routine takes the disordered molecules into account as diffuse electron density and adds this contribution to the F_c^2 values through back-Fourier transformation. The final F_o^2/F_c^2 data include the disordered solvent contribution.

H atoms were located using a difference Fourier map and were included in the refinement with isotropic displacement parameters equal to 1.2 (or 1.5 for methyl-H atoms) times the equivalent isotropic parameter of the atom to which they were attached. The H atoms involved in the [N—H···N]$^+$ and the [O—H···O]$^-$ hydrogen bonds were originally located on the symmetry elements. The difference Fourier map in the C2—C1—N1 plane (H atom exluded) showed a broad net electron density indicating two H-atom positions slightly off the axis running through the central C—C bond. Therefore, in the next refining step, a disordered model was introduced for the H atom. The [O—H···O]$^-$ hydrogen was treated in a similar way. The *R* and *wR* values showed a significant (Hamilton, 1965) improvement upon introducing disorder (from 0.0584 and 0.1211 to 0.0580 and 0.1201, respectively).

Data collection: *KappaCCD Server* (Nonius, 1997). Cell refinement: *DIRAX* (Duisenberg, 1992). Data reduction: *EVAL* (Schreurs & Duisenberg, 1999). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1044). Services for accessing these data are described at the back of the journal.

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1,8-Bis(dimethylaminomethyl)naphthalene bis(squaric acid) dihydrate

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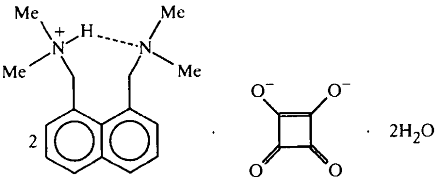
Abstract

In the crystal structure of the title compound, bis[(1-dimethylamino-8-naphthyl)dimethyl ammonium] 3,4-dihydroxy-3-cyclobutene-1,2-dionate(2−) dihydrate, $2C_{16}H_{23}N_2^+\cdot C_4O_4^{2-}\cdot 2H_2O$, 1,8-bis(dimethylaminomethyl)naphthalene acts as a proton sponge by accepting protons from squaric acid. The protons form disordered asymmetric [N—H···N]$^+$ hydrogen bonds. The crystal water is hydrogen bonded to the squarate anion in a 2:1 cluster.

Comment

1,8-Bis(dimethylaminomethyl)naphthalene (DMAMN) is a modification of the more widely used compound 1,8-bis(dimethylamino)naphthalene (DMAN). This class of compounds is given the nickname 'proton sponge' due to the compound trapping an H$^+$ ion in a very strong intramolecular [N—H···N]$^+$ hydrogen bond. The strength of the hydrogen bond is determined by the favorable geometry of two chemically equivalent basic centres. Upon binding a proton, the repulsion between the nitrogen lone-pair electrons is released, adding to the strength of the hydrogen bond. Complexes containing DMANH$^+$ ions, reported in the Cambridge Structural Database (Allen *et al.*, 1983, version October 1998), show that in some cases the proton tends to move to a central position between the two N atoms, in order to form strong, symmetrical hydrogen bonds (*e.g.* Bartoszak *et al.*, 1994). In a number of low-temperature studies a truly asymmetric hydrogen bond was found (*e.g.* Kanters *et al.*, 1991) or an (asymmetric) distribution over two proton positions (*e.g.* Kanters *et al.*, 1992). The basicity of DMAMN is slightly stronger than that of DMAN (Sawka-Dobrowolska *et al.*, 1995). The separation of the amino groups from the naphthalene ring system by the methylene moiety causes an increase in the basicity of these amino groups, but it also leads to a steric disturbance which does not favour the formation of the most stable [N—H···N]$^+$ bond (Brzezinski *et al.*, 1991).

The asymmetric unit of the studied crystal, (I), contains one protonated DMAMN ion, half a squarate ion (Sq^{2-}), located at a crystallographic inversion centre and a solvent water molecule.



(I)

Geometrical analysis of the molecules revealed no significant differences compared with structures reported earlier. In the crystal structure of unprotonated DMAMN (van Meervelt *et al.*, 1994), the dimethylamine moieties are located on opposite sides of the naphthalene ring system. In the protonated DMAMN these groups are located on the same side of the ring system. The repulsion between the dimethylaminomethyl groups is reduced by opening of the C9—C1—C11 and C9—C8—C14 angles (see Table 1) and by a slight distortion of the naphthalene skeleton, resulting in out-of-plane positions of C11 and C14 [0.1980(16) above and 0.1222(14) Å below the least-squares plane through the ring system, respectively].

The hydroxyl protons of squaric acid have been transferred to DMAMN residues. Difference Fourier plots of the region between the two N atoms of DMAMNH$^+$ revealed the presence of two more or less symmetrically located H atom sites, indicated by H1*A* and H1*B* which are unevenly occupied in a ratio 3:1. The resulting hydrogen-bond geometry is given in Table 2. In room-temperature studies of structures containing monoprotonated DMAMN, the proton is reported to be located asymmetric, but considerably shifted towards the centre of the hydrogen bond (perchlorate complex; Sawka-Dobrowolska *et al.*, 1994) or to be close to the centre of the N—H···N bond (pentachlorophenolate complex; Sawka-Dobrowolska *et al.*, 1995 and nitrate complex; Brzezinski *et al.*, 1991). In a low-temperature study of this last structure (Salas *et al.*, 1992), the proton was found to be disordered over two positions, like in the structure reported in this paper.

In the crystal structures of [DMANH]$^+$·[HSq]$^-$·H_2O (Kanters *et al.*, 1991) and 2[DMANH]$^+$·[Sq]$^{2-}$·4H_2O (Kanters *et al.*, 1992) the [N—H···N]$^+$ protons are also involved in a weak hydrogen-bond interaction with either a charged O atom of the squarate ion or with the O atom of a co-crystallized water molecule. This kind of bifurcation is not observed in the structure of 2[DMAMNH]$^+$·[Sq]$^{2-}$ presented here, although the O atom of the water molecule is only 3.2 Å removed from each of the disordered H-atom positions. The increased flexibility of DMAMN with respect to DMAN allows the molecule to obtain a more linear hydrogen-bond geometry, although the observed N···N distance in DMAMN is somewhat longer than the average observed for DMAN structures. Due to the more linear geometry of the intramolecular hydrogen bond in DMAMN the methyl groups are oriented so that they effectively shield the N—H···N moiety. Instead of the bifurcated bond from the N—H proton, the water oxygen now receives a C—H···O hydrogen bond from C16. Geometrical details are given in Table 2. The water molecule in turn donates two hydrogen bonds to the squarate ion. Two water molecules and the squarate anion form an isolated O—H···O hydrogen-bonded cluster, unlike 2[DMANH]$^+$·[Sq]$^{2-}$, where an infinite three-dimensional network is formed.

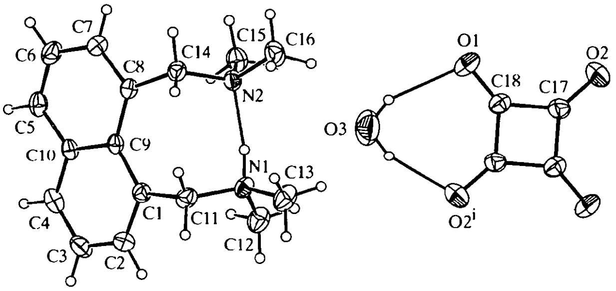


Fig. 1. Atomic displacement plot of 2[DMAMN]$^+$·[Sq]$^{2-}$·2H_2O drawn at the 30% probability level. The minor component of the disordered [N—H···N]$^+$ H atom has been excluded for clarity. [Symmetry code: (i) $1-x, -y, 1-z$.]

Experimental

Crystals have been grown from a solution in water of DMAMN and squaric acid, present in a molar ratio of 2:1.

Crystal data

$2C_{16}H_{23}N_2^+·C_4O_4^{2-}·2H_2O$
M_r = 634.80
Monoclinic
$P2_1/c$
a = 10.361 (6) Å
b = 8.144 (4) Å
c = 20.158 (3) Å
β = 101.299 (8)°
V = 1668.0 (13) Å^3
Z = 2
D_x = 1.264 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.45–19.40°
μ = 0.086 mm^{-1}
T = 295 K
Block
0.6 × 0.5 × 0.3 mm
Pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6690 measured reflections
3819 independent reflections
2610 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\rm max} = 27.46°$
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 26$
3 standard reflections frequency: 60 min intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.137$
$S = 1.043$
3819 reflections
221 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 0.0235P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.225$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.177$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (°)*

H3*A*—O3—H3*B*	107 (3)	N2—C14—C8	114.49 (12)
C9—C1—C11	126.53 (13)	O2—C17—C18$^{\rm i}$	135.51 (16)
C9—C8—C14	126.26 (12)	O2—C17—C18	133.88 (16)
C1—C9—C8	127.62 (12)	O1—C18—C17$^{\rm i}$	135.98 (16)
N1—C11—C1	114.01 (12)	O1—C18—C17	134.63 (16)
C9—C1—C11—N1	−83.48 (18)	C9—C8—C14—N2	67.50 (18)
C11—C1—C9—C8	6.1 (2)	C14—C8—C9—C1	4.1 (2)

Symmetry code: (i) $1 - x, -y, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N2	0.97 (3)	1.72 (3)	2.671 (2)	167 (3)
N2—H1*B*···N1	0.86 (10)	1.83 (10)	2.671 (2)	165 (8)
O3—H3*A*···O2$^{\rm i}$	0.87 (3)	1.95 (3)	2.753 (3)	153 (3)
O3—H3*B*···O1	0.86 (3)	2.11 (3)	2.877 (3)	149 (3)
*C*13—H13*A*···O2$^{\rm ii}$	0.96	2.25	3.188 (3)	166
C16—H16*A*···O2$^{\rm ii}$	0.96	2.42	3.341 (3)	161
C16—H16*C*···O3	0.96	2.54	3.384 (3)	146

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

The H atoms bonded to N and O atoms have been located on a difference Fourier map; their coordinates have been subsequently introduced as parameters in the refinement. A two-site disorder model was introduced for the $[\rm N—H\cdots N]^+$ moiety; the occupation factor for atom H1*A* refined to 0.75 (4). All other H atoms have been introduced at calculated positions riding on their carrier atoms. The isotropic atomic displacement factor of the H atoms is related to the equivalent isotropic displacement of the carrier atoms by a factor of 1.5 for ammonium, water and methyl-H atoms and 1.2 for all other H atoms.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

Diffraction data were kindly collected by A. M. M. Schreurs.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1043). Services for accessing these data are described at the back of the journal.

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3′-(2,3-Dimethyl-5-oxo-1-phenyl-3-pyrazolin-4-yl)-5-fluorospiro[3*H*-indole-3,2′-thiazolidine]-2(1*H*),4′-dione

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Abstract

The synthesis and structure of the title compound, $C_{21}H_{17}FN_4O_3S$, is described. It is a novel spiro-indole in which the sp^3 spiro-C atom is linked to S and N atoms. The pyrazole ring is aligned at 76.8 (1)° with respect to the attached phenyl ring and at 87.7 (1)° with respect

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