the spectra of the solid 2:1 complex revealed incomplete protonation of DMAN with the appearance of two broad absorptions representing $\nu(NHN)^+$ and $\nu(OHN)$ in the ranges 700–400 and 1600–700 cm^{-1} respectively, while the 1:2 complex indicated the complete protonation of DMAN with the appearance of two broad absorptions representing $\nu(NHN)^+$ and $\nu(OHO^-)$ in the ranges 700–400 and 1600–700 cm^{-1} respectively. On the other hand the IR spectra in acetonitrile indicated that the 1:2 complex is more stable than the 2:1 complex.

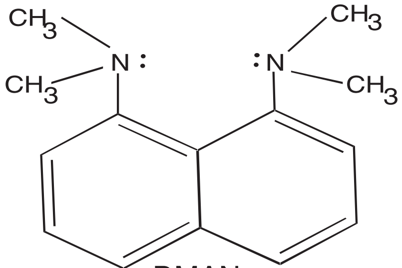
Keywords: DMAN, DHN, hydrogen bond

The attachment of a proton to two-centre bases seems to be of great interest especially in acid–base equilibria[1-5] and in studying potentially symmetrical hydrogen bonds.[6,7] DMAN is a particularly interesting compound including two centre bases. The higher aqueous pK_a of 12.34 and proton affinity of 242 kcal/mol for DMAN[8-10] confirm that this proton sponge is considered as one of the strongest nitrogen bases. These higher values correlate with the short distance between the two nitrogen atoms (2.79 A°).[11] In the solid state, protonation of DMAN forms strongly non linear hydrogen bonds with an extremely low value for $\nu(NHN)^+$, suggesting a peculiar shape of the potential energy curve for the protonation. The (NHN^+) hydrogen bond in protonated proton sponge is interesting from both the crystallographic[12-16] and spectroscopic points of view.[17-22] DMAN as a strong proton acceptor has been used frequently for the abstraction of a proton from various systems. Consequently the aim of the current contribution was to add new hydrogen-bonded complexes, including the proton sponge DMAN, through the synthesis of 2:1 and 1:2 complexes with DHN. An important aim of this work was the analysis of the IR spectra of these complexes in the crystalline form in different regions to predict the ability of DMAN to abstract the proton from DHN by studying the produced broad absorptions and its interaction with the naphthalene π–electron system. The work also aimed to study these complexes in acetonitrile to give more information about the stability of these complexes in solution.

Experimental

DMAN and DHN were of Aldrich spectroscopic grade and were crystallised from ethanol twice before use. Acetonitrile also was Aldrich spectroscopic grade and was dried over 3A° molecular sieves. KBr was Perkin –Elmer spectroscopic grade which was oven dried at 140°C. The 2DMAN : 1DHN and 1DMAN : 2DHN solid complexes were prepared by mixing molar concentrations in the same ratios in acetonitrile. The 2:1 complex was pale brown crystals while the 1:2 complex was dark brown crystals which were grown slowly. The two complexes have uncorrected melting points and gave good carbon, hydrogen and nitrogen elemental analyses. The IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer. KBr pellets were used to measure the spectra of the solid complexes. The IR spectra of 0.01M solution of the 2:1 complex was measured in acetonitrile using KBr windows of 0.02 cm thickness. The 1:2 complex has poor solubility in acetonitrile, hence 0.01M DMAN was mixed with 0.02M DHN in 10 ml volumetric flask, the mixture stood overnight to complete the reaction and the IR spectra of the resulting solution measured.

Results and discussion



DMAN

The protonation of DMAN can be clearly understood from the intensity of Bohlmann bands[23] in the range 2700-3000 cm^{-1}. These bands are attributed to the stretching vibrations of the methyl groups attached to the nitrogen atoms *trans* to the nitrogen lone electron pair. Fig. 1 shows the IR spectra in the Bohlmann bands region. Fig. 1a represents the IR spectrum of DMAN where the Bohlmann bands are clearly observed with higher intensities. Fig. 1b represents the spectrum of the 2:1 solid complex where a reduction in the Bohlmann band intensities confirm the incomplete protonation of DMAN. The complete protonation of DMAN led to the complete vanishing of Bohlmann bands as reported by Brzezinski *et al*. upon protonation of DMAN by HBF_4.[17] The incomplete protonation of DMAN in the 2:1 complex strongly suggests the sharing of the DHN proton between the two nitrogen atoms of DMAN and the O^- of DHN leading to the formation of two hydrogen bonds (NHN^+) and (OHN). These results are based on the appearance of two broad absorptions extending from 1700–700 and 700–400 cm^{-1} representing $\nu(OHN)$ and $\nu(NHN^+)$ respectively. Fig. 2 represents the IR spectra in the range 1700–700 cm^{-1} where the broad absorption representing the $\nu(OHN)$ is clearly seen with a center at 1145 cm^{-1}, the

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

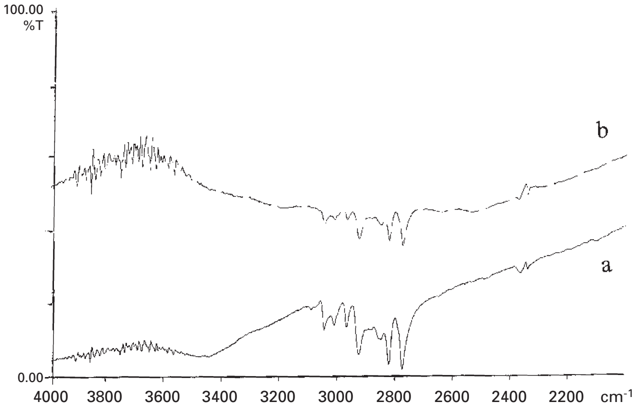


Fig. 1 IR spectra in the region of Bohlmann bands: (———) DMAN, (--------) 2:1 complex.

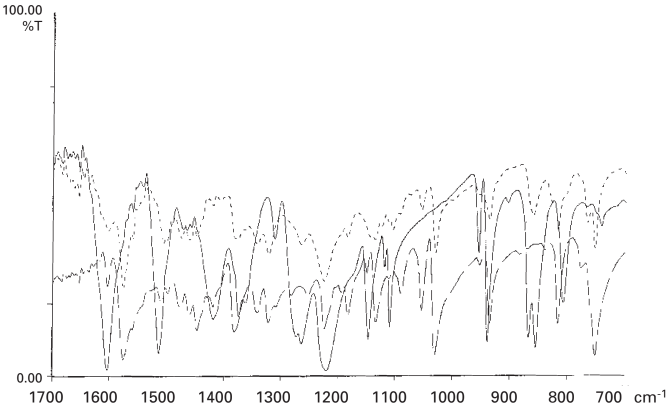


Fig. 2 IR spectra in the 1700-700 cm^{-1} range: (———) DHN, (--------) DMAN, (......) 2:1 complex.

gravity centre of the broad absorption ν_{cg} was calculated using the equation

$$vcg = \frac{\Sigma A v}{\Sigma A}\ \text{cm}^{-1}$$

where A is the absorbance and ν is the frequency within the studied frequency range. This absorption continua is mainly produced from the perturbation of the in-plane and out of plane deformation modes of DHN near 935 and 1520 cm^{-1} as well as the $\nu_{C\text{-}O}$ modes between 1200-1300 cm^{-1}. Fig. 3 shows the absorption continua representing $\nu(NHN^+)$ of the 2:1 complex with a centre at 483 cm^{-1} . This broad absorption is produced from the strong coupling between the protonic vibration and the deformation modes of the naphthalene rings leading to the perturbation of these modes at 480, 580, 660, and 680 cm^{-1} for DHN and at 480, 530, 650, and 670 cm^{-1} for DMAN. This broad absorption is characterised by the appearance of various Evan windows at 430, 500, 560, and 650cm^{-1}.[12-22] For the 1DMAN : 2DHN complex in the Bohlmann region, (Fig. 4), complete vanishing of the Bohlmann bands is clearly seen confirming the complete protonation of DMAN. The broad absorption band at 3410 cm^{-1} is attributed to $\nu_{O\text{-}H}$ of the DHN moiety overlapped with the $\nu_{C\text{-}H}$ of the aromatic rings. Two broad absorptions are recorded, the first lies in the range 1600–700 cm^{-1} and is attributed to the homoconjugated anion $\nu_{(O\text{-}H\text{-}O^-)}$ with a centre at 1182 cm^{-1}. The second lies in the range 700–400 and is attributed to the homoconjugated cation $\nu_{(N\text{-}H\text{-}N+)}$ vibration band with characteristic windows at 432, 501, 535 and 550 cm^{-1} and centered at 469 cm^{-1}. Concerning the absorption continua representing $\nu_{(O\text{-}H\text{-}O^-)}$, one can not observe any absorption near 2000 cm^{-1} although some absorption must be expected according to the Novak correlation.[24] This observation could be interpreted in terms of a strong coupling between (OHO$^-$) and the naphthalene π-electron system leading to increase of the width and decrease of the intensity of the $\nu_{(O\text{-}H\text{-}O^-)}$ continua. This led to the vanishing of the 2000 cm^{-1} OHO$^-$ stretching vibration.[25,26] Hence the formed 1:2 complex most probably the following structure.

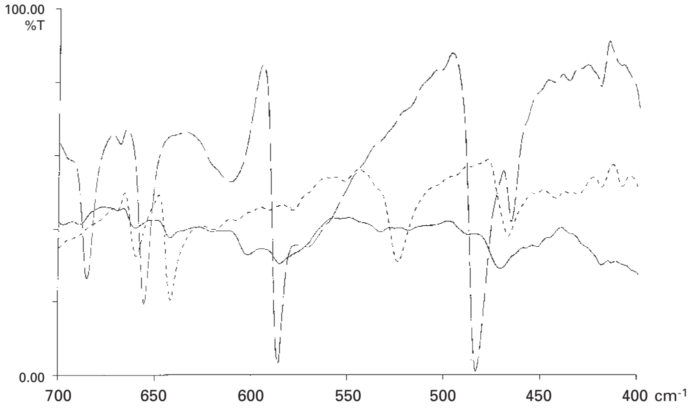


Fig. 3 IR spectra in the range 700–400 cm^{-1}: (-----) DHN, (....) DMAN, (———) 2:1 complex

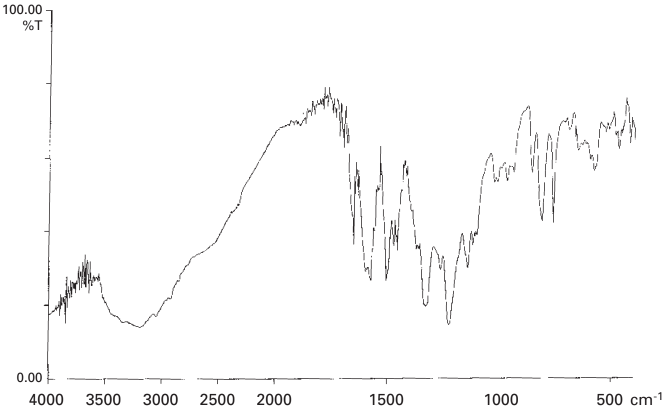
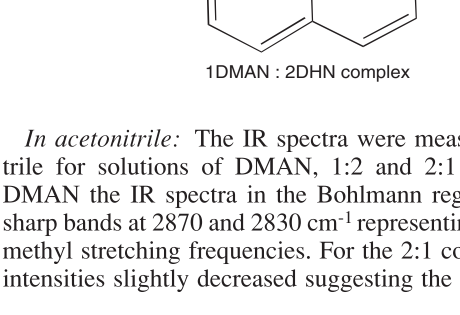
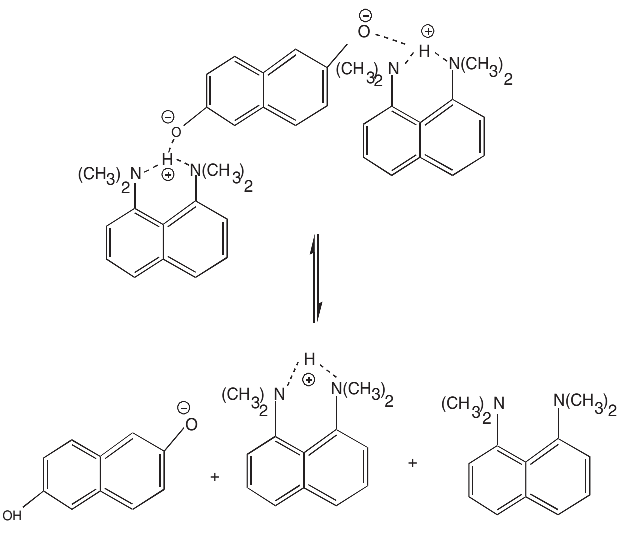


Fig. 4 IR spectrum of the 1:2 complex in the range 4000–400 cm^{-1}.



1DMAN : 2DHN complex

In acetonitrile: The IR spectra were measured in acetonitrile for solutions of DMAN, 1:2 and 2:1 complexes. For DMAN the IR spectra in the Bohlmann region showed two sharp bands at 2870 and 2830 cm^{-1} representing the Bohlmann methyl stretching frequencies. For the 2:1 complex, the band intensities slightly decreased suggesting the existence of free



Scheme 1

DMAN. The DHN $\nu_{O\text{-}H}$ band was found at 3400 cm^{-1} confirming the presence of free naphthoxide anion. The IR spectra between 800 and 400 cm^{-1} were measured where the broad absorption representing the frequency $\nu_{(N\text{-}H\text{-}N+)}$ was recognised with a centre at 460 cm^{-1}. Hence one concludes that the 2:1 complex is unstable in acetonitrile where it decomposes to free DMAN, protonated DMAN and free naphthoxide anion in 1:1:1 ratio according to Scheme I.

Although there was a strong reduction in the intensity of the Bohlmann methyl bands of the 1:2 complex in the range 4000–2000 cm^{-1} , nevertheless the $\nu_{(N\text{-}H\text{-}N+)}$ absorption band with a centre at 478 cm^{-1} was clearly recorded between 700 and 400 cm^{-1}, asserting the stability of this complex. Good evidence for this stability in acetonitrile comes from the appearance of a broad band between 1470 and 1370 cm^{-1} attributed to $\nu_{(O\text{-}H\text{-}O^-)}$. Information about the stability of the 1:2 complex can be obtained from the analysis of the absorption band at 1575 cm^{-1} attributed to the Ag(ν_{12}) naphthalene ring vibration.[27,28] The appearance of this band (Fig.5) is due to the fact that the $N(CH_3)_2$ groups in DMAN are markedly twisted with respect to the naphthalene ring causing a lowering of the symmetry. The protonation of the DMAN molecules makes the hydrogen–bonded NHN^+ chelate ring almost coplanar with the naphthalene ring and this leads to an increase in symmetry. Hence there is a lowering in the intensity of the Ag(ν_{12}) band as clearly seen in Fig.5. The small reduction observed for the 2:1 complex suggests the decomposition of the complex to DMAN, protonated DMAN and naphthoxide anion in a 1:1:1 ratio. On the other hand the drastic lowering of the intensity of Ag(ν_{12}) in the 1:2 complex band confirms the stability of this complex in acetonitrile.

Conclusions

(1) The 2:1 and 1:2 complexes between DMAN and DHN have been successfully synthesized

(2) Incomplete protonation of DMAN occurs in the 2:1 complex but complete is in the 1:2 complex

(3) The 2:1 complex is unstable in acetonitrile where it decomposes to DMAN, protonated DMAN and free naphthoxide in a 1:1:1 ratio

(4) The 1:2 complex is stable in acetonitrile as confirmed from the appearance of broad absorptions assigned to the homoconjugated cation ($N\text{-}H\text{-}N^+$) and homoconjugated anion ($O\text{-}H\text{-}O^-$).

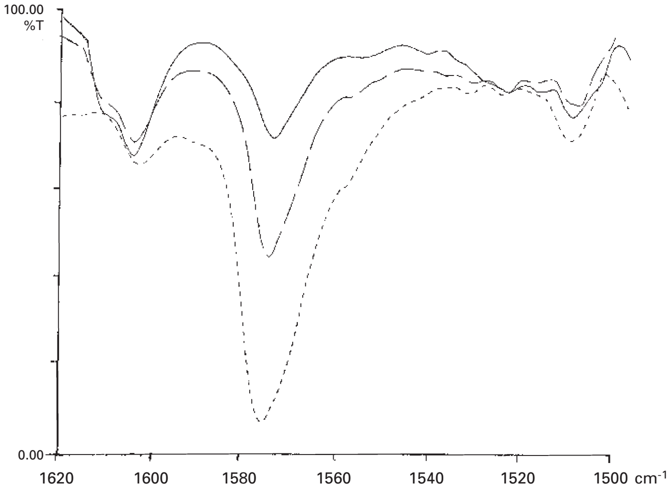


Fig. 5 IR spectra in the Ag (ν_{12}) region band: (....) DMAN, (-------), 2:1 complex and (——) 1:2 complex.

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