1,8-Bis(dimethylaminomethyl)naphthalene: A New Proton Sponge

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1,8-bis(dimethylaminomethyl)naphthalene (DMAMN), which exhibits the features of a proton sponge, has been synthesized. ^{1}H NMR, infrared and X-ray diffraction studies on protonated DMAMN indicate the formation of intramolecular NHN$^+$ hydrogen bonds which are a little weaker than those in protonated 1,8-bis(dimethylamino)naphthalene (DMAN). This is particularly apparent in the IR spectra of solid salts (appearance of an absorption above 2000 cm^{-1}). One should emphasize that in CH_3CN solution the intensity of the broad continuum for DMAMN·H$^+$ is larger than that for DMAN·H$^+$. In the latter case a π-electron conjugation contributes, which in intramolecular hydrogen bonds reduces the transition moment of the protonic stretching vibrations. The structure of DMAMN nitrate was determined by X-ray diffraction. Crystals of DMAMN·HNO_3 are monoclinic, space group $P2_1/c$ with a = 10.938(3), b = 11.829(3), c = 12.497(3) Å, β = 90.40(3)° and Z = 4. The intramolecular [NHN]$^+$ hydrogen bond length is 2.642(3) Å.

The characteristic behaviour of proton sponges results from the presence of two basic centres arranged in a favourable geometry. The high basicity arises from the fact that the proton is shared between two basic centres forming strong NHN$^+$ hydrogen bonds, particularly when both centres are chemically equivalent. Simultaneously, the repulsion of lone electron pairs is eliminated. In the present paper we report the synthesis of the analogue of the well known 1,8-bis(dimethylamino)naphthalene (DMAN) by isolation of the basic amino groups from the naphthalene ring by methylene groups. Such an operation on one hand causes an increase in basicity of the amino groups, but on the other hand leads to a steric disturbance which does not favour the formation of the most stable NHN$^+$ bridge. The studies performed so far on various groups of compound[1–5] seem to indicate that the steric factor is more important than the chemical one. DMAN, for instance, is a weak proton acceptor when non-ionized hydrogen-bonded complexes are formed[6] while its proton affinity is extremely high. The nature of the solvent plays an important role in the protonation of a proton sponge and ionic equilibria.[7,8]

In the present paper DMAMN protonated by means of strong acids was studied by using IR and ^{1}H NMR spectroscopy in CH_3CN solution and the results were compared with those for DMAN·H$^+$. In addition, the crystal and molecular structure of the DMAMN·HNO_3 salt was determined providing information about the geometry of the NHN$^+$ bridge and the packing of molecules.

Experimental

Preparation of 1,8-bis(dimethylaminomethyl)naphthalene (DMAMN).—(1) Naphthalene-1,8-dicarbonyl dichloride was obtained as described previously.[9]

(2) *N,N,N′,N′*-Tetramethylnaphthalene-1,8-dicarboxamide. Anhydrous dimethylamine hydrochloride (23 g, 0.14 mol) and naphthalene-1,8-dicarbonyl dichloride (18 g, 0.07 mol) was dissolved in 150 cm^3 of chloroform and refluxed for 30 h. Then a saturated aqueous solution of Na_2CO_3 (100 cm^3) was added slowly on stirring and cooling. The obtained solution was transferred to a separating funnel, the organic layer was collected and the aqueous layer was extracted 3 times with 50 cm^3 of chloroform. The combined chloroform extracts were evaporated to dryness under reduced pressure and the residue was recrystallised from benzene as colourless needles, m.p. 159–160 °C, yield 56%.

(3) 1,8-*bis(dimethylaminomethyl)naphthalene* (DMAMN). To anhydrous diethyl ether (500 cm^3), lithium aluminium hydride ($LiAlH_4$, 10 g, 0.26 mol) and *N,N,N′,N′*-tetramethylnaphthalene-1,8-dicarboxamide (30 g, 0.11 mol) were added. The reaction mixture was heated at reflux and stirred for 60 h, then cooled to −10 °C and decomposed carefully (stirring) with

Table 1 Crystal data, data collection details and refinement for $C_{16}H_{23}N_3O_3$

M_r	307.2
a/Å	10.938(3)
b/Å	11.829(3)
c/Å	12.497(3)
β/°	90.40(3)
V/Å^3	1616.9(7)
Space group	$P2_1/c$
Z	4
F(000)	656
T/K	298
15 ref. to determine cell constants, range (2θ)/°	21–30
D_m/mg m^{-3} (flotation $C_6H_6/CHCl_3$)	1.25(1)
D_c/mg m^{-3}	1.254(1)
$\bar{\lambda}$/Å (Mo-Kα)	0.71069
Monochromator	Graphite
Crystal size/mm	0.25 × 0.35 × 0.50
Linear absorption coefficient/cm^{-1}	0.95
Data collection method	$\theta - 2\theta$ scan
2θ limit/°	52
h range	0–13
k range	0–14
l range	−15–15
Scan rate/° min^{-1}	2.0–29.3
Number of standard reflections	2 (50 ref.)
Variation in standard reflections (%)	6
Number of unique reflections collected	3190
Number of unique reflections with $I \geq 3\sigma(I)$	2143
Variable parameters	291
Final $R\Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.064
Final $R_w[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.060
Final $S[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-\rho)]^{\frac{1}{2}}$	4.972
Function minimized $w = 1/\sigma^2 (F_o)$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Final (Δ/δ) for non-H atoms	0.01
for H atoms	0.07
Final (Δ/ρ)	−0.33 and 0.42

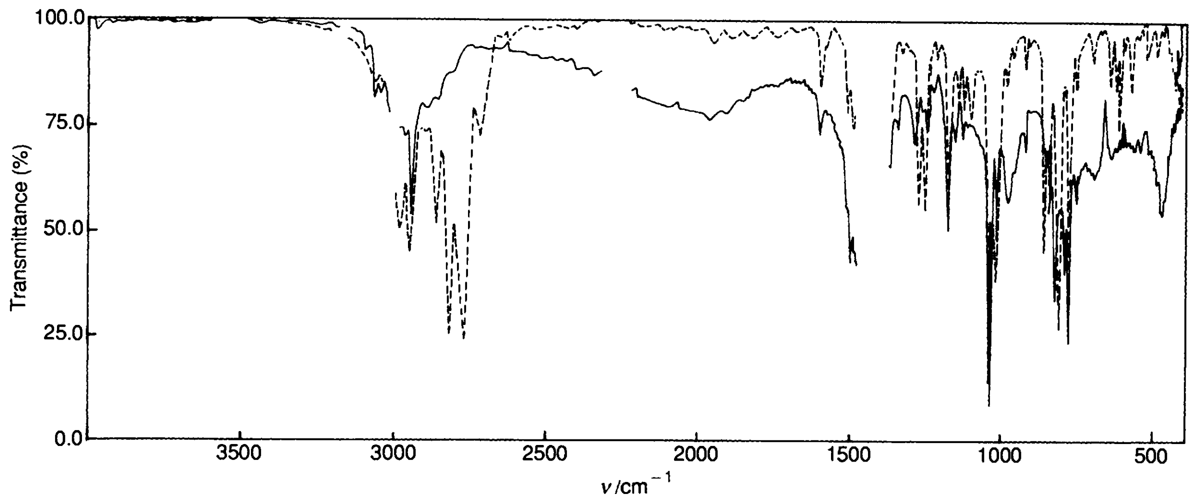

Fig. 1 IR spectra in acetonitrile: (– – – –) DMAMN, (——) DMAMN· $HAuCl_4$

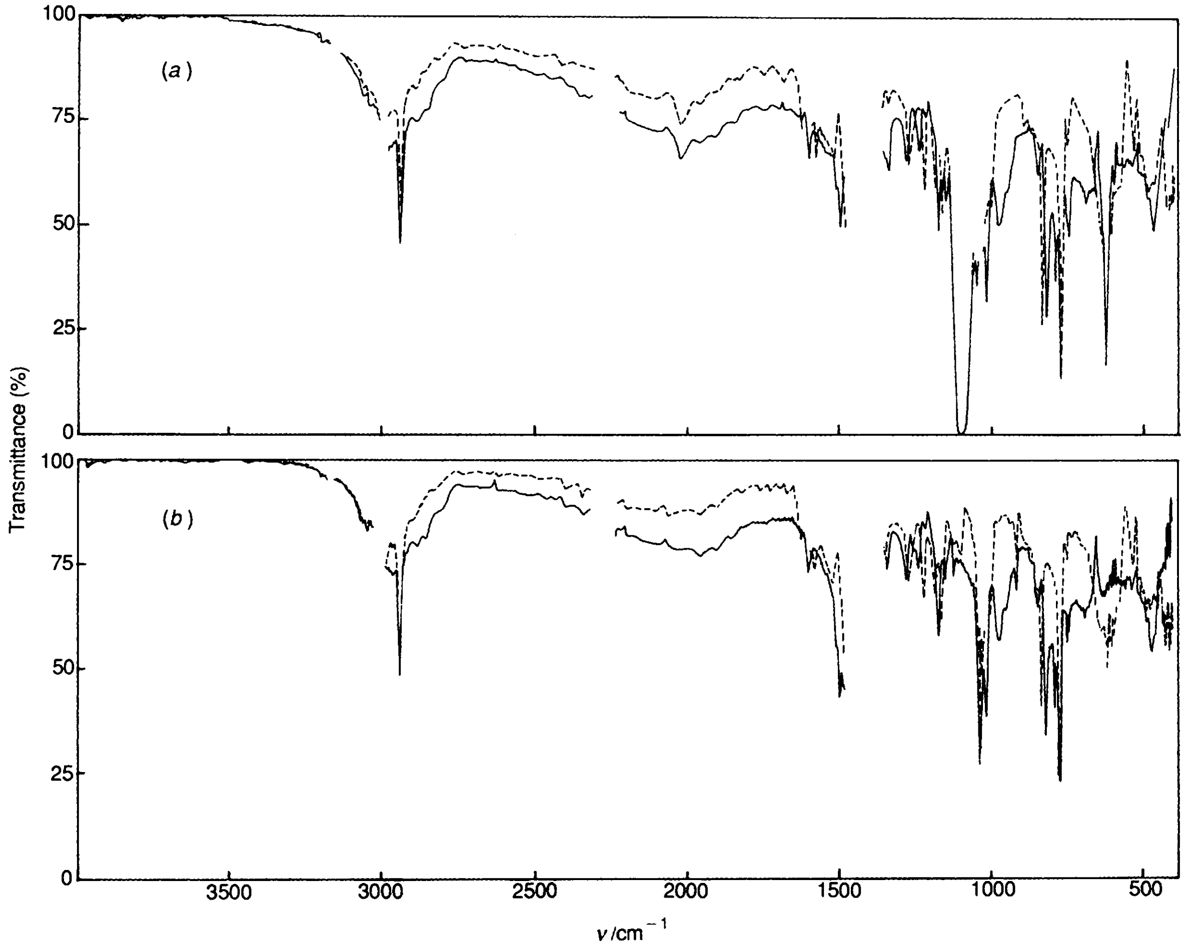

Fig. 2 Comparison of IR spectra of protonated DMAMN (——) and DMAN (– – – –) with (*a*) $HClO_4$, (*b*) $HAuCl_4$

Table 2 Chemical shifts of N^+–H, aromatic, and CH_2 and CH_3 protons of DMAMN and its perchlorates in acetonitrile

		δ (ppm)					
Compound	Conc./mol dm^{-3}	N^+–H	H-2.7	H-3.6	H-4.5	CH_2	CH_3
DMAMN	0.3		7.39	7.30	7.77	4.04s	2.17
DMAMN·$HClO_4$	0.1	15.80	7.59	7.52	8.07	4.50s	2.50s
DMAMN·$HClO_4$	0.6	15.80	7.59	7.52	8.07	4.50s	2.50s
DMAMN·$2HClO_4$	0.3	7.19	7.78	7.67	8.16	4.85d	2.73d

s, singlet; d, doublet.

Table 3 Atomic positions (fraction coordinates) with standard deviations in parentheses

Atom	x	y	z
O(1)	0.3615(3)	0.2793(3)	−0.0681(3)
O(2)	0.4300(4)	0.1208(3)	−0.1051(3)
O(3)	0.5463(3)	0.2582(4)	−0.1006(3)
N(1)	0.2655(2)	0.0179(2)	0.1888(2)
N(2)	0.3480(2)	−0.1127(2)	0.3499(2)
N(3)	0.4454(3)	0.2218(2)	−0.0918(2)
C(1)	0.0580(3)	0.0073(2)	0.2758(3)
C(2)	−0.0442(3)	0.0242(3)	0.2114(3)
C(3)	−0.1546(4)	−0.0286(3)	0.2281(3)
C(4)	−0.1669(3)	−0.0989(3)	0.3124(3)
C(5)	−0.0861(3)	−0.1914(3)	0.4723(3)
C(6)	0.0053(3)	−0.2148(3)	0.5425(3)
C(7)	0.1204(3)	−0.1693(3)	0.5242(2)
C(8)	0.1458(3)	−0.0986(2)	0.4394(2)
C(9)	0.0507(2)	−0.0686(2)	0.3644(2)
C(10)	−0.0666(3)	−0.1203(3)	0.3830(3)
C(11)	0.1677(3)	0.0796(2)	0.2459(2)
C(12)	0.3670(3)	0.0975(3)	0.1658(3)
C(13)	0.2008(4)	−0.0321(4)	0.0881(3)
C(14)	0.2274(3)	−0.0604(3)	0.4349(2)
C(15)	0.3317(3)	−0.2371(3)	0.3383(3)
C(16)	0.4799(3)	−0.0816(3)	0.3574(3)

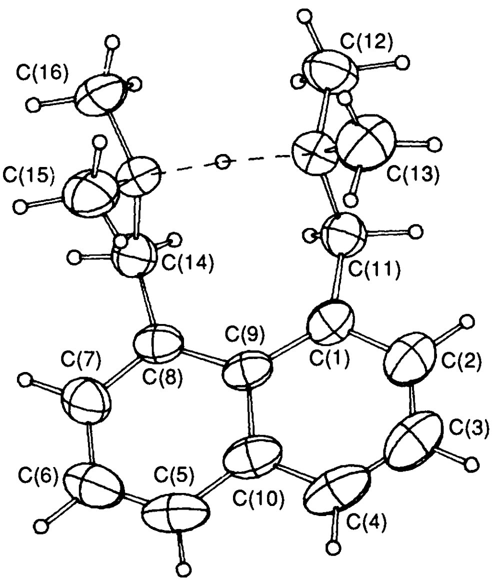

Fig. 3 Schematic representation of protonated DMAMN with numbering of atoms

50 cm^3 of water. The obtained suspension was filtered, washed three times with 30 cm^3 of diethyl ether, and the filtrate evaporated to dryness under reduced pressure; yield 90%, m.p. 58–59 °C. (Found: C, 79.3; H, 9.1; N, 11.6. Calc. for DMAMN: C, 79.3; H, 9.15; N, 11.55%.)

The IR spectra were recorded by means of a Bruker FTIR spectrometer IFS 113v. ^{1}H NMR spectra were recorded using a JEOL FX 90Q spectrometer. The X-ray diffraction studies were performed on DMAMN nitrate by using a Syntex P2$_1$ diffractometer. Crystals of the salt were grown from an acetonitrile–methanol mixture. Details relating to the diffraction experiments, the crystal data, data collection and refinement are given in Table 1. The intensities were corrected for Lorentz and polarization effects, but no corrections were made for extinction or absorption.

The structure was solved by direct methods using the program SHELXS 86[10] and refined by the full-matrix least-squares technique using the SYNTEX XTL/XTLE structure determination system[11] locally adapted by Mr. A. Kowalski for calculation on an IBM PC/AT computer. The positions of all hydrogen atoms were determined from the difference Fourier synthesis. Several cycles of refinement of the co-ordinates and thermal parameters (anisotropic for non-hydrogen and isotropic for hydrogen atoms) reduced the R value to 0.064 and R_w to 0.060. Neutral atomic scattering factors for all atoms were taken from ref. 12.

Results and Discussion

In Fig. 1 the IR spectra of DMAMN with its $HAuCl_4$ 1 : 1 salt in acetonitrile are compared. In the case of the free base the intense Bohlmann bands below 2900 cm^{-1} are very characteristic; they vanish completely after monoprotonation. This means that the attached proton is equally shared between the two nitrogen atoms in a stable NHN^+ bridge. Simultaneously, a broad 'continuum' over the frequency region 400–3000 cm^{-1} appears. One should emphasize that the intensity of that continuum for the DMAMN salt is considerably larger than that for the DMAN salt, as can be seen in Fig. 2. It seems that this is due to the fact that in the DMAN salt the nitrogen atoms are directly attached to the π-electron system of the naphthalene ring. The NHN^+ hydrogen bridges, in such cases, act as π-electron conjugating chains, and it is well known[13] that the intensity of the stretching ν_{XH} vibration band is thus markedly diminished. The spectral features shown in Figs. 1 and 2 do not depend on the type of proton donor if strong acids are used.

Data related to ^{1}H NMR spectra are presented in Table 2. Note that the chemical shift for the 1 : 1 salt does not depend on concentration, confirming the stability of the NHN^+ bridge. No splitting of CH_2 and CH_3 signals is observed in contrast with the spectra of DMAN salts.[14] It was shown that the splitting arises from spin–spin coupling with the bridge protons. The reason for the splitting of CH_2 and CH_3 signals is not clear. However, it seems that the doublet occurs when the proton is localized at one nitrogen atom or when it is symmetrically distributed between the nitrogen atoms.[15]

Note also that the chemical shift of the bridge proton in protonated DMAMN is lower than that in protonated DMAN. This fact may be due to the larger contribution in $DMAN\cdot H^+$ of π-electron anisotropy. It may also arise from the fact that the NHN^+ bridge in protonated DMAMN is a little weaker than that in protonated DMAN.

In the case of DMAMN it is possible to form 2 : 1 salts with $HClO_4$. The signal of the N^+H protons is localised in such a case at a much higher magnetic field. The chemical shifts of the remaining protons in the cations behave similarly.

The atomic positions (fractional coordinates) with standard deviations in parentheses, in the crystal of $DMAN\cdot HNO_3$ are collected in Table 3. Tables of thermal parameters, hydrogen atom coordinates and least-squares planes have been deposited at the Cambridge Crystallographic Data Centre (CCDC).* The atom numbering in the $DMAMN\cdot H^+$ cation is shown in Fig. 3 and the packing of molecules in the unit cell is shown in Fig. 4, while the bond lengths and angles are collected in Table 4.

The $N \cdots N$ distance in $DMAMN\cdot HNO_3$ is relatively long [2.642(3) Å]. This length seems to correspond to the upper limit of symmetric NHN hydrogen bonds.[16] It seems interesting, however, that the proton is located close to the centre of the bridge. The N–H bond lengths are 1.39(3) and 1.28(3) Å. The slight asymmetry of the proton position may be related to the positions of the nitrate anions, which are arranged slightly asymmetrically with respect to the nitrogen atoms.

The NO_3^- anions are almost ideally planar and form an angle of 79.2° with respect to the C(11)–C(14)–N(1)–N(2) plane.

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* For details of the CCDC deposition scheme see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 2*, issue 1.

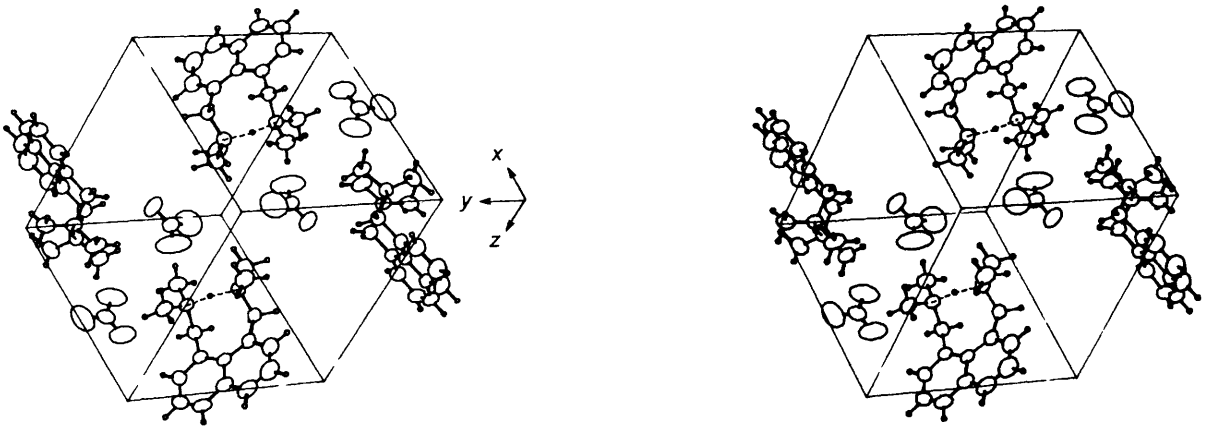

Fig. 4 Stereoview of the packing of molecules in DMAMN·HNO_3

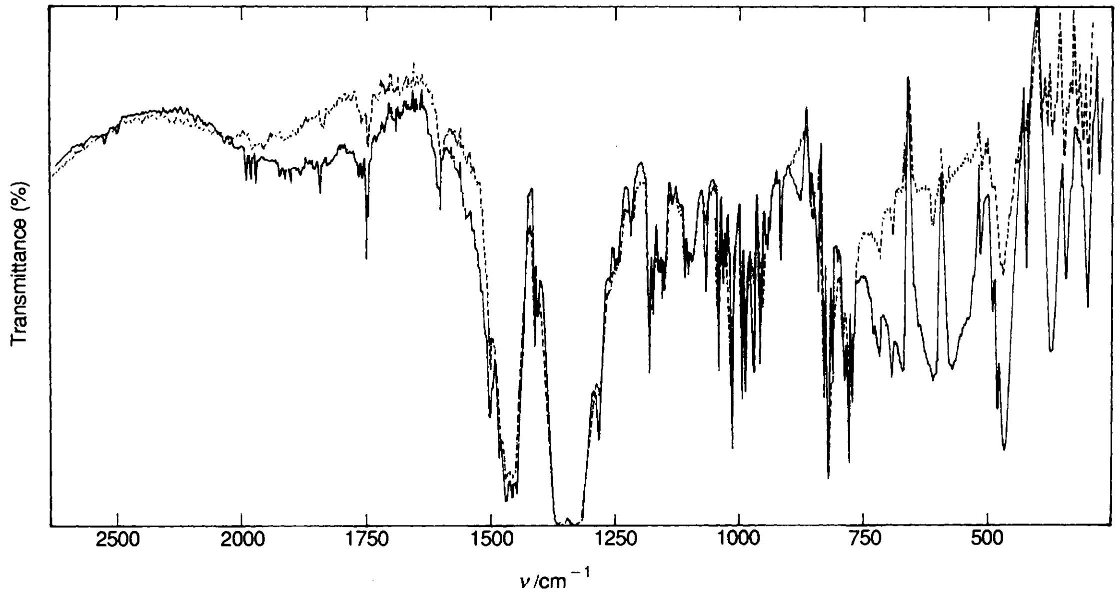

Fig. 5 IR spectra of solid DMAMN·HNO_3 (in KBr) at room temperature (– – – –) and at liquid nitrogen temperature (——)

Table 4 Bond lengths and angles in DMAMN·HNO_3

Bond length/Å		Bond angle/°	
C(1)–C(2)	1.387(4)	C(2)–C(3)–C(4)	119.3(4)
C(3)–C(4)	1.350(6)	C(4)–C(10)–C(9)	120.5(3)
C(5)–C(10)	1.415(5)	C(10)–C(5)–C(6)	121.1(3)
C(6)–C(7)	1.389(5)	C(6)–C(7)–C(8)	123.3(3)
C(8)–C(9)	1.439(4)	C(8)–C(9)–C(10)	115.5(2)
C(1)–C(11)	1.522(4)	C(4)–C(10)–C(5)	118.2(3)
C(2)–C(3)	1.377(5)	C(5)–C(8)–C(14)	125.9(2)
C(4)–C(10)	1.426(4)	C(1)–C(2)–C(3)	123.4(3)
C(5)–C(6)	1.354(5)	C(3)–C(4)–C(10)	120.8(3)
C(7)–C(8)	1.380(4)	C(9)–C(1)–C(2)	119.4(3)
C(9)–C(10)	1.441(4)	C(5)–C(6)–C(7)	118.7(3)
C(8)–C(14)	1.510(4)	C(7)–C(8)–C(9)	120.1(3)
C(11)–N(1)	1.482(4)	C(1)–C(5)–C(8)	128.0(3)
C(14)–N(2)	1.502(4)	C(9)–C(1)–C(11)	126.3(3)
N(1)–C(12)	1.486(4)	C(11)–N(1)–C(12)	108.9(2)
N(1)–C(13)	1.471(4)	C(11)–N(1)–C(13)	111.9(2)
N(2)–C(15)	1.484(4)	C(12)–N(1)–C(13)	109.5(2)
N(2)–C(16)	1.496(4)	C(14)–N(2)–C(16)	108.7(2)
N(1)–H(1)	1.39(3)	C(14)–N(2)–C(15)	112.8(2)
N(2)–H(1)	1.28(3)	C(15)–N(2)–C(16)	111.4(2)
N(3)–O(1)	1.182(4)	O(1)–N(3)–O(2)	119.4(3)
N(3)–O(2)	1.219(5)	O(3)–N(3)–O(1)	122.5(3)
N(3)–O(3)	1.190(4)	O(2)–N(3)–O(3)	118.0(3)
N(1) ··· N(2)	2.642(3)	N(1) ··· H(1) ··· N(2)	164(2)

The N(1) atom is sitting next to one oxygen atom (if the distances above 4 Å can be omitted) with $R_{N(2)-O(2)^{3100}}$ = 3.863(5) Å while the second nitrogen atom N(2) possesses three oxygen atoms with the distance below 4 Å. Thus the distances N(2) ··· $O(2)^{3100,}$ N(2) ··· $O(3)^{211\bar{0}}$ and N(2) ··· $O(3)^{3100}$ equal to 3.871(5), 3.719(4) and 3.698(4) Å, respectively.

The bridge length 2.642(3) Å is characteristic of the transition region and is well reflected in the IR spectrum of the solid nitrate shown in Fig. 5. Note the absorption band above 2000 cm⁻¹ which is sensitive to temperature (increases in intensity and shifts to lower frequencies on cooling). Most spectacular, however, is the behaviour of the absorption in the 500–600 cm⁻¹ region, typical of strong (symmetric or nearly symmetric) NHN^+ bridges. The intensity of this absorption increases dramatically at low temperatures.

The final conclusion is that the behaviour of the NHN^+ hydrogen bridge in protonated DMAMN is similar to that in intermolecular homoconjugated NHN^+ cations, such as 3-oxo-azabicyclo[2.2.2]octane hemiperchlorate.[17]

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