Structure and IR Spectra of Protonated 1,8-Bis(dimethylamino)naphthalene Proton Sponge*


aFaculty of Chemistry, A. Mickiewicz University, 60-780 Poznań, Poland
bInstitute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland
bInstitute of Fundamental Chemistry, Technical University, 71-065 Szczecin, Poland

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A review of X-ray diffraction studies (including those not published so far) on a number of salts composed of 1,8-bis(dimethylamino)naphthalene (DMAN) and various proton donors is presented. The symmetry of intramolecular NHN^+ bridges in protonated DMAN changes depending on the counterion and the resulting lattice potential in the neighbourhood of a bridge. Symmetrical NHN^+ bridges in solid protonated DMAN are characterized by a low frequency ν(NHN) stretching vibration at about 500–600 cm⁻¹. The symmetry causes a broadening and some diminishing of integrated intensity of the band and a shift of its centre of gravity towards higher frequencies. In some cases, an additional absorption at about 2000 cm⁻¹ appears. Quite differently behave the protonated DMAN species in acetonitrile solution. In all cases, the so called continua appear, extending between 200–3000 cm⁻¹. In the case of moderately strong proton donors (both for OH and N–N acids) complicated ionic equilibria are evidenced, in which protonated DMAN.H^+ cations, free molecules of DMAN and homoconjugated OHO^- or NHN^- anions participate.

INTRODUCTION

1,8-bis(dimethylamino)naphthalene (DMAN) belongs to the best recognized proton sponges. Its basicity is extremely high (pK_a = 12.34–12.1 in water,¹,² and 18.18 in acetonitrile,³ the proton affinity in gas phase PA = 242 kcal/mol.⁴ Several studies aimed at explaining the high basicity of DMAN and solvent effects upon pK_a were reported. These studies were summarized by Alder⁵ and Stewart.⁶ The high basicity of DMAN seems to be due to the fact that the trapped proton is shared between the two equivalent basic centres. Simultaneously, the repulsion between the two electron pairs of nitrogen atoms in the free molecule is neutralized.

* Dedicated to Professor Dušan Hadži on the occasion of his 70th birthday.
** To whom correspondence should be addressed.
The crystallographic studies reported so far\(^7\) show that the NH\(^+\) bridges are either symmetrical (equal distances between proton and nitrogen atoms) or asymmetrical (the proton is shifted more or less to one of nitrogen atoms). The asymmetry scale in known cases is broad.

The potential energy for the proton motion in symmetrical or close to symmetrical NH\(^+\) bridges is characterized by a peculiar shape that is reflected in the position and the structure of the \(v_s\) (NHN) band as well as in the unusual isotope effect \(v_{s}(\text{NHN})/v_{s}(\text{NDN})\) reaching high values, markedly exceeding \(\sqrt{2}\).\(^8\) In one case, it is higher than 2. One could expect the potential to be close to a rectangular one. The studies also showed that the IR spectroscopic behaviour depends substantially on the counteranion, which can affect the shape of the potential. However, it seems that a decisive factor affecting the bridge geometry and, hence, the spectroscopic behaviour is the resulting lattice potential in the direct neighbourhood of a bridge. Thus, it seemed justified to undertake systematic studies of the geometry and IR spectra of various salts of DMAN.

On the other hand, it appeared\(^9\) that the IR spectra of protonated DMAN in solution differ substantially from those recorded in the solid state. In such a polar solvent as acetonitrile, one observes a very broad protonic absorption extended over almost whole infrared region. The frequency isotopic ratio is about 1. This is a typical behaviour of homoconjugated NH\(^+\) cations like that in [PyHPy\(^+\)] and other hemiprotonated pyridines. Moreover, it was shown\(^10-12\) that salts of DMAN undergo complicated ionic equilibria with participation of homoconjugated OHO\(^-\) or NHN\(^-\) anions. Based on the studies performed so far by using various proton donors, one could attempt more general conclusions related to the solvent effects and the influence of the donor properties of acids on the ionic equilibria.

**STRUCTURE OF DMAN·H\(^+\) CATIONS**

The data related to the geometry of NH\(^+\) bridges in protonated DMAN collected so far, as well as the positions of the gravity centres for the \(v_s\) (NHN) bands, are presented in Table I.

All N···N distances found to date are comprised in a relatively narrow range of 2.55–2.65 Å. It has been suggested\(^7\) that the length of 2.65 Å for NHN bridges is the upper limit of symmetrical bridges. The results quoted in Table I seem to indicate that there is no direct correlation between the bridge length and the bond length r(N–H), although the symmetry is preferred for the shortest bridges, below 2.60 Å. However, one can find examples of strongly asymmetric bridges with the length below 2.60 Å. As a measure of symmetry, we accept the ratio of the distances of the proton between the respective nitrogen atoms. For symmetric bridges, this ratio equals 1.

All salts of the DMAN investigated so far possess bridges which are markedly bent. The \(\angle\)NHN values are included in the limits of 150–160°. In one case, namely for salt \(XII\) (see Table I), this angle is much less but the estimated error for this salt is particularly high. Generally, displacement of the proton from N···N axis does not provide any criterion for bridge asymmetry. The bridges for salts \(I–VI\), with symmetric localization of the proton, show the mean value of the NHN angles found out so far. It is particularly worth emphasizing that in all cases – even in those with strongly asymmetric bridges – the proton is shifted towards the centre of the bridge. We have to remember that the X-ray N–H bond lengths are, as a rule, somewhat shorter than virtual distances between N and H nuclei.\(^7\)
TABLE I

Geometry of NHN⁺ bridges in various salts of 1,8-bis(dimethylamino)naphthalene and localization of protonic νₙ (NHN) bands

<table>
<thead>
<tr>
<th>Proton donor</th>
<th>RₕN···Nₖ</th>
<th>RₕN·II</th>
<th>RₕN·II</th>
<th>ΔNHN, cm⁻¹</th>
<th>νₙ(NHN), cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I: IVBr·2H₂O</td>
<td>2.554(1)</td>
<td>1.31(1)</td>
<td>1.31(1)</td>
<td>153(3)</td>
<td>480</td>
<td>13</td>
</tr>
<tr>
<td>II: HF₄</td>
<td>2.562(3)</td>
<td>1.30(3)</td>
<td>1.31(3)</td>
<td>159(2)</td>
<td>514</td>
<td>14</td>
</tr>
<tr>
<td>III: HNC₅, 290K</td>
<td>2.556(3)</td>
<td>1.302(5)</td>
<td>1.302(5)</td>
<td>160(2)</td>
<td>533</td>
<td>15</td>
</tr>
<tr>
<td>IV: 188K</td>
<td>2.573(3)</td>
<td>1.316(4)</td>
<td>1.316(4)</td>
<td>156(2)</td>
<td>480</td>
<td>16</td>
</tr>
<tr>
<td>V: 5-Mercapto-1-methyl-tetrazole·1/2 H₂O</td>
<td>2.590(3)</td>
<td>1.33(1)</td>
<td>1.33(1)</td>
<td>152(3)</td>
<td>500</td>
<td>16</td>
</tr>
<tr>
<td>VI: 2,4,5,7-Tetranitro-1,8-diaminonaphthalene</td>
<td>2.577(3)</td>
<td>1.30(2)</td>
<td>1.33(2)</td>
<td>158(2)</td>
<td>529</td>
<td>17</td>
</tr>
<tr>
<td>VII: HOF Te₅</td>
<td>2.574(−)</td>
<td>1.17(−)</td>
<td>1.45(−)</td>
<td>159(−)</td>
<td>159(−)</td>
<td>18</td>
</tr>
<tr>
<td>VIII: X: 1,8-Bis(2,2,2-trifluoroacetamido)naphthalene</td>
<td>2.577(3)</td>
<td>1.17(−)</td>
<td>1.45(−)</td>
<td>159(−)</td>
<td>159(−)</td>
<td>19</td>
</tr>
<tr>
<td>IX: CHLORAMINE ACID (12) H₂O 300 K</td>
<td>2.590(2)</td>
<td>1.14(3)</td>
<td>1.51(3)</td>
<td>155(2)</td>
<td>550,2000</td>
<td>20</td>
</tr>
<tr>
<td>X: 180 K</td>
<td>2.588(1)</td>
<td>1.07(3)</td>
<td>1.59(2)</td>
<td>152(2)</td>
<td>550,2000</td>
<td>21</td>
</tr>
<tr>
<td>XI: H Tris(hexafluoroglycolylacetatono) Cu²⁺</td>
<td>2.65(2)</td>
<td>1.27(17)</td>
<td>148(12)</td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>XII: H Tris(hexafluoroglycolylacetatono) Mg²⁺</td>
<td>2.60(1)</td>
<td>1.25(11)</td>
<td>134(8)</td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>XIII: Di-4-nitroimidazole-5-sulphide</td>
<td>2.50(7)</td>
<td>1.24(5)</td>
<td>1.39(5)</td>
<td>152(4)</td>
<td>550,2000</td>
<td>22</td>
</tr>
<tr>
<td>XIV: 1,8-Dinitroimidazole</td>
<td>2.587(7)</td>
<td>1.05(4)</td>
<td>1.68(4)</td>
<td>160(4)</td>
<td>obscured</td>
<td>23</td>
</tr>
<tr>
<td>XV: Squaric acid</td>
<td>2.589(3)</td>
<td>1.08(2)</td>
<td>157(2)</td>
<td>600,2000</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>XVI: 3,4-Furandicarboxylic acid. H₂O</td>
<td>2.521(3)</td>
<td>1.06(2)</td>
<td>1.62(2)</td>
<td>155(2)</td>
<td>600,2000</td>
<td>25</td>
</tr>
<tr>
<td>XVII: 1,8-Bis(4-toluene sulfonamido) 2,4,5,7-tetranitronaphthalene</td>
<td>2.610(5)</td>
<td>1.05(5)</td>
<td>1.63(5)</td>
<td>152(5)</td>
<td>600,2000</td>
<td>25</td>
</tr>
</tbody>
</table>

For two salts, III and IX, the temperature effect upon the packing and geometry of the NHN bridge was studied. In the case of II, practically no temperature effect was detected on the length and symmetry of the bridge. The lowering of temperature in the case of salt IX does not change the bridge length, but leads to a marked increase of asymmetry. The analysis shows that this is due to some shortening of the distance between one of the oxygen atoms of chloranilic anion and one of the two bridge nitrogen atoms. The relationship between the asymmetry of the environment around the bridge and the asymmetry of the bridge itself can be seen in other salts of DMAN.

**INFRARED SPECTRA OF SOLID SALTS OF DMAN**

There is a clear correlation between the changes of the NHN bridges and the evolution on the νₙ (NHN) band. For the symmetric and close to symmetric bridges, a relatively narrow band at very low frequencies (with the maximum at about 500 cm⁻¹) is observed with a rich structure of Evans holes. The half-width Δν₁/₂ is of the order of 300–400 cm⁻¹. Asymmetrization of the bridge leads to broadening of the band and a shift towards higher frequencies. Simultaneously, as it can be seen for salts IX, XIII – XVII, a high frequency absorption region at about 2000 cm⁻¹ appears, which is typical of homoconjugated NHN⁺ cations. The evolution of spectral changes is illustrated in Figure 1.
It is worth mentioning that for symmetric or close to symmetric NHN bridges in DMAN·H⁺ the isotopic ratio $\nu_s$ (NHN)/$\nu_s$ (NDN) reaches unusually high values. The asymmetrization causes a drastic drop in the isotopic ratio and in the cases of broad absorption («continua») reaches values about 1 or even less.
PROTONATION OF DMAN IN ACETONITRILE BY MINERAL ACIDS

DMAN forms with mineral acids 1:1 salts that can be easily isolated in a crystalline form. Salts with such acids as HBF$_4$, HClO$_4$, HAuCl$_4$, HNO$_3$, HCl, HBr and HBPh$_4$ were studied in acetonitrile. IR spectra are almost identical for all acids and are characterized – in contrast to the spectra in solid state – by a continuum of absorption extended over the frequency range of 3000–200 cm$^{-1}$, as shown in Figure 2. In the region 600–400 cm$^{-1}$, intense Evans windows are observed. These results indicate that the DMAN salts undergo a complete ionic dissociation in acetonitrile and the continua should be assigned to free DMAN.H$^+$ species. Simultaneously, the character of continuous absorption indicates that the intramolecular NHN hydrogen bonds are very strong and similar to those frequently observed for homoconjugated intermolecular NHN$^+$ cations.

![Figure 2. Protonic broad absorption in acetonitrile for DMANxHClO$_4$ (dashed), DMANxDCIO$_4$ (dotted), compared with the DMAN spectrum (solid line).](image)

For free base, three Bohlmann bands at 2780, 2831 and 2869 cm$^{-1}$ are visible. Among them the first two bands are particularly strong. These bands can be used in the quantitative analysis of the protonation degree of DMAN because they completely vanish in DMAN.H$^+$. In some cases, particularly for HNCS and HNO$_3$ salts dissolved in acetonitrile, traces of free DMAN are present. One can conclude that in acetonitrile a slight deprotonation of DMAN·H$^+$ takes place with formation of homoconjugated anions according to the equation

$$2\text{DMAN} \cdot \text{H}^+ + 2\text{X}^- \rightleftharpoons \text{DMAN} + [\text{XHX}]^- + \text{DMAN} \cdot \text{H}^+$$

Formation of homoconjugated anions can be univocally evidenced for organic acids (see subsequent section).

For further characterization of intramolecular NHN hydrogen bonds, the $^1$H and $^{13}$C NMR studies were performed on DMAN salts with mineral acids. The results obtained show that chemical shifts of the bridge proton and ring protons, as well as
chemical shifts of the carbon atoms, are almost identical for all salts. These results confirm the conclusions drawn from IR studies, that salts with mineral acids undergo complete ionic dissociation.

Of particular interest seems to be the splitting of 'H NMR signals assigned to the methyl groups of DMAN·H⁺. The decoupling procedure proves that the doublet results from the spin-spin coupling between the bridge and methyl protons. The coupling constant equals 2.5 Hz. The appearance of a doublet suggests that the proton in the intramolecular hydrogen bond is localized and can be described by a single minimum potential. The alternative would be a situation with a double minimum but the residence time at respective nitrogen atom should be sufficiently long, which seems to be less probable.

PROTONATION OF DMAN BY PHENOLS AND CARBOXYLIC ACIDS

The protonation of DMAN by acids other than mineral ones is accompanied in various solvents by several equilibria. A comparison of the spectra for the complexes of DMAN formed with phenols and carboxylic acids with those of hydrogen tetrabutylammonium phenolates and carboxylates clearly shows that the protonation of DMAN by phenols and carboxylic acids is accompanied by homoconjugated anions [RO···HOR]⁻. Such anions are characterized by an intense background absorption below 1800 cm⁻¹. The creation of homoconjugated anions proceeds in the case of phenolate according the equation

2DMAN·HOPh ⇌ DMAN·H⁺ + DMAN + [PhO···HOPh]⁻

Based on the intensity of the Bohlmann bands, the percentage of protonated DMAN was estimated for the solutions DMAN-acid of 1:1 and 1:2 ratios. It was found that the contribution of DMAN·H⁺ in the reaction with acids increases with a decrease of the pKₐ – value of the acid. However, for comparable pKₐ values of phenols and carboxylic acids, the contribution of DMAN·H⁺ is considerably larger for the reaction with phenols. The contribution of protonated DMAN increases when dicarboxylic acids are used in the reaction instead of monocarboxylic acids. Protonation ability of dicarboxylic acids is certainly due to the formation of intramolecular homoconjugated anions. These results show that the pKₐ value cannot be a decisive factor governing the protonation of DMAN.

From the spectra of DMAN with acids it was possible, using the difference technique, to isolate the spectrum of DMAN·H⁺ itself. This spectrum is analogous to that observed for the salts of DMAN with mineral acids. This proves that the character of intramolecular hydrogen bonds in DMAN·H⁺ does not depend on the counteranion and can be most probably described by a single minimum potential for the proton motion.

PROTONATION OF DMAN BY N–H ACIDS

Protonation of DMAN by means of compounds containing acidic N–H groups seems to be interesting not only because the formation of DMAN·H⁺ takes place but also because of the formation of [NHN]⁻ bridges which are very difficult to obtain in other reactions. The application of DMAN to deprotonation of N–H groups extends our knowledge about [NHN]⁻ hydrogen bonds.
In the case of 4,5-dinitroimidazole, which is a strong proton donor, at the ratio 1:1 with DMAN, protonation of DMAN reaches 94%. This means that the absorption continuum arises almost quantitatively from DMAN·H⁺. The broad absorption is analogous in all details to that found for salts with mineral acids. Addition of the excess of acid (2:1 complex) changes substantially the IR spectrum: an increase of the intensity of continuous absorption below 3000 cm⁻¹ and appearance of a broad doublet with submaxima at about 1950 and 2500 cm⁻¹ take place. This doublet is particularly well seen in the difference spectra and can be assigned to the νₛ (NHN)⁻ vibrations. Absorption in this region is very similar to that observed for the NHN⁺ bridges formed by aromatic nitrogen bases. The doublet structure of the νₛ (NHN)⁻ band is most probably caused by the Fermi resonance with the δ(NHN)⁻ overtone.

In the case of 1:1 complex DMAN-tetrazole in acetonitrile, 60% of DMAN is protonated, while for the 2:1 complex 90%. This result indicates that in the protonation reaction of DMAN the [NHN]⁻ anion is initially formed. The results obtained for other N–H acids show that the percentage of protonation increases with a decrease of pKₐ of the acid. The contribution of DMAN·H⁺ is comparable with those obtained for phenols of similar pKₐ values. The tendency of N–H acids to form homoconjugated anions [NHN]⁻ is also similar to the tendency to homoconjugation of phenols [OHO]⁻.

The tetrazole-DMAN complex has been studied by the multinuclear NMR technique both in the solid state and in solution in acetonitrile. The results are in very good agreement with IR spectroscopic behaviour. Thus, an equilibrium takes place after dissolution of the salt in acetonitrile.

Summarizing, one could say that our knowledge of ionic equilibria existing in non-aqueous solutions of DMAN and moderately strong acids is far from quantitative. However, there are no doubts about the substantial role of simple homoconjugated anions and, maybe, more complicated selfsolvated anions.

REFERENCES


SAŻETAK

Struktura i infracrveni spektri protoniranih 1,8-bis(dimetilaminol)naftalen (protonska spužva)

B. Brzeziński, T. Głowiaık, E. Grech, Z. Malarski i L. Sobczyk

Dan je prikaz studija rendgenske difrakcije (uključujući one nepublicirane) za niz soli sastavljenih od 1,8-bis(dimetilamino)naftalen (DMAN) i raznih protonskih donora. Simetrija intramolekulskih mostova NH₄⁺ u protoniranim DMAN mijenja se ovisno o suprotnom ionu i rezultantnom potencijalu rešetke u susjedstvu mosta. Simetrične mostove NH₄⁺ u čvrstim protoniranim DMAN karakterizira niska frekvencija v(NH₄) pri oko 500-600 cm⁻¹. Nesimetrija uzrokuje proširenje i sniženje integriranog intenziteta vrpce, te pomak njezina težišta prema višim frekvencijama. U nekim slučajevima pojavljuje se dodatna absorpcija pri oko 2000 cm⁻¹. Sasvim različito ponašaju se protonirane vrste DMAN u acetonitrilnoj otopini. U svim slučajevima javljaju se tzv. kontinua koja se prostiru između 200 i 3000 cm⁻¹. U slučaju umjereno jakih protonskih donora (i OH i NH kiselina) dokazane su složene ionske ravnoteže, u kojima participiraju protonirani kationi DMAN H⁺, slobodne molekule DMAN i homokonjugirani anioni OHO⁻ ili NHN⁻.