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SOLID-STATE NMR AND X-RAY DIFFRACTION STUDIES OF IONIC COMPLEX OF 1,8-BIS(DIMETHYLAMINO)NAPHTHALENE (DMAN) WITH PICROLONIC ACID

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An ionic complex of 1,8-bis(dimethylamino)naphthalene with picrolonic acid was studied by ^{13}C and ^{1}H magic angle spinning and x-ray diffraction. Structural and spectroscopic features of this compound were investigated. The detailed x-ray structure of this complex is described. A multicentre model of hydrogen bonding in proton sponges $\{[Me_2N—H\cdots NMe_2]^+\cdots X^{\delta -}\}$ is proposed and the influence of weak intermolecular intractions with the nearest electronegative atom in crystal lattice of a proton sponge on the strong intramolecular $[N—H\cdots N]^+$ hydrogen bonding is demonstrated. It appears that weak interactions of electronegative atoms with the nearest methyl hydrogen atoms can influence the localization of the proton in the intramolecular $[N—H\cdots N]^+$ hydrogen bridge. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

An aromatic diamine, 1,8-bis(dimethylamino)naphthalene (DMAN), is the parent molecule of proton sponges,[1–3] model compounds which have attracted considerable interest owing to their very high proton affinity. With mineral or organic acids they form very stable ionic complexes containing intramolecular $[N\cdots H\cdots N]^+$ hydrogen bonding.[4–7] The properties of these hydrogen bonds are used in the discussion of the role of hydrogen bonding in enzymatic catalysis.[8, 9] Already more than 180 papers have been published on proton sponges and their complexes (including about 100 structural papers). DMAN and its complexes have been examined by several spectroscopic and diffractometric methods in solution and in the solid state. Among other things, some regularities in the variation of binding energies of donor and acceptor core electrons, ^{1}H and ^{13}C magic angle spinning (MAS) NMR chemical shifts and structural parameters for a series of ionic complexes of DMAN have been examined.[4–7] Also, some neutron[10] and *ab initio* data for such complexes and the reference amines[11] are available.

DMAN itself and its complexes are very good model systems for studying a number of interesting chemical phenomena such as unusual proton affinity, interesting ionic $[N—H\cdots N]^+$ hydrogen bonding and its short- and long-range consequences, aromaticity and conjugation between electron density in the aromatic part and the H-bonding. In particular, we are intersted in the molecular response to small structural changes. The reason for such small molecular changes of the DMANH$^+$ cation is possible minor interactions of the H-bonded fragment with the nearest counterion in the crystal lattice. In this context, solid-state NMR can supply some interesting information regarding the rearrangement of electron density in the aromatic part of the cation.

Our aim is to present the detailed x-ray structure of the complex of DMAN with picrolonic acid (DMANH$^+$*x*PA$^-$) (the labelling scheme and an ORTEP illustration of the complex studied are shown in Figure 1) and to discuss the multicentre character of $[N—H\cdots N]^+$ H-bonding in ionic complexes of DMAN (Figure 2). It appears that the acidic proton in DMAN complexes is extremely well shielded by bulky methyl groups, which might suggest that the H-

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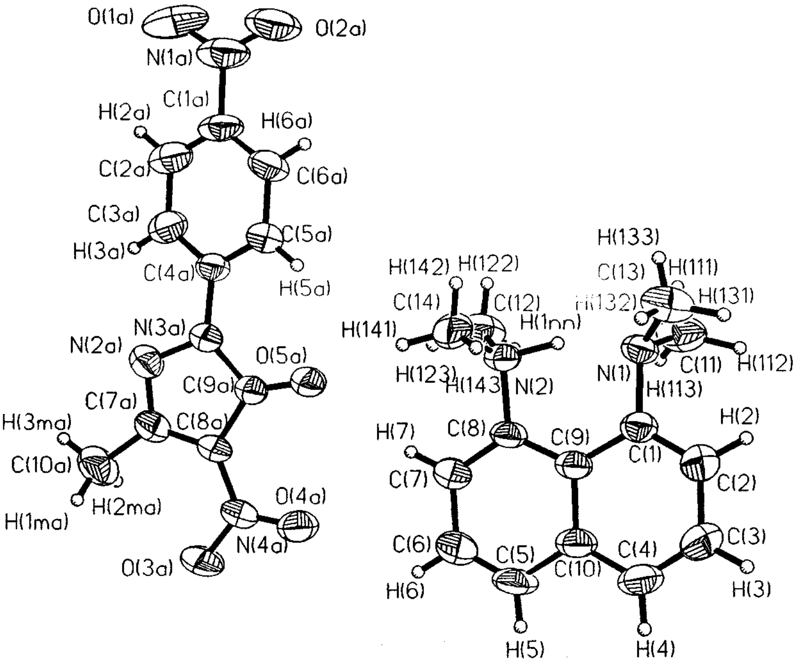


Figure 1. Labelling of atoms and ORTEP illustration of thermal motions of atoms in the complex of DMAN with picrolonic acid

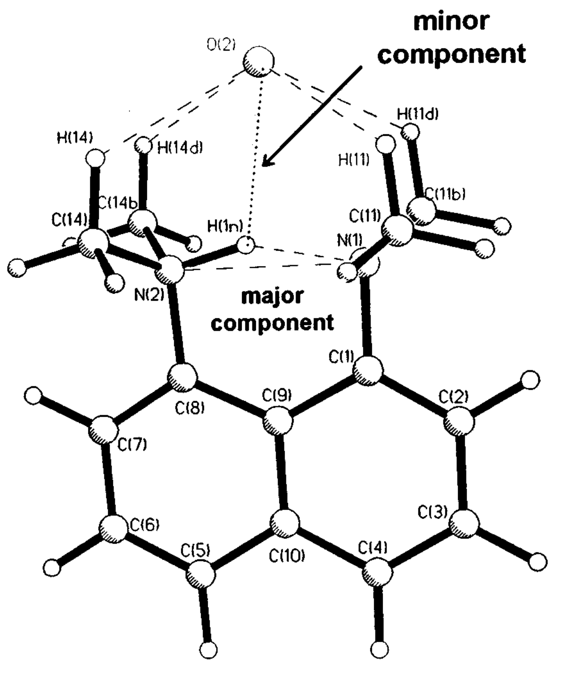


Figure 2. Multicentre character of [N—H · · · N]$^+$ H-bonding in ionic complexes of DMAN

bonding in the complexes of proton sponges in general (and in DMAN complexes in particular) has a two-centre character. This is not only suggested by the common formal formula of this bonding, [N—H · · · N]$^+$, but also by its description in the literature.[1–3] In this paper, however, we also discuss the role of a minor secondary interaction, [Me$_2$N—H · · · NMe$_2$]$^+$ · · · X$^{\delta-}$ of the [Me$_2$N—H · · · NMe$_2$]$^+$ fragment, with the nearest electronegative

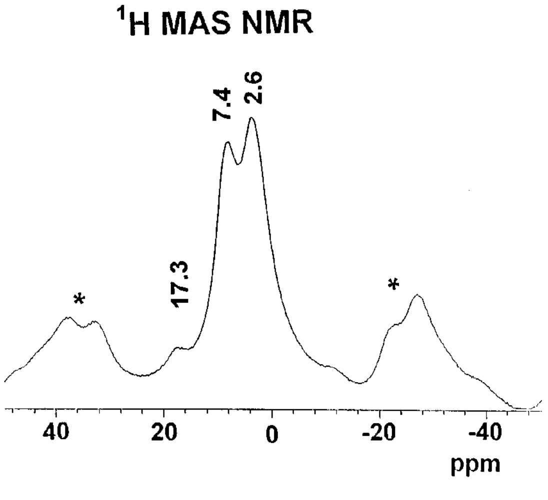


Figure 3. ^{1}H MAS NMR spectrum of the complex of DMAN with picrolonic acid. Asterisks denote spinning sidebands

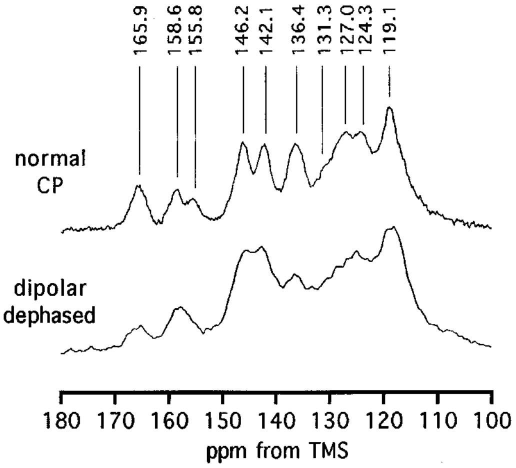


Figure 4. Aromatic region of ^{13}C CP/MAS NMR spectra of the complex of DMAN with picrolonic acid

atom ($X^{\delta-}$) in space. In most structures of DMAN complexes, retrieved from the Cambridge Structural Database (CSD[12]), oxygen is the nearest electronegative atom.

EXPERIMENTAL

Solid-state NMR. The ^{1}H spectrum with MAS was recorded at room temperature at 399·9 MHz using a Chemamagnetics CMX-400 spectrometer. A zirconia rotor was used which spun in nitrogen gas at different rates in order to identify sidebands and resonance overlaps. The ^{1}H NMR spectrum was measured with spinning at *ca* 10 kHz using 2 μs (30°) pulses and 3 s recycle delays. The ^{13}C NMR spectra [with cross-polarisation (CP)] were recorded at 50·3 MHz with a Varian UNITY-200 spectrometer using a high-speed double-bearing probehead and silicon nitride rotors spun in dry air. The single contact ^{13}C CP/MAS experiments were performed at 298 K with an optimized contact time of 4 ms. The length of ^{1}H and ^{13}C $\pi/2$ pulses was 5 μs, the recycle delay 3 s and the MAS rate 5 kHz. The ^{13}C dipolar-dephased spectra[13] (DD) were recorded with a 50 μs delay prior to acquisition. They expose quaternatry carbon lines.

X-ray diffraction. The crystals of $DMANH^{+}xPA^{-}$ suitable for x-ray work were crystallized from acetonitrile by

Table 1. Crystal data and structure refinement details for $DMANH^{+}xPA^{-}$

Empirical formula	$C_{24}H_{26}N_6O_5$
Formula weight	478·51
Temperature (K)	293(2)
Wavelength (Å)	1·54178
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10{\cdot}282(1)$ Å, $\alpha = 92{\cdot}72(1)^0$ $b = 10{\cdot}606(1)$ Å, $\beta = 104{\cdot}25(1)^0$ $c = 11{\cdot}435(1)$ Å, $\gamma = 99{\cdot}53(1)^0$
Volume (Å^3)	1186·9(2)
Z	2
Density (calculated) (mg/m^{-3})	1·339
Absorption coefficient (mm^{-1})	0·798
$F(000)$	504
Crystal size (mm^3)	0·20×0·30×0·25
Theta range for data collecton (°)	4·01–57·49
Index ranges	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 0$
Reflections collected	3387
Independent reflections	3186 [R(int) = 0·0396]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3158/0/421
Goodness-of-fit on F^2	1·054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0{\cdot}0590$, $wR_2 = 0{\cdot}1570$
R indices (all data)	$R_1 = 0{\cdot}0636$, $wR_2 = 0{\cdot}1775$
Extinction coefficient	0·068(5)
Largest diff. peak and hole (e Å^{-3})	0·33 and −0·23

Table 2. ^{13}C and ^{1}H MAS NMR chemical shifts in DMANH^{+}xPA^{-} and the average values of chemical shifts for a sries of ionic complexes of DMAN

Nucleus	DMANH^{+}xPA^{-}	Average[6]
C(1), C(8)	146·2	145·1
C(2), C(7)	124·3	122·3
C(3), C(6)	127·0	127·1
C(4), C(5)	131·3	129·1
C(9)	118·9	118·7
C(10)	136·5	134·9
C(Me)	45·3, 47·5	46·9, 45·8
H(acidic)	19·2	18·9

slow evaporation. The x-ray measurements were made on a KM-4 KUMA diffractometer with graphite monochromated Cu Kα radiation. The data were collected at room temperature using the $\omega - 2\theta$ scan technique. The intensity of the control reflections varied by less than 3% and a linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was applied. The structure was solved by direct methods[14] and refined using SHELXL.[15] The refinement was based on F^2 for all reflections except those with very negative F^2. The weighted *R* factors *wR* and all goodness-of-fit *S* values are based on F^2. Conventional *R* factors are based on *F* with *F* set to zero for negative F^2. The criterion $F_o^2 > 2\sigma(F_o^2)$ was used only for calculating the *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on F^2 are about twice as large as those based on *F*. All hydrogen atoms were located from a difference map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. 16. Experimental details concerning data collection and refinement are summarized in Table 1.

RESULTS AND DISCUSSION

Solid-state NMR

The ^{1}H MAS NMR spectrum of the complex of DMAN with picrolonic acid (PAH) is shown in Figure 3. There are two peaks from hydrogen atoms bound to the aliphatic (lower chemical shifts at *ca* 2·6 ppm) and aromatic (higher chemical shifts at *ca* 7·4 ppm) carbons. Note a small high-frequency peak from the acidic proton (at *ca* 17·3 ppm) which has a similar chemical shift to that from other proton sponge complexes.[4,7]

The ^{13}C resonances were assigned by analysis of the dipolar-dephased spectra and by reference to the literature.[7,16–21] Conventional ^{1}H–^{13}C CP/MAS and

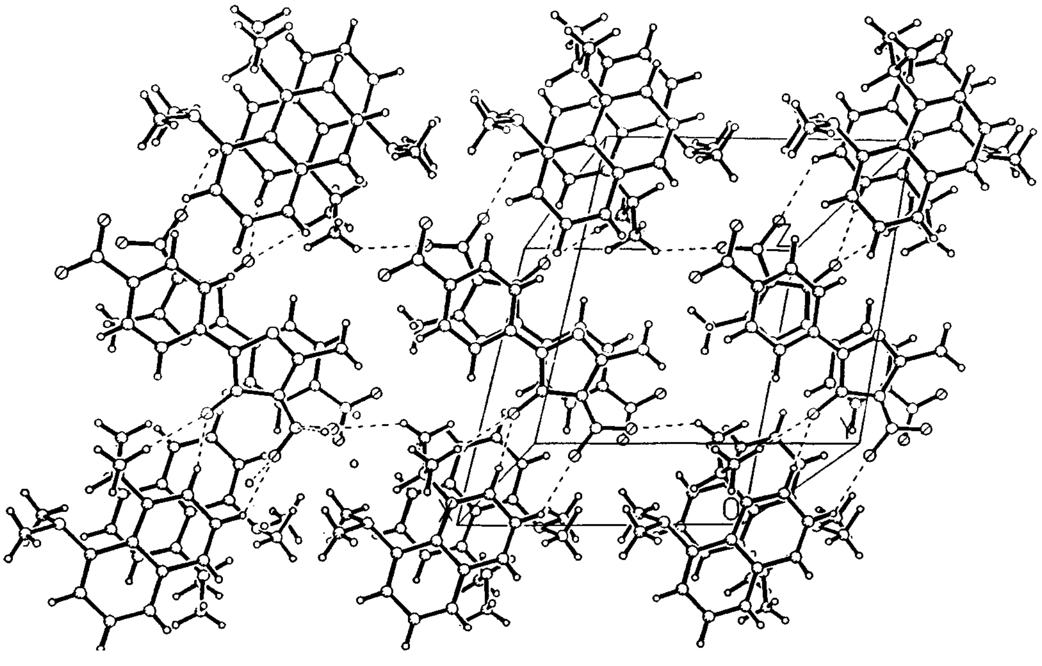


Figure 5. 3D packing of molecules: view along *y*-axis showing layers of pairs of stacked cations and anions which form molecular planes

dipolar-dephased spectra of the aromatic region of the complex are shown in Figure 4. The first carbon spectrum contains peaks from all the aromatic carbons in the complex, while the dipolar-dephased spectra show only resonances from quaternary carbons.

The final peak assignment in the MAS NMR spectra for the complex of DMANH$^+$*x*PA$^-$ and the average values of chemical shifts for the whole series of DMAN complexes[6] are shown in Table 2. The average chemical shift of the carbon nuclei at the *peri* positions (1 and 8) is 145·1(5) ppm, whereas in DMANH$^+$*x*PA$^-$ it is 146·2 ppm. The chemical shift of C(2) and C(7) is 124·4 ppm. Similarly, the average chemical shifts of C(9) and C(10) are 118·7(4) and 134·9(2) ppm, respectively, wheras in DMANH$^+$*x*PA$^-$ they amount to 118·9 and 136·5 ppm, respectively. C(3) and C(6) give a peak at 127·2 ppm whereas C(4) and C(5) probably give a signal near 131 ppm overlapped with some other signals from the counterion. The chemical shifts for methyl carbon nuclei are in the range 45·4–50·0 ppm. The variation of chemical shifts is a measure of the sensitivity of a given carbon site to small changes in the properties of the [N—H · · · N]$^+$ hydrogen bond. The averaging out of the ^{13}C MAS NMR signals from almost equivalent nuclei supports the dynamic character of the major component of hydrogen bonding in DMAN complexes. For a more numerous set of DMAN complexes with the oxygen atom as part of a counterion, it is likely that there will be a correlation between structural parameters of the weaker component of the H-bonding and chemical shifts of the aromatic fragment.

X-ray analysis

The complex of DMAN with picrolonic acid (DMANH$^+$ *x*PA$^-$) crystallizes in the triclinic $P\bar{1}$ space group with two molecules in the unit cell (Table 1). The labelling scheme of atoms in the asymmetric unit and the ORTEP illustration of thermal motions of the atoms are shown in Figure 1. The coordinates of atoms and the equivalent/isotropic temperature factors are given in Table 1 in the Supplementary

Table 3. Structural parameters of hydrogen bonds and close contacts

Hydrogen bond D—H · · · A Sym. code	Donor-H D—H (Å)	Acceptor · · · H A · · · H (Å)	Donor · · ·acceptor D · · · A (Å)	D—H · · · A (°)
N2—H1n · · · N1	N2—H1 1·09(3)	H1 · · · N1 1·56(3)	N2 · · · N1 2·610(3)	N2—H1 · · · N1 161(2)
C5—H5 · · · O1a *H*+1, 1+*Y*, 1+*Z*	C5—H5 0·84(3)	H5 · · · O1a 2·66(3)	C5 · · · O1a 3·245(4)	C5—H5 · · · O1a 159(2)
C6—H6 · · · O4a	C6—H6 0·95(3)	H6 · · · O4a 2·52(3)	C6 · · · O4a 3·186(4)	C6—H6 · · · O4a 127(2)
C7—H7 · · · O4a	C7—H7 0.96(3)	H7 · · · O4a 2.66(3)	C7 · · · O4a 3.242(4)	C7—H7 · · · O4a 120(2)
C7—H7 · · · O5a	C7—H7 0.96(3)	H7 · · · O5a 2.42(3)	C7 · · · O5a 3.298(4)	C7—H7 · · · O5a 152(2)
C11—H111 · · · O1a −1−*X*, 1−*Y*, 1−*Z*	C11—H111 0.97(4)	H111 · · · O5a 2.85(4)	C11 · · · O1a 3.383(4)	C11—H111 · · · O1a 115(2)
C11—H111 · · · O3a *X*−1, *Y*, *Z*	C11—H111 0.97(4)	H111 · · · O3a 2.87(4)	C11 · · · O3a 3.549(4)	C11—H111 · · · O3a 128(2)
C11—H111 · · · O4a *X*−1, *Y*, *Z*	C11—H111 0.97(4)	H111 · · · O4a 2.85(4)	C11 · · · O1a 3.648(4)	C11—H111 · · · O1a 140(2)
C12—H122 · · · O3a *X*−1, *Y*, *Z*	C12—H122 0.94(4)	H122 · · · O3a 2.56(4)	C12 · · · O3a 3.353(3)	C12—H122 · · · O3a 143(2)
C12—H123 · · · O5a	C12—H123 1.03(3)	H123 · · · O5a 2.72(3)	C12 · · · O5a 3.592(3)	C12—H123 · · · O5a 143(2)
C13—H132 · · · O3a −*X*, 1−*Y*, 2−*Z*	C13—H132 1.02(4)	H132 · · · O3a 2.62(4)	C13 · · · O3a 3.493(4)	C13—H123 · · · O3a 143(2)
C13—H133 · · · O3a *X*−1, *Y*, *Z*	C13—H133 0.91(4)	H133 · · · O3a 2.85(2)	C13 · · · O3a 3.451(4)	C13—H123 · · · O3a 140(2)
C14—H141 · · · O5a	C14—H141 1.01(3)	H141 · · · O5a 2.33(3)	C14 · · · O5a 3.315(3)	C14—H141 · · · O5a 165(2)
C14—H143 · · · O4a −*X*, 1−*Y*, 2−*Z*	C14—H143 1.04(4)	H141 · · · O4a 2.33(4)	C14 · · · O4a 3.421(3)	C14—H143 · · · O4a 165(2)
C2a—H2a · · · O4a −*X*, 1−*Y*, 1−*Z*	C2A—H2A 0.97(3)	H2A · · · O4a 2.93(3)	C2A · · · O4a 3.288(3)	C2a—H2a · · · O4a 127(2)

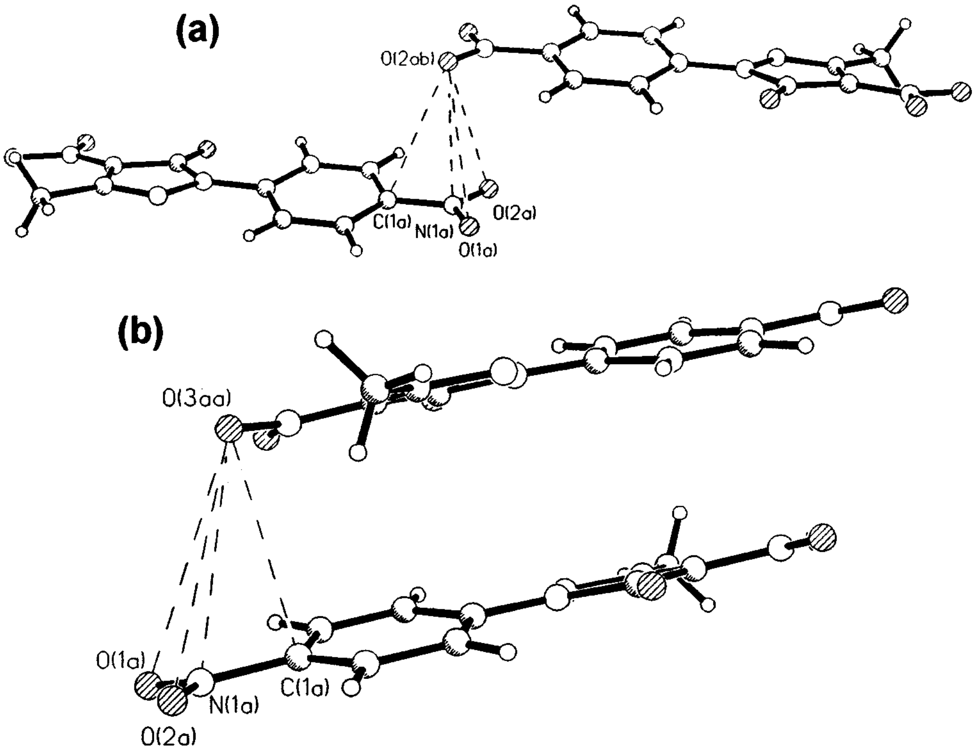
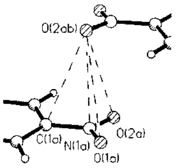
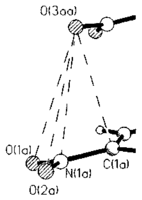


Figure 6. N · · · Ointeractions in the complex of DMAN with picrolonic acid

Table 4. Structural parameters of the N · · · O interactions in the complex of DMAN with picrolonic acid

Definition of N · · · O interaction		
Symmetry	$-1-X,\ -Y, Z+1$	$-X, 1-Y, 1-Z$
N1 · · · O (Å)	3·171(4)	3·747(4)
O · · · N1—C1 (°)	86·6(3)	69·4(3)
O · · · N1=O1, O · · · N1=O2 (°)	97·3(3), 85·6(3)	92·1(3), 107·5(3)
C1N1 (Å)	1·463(3)	1·463(3)
N1O1, N1O2 (Å)	1·235(4), 1·223(3)	1·235(4), 1·223(3)
C1N1O1, C1N1O2 (°)	117·9(3), 118·6(3)	117·9(3), 118·6(3)
O1N1O2 (°)	123·5(3)	123·5(3)

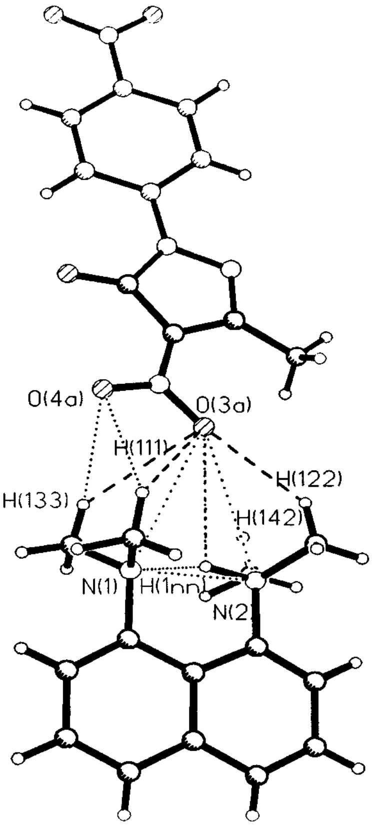


Figure 7. [Me$_2$N—H · · · NMe$_2$]$^+$ · · · X$^{\delta-}$ interactions in DMANH$^+$*x*PA$^-$

Material, which also contains structural parameters for DMANH$^+$*x*PA$^-$ (Table 2) and anisotropic thermal parameters (Table 3).

The crystal structure of DMANH$^+$*x*PA$^-$ is built of layers of pairs of stacked cations and anions which form molecular planes (Figure 5). In each pair, two cations and two anions are placed in an antiparallel manner due to strong dipole–dipole interactions and other kinds of weak interactions (such as N · · · Ointeractions or interactions in stacks). Such molecular planes (slightly shifted) are overlaid, forming a 3D structure. This is not a typical 3D arrangement of molecules for a structure of a complex of DMAN. Usually, a single DMANH$^+$ cation interacts with six anions in the closest 3D neighbourhood and one anion interacts with six cations, which resembles close packing characteristic of ionic inorganic compounds.

As a result of strong electrostatic interactions and the weak interactions mentioned above, some relatively short intermolecular contacts occur. The shortest of them can be considered as weak C—H · · · O hydrogen bonds. The geometry of these close contacts is given in Table 3.

There is strong, asymmetric [N—H · · · N]$^+$ H-bonding in the cation: N(2)H(1n) = 1.09(3) Å, N(1) · · ·H(1n) = 1.56(3) Å and N(2)H(1n) · · ·N(1) angle and N(1) · · ·N(2) contacts are 161(2)° and 2·610(3) Å, respectively.

Another type of weak interaction which is present in the DMANH$^+$*x*PA$^-$ structure is weak N · · · Ointeractions.[21,22] It appears that there is a tendency in nitro derivatives to form regular 3D structural patterns (such as pyramids and bipyramids) with a heteroatom located above or below the centre of a nitro group. This is also the case for DMANH$^+$*x*PA$^-$ (Figure 6). The geometrical parameters describing these interactions are collected in Table 4.

The DMANH$^+$ cation is almost planar [with the largest deviation from planarity being $-0{\cdot}200(3)$ Å for N(1) and $-0{\cdot}145(3)$ Å for C(2)] and almost symmetric with all the structural parameters in the left and right parts of the moiety deviating less than 3σ from one another, with the exception of CN bonds and C(1) and C(8) *ipso* angles. These two structural parameters reflect the consequences of the asymmetry of the [N(2)—H(1n) · · ·N(1)]$^+$ H-bonding. The asymmetry of the hydrogen bonding is transmitted over the nearest fragments of the cation and also to the other part of the molecule [C(3)C(4) and C(5)C(6) bonds]. The values of structural parameters for the cation are similar to those found in some other DMAN complexes.[4–7,23–32]

The most characteristic feature of the anion is its high planarity. The torsion angles between the best planes of four distinct fragments of the anion (two nitro groups and two aromatic fragments) are in the range 0–12°. The planarity of the pyrazole fragment containing only one relatively short localized C(7a)N(2a) double bond supports the idea that the negative charge associated wtih the anion is smeared all over the whole moiety.

The structure of DMANH$^+$*x*PA$^-$, together with the other structures of the ionic complexes of DMAN, may be used to find possible relationships between major and minor components of [N—H · · · N]$^+$ H-bonding in these complexes (Figure 7). Let us concentrate on a slightly larger fragment of the cation than just these three atoms; in fact *peri*-amino derivatives of naphthalene do not have proton sponge properties unless they are fully substituted. This means that the alkyl groups attached to the nitrogen atoms play a very important role. If so, one should look at the arrangement and structural parameters of [Me$_2$N—H · · · NMe$_2$]$^+$ · · · X$^{\delta-}$ H-bonding, where X$^{\delta}$ is the nearest electronegative atom. Since in most cases of the DMAN complexes this is oxygen, we will concentrate on such structures where X = O. Then, we will call the [Me$_2$N—H · · · NMe$_2$]$^+$ the major component and the · · · X$^{\delta}$ the minor component of the [Me$_2$N—H · · · NMe$_2$]$^+$ · · · X$^{\delta-}$ H-bonding. The reference data describing the geometry of this hydrogen bonding are shown in Table 5. Figure 8 illustrates such interactions in a few structures.

According to Table 5, there are some trends among structural parameters describing the [Me$_2$N—H · · · NMe$_2$]$^+$ · · · X$^{-\delta}$ fragment. First, it appears that the nearest electonegative atom (oxygen) is located more or less

Table 5. Structural parameters describing $[(CH_3)_2N—H\cdots N(CH_3)_2]^+\cdots O$ interactions[a]

No.	Refcode and reference	O · · · H (Å)	O · · · H · · · N2 (°)	O · · · H · · · N1 (°)	N · · · N (Å)	N—H · · · N (°)	O · · · N1 (Å)	O · · · N2 (Å)	O · · · H1 methyl (Å)	O · · · H2 methyl (Å)	O · · · H3 methyl (Å)	O · · · H4 methyl (Å)
1	FIJWAW[23]	2·601	103	99	2·577	140	3·207	3·115	2·421	2·541	2·634	2·805
2	GADHEY[24]	2·747	102	98	2·606	160	3·294	3·200	2·451	2·533	2·627	2·728
3	GEKZIF[25]	2·790	99	101	2·574	159	3·378	3·193	2·522	2·577	2·598	2·934
4	JIXCAU[26]	2·757	109	98	2·588	152	3·374	3·271	2·408	2·467	2·945	3·171
5	JIXCAU01[27]	2·860	105	99	2·589	155	3·428	3·347	2·443	2·492	3·004	3·169
6	KICBED[28]	2·746	107	99	2·610	153	3·421	3·205	2·494	2·513	2·689	2·860
7	KINKEX[29]	2·574	108	95	2·582	157	3·129	3·065	2·362	2·471	2·681	2·715
8	KUTBEG[30]	2·494	115	89	2·604	155	3·013	3·016	2·400	2·463	2·544	2·591
9	PEJBOV[31]	2·642	106	96	2·606	158	3·170	3·171	2·487	2·507	2·611	2·685
10	YOSNOJ[32]	2·770	103	100	2·588	157	3·327	3·264	2·413	2·563	2·588	2·778
11	$DMANH^+ x PA^-$	3·063	105	94	2·610	161	3·529	3·509	2·556	2·847	2·869	3·142
12	CLMH2[4]	2·619	113	87	2·638	161	3·048	3·113	2·511	2·511	2·618	2·618
13	$DMANH^+$ [22]	3·680	81	121	2·573	158	3·665	4·679	2·452	2·560	4·130	4·330
14	PICIIRT[7 b]	2·844	102	106	2·570	152	3·549	3·295	2·412	2·486	2·724	3·184
	Average	2·80	104	99	2·593	156	3·33	3·32	2·46	2·54	2·80	2·97
	Standard error	0·08	2	2	0·005	2	0·05	0·11	0·02	0·03	0·12	0·12
	Range	1·19	34	34	0·065	21	0·65	1·66	0·19	0·38	1·59	4·33

[a] O · · · H is the distance between the nearest oxygen atom and the acidic proton in the $[N—H\cdots N]^+$ bridge, O · · · H—N2 and O · · · H · · · N1 are angles formed by O · · · H and components of $[N—H\cdots N]^+$ hydrogen bonding, N · · · N and N—H · · · N are structural parameters of the major component of the $[N—H\cdots N]^+$ hydrogen bonding, O · · · N1 and O · · · N2 are interatomic distances between the nearest oxygen atom and the nitrogen atoms, O · · · Hi(methyl) are the shortest distances from the nearest oxygen atom to methyl hydrogen atoms.

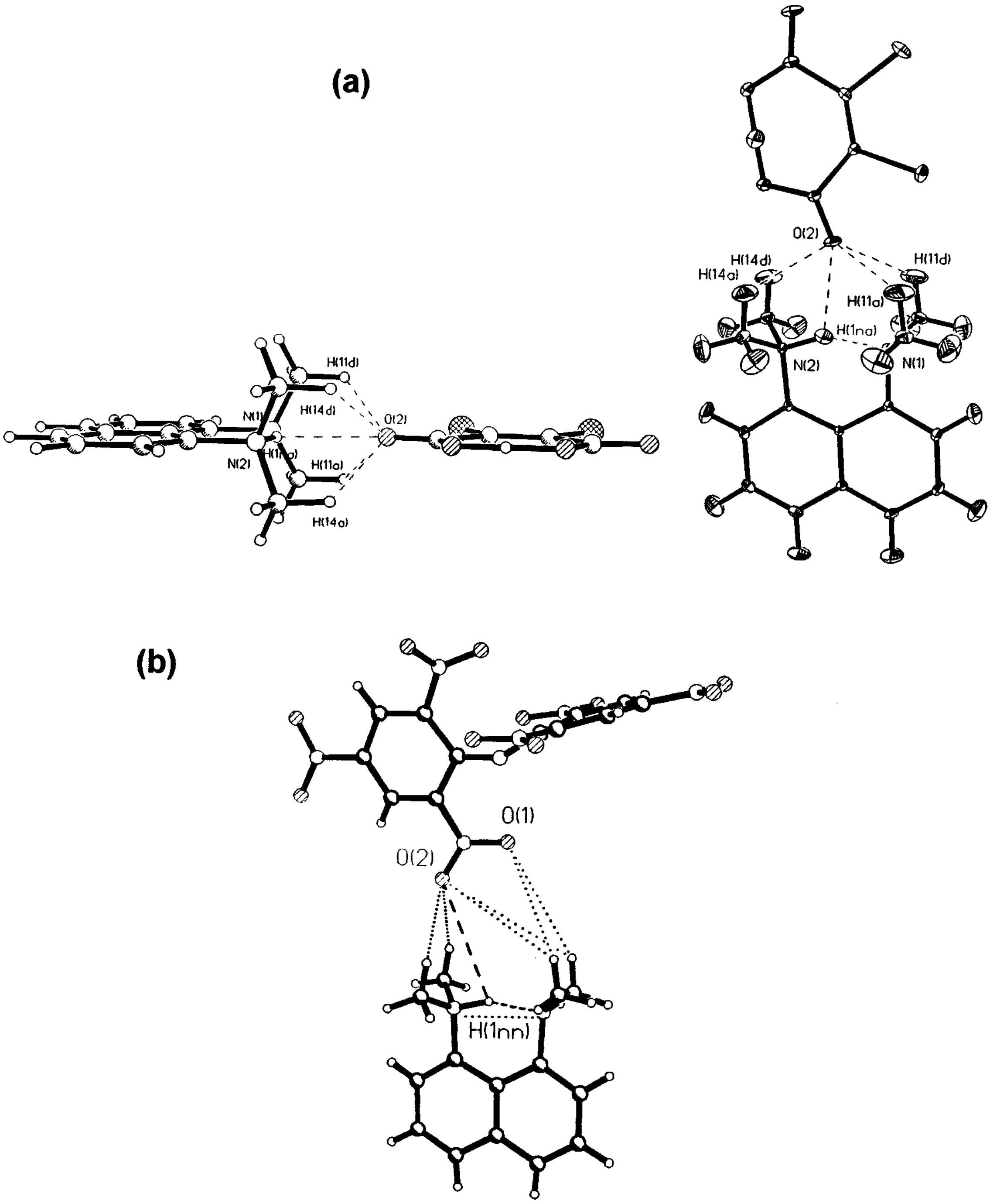


Figure 8. $[Me_2N—H \cdots NMe_2]^+ \cdots X^{\delta -}$ interactions in model complexes of DMAN with (a) dichloromaleic acid[4] and (b) dipicrylamine[23]

at the central position in front of four hydrogens which stick outside the cation from the methyl groups. In fact, the electronegative atom is almost always slightly shifted towards this nitrogen atom in the [Me_2N—H · · · NMe_2]$^+$ hydrogen bridge which is the donor of hydrogen [the N(2) · · · O distance is less than the N(1) · · · O distance]. This means that the N(2)—H · · · O angle is larger than the N(1) · · · H · · · O angle unless there is more than one electronegative atom close to the [Me_2N—H · · · NMe_2]$^+$ fragment. Additionally, the nearest oxygen atom always has shorter distances to hydrogen atoms from bulky methyl groups attached to the nitrogen atom [N(2)] in comparison with those attached to the nitrogen acceptor atom [N(1)]. It is interesting that the distance from the nearest oxygen atom to the acidic proton is longer than distances from the oxygen atom to the nearest hydrogen atoms from the methyl groups. This means that the major component of the [Me^2N—H · · · NMe_2]$^+$ · · · O hydrogen bonding can be influenced by the weaker component not only via direct interaction with the acidic proton but also via indirect interactions with the methyl hydrogen atoms. This is the case for DMAN complexes with some simple anions containing a small number of electronegative atoms. In general, the DMAN methyl groups can interact with a few electronegative atoms in an independent manner and such electrostatic interactions can induce localization of the acidic proton at one of the nitrogen atoms. More than one electronegative atom located close to the [Me_2N—$HNMe_2$]$^+$ fragment can change the relatonships between structural parameters describing minor interactions. In consequence, one can try to synthesize proton sponge complexes of DMAN with either ordered or disordered hydrogen bonding playing with the number of electronegative atoms in an anion. Another important factor influencing proton localization is the charges associated with the hydrogen and the electronegative atoms. A formal positive charge (+1) associated with the acidic proton is smeared over the whole cation which increases the charges also at the methyl hydrogen atoms. An estimation of atomic charges obtained for a complex of DMAN with dichloromaleic acid from charge density studies[33] gives *ca* +0·45 for the acidic proton and the values of charges about two times smaller for the methyl hydrogen atoms. This means that the final situation in the [Me_2N—N · · · NMe_2]$^+$ · · · $O^{-\delta}$ hydrogen bonding results from a delicate balance between electrostatic and steric factors. Unfortunately, as the x-ray hydrogen positions suffer from obvious systematic errors (shortenting of X—H' bonds), it is difficult to quantify the role of the weaker component of hydrogen bonding in proton sponge complexes.

We conclude that strong ionic intramolecular [N—H · · · N]$^+$ hydrogen bonding in proton sponge complexes of DMAN has in fact a multicentre character: [Me_2N—H· · · NMe_2]$^+$ · · · X(O)$^{\delta-}$. This is due to electrostatic interactions with the nearest electronegative atoms in the crystal lattice. Such interactions seem to affect the localization of the proton in the [N—H · · · N]$^+$ hydrogen bridge. There are regularities in structural parameters describing the weaker component of the [Me_2N—H · · · NMe_2]$^+$ · · · $O^{\delta-}$ hydrogen bonding.

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REFERENCES

1. H. A. Staab and T. Saupe, *Angew. Chem., Int. Ed. Engl.* **27**, 865 (1988).
2. R. Alder, *Chem. Rev.* **89**, 1215 (1989).
3. A. L. Llamas-Saiz, C. Foces-Foces and J. Elguero, *J. Mol. Struct.* **328**, 297 (1994).
4. K. Woźniak, H. He, J. Klinowski, W. Jones and T. L. Barr, *J. Phys. Chem.* **99**, 14667 (1995).
5. K. Woźniak, H. He, J. Klinowski, W. Jones, T. L. Barr and S. Hardcastle, *J. Phys. Chem.* **100**, 11408 (1996).
6. K. Woźniak, H. He, J. Klinowski, T. L. Barr and P. Milart, *J. Phys. Chem.* **100**, 11420 (1996).
7. C. Lopez, R. M. Claramunt, A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, I. Sobrados, F. Aguilar-Parrilla and H.-H. Limbach, *New J. Chem.* **20**, 523 (1996).
8. W. W. Cleland and M. M. Kreevoy, *Science* **269**, 104 (1995).
9. P. A. Frey, *Science* **269**, 104 (1995).
10. K. Woźniak, C. C. Wilson, K. S. Knight and E. Grech, *Acta Crystallogr. Sect. B* **52**, 691 (1996).
11. J. A. Platts, S. T. Howard, K. Woźniak, *J. Org. Chem.* **59**, 4647 (1994).
12. F. H. Allen, J. E. Davies, J. J. Galloy, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.* **31**, 187 (1991).
13. S. J. Opella and M. H. J. Frey, *J. Am. Chem. Soc.* **101**, 5854 (1979).
14. G. M. Sheldric, *Acta Crystallogr., Sect. A* **46**, 467 (1990).
15. G. M. Sheldrick, *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Göttingen (1993).
16. A. J. C. Wilson (Ed.), *International Tables for Crystallography*, Kluwer, Dordrecht (1992).
17. K. Woźniak, H. He, J. Klinowski, B. Nogaj, D. Lemanski, D. Hibbs, M. B. Hursthouse and S. T. Howard, *J. Chem. Soc., Faraday Trans.* **91**, 3925 (1995).
18. E. Grech, L. Stefaniak, I. Ando, H. Yoshimizu, G. Webb and L. Sobczyk, *Bull. Chem. Soc. Jpn* **63**, 2716 (1990).
19. E. Grech, L. Stefaniak, I. Ando, H. Yoshimizu and G. Webb, *Bull. Chem. Soc. Jpn* **64**, 3761 (1991).
20. K. Woźniak, H. He, J. Klinowski and E. Grech, *J. Phys. Chem.* **99**, 1403 (1995).
21. K. Woźniak, *J. Mol. Struct.* **374**, 227 (1996).
22. S. T. Howard, J. A. Plats and K. Woźniak, *Chem. Phys. Lett.* **232**, 479 (1995).
23. K. Woźniak, H. He, J. Klinowski, W. Jones and E. Grech, *J. Phys. Chem.* **98**, 13755 (1994).
24. D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, J. R. Stephenson and K. Wade, *J. Chem. Soc., Chem Commun.* 889 (1987).
25. T. Glowiak, Z. Malarski, L. Sobczyk and E. Grech, *J. Mol. Struct.* **157**, 329 (1987).
26. P. K. Miller, K. D. Abney, A. K. Rappe, O. P. Anderson and S. B. Strauss, *Inorg. Chem.* **27**, 2255 (1988).

27. J. A. Kanters, A. Schouten, A. J. M. Duisenberg, T. Glowiak, Z. Malarski, L. Sobczyk and E. Grech, *Acta Crystallogr., Sect. C* **47**, 2148 (1991).
28. Z. Malarski, T. Lis, E. Grech, J. Nowicka-Scheibe and K. Majewska, *J. Mol. Struct.* **221**, 227 (1990).
29. J. A. Kanters, A. Schouten, J. Kroon and E. Grech, *Acta Crystallogr., Sect. C* **47**, 807 (1991).
30. M. L. Raves, J. A. Kanters and E. Grech, *J. Mol. Struct.* **271**, 109 (1992).
31. E. Bartoszak, Z. Dega-Szafran, M. Grundwald-Wyspianska, M. Jaskolski and M. Szafran, *J. Chem. Soc., Faraday Trans.* **89**, 2085 (1993).
32. B. Brzezinski, E. Grech, J. Nowicka-Scheibe, T. Glowiak, Z. Malarski and L. Sobczyk, *J. Mol. Struct.* **327**, 71 (1994).
33. P. Mallinson, K. Woźniak and K. McCormack, *J. Am. Chem. Soc.*, in press.