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

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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  $\text{NHN}^+$  bridges in protonated DMAN changes depending on the counteranion and the resulting lattice potential in the neighbourhood of a bridge. Symmetrical  $\text{NHN}^+$  bridges in solid protonated DMAN are characterized by a low frequency  $\nu(\text{NHN})$  stretching vibration at about  $500\text{--}600\text{ cm}^{-1}$ . 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  $2000\text{ cm}^{-1}$  appears. Quite differently behave the protonated DMAN species in acetonitrile solution. In all cases, the so called continua appear, extending between  $200\text{--}3000\text{ cm}^{-1}$ . In the case of moderately strong proton donors (both for OH and N-N acids) complicated ionic equilibria are evidenced, in which protonated  $\text{DMAN.H}^+$  cations, free molecules of DMAN and homoconjugated  $\text{OHO}^-$  or  $\text{NHN}^-$  anions participate.

### INTRODUCTION

1,8-bis(dimethylamino)naphthalene (DMAN) belongs to the best recognized proton sponges. Its basicity is extremely high ( $\text{p}K_{\text{a}} = 12.34\text{--}12.1$  in water,<sup>1,2</sup> and  $18.18$  in acetonitrile;<sup>3</sup> the proton affinity in gas phase  $PA = 242\text{ kcal/mol}$ .<sup>4</sup> Several studies aimed at explaining the high basicity of DMAN and solvent effects upon  $\text{p}K_{\text{a}}$  were reported. These studies were summarized by Alder<sup>5</sup> and Stewart.<sup>6</sup> 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.

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The crystallographic studies reported so far<sup>7</sup> show that the  $\text{NHN}^+$  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  $\text{NHN}^+$  bridges is characterized by a peculiar shape that is reflected in the position and the structure of the  $\nu_s$  (NHN) band as well as in the unusual isotope effect  $\nu_s(\text{NHN})/\nu_s(\text{NDN})$  reaching high values, markedly exceeding  $\sqrt{2}$ .<sup>8</sup> 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<sup>9</sup> 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  $\text{NHN}^+$  cations like that in  $[\text{PyHPy}]^+$  and other hemiprotonated pyridines. Moreover, it was shown<sup>10-12</sup> that salts of DMAN undergo complicated ionic equilibria with participation of homoconjugated  $\text{OHO}^-$  or  $\text{NHN}^-$  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 $\text{DMAN}\cdot\text{H}^+$ CATIONS

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

All  $\text{N}\cdots\text{N}$  distances found to date are comprised in a relatively narrow range of 2.55–2.65 Å. It has been suggested<sup>7</sup> 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  $r(\text{N}-\text{H})$ , 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  $\angle\text{NHN}$  values are included with 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  $\text{N}\cdots\text{N}$  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.<sup>7</sup>

TABLE I

*Geometry of NHN<sup>+</sup> bridges in various salts of 1,8-bis(dimethylamino)naphthalene and localization of protonic  $\nu_s$  (NHN) bands*

Proton donor	$R_{N \cdots N}$ , $\text{\AA}$	$r_{N-II}$ , $\text{\AA}$	$r_{N \cdots II}$ , $\text{\AA}$	$\angle \text{NHIN}$ , <sup>o</sup>	$\nu_s(\text{NHN})$ , $\text{cm}^{-1}$	Reference
I. HBr · 2H <sub>2</sub> O	2.554(4)	1.31(1)	1.31(1)	153(3)		13
II. HBF <sub>4</sub>	2.562(3)	1.30(3)	1.31(3)	159(2)	480	14
III. HNCS, 290K	2.566(3)	1.302(5)	1.302(5)	160(2)	514	15
188K	2.573(3)	1.316(4)	1.316(4)	156(2)	533	
IV. Tetrazole · H <sub>2</sub> O	2.573(2)	1.312(5)	1.312(5)	157(2)	480	16
V. 5-Mercapto-1-methyl-tetrazole · 1/2 H <sub>2</sub> O	2.590(3)	1.33(1)	1.33(1)	152(3)	500	16
VI. 2,4,5,7-Tetranitro-1,8-diaminonaphthalene	2.577(3)	1.30(2)	1.33(2)	158(2)	520	17
VII. HOTeF <sub>5</sub>	2.574(-)	1.17(-)	1.45(-)	159(-)		18
VIII. 1-HO-2-Ph-C <sub>2</sub> B <sub>10</sub> H <sub>10</sub>	2.577(3)	1.22(3)		140(3)		19
IX. Chloranilic acid (1:2)2H <sub>2</sub> O						
300 K	2.590(2)	1.14(3)	1.51(3)	155(2)	550,2000	20
150 K	2.588(1)	1.07(3)	1.59(2)	152(2)		
X. 1,8-Bis(2,2,2-trifluoroacetamido)naphthalene	2.589(3)	1.21(3)	1.43(3)	158(3)	530	17
XI. H Tris(hexafluoroacetyl-acetonato) <sup>2-</sup> Cu <sup>2+</sup>	2.65(2)	1.27(17)		148(12)		21
XII. H Tris(hexafluoroacetyl-acetonato) <sup>2-</sup> Mg <sup>2+</sup>	2.60(1)	1.25(11)		134(8)		21
XIII. Di-4-nitroimidazolyl-5-sulphide	2.562(7)	1.24(5)	1.39(5)	152(4)	550,2000	22
	2.587(7)	1.05(4)	1.58(4)	160(4)	obscured	
XIV. 2,4-Dinitroimidazole	2.606(3)	1.17(3)	1.47(1)	160(3)	650, 1950	23
XV. Squaric acid	2.583(2)	1.08(2)		157(2)	600, 2000	24
XVI. 3,4-Furandicarboxylic acid · H <sub>2</sub> O	2.621(3)	1.06(2)	1.62(2)	155(2)	600, 2000	16
XVII. 1,8-Bis(4-toluenesulphonamido)2,4,5,7-tetranitro naphthalene	2.610(5)	1.05(5)	1.63(5)	152(5)	600,2000 obscured	25

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  $\nu_s$  (NHN) band. For the symmetric and close to symmetric bridges, a relatively narrow band at very low frequencies (with the maximum at about 500  $\text{cm}^{-1}$ ) is observed with a rich structure of Evans holes.<sup>26</sup> The half-width  $\Delta\nu_{1/2}$  is of the order of 300–400  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$  appears, which is typical of homoconjugated NHN<sup>+</sup> cations. The evolution of spectral changes is illustrated in Figure 1.

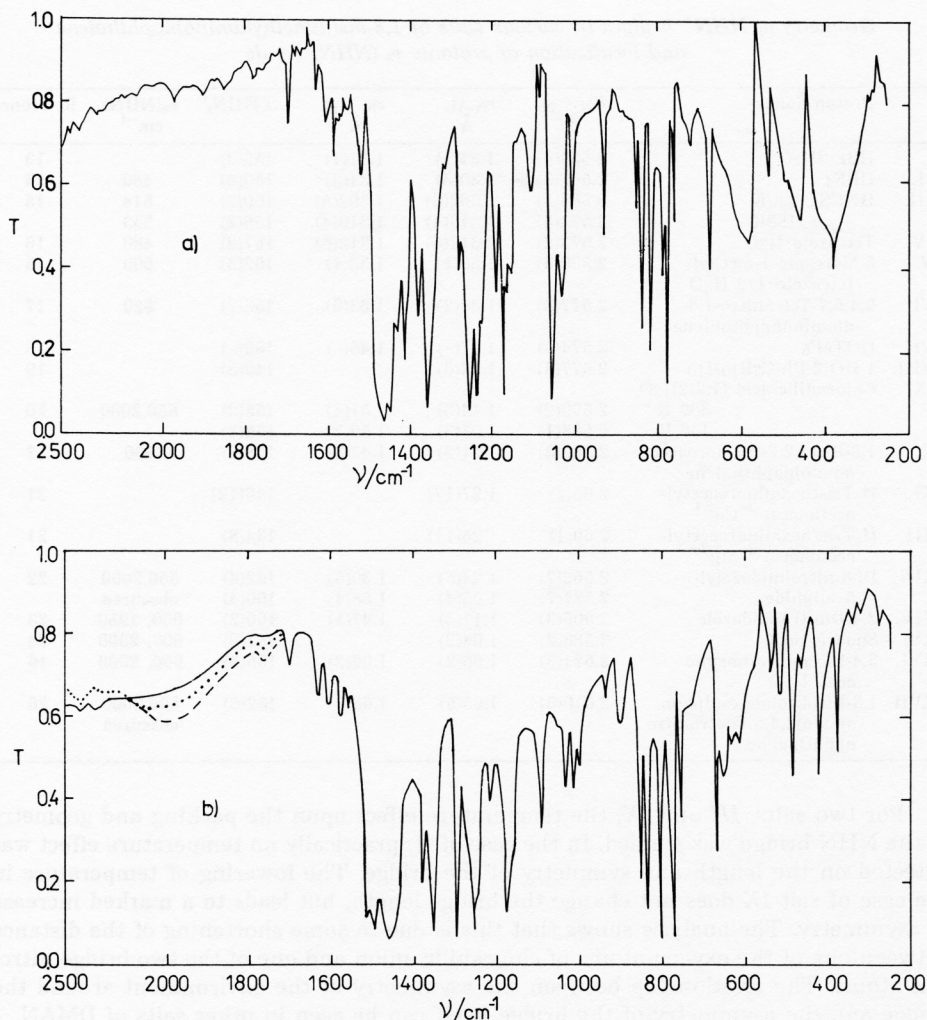


Figure 1. IR spectra in Nujol of DMAN $x$ (4,5)-chloronitroimidazole complex (a) and DMAN $x$ 4,5-dinitroimidazole complex (b). In the case of (a), the band centred between 400–600  $\text{cm}^{-1}$  with deep Evans holes is visible without any absorption above 1800  $\text{cm}^{-1}$ . For complex (b), the low frequency absorption (weaker than that of (a)) is shifted to the region 600–800  $\text{cm}^{-1}$ ; the temperature effect upon additional high frequency absorption at about 2000  $\text{cm}^{-1}$  is shown: solid line at 300 K, dotted at 200 K and dashed at 80 K.

It is worth mentioning that for symmetric or close to symmetric NHN bridges in DMAN $\cdot$ H $^+$  the isotopic ratio  $\nu_s(\text{NHN})/\nu_s(\text{NDN})$  reaches unusually high values.<sup>8</sup> The asymmetrization causes a drastic drop in the isotopic ratio and in the cases of broad absorption ( $\gg$ continua $\ll$ ) 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.<sup>26</sup> Salts with such acids as  $\text{HBF}_4$ ,  $\text{HClO}_4$ ,  $\text{HAuCl}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HBPh}_4$  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  $3000\text{--}200\text{ cm}^{-1}$ , as shown in Figure 2. In the region  $600\text{--}400\text{ cm}^{-1}$ , 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  $\text{DMAN}\cdot\text{H}^+$  species. Simultaneously, the character of continuous absorption indicates that the intramolecular  $\text{NHN}$  hydrogen bonds are very strong and similar to those frequently observed for homoconjugated intermolecular  $\text{NHN}^+$  cations.

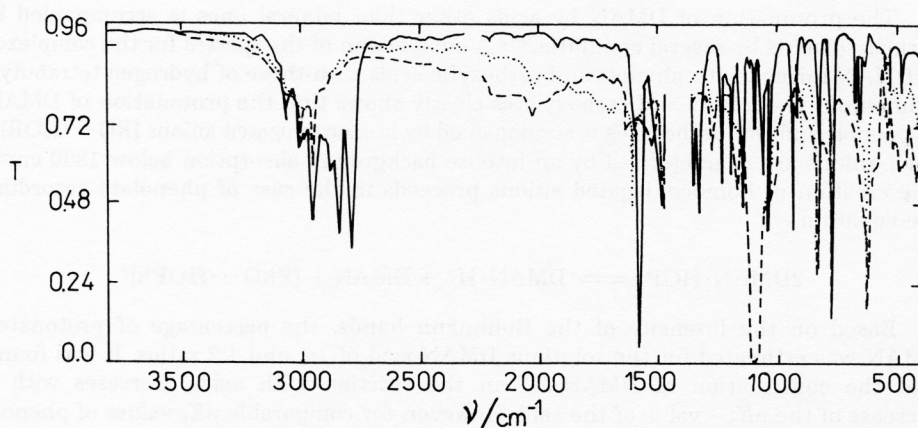


Figure 2. Protonic broad absorption in acetonitrile for  $\text{DMAN}\cdot\text{HClO}_4$  (dashed),  $\text{DMAN}\cdot\text{DClO}_4$  (dotted), compared with the DMAN spectrum (solid line).

For free base, three Bohlmann bands<sup>27</sup> at  $2780$ ,  $2831$  and  $2869\text{ cm}^{-1}$  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  $\text{DMAN}\cdot\text{H}^+$ . In some cases, particularly for  $\text{HNCS}$  and  $\text{HNO}_3$  salts dissolved in acetonitrile, traces of free DMAN are present. One can conclude that in acetonitrile a slight deprotonation of  $\text{DMAN}\cdot\text{H}^+$  takes place with formation of homoconjugated anions according to the equation



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

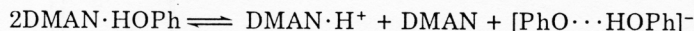
For further characterization of intramolecular  $\text{NHN}$  hydrogen bonds, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies were performed on DMAN salts with mineral acids. The results obtained show<sup>28</sup> that chemical shifts of the bridge proton and ring protons, as well as

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  $^1\text{H}$  NMR signals assigned to the methyl groups of  $\text{DMAN}\cdot\text{H}^+$ . 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.<sup>9-12</sup> 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  $[\text{RO}\cdots\text{HOR}]^-$ . Such anions are characterized by an intense background absorption below  $1800\text{ cm}^{-1}$ . The creation of homoconjugated anions proceeds in the case of phenolate according to the equation



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  $\text{DMAN}\cdot\text{H}^+$  in the reaction with acids increases with a decrease of the  $\text{p}K_a$  - value of the acid. However, for comparable  $\text{p}K_a$  values of phenols and carboxylic acids, the contribution of  $\text{DMAN}\cdot\text{H}^+$  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  $\text{p}K_a$  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  $\text{DMAN}\cdot\text{H}^+$  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  $\text{DMAN}\cdot\text{H}^+$  does not depend on the counteranion and can be most probably described by a single minimum potential for the proton motion.

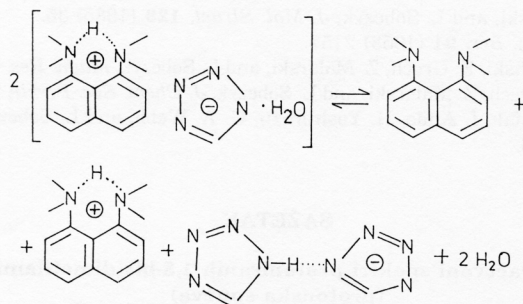
### PROTONATION OF DMAN BY N-H ACIDS

Protonation of DMAN by means of compounds containing acidic N-H groups seems to be interesting not only because the formation of  $\text{DMAN}\cdot\text{H}^+$  takes place but also because of the formation of  $[\text{NHN}]^-$  bridges which are very difficult to obtain in other reactions. The application of DMAN to deprotonation of N-H groups extends our knowledge about  $[\text{NHN}]^-$  hydrogen bonds.

In the case of 4,5-dinitroimidazole,<sup>29</sup> 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  $\text{DMAN} \cdot \text{H}^+$ . 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  $3000 \text{ cm}^{-1}$  and appearance of a broad doublet with submaxima at about  $1950$  and  $2500 \text{ cm}^{-1}$  take place. This doublet is particularly well seen in the difference spectra and can be assigned to the  $\nu_s$  ( $\text{NHN}^-$ ) vibrations. Absorption in this region is very similar to that observed for the  $\text{NHN}^+$  bridges formed by aromatic nitrogen bases. The doublet structure of the  $\nu_s$  ( $\text{NHN}^-$ ) band is most probably caused by the Fermi resonance with the  $\delta(\text{NHN}^-)$  overtone.

In the case of 1:1 complex DMAN-tetrazole<sup>29</sup> 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  $[\text{NHN}]^-$  anion is initially formed. The results obtained for other N-H acids show that the percentage of protonation increases with a decrease of  $\text{p}K_a$  of the acid. The contribution of  $\text{DMAN} \cdot \text{H}^+$  is comparable with those obtained for phenols of similar  $\text{p}K_a$  values. The tendency of N-H acids to form homoconjugated anions  $[\text{NHN}]^-$  is also similar to the tendency to homoconjugation of phenols  $[\text{OHO}]^-$ .

The tetrazole-DMAN complex has been studied by the multinuclear NMR technique<sup>30</sup> 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.

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## SAŽETAK

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

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