

Complexes of the 'Proton Sponge' 1,8-Bis(dimethylamino)naphthalene (DMAN). IV. Structure of $[\text{DMANH}]_2^+ \cdot [\text{Squarate}]^{2-}$ Tetrahydrate at 100 K*

BY J. A. KANTERS,† A. SCHOUTEN AND J. KROON

Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Rijksuniversiteit Utrecht, Transitorium 3, Padualaan 8, 3584 CH Utrecht, The Netherlands

AND E. GRECH

Institute of Fundamental Chemistry, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland

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Abstract. Bis[(8-dimethylamino-1-naphthyl)dimethylammonium] 3,4-dioxocyclobut-1-ene-1,2-diolate tetrahydrate, $2\text{C}_{14}\text{H}_{19}\text{N}_2^+ \cdot \text{C}_4\text{O}_4^{2-} \cdot 4\text{H}_2\text{O}$, $M_r = 614.74$, orthorhombic, $Cmc2_1$, $a = 11.2191(4)$, $b = 15.9824(5)$, $c = 17.7311(7)$ Å, $V = 3179.3(2)$ Å³, $Z = 4$, $D_x = 1.284$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.0$ cm⁻¹, $F(000) = 1320$, $T = 100$ K, $R = 0.033$ for 1790 reflections with $I > 2.5\sigma(I)$. The asymmetric unit consists of two half DMANH^+ cations, one half squarate anion and four half water molecules. The crystallographic mirror plane bisects the two independent DMANH^+ cations through the central C—C bond and contains the squarate anion and the four water molecules. The H atoms in the two $[\text{N—H}\cdots\text{N}]^+$ intramolecular hydrogen bonds are disordered and located at about 0.35 Å from the mirror plane.

Introduction. Recently we reported the low-temperature structure at 150 K of the complex of the 'proton sponge' 1,8-bis(dimethylamino)naphthalene (DMAN) with squaric acid (H_2SQ), $\text{DMANH}^+ \cdot \text{HSQ}^-$ (Kanters, Schouten, Kroon & Grech, 1991). As in other DMAN complexes (Kanters, Schouten, Kroon & Grech, 1991; Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech, 1991; Kanters, ter Horst, Kroon & Grech, 1992; Woźniak, Krygowski, Kariuki, Jones & Grech, 1990), a proton is transferred to the DMAN residue with the formation of a strong intramolecular $[\text{N—H}\cdots\text{H}]^+$ hydrogen bond. In the room-temperature structures these intramolecular hydrogen bonds have elongated N—H distances which for eight complexes (Kanters, Schouten, Kroon & Grech, 1991; Woźniak, Krygowski, Kariuki, Jones & Grech, 1990) are in the range 1.17–1.31 Å, the N \cdots N

range being 2.55–2.65 Å. On the other hand, in two low-temperature structures, $\text{DMANH}^+ \cdot \text{HSQ}^-$ (Kanters, Schouten, Kroon & Grech, 1991) and $2\text{DMANH}^+ \cdot \text{chloroanilate}^{2-}$ (Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech, 1991) the N—H distances have normal values of 1.08(2) and 1.07(3) Å, respectively. A very long N—H distance was reported for the 143 K structure of $\text{DMANH}^+ \cdot \text{OTeF}_5^-$ (Kellett, Anderson, Strauss & Abney, 1989) where space-group symmetry requires the H atom to lie at the mirror plane passing through the central C—C bond of the DMANH^+ residue or alternatively to be disordered at opposite sides of the mirror plane; the H atom was located in the mirror plane (N—H 1.37 Å, N—H \cdots N 140°) and no mention is made about a possible disorder of the H atom. In the room-temperature triclinic modification (Miller, Abney, Rappé, Anderson & Strauss, 1988), where no symmetry constraint is operative, the $[\text{N—H}\cdots\text{N}]^+$ bridge is asymmetric with an N—H distance of 1.17 Å. The results of the room-temperature and low-temperature analyses seem to indicate that the N—H \cdots N potential well is fairly skew, resulting in elongated N—H distances in room-temperature structures and normal N—H distances in low-temperature structures, provided that no symmetry constraints are present.

In order to obtain accurate information on the electron-density distribution in the $[\text{N—H}\cdots\text{N}]^+$ hydrogen bond, we undertook the structure analysis of the title complex at 100 K.

Experimental. A colourless crystal of dimensions 0.7 × 0.5 × 0.4 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation. Lattice parameters were determined from the setting angles of 25 reflections in the range $14.04 \leq \theta \leq 19.66^\circ$. Systematic absences (hkl , $h + k$ odd; $h0l$, l odd) are consistent with space

* Part III: Kanters, ter Horst, Kroon & Grech (1992).

† Author to whom correspondence should be addressed.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
N(1)	0.1147 (2)	0.0605 (1)	0.3693 (3)	0.0147 (5)
C(1)	0.1136 (2)	-0.0281 (1)	0.3908	0.0131 (5)
C(2)	0.2177 (2)	-0.0703 (1)	0.4030 (2)	0.0150 (6)
C(3)	0.2157 (2)	-0.1553 (1)	0.4246 (2)	0.0163 (6)
C(4)	0.1102 (2)	-0.1961 (1)	0.4333 (2)	0.0155 (5)
C(5)	0	-0.1543 (2)	0.4221 (3)	0.0133 (6)
C(6)	0	-0.0676 (2)	0.3999 (2)	0.0127 (6)
C(7)	0.1760 (3)	0.1131 (2)	0.4261 (2)	0.031 (1)
C(8)	0.1639 (2)	0.0736 (2)	0.2926 (2)	0.0277 (6)
N(2)	0.1156 (2)	0.7977 (1)	0.1668 (2)	0.0139 (5)
C(9)	0.1133 (2)	0.8861 (1)	0.1395 (1)	0.0126 (5)
C(10)	0.2176 (2)	0.9281 (1)	0.1255 (2)	0.0163 (6)
C(11)	0.2158 (2)	1.0123 (1)	0.1011 (2)	0.0177 (6)
C(12)	0.1098 (2)	1.0529 (1)	0.0922 (2)	0.0157 (6)
C(13)	0	1.0107 (2)	0.1043 (2)	0.0140 (6)
C(14)	0	0.9253 (2)	0.1284 (2)	0.0130 (6)
C(15)	0.1686 (2)	0.7403 (2)	0.1118 (2)	0.0243 (6)
C(16)	0.1749 (2)	0.7944 (1)	0.2415 (2)	0.0230 (6)
O(1)	0	0.3588 (1)	0.2319 (2)	0.0310 (8)
O(2)	0	0.4982 (1)	0.3661 (2)	0.0187 (6)
O(3)	0	0.6449 (2)	0.2407 (2)	0.0327 (8)
O(4)	0	0.5081 (1)	0.1072 (2)	0.0180 (6)
C(17)	0	0.4379 (2)	0.2349 (2)	0.0173 (6)
C(18)	0	0.5002 (2)	0.2951 (2)	0.0147 (6)
C(19)	0	0.5680 (2)	0.2383 (2)	0.0173 (6)
C(20)	0	0.5049 (2)	0.1780 (2)	0.0137 (6)
O(5)	0	0.2608 (2)	0.1034 (2)	0.0373 (8)
O(6)	0	0.2540 (2)	0.3548 (2)	0.0270 (8)
O(7)	0	0.3775 (1)	0.4801 (2)	0.0210 (6)
O(8)	0	0.6090 (2)	0.4904 (2)	0.0390 (8)

Table 2. Bond distances (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

N(1)—C(1)	1.466 (2)	N(2)—C(9)	1.463 (3)
N(1)—C(7)	1.481 (4)	N(2)—C(15)	1.485 (4)
N(1)—C(8)	1.483 (5)	N(2)—C(16)	1.485 (5)
C(1)—C(2)	1.366 (3)	C(9)—C(10)	1.372 (3)
C(1)—C(6)	1.431 (3)	C(9)—C(14)	1.431 (3)
C(2)—C(3)	1.412 (3)	C(10)—C(11)	1.414 (3)
C(3)—C(4)	1.360 (3)	C(11)—C(12)	1.364 (3)
C(4)—C(5)	1.419 (3)	C(12)—C(13)	1.421 (3)
C(5)—C(6)	1.440 (5)	C(13)—C(14)	1.430 (5)
O(1)—C(17)	1.265 (4)	C(17)—C(18)	1.460 (5)
O(2)—C(18)	1.259 (5)	C(17)—C(20)	1.471 (5)
O(3)—C(19)	1.230 (5)	C(18)—C(19)	1.479 (5)
O(4)—C(20)	1.256 (5)	C(19)—C(20)	1.470 (5)
C(1)—N(1)—C(7)	112.1 (2)	C(9)—N(2)—C(15)	113.1 (3)
C(1)—N(1)—C(8)	112.2 (2)	C(9)—N(2)—C(16)	110.9 (2)
C(7)—N(1)—C(8)	111.8 (2)	C(15)—N(2)—C(16)	111.7 (2)
N(1)—C(1)—C(2)	120.7 (2)	N(2)—C(9)—C(10)	120.4 (2)
N(1)—C(1)—C(6)	117.6 (2)	N(2)—C(9)—C(14)	118.3 (2)
C(2)—C(1)—C(6)	121.7 (2)	C(10)—C(9)—C(14)	121.2 (2)
C(1)—C(2)—C(3)	120.3 (2)	C(9)—C(10)—C(11)	120.6 (2)
C(2)—C(3)—C(4)	120.4 (2)	C(10)—C(11)—C(12)	120.0 (2)
C(3)—C(4)—C(5)	121.1 (2)	C(11)—C(12)—C(13)	120.8 (2)
C(4)—C(5)—C(6)	119.4 (1)	C(12)—C(13)—C(14)	119.9 (1)
C(4)—C(5)—C(4')	121.2 (3)	C(12)—C(13)—C(12')	120.2 (3)
C(1)—C(6)—C(5)	117.1 (1)	C(9)—C(14)—C(13)	117.3 (1)
C(1)—C(6)—C(1')	125.8 (2)	C(9)—C(14)—C(9')	125.4 (3)
O(1)—C(17)—C(18)	135.4 (3)	O(3)—C(19)—C(18)	135.1 (3)
O(1)—C(17)—C(20)	134.3 (3)	O(3)—C(19)—C(20)	135.3 (3)
C(18)—C(17)—C(20)	90.3 (3)	C(18)—C(19)—C(20)	89.6 (3)
O(2)—C(18)—C(17)	135.5 (3)	O(4)—C(20)—C(17)	135.6 (3)
O(2)—C(18)—C(19)	134.4 (3)	O(4)—C(20)—C(19)	134.3 (3)
C(17)—C(18)—C(19)	90.1 (3)	C(17)—C(20)—C(19)	90.0 (3)

Symmetry code: (i) $-x, y, z$.

groups $Cmc2_1$, $Cmcm$ and $C2cm$ (alternative setting of $Ama2$, No. 40). The intensities of 2484 reflections (1979 unique, $R_{int} = 0.025$) were collected at liquid-nitrogen temperature (100 K) using the ω - 2θ scan mode, $\Delta\omega = (0.89 + 0.35\tan\theta)^\circ$, $2\theta_{max} = 55^\circ$ and $0 \leq h \leq 14$, $0 \leq k \leq 20$, $-23 \leq l \leq 0$, 1790 with $I > 2.5\sigma(I)$. Three standard reflections (154, 400 and 042), measured every hour, showed an average deviation of less than 2% during 33 h of X-ray exposure. Intensities were corrected for Lp effects, but not for absorption. The structure was solved in space group $Cmc2_1$ by direct methods using *SHELXS86* (Sheldrick, 1986). The difference Fourier syntheses showed peaks at the expected positions of H atoms; all but two were included in the refinement with an overall isotropic thermal parameter which refined to $0.031(2) \text{\AA}^2$. In the regions between the N atoms of the two [DMANH] $^+$ residues two maxima of 0.35 e \AA^{-3} were found at a distance of 0.35 \AA from the mirror plane which indicates disordering of the H atom in each [N—H...N] $^+$ hydrogen bond. These two H atoms were included in the refinement with a fixed occupancy of 0.5. Anisotropic full-matrix least-squares refinement on F of 299 parameters converged at $R = 0.033$ and $wR = 0.042$ with $w = 1/\sigma^2(F_o)$, $S = 0.99$, $(\Delta/\sigma)_{av} = 0.006$, $(\Delta/\sigma)_{max} = 0.08$, $-0.24 \leq \Delta\rho \leq 0.36 \text{ e \AA}^{-3}$. The scattering factors were those of Cromer & Mann (1968) and anomalous-dispersion terms from Cromer & Liberman (1970). Calculations were performed with *SHELX76* (Sheldrick, 1976) (refinement) and the *EUCLID* program package

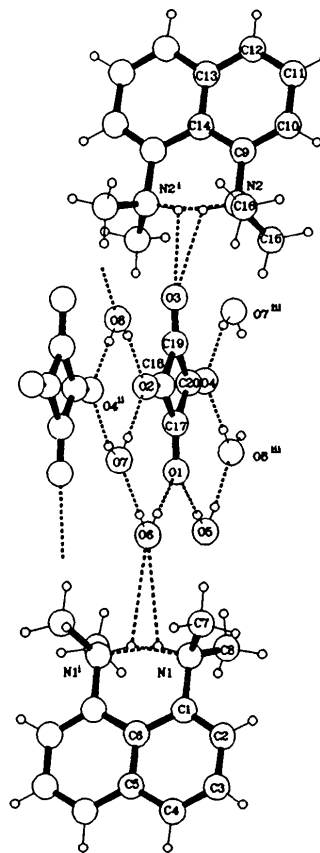


Fig. 1. Projection of part of the structure with atom numbering, showing the hydrogen-bond network.

(Spek, 1982) (geometry and illustrations) on a MicroVAX II computer.

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1* and bond distances and angles are listed in Table 2. Part of the hydrogen-bond network of the complex with the adopted numbering scheme is shown in Fig. 1. The crystallographic mirror plane perpendicular to the *a* axis bisects the two independent DMANH⁺ residues through the central C—C bond and contains the squarate anion and the four water molecules. The naphthalene rings of the two independent half DMANH⁺ residues are planar and the N atoms of the two residues deviate only 0.010 (5) and 0.06 (1) Å from the naphthalene planes. The bond distances and angles agree with those observed in other DMANH⁺ complexes, the C(1)—C(6)—C(1') and C(9)—C(14)—C(9') angles being opened to 125.8 (2) and 125.4 (3)°. The squarate anion lies in

* Lists of structure factors, anisotropic thermal parameters and coordinates of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54924 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0295]

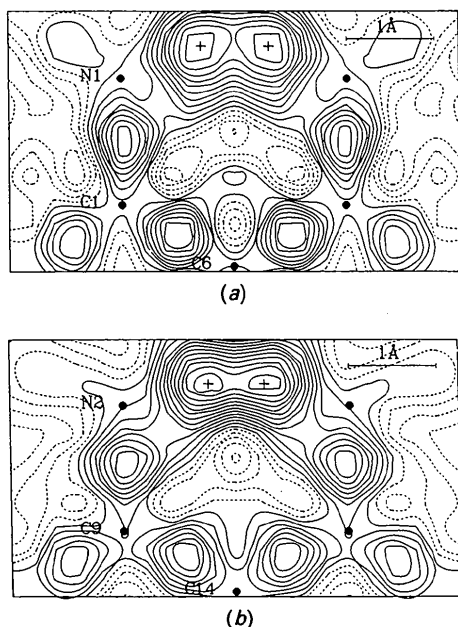


Fig. 2. Difference Fourier maps in the region of the intramolecular hydrogen bonds. The lines indicate electron density in steps of $0.03 \text{ e } \text{Å}^{-3}$. Dashed lines indicate negative electron densities. The crosses mark the maxima at a displacement of 0.08 Å from the H-atom positions after refinement. (a) Section in the plane C(1)—N(1)···N(1')—C(1'); (b) section in the plane C(9)—N(2)···N(2')—C(9'). (Note the residual densities on the C—N and C—C bonds.)

Table 3. *Hydrogen bond geometry* (Å, °) *with e.s.d.'s in parentheses*

D—H···A	D—H	D···A	H···A	D—H···A
N(1)—H···N(1')	0.94 (6)	2.574 (3)	1.69 (6)	156 (5)
N(1)—H···O(6)	0.94 (6)	3.359 (3)	2.88 (5)	113 (4)
N(2)—H···N(2')	0.97 (6)	2.594 (3)	1.66 (6)	162 (5)
N(2)—H···O(3)	0.97 (6)	3.085 (4)	2.63 (5)	109 (4)
O(5)—H···O(8 ⁱⁱⁱ)	0.96 (5)	2.889 (5)	1.93 (5)	174 (5)
O(5)—H···O(1)	0.75 (5)	2.765 (5)	2.01 (5)	179 (5)
O(6)—H···O(1)	0.93 (5)	2.748 (5)	1.82 (5)	179 (5)
O(6)—H···O(7)	0.84 (5)	2.972 (4)	2.13 (5)	178 (5)
O(7)—H···O(2)	0.87 (5)	2.794 (4)	1.93 (5)	178 (5)
O(7)—H···O(4 ⁱⁱ)	0.91 (5)	2.902 (4)	2.03 (5)	159 (4)
O(8)—H···O(4 ⁱⁱ)	0.86 (5)	2.791 (4)	1.93 (5)	179 (5)
O(8)—H···O(2)	0.90 (5)	2.827 (5)	1.95 (5)	165 (5)

Symmetry code: (i) $-x, y, z$; (ii) $x, 1-y, \frac{1}{2}+z$; (iii) $x, 1-y, -\frac{1}{2}+z$.

the mirror plane and has almost fourfold symmetry. Special attention was devoted to the location of the H atoms in the two intramolecular [N—H···N]⁺ hydrogen bonds. The space group requires *m* symmetry, which would lead to considerably elongated N—H distances in the linear N—H···N arrangement if the H atom were to lie in the mirror plane [see, for DMANH⁺·OTeF₅⁻, Kellett, Anderson, Strauss & Abney (1989)].

Careful inspection of the (total) difference electron-density synthesis revealed two broad smeared maxima considerably extending outside the mirror plane. These difference maps [Fig. 2(a) and (b)] clearly reveal that the bridging H atoms are disordered. Inclusion of the H atoms with half occupancy in the refinement resulted in stable N—H distances of 0.94 (6) and 0.97 (6) Å for the two residues and N—H···N angles of 156 (5) and 162 (5)°, these values being more acceptable than those postulated for DMANH⁺·OTeF₅⁻ (Kellett, Anderson, Strauss & Abney, 1989).

The complex pattern of intermolecular hydrogen bonds (Table 3 and Fig. 1) involving all constituents of the title compound lies entirely in the mirror plane. An endless one-dimensional chain is formed by four hydrogen bonds from the donating O(7) and O(8) water molecules to the accepting O(2) and O(4ⁱⁱ) of neighbouring squarates. The two other water molecules, O(5) and O(6), each donate a hydrogen bond to squarate O(1), O(5) donates one bond to water O(8ⁱⁱⁱ) and similarly water O(6) to water O(7). The N—H···N system of one DMANH⁺ residue is involved in a weak bifurcated interaction *via* the disordered bridging H atoms with squarate O(3) and the same holds for the other DMANH⁺ residue which interacts with water molecule O(6). Both four-atom configurations are planar; the sum of angles around the central H atom amounts to 360 (7)°.

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Structure of 3-Benzoyl-4-methyl-1-phenyl-1,2,3,4-tetrahydro-5H-indeno-[1,2-*b*]pyridine-2,5-dione

BY MICHAEL B. HURSTHOUSE AND A. I. KARAULOV

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, England

M. CIECHANOWICZ-RUTKOWSKA

Regional Laboratory of Physicochemical Analysis and Structural Research, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland

AND A. KOLASA AND W. ZANKOWSKA-JASIŃSKA

Faculty of Chemistry, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland

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Abstract. C₂₆H₁₉NO₃, *M_r* = 393.442, triclinic, *P* $\bar{1}$, *a* = 8.630 (1), *b* = 9.908 (4), *c* = 13.549 (16) Å, α = 107.73 (3), β = 94.96 (5), γ = 112.51 (3)°, *V* = 991.85 (1.31) Å³, *Z* = 2, *D_m* = 1.30, *D_x* = 1.317 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.080 mm⁻¹, *F*(000) = 412, *T* = 293 K, *R* = 0.050 for 2110 unique observed reflections. The pyridone ring has a half-chair conformation with in-ring torsions in the N—C(carbonyl) and N—C(indenyl) bonds of 6.3 (5) and 15.6 (5)°, respectively. The phenyl-substituted N is planar to within 0.013 (3) Å.

Introduction. Both 5*H*- and 1*H*-indeno[1,2-*b*]pyridine derivatives have a wide spectrum of biological activity, e.g. antidepressant (Leven & Schacht, 1984), antihistaminic (Vinogradova, Gaivoronskaya, Kirillova, Bu Habib & Prostavkov, 1984), plant-growth regulatory (Wieczorek, Boduszek, Gancarz & Zukiewicz, 1984), and are present in many alkaloids (Koyama, Sugita, Suzuta & Irie, 1979; Waterman & Muhammad, 1985; Goulart, Sant'ana, De Oliveira, De Oliveira & Maia, 1986; Wu, 1989; Bon-Abdullah, Jossang, Tadic, Lebceuf & Cave, 1989). In a study of the reaction of methylene-bis-anilides of benzoyl-acetic derivatives with excess phosphorus oxychloride,

elemental and spectral analysis as well as isotopic and chemical evidence suggested that 2*H*-pyrano[2,3-*b*]quinolin-2-one was the reaction product (Zankowska-Jasińska & Kolasa, 1976). Because this relatively simple and very efficient synthesis should lead, according to our assumption, to a common constituent of alkaloid structures we decided to choose a stereochemically interesting derivative for X-ray investigation. Much to our surprise the result revised the previously postulated structure of the reaction product of 2,4-dibenzoyl-3-methyl-pentanedioic acid dianilide with POCl₃ and thus revealed indirectly the course of the reaction, i.e. that aniline and not water is eliminated first.

Experimental. The compound crystallizes from methanol at room temperature as orange prisms. A crystal 0.2 × 0.1 × 0.05 mm was chosen. X-ray measurements were made using an Enraf–Nonius FAST area detector and graphite-monochromated Mo *K*α radiation from a rotating-anode generator operating at 47 kV, 47 mA with a 300 μm focus. With a detector-to-crystal setting (= DET) of 40 mm and a swing angle (= θ_D) of -18°, reflections were found in two 5° ω -rotation regions separated by 90°.