

X-Ray and Fourier-transform Infrared Studies of 1,8-Bis(dimethylaminomethyl)naphthalene. Comparison with 1,8-Bis(dimethylamino)naphthalene

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The X-ray structure of a proton sponge, 1,8-bis(dimethylaminomethyl)naphthalene (DMAMN) has been determined and its FTIR spectrum investigated. The results are compared with previously reported data on 1,8-bis(dimethylamino)naphthalene (DMAN). The X-ray results show that in DMAMN, the naphthalene ring is almost planar in contrast with DMAN. The IR spectra of these two molecules are markedly different and the decrease in the intensity of some ring and CH vibrational modes in DMAMN is discussed as a function of the higher symmetry of the naphthalene skeleton of the molecule.

The title compounds, 1,8-bis(dimethylamino)naphthalene (DMAN) and 1,8-bis(dimethylaminomethyl)naphthalene (DMAMN) are of special interest owing to their unusual basic properties.¹⁻¹⁴ An X-ray crystallographic study¹⁵ of DMAN has shown that the molecule adopts a conformation in which one carbon atom of each of the dimethylamino groups lies in the plane of the naphthalene ring. This ring is considerably twisted out of the planar conformation. The high basicity of DMAN which is one of the strongest organic nitrogen bases, arises from the fact that the proton is shared between the two basic centres, forming strong NHN⁺ hydrogen bonds. Simultaneously, the repulsion of lone pairs is eliminated. Infrared studies in solution have shown that DMAN is a weak proton acceptor when non-ionized hydrogen bonds are formed. When strong proton donors are used, there is a marked tendency to form DMANH⁺ and homoconjugated anions.^{8,9} In DMAMN the separation of the basic amino groups from the naphthalene ring by methylene groups increases their basicity. Recent results obtained in our laboratory¹⁶ have however proved that the tendency of DMAMN to form complexes of higher stoichiometry is less than in the case of DMAN. Further, the NHN⁺ bridge in protonated DMAMN is slightly weaker than in protonated DMAN.¹⁴ These experimental results indicate that the proton sponge properties of DMAMN are less pronounced than those of DMAN. This effect can originate from different structural parameters in the neutral molecules. It seemed therefore interesting to determine the crystal structure and to study the IR spectrum of DMAMN. These two techniques provide information on the geometry and the symmetry of the molecule.

Experimental

Crystal Data.—C₁₆H₂₂N₂, *M* = 242.36. Orthorhombic, *a* = 15.620(3), *b* = 9.857(2), *c* = 19.401(4) Å, *V* = 2987.1(10) Å³ (by least-squares refinement on diffractometer angles of 20 centred reflections, λ = 1.541 78 Å), space group *Pbca*, *Z* = 8, *D*_x = 1.078 g cm⁻³. Transparent crystals, 0.35 × 0.20 × 0.15 mm, $\mu(\text{Cu-K}\alpha)$ = 0.482 mm⁻¹.

Data Collection and Processing.—Siemens P4-PC diffractometer, graphite monochromatized Cu-K α -radiation, θ -2 θ mode, 2162 reflections measured (4.5 < θ < 50.5°, +*h*, *k*, *l*), 1558 unique reflections (*R*_{merge} = 0.0037), no absorption

correction applied. Three check reflections measured every 100 reflections showed no significant decrease in intensity.

Structure Analysis and Refinement.—Structure solved by direct methods and refined by full-matrix least-squares on *F*², with all non-hydrogen atoms anisotropic, and hydrogens with isotropic temperature factors fixed at 1.2 times *U*_{eq} of their parent atoms. Aromatic and methylene hydrogens placed at calculated positions with C-H distance free and torsion angle which maximizes the sum of the electron density at the three calculated positions. Extinction correction as described by Larson.¹⁷ Final *R* indices *R*₁ = 0.044, *wR*₂ = 0.109 for *I* > 2 σ (*I*) data and *R*₁ = 0.062, *wR*₂ = 0.117 for all data. Weighting scheme used: $w[\sigma^2(F_o^2) + 0.0730P^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Program package SHELXTL-PC¹⁸ used for structure solution and drawings, SHELXL-93¹⁹ used for refinement.

IR Spectra.—The IR spectra were recorded on a Bruker FTIR spectrometer IFS 88 at a resolution of 1 cm⁻¹. The spectrum of DMAMN was taken in KBr suspension (3200–700 cm⁻¹) or in C₂Cl₄ (700–400 cm⁻¹).

Materials.—DMAMN was synthesized following a previously described procedure.¹⁴ The purity was checked by ¹H NMR spectroscopy.

Results and Discussion

The atom numbering in DMAMN is shown in Fig. 1. Selected bond lengths and angles are collected in Table 1. Fig. 2 shows the deviations (Å) from the mean plane of the ring system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

The FTIR spectrum of DMAMN from 3200 to 2600 cm⁻¹ and from 1800 to 400 cm⁻¹ is reproduced in Fig. 3. The spectrum of DMAN, useful for comparison, is shown in the same figure.

The X-ray results indicate that the naphthalene ring of

* For details of the CCDC deposition scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue 1.

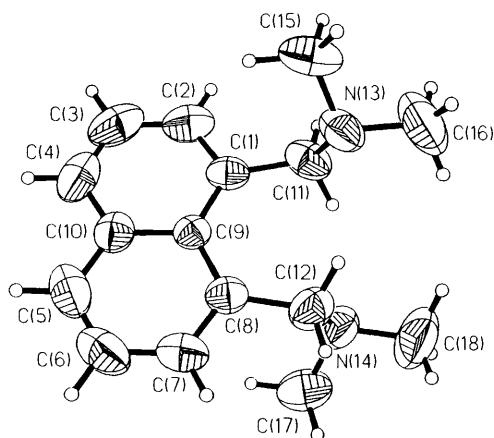


Fig. 1 ORTEP drawing and numbering of the atoms in DMAMN

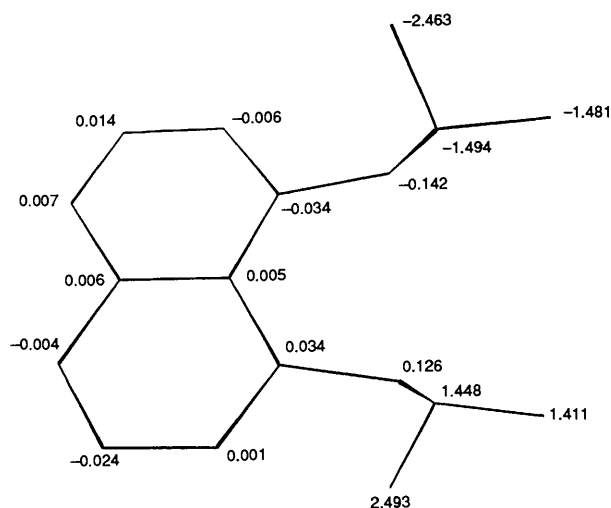


Fig. 2 Deviations (Å) from the mean plane of the ring in DMAMN

DMAMN is nearly planar, the mean deviation from the plane of the ring system being 0.018 Å. In DMAN, the mean deviation of the ring system is markedly higher, about 0.086 Å and the deviation from the ring system for the C(1) and C(8) atoms is ± 0.15 Å.¹⁵ This value is higher than the value of ± 0.034 Å found in this work for DMAMN.

In the case of DMAMN, the steric repulsion between the electron-pairs of the nitrogen atoms is reduced by opening the C(9)–C(1)–C(11) and C(9)–C(8)–C(12) angles to a value of about 125° and by an out-of-plane torsion of C(11) (–0.142 Å) and C(12) (+0.126 Å). These angles and the out-of-plane deviation are not strongly different from those recently determined at low temperatures for DMAMN protonated by nitric acid.²⁰ In DMAN, the C(9)–C(8)–N(11) angle is 120° and steric repulsion is prevented by a rotation of the dimethylamino groups so as to bring two of the methyl groups in the plane of the aromatic ring and the two other ones above and below this ring.¹⁵ The N...N distance is markedly higher in DMAMN (3.854 Å) than in DMAN (2.790 Å).¹⁵

Owing to the delocalization of the free electron pairs into the aromatic ring, the C(1)–N(11) and C(8)–N(12) distances in DMAN are markedly shorter than the C(11)–N(13) (1.471 Å) and C(12)–N(14) (1.466 Å) distances in DMAMN. This delocalization effect has also an influence on the C–N–C angle in the N(CH₃)₂ group. This average angle is 116° in DMAN, larger than would be expected for sp³ hybridization.¹⁵ In

Table 1 Bond lengths (Å) and angles (°)

C(1)–C(2)	1.367(3)	C(1)–C(9)	1.439(3)
C(1)–C(11)	1.506(3)	C(2)–C(3)	1.391(4)
C(3)–C(4)	1.343(4)	C(4)–C(10)	1.413(3)
C(5)–C(6)	1.351(4)	C(5)–C(10)	1.418(3)
C(6)–C(7)	1.378(4)	C(7)–C(8)	1.375(3)
C(8)–C(9)	1.436(3)	C(8)–C(12)	1.514(3)
C(9)–C(10)	1.426(3)	C(11)–N(13)	1.471(3)
C(12)–N(14)	1.466(3)	N(13)–C(15)	1.455(3)
N(13)–C(16)	1.465(3)	N(14)–C(17)	1.451(3)
N(14)–C(18)	1.465(3)		
C(2)–C(1)–C(9)	119.5(2)	C(2)–C(1)–C(11)	115.1(2)
C(9)–C(1)–C(11)	125.4(2)	C(1)–C(2)–C(3)	122.8(3)
C(4)–C(3)–C(2)	119.5(3)	C(3)–C(4)–C(10)	121.0(3)
C(6)–C(5)–C(10)	121.3(3)	C(5)–C(6)–C(7)	118.8(3)
C(8)–C(7)–C(6)	123.6(3)	C(7)–C(8)–C(9)	119.2(2)
C(7)–C(8)–C(12)	115.7(2)	C(9)–C(8)–C(12)	125.1(2)
C(10)–C(9)–C(8)	116.7(2)	C(10)–C(9)–C(1)	116.7(2)
C(8)–C(9)–C(1)	126.6(2)	C(4)–C(10)–C(5)	119.2(3)
C(4)–C(10)–C(9)	120.5(2)	C(5)–C(10)–C(9)	120.3(2)
N(13)–C(11)–C(1)	113.2(2)	N(14)–C(12)–C(8)	114.1(2)
C(15)–N(13)–C(11)	109.5(2)	C(15)–N(13)–C(11)	111.6(2)
C(16)–N(13)–C(11)	109.3(2)	C(17)–N(14)–C(18)	109.5(2)
C(17)–N(14)–C(12)	112.4(2)	C(18)–N(14)–C(12)	109.1(2)

Table 2 Selection rules for the aromatic ring vibrations of naphthalene, DMAMN and DMAN

D_{2h}^a	C_{2v}	C_2
9 A _g (R)	↘	24 A (IR, R)
8 B _{1u} (IR)	↗	
4 A _w (R)	↘	24 B (IR, R)
3 B _{1g} (IR)	↗	
4 B _{2g} (R)	↘	8 B ₂ (IR)
4 B _{3u} (IR)	↗	
8 B _{2u} (IR)	↘	
8 B _{3g} (R)	↗	

^a B_{1u} and B_{2u} are the vibrations polarized along the short and long axis of naphthalene and B_{3u}, B_{1g} and B_{2g} are perpendicular vibrations. IR = Infrared active, R = Raman active.

DMAMN, the C–N–C angle has a mean value of 111°, indicating an almost pure sp³ hybridization.

As illustrated in Fig. 3, the IR spectra of DMAN and DMAMN show marked differences which cannot be explained only by the vibrations arising from the two CH₂ groups. The assignments of the ring skeleton vibrations of the two proton sponges is made by comparison with the vibrations of naphthalene^{21–25} which has D_{2h} symmetry. Owing to its almost planar structure the ring skeleton of DMAMN can be considered as having C_{2v} symmetry while DMAN, having only one twofold axis, belongs to the C_2 group. The selection rules for the aromatic ring vibrations of naphthalene, DMAMN and DMAN are indicated in Table 2.

Table 3 lists the wavenumber of some vibrational modes useful for the comparison of the three molecules, along with their probable assignments. The other absorptions between 1480 and 1350 cm^{–1} can be ascribed to the deformation vibration of the CH₃ and CH₂ groups. The bands at 1185 (DMAN) and 1176 cm^{–1} (DMAMN) probably originate from the rocking motion of the CH₃ groups. The absorptions at 1008

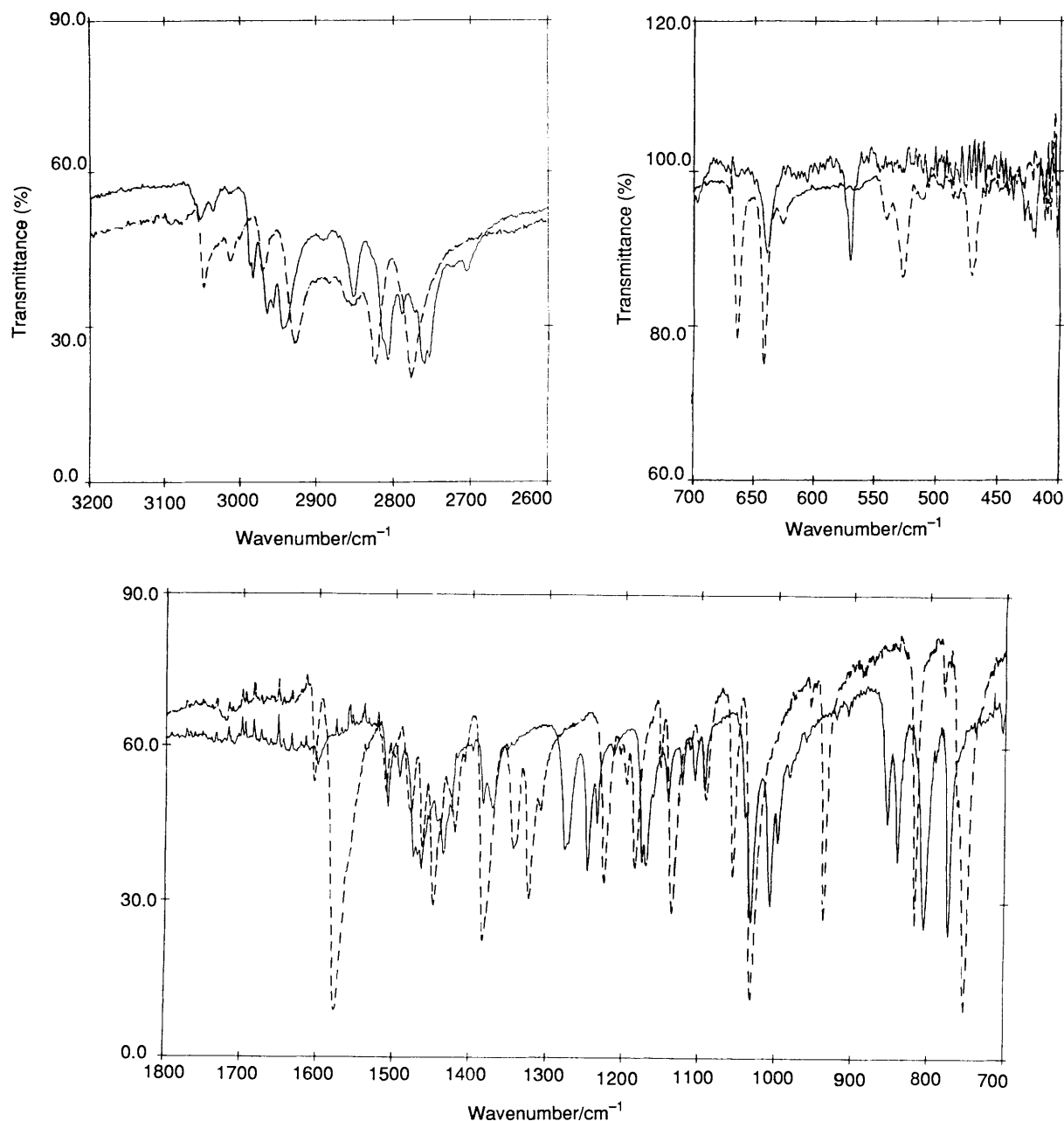


Fig. 3 IR spectrum of DMAMN (—) and DMAN (---); 3200–700 cm^{-1} in KBr suspension; 700–400 cm^{-1} in C_2Cl_4

and 841 cm^{-1} observed only in DMAMN are ascribed to the skeletal vibrations of the C–C–N aliphatic skeleton and will not be discussed here.

Inspection of the results in Table 3 shows that several absorptions assigned to vibrations of the aromatic skeleton or to vibrations involving the aromatic CH bonds are characterized by a much higher intensity in DMAN than in DMAMN. This is the case for the ν_{CH} vibrations, the ring stretching vibrations at 1577 and 1448 cm^{-1} , the δ_{CH} vibrations at 1384 and 1136 cm^{-1} , the γ_{CH} vibration at 753 cm^{-1} and the out-of-plane deformation of the ring skeleton whose assignment is more doubtful. The A_g vibration of the ring (observed at 1570 cm^{-1} in the Raman spectrum of naphthalene) is theoretically active in DMAMN but is not observed owing to its weak intensity. Interestingly, the intensity of this band strongly decreases when DMAN is protonated.^{8,9} This can be ascribed to an increase of the symmetry of the aromatic ring brought about by protonation. It must be pointed out here that the absorption observed at 1448 cm^{-1} in DMAN has been ascribed

to the δ_{CH_2} vibration.⁶ This absorption is observed in DMAMN with a very weak intensity and is therefore assigned to a ring vibration. Finally the Bohlmann bands observed between 2883 and 2760 cm^{-1} have comparable intensities in the two proton sponges.

Conclusions

This work has shown that the ring skeleton of DMAMN is almost planar in contrast to DMAN. The remarkable basicity of DMAN is ascribed to the relief of the steric strain between the two dimethylamino groups upon protonation which also increases its planarity. Previous studies performed in solution have shown that DMAN forms with AH proton donors, protonated and homoconjugated AHA species. This tendency is less pronounced in the DMAMN complexes.¹⁶ DMAMN can be considered as a proton sponge with basic properties intermediate between those of DMAN and monofunctional aliphatic amines such as triethylamine.²⁶

Table 3 IR data for DMAN, DMAMN and naphthalene^a

DMAN	DMAMN	Naphthalene	Symmetry and assignment	
3048m	3053w	3056	B _{1u}	ν_{CH}
3013w	3015vw	3029	B _{2u}	ν_{CH}
2883m	2870m			ν_{NMe}
2778m	2760m			
1605mw	1600vw	1595	B _{1u}	ν_{ring}
1577vs		1566 ^b	A _g	ν_{ring}
1512w	1508w	1509	B _{2u}	ν_{ring}
1448m	1445vw	1460(R) ^c	A _g	ν_{ring}
1384s	1384w	1390	B _{1u}	δ_{CH}
1345		1361	B _{2u}	δ_{ring}
1325				$\nu_{\text{C(ar)-N}}$
1136s	1142 or 1123w	1144	B _{2u}	δ_{CH}
1032vs	1033vs			$\nu_{\text{C(aliph)-(N)}}$ ^d
753vs	774s	782	B _{3u}	γ_{CH}
663mw		717?(R)	B _{1g}	γ_{ring}
641mw	639w	618?	B _{2u}	δ_{ring}
527	570			δ_{CNC}
471w		461(R)	B _{2g}	γ_{ring}

^a w = weak, vw = very weak, m = medium, s = strong, vs = very strong, ν , δ and γ are stretching, in-plane and out-of-plane bending modes. ^b Probably the overtone of the 790 cm⁻¹ (ν_{CH}) vibration. ^c Raman active. ^d Ref. 6.

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