

ORGANIC COMPOUNDS

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1,8-Bis(dimethylamino)naphthalene bis[6-fluoro-2-(trifluoromethyl)-4-quinolinol] acetonitrile solvate

PETER VERGEER,^a HUUB KOOIJMAN,^a ANTOINE M. M. SCHREURS,^a JAN KROON^a AND EUGENIUSZ GRECH^b

^a*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands, and* ^b*Institute of Fundamental Chemistry, University of Szczecin, al. Piastów 42, 71-065 Szczecin, Poland. E-mail: h.kooijman@chem.uu.nl*

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Abstract

In the crystal structure of the title compound, (1-dimethylamino-8-naphthyl)dimethylammonium 6-fluoro-2-(trifluoromethyl)-4-quinolinolate 6-fluoro-2-(trifluoromethyl)-4-quinolinol acetonitrile solvate, $C_{14}H_{19}N_2^+ \cdot C_{10}H_4F_4NO^- \cdot C_{10}H_5F_4NO \cdot C_2H_3N$, 1,8-bis(dimethylamino)naphthalene (DMAN) acts as a proton sponge by accepting a proton from the quinolinol moiety. In the $[DMANH^+]$ cation, a strong disordered intramolecular hydrogen bond is formed. The quinolinolate anion forms a dimer with a quinolinol molecule by sharing an H atom in a disordered hydrogen bond.

Comment

The term 'proton sponge' is a common name for a class of compounds, mostly diamines, which combines an unusual high basicity with a low nucleophilic character. One of the major reasons for the high level of basicity of these proton sponges in general and 1,8-bis(dimethylamino)naphthalene (DMAN) in particular, is the high degree of stability of the intramolecular $[N-H \cdots N]^+$ hydrogen bond of the protonated form of DMAN. The location and the possible disorder of this hydrogen bond in $DMANH^+$ has been the focus of a number of studies (Llamas-Saiz *et al.*, 1994, and references therein).

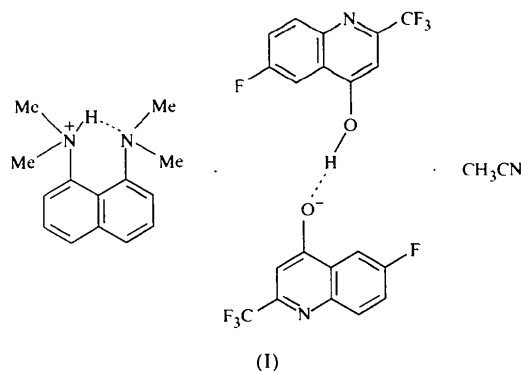
The average value for intramolecular N—H bond lengths of hydrogen bonds in 63 organic crystals has been found to be 1.02 (12) Å (Llamas-Saiz *et al.*, 1994). Structural studies at low temperature on this protonated proton sponge, performed for various salts (Kanters, Schouten, Duisenberg *et al.*, 1991; Kanters, Schouten, Kroon & Grech, 1991; Kanters, Horst *et al.*, 1992; Mallinson *et al.*, 1997; Miller *et al.*, 1988) report fairly large values of the N—H bond length in the

$[N-H \cdots N]^+$ hydrogen bond ranging from 1.07 (3) to 1.16 (5) Å.

Conversely, in $[DMANH]_2^+ \cdot [squate]^{2-}$ (Kanters, Schouten *et al.*, 1992) fairly short N—H distances of 0.94 (6) and 0.97 (6) Å for two independent $DMANH^+$ ions are found. A neutron study at 100 K gives an N—H distance of 1.106 (5) Å (Wozniak *et al.*, 1996).

It is believed that the unusual variety in N—H distances (symmetry-constrained H atoms excluded) could be due to the flatness of the potential energy surface between the two N atoms (Jeffrey, 1997).

The subject of the present study (I) is the 1:2 complex of DMAN with 6-fluoro-2-(trifluoromethyl)-4-quinolinol [TFMQ-OH]. In this complex DMAN accepts a hydrogen from a quinolinol moiety. The resulting quinolate anion forms a dimer with a quinolinol molecule by sharing a hydrogen in a disordered hydrogen bond. The asymmetric unit contains one half of a $DMANH^+$ cation and one quinolinolate moiety as a counterion. The central C—C bond of the $DMANH^+$ structure is located on a twofold rotation axis (Fig. 1). The structure also contains a disordered acetonitrile molecule, located on the twofold rotation axis (see *Experimental*).



The most satisfactory models for the $[N-H \cdots N]^+$ and the $[O-H \cdots O]^-$ hydrogen bonds involve a hydrogen disordered over a twofold axis and an inversion centre, respectively (see *Experimental*). The intermediate value found for the N—H distance (Table 2), in combination with the N—H distances listed above, fits well in a flat potential model.

The $[O-H \cdots O]^-$ hydrogen bond is nearly linear (Table 2). This has also been observed in $DMANH^+ \cdot TFMQ-O^- \cdot TFMQ-OH$ [$TFMQ-O^-$ is 2,8-bis(trifluoromethyl)quinoline-4-olate] [$O-H$ 0.819 (13), $O \cdots O$ 2.4528 (3) Å, $O-H \cdots O$ 167.5 (12)°] (Klewinghaus *et al.*, 1999). NMR measurements of $TFMQ-OH$ with DMAN in 2:1 and 1:1 molar ratios also show dimers of the 4-hydroxyquinolinoline form (Stefaniak *et al.*, 1999).

The naphthalene ring of $DMANH^+$ is planar ($\sigma_{plane} = 0.015$ Å) and the symmetry-related $N1$ and $N1^i$

atoms lie 0.033(2) Å from this plane. This agrees well with [DMANH]⁺·[HSQ]⁻ (Kanters, Schouten, Kroon & Grech, 1991), but is in contrast with [DMANH]⁺·[PCP]⁻·[PCP]₂ [0.19(1) and 0.25(1) Å] (Kanters, Horst *et al.*, 1992).

The quinoline ring is planar as well ($\sigma_{\text{plane}} = 0.023$ Å). This has also been observed in similar compounds (Fan & Chen, 1987; Karle & Karle, 1991; Klewinghaus *et al.*, 1999). The trifluoromethyl group at the C17 position (Fig. 1) appeared to be ordered, in contrast with the situation in the three crystal structures referred to above.

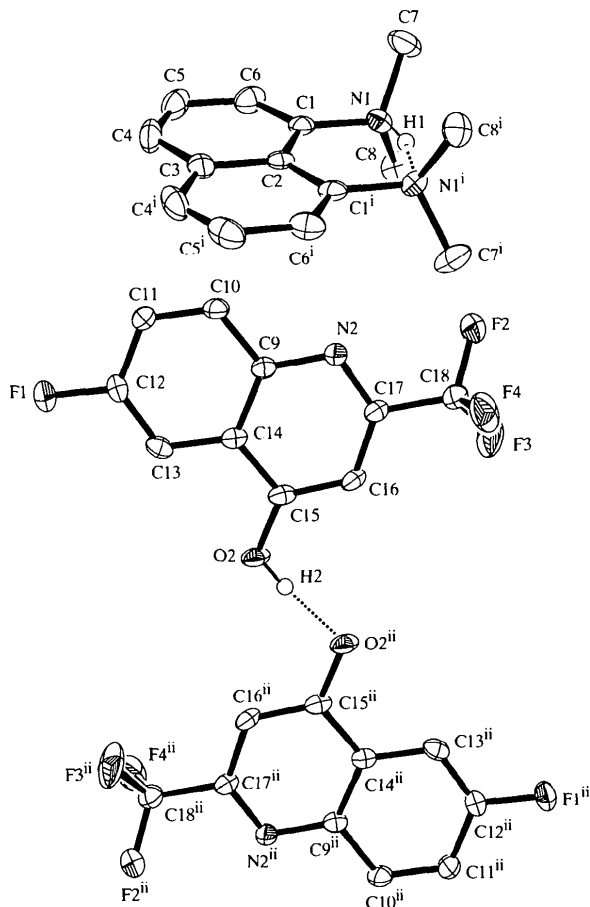


Fig. 1. A perspective view of the title compound with the atomic numbering scheme; displacement ellipsoids are at the 50% probability level. For clarity, only the disordered H1 and H2 atoms are shown. [Symmetry codes: (i) $1 - x, y, -z + \frac{1}{2}$; (ii) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$.]

The crystal structure is further stabilized by three intermolecular C—H...A contacts ($A = \text{F}$ or O) (see Table 2).

Experimental

A single crystal of the 1:2 complex of DMAN with FTFMQ-OH was obtained from 1:2 molar ratio solutions in acetonitrile by slow evaporation of the solvent.

Crystal data

$\text{C}_{14}\text{H}_{19}\text{N}_2 \cdot \text{C}_{10}\text{H}_4\text{F}_4\text{NO}^-$
 $\text{C}_{10}\text{H}_5\text{F}_4\text{NO} \cdot \text{C}_2\text{H}_3\text{N}$
 $M_r = 717.66$
 Monoclinic
 $C2/c$
 $a = 9.8833(10)$ Å
 $b = 17.9581(10)$ Å
 $c = 19.2752(10)$ Å
 $\beta = 90.578(10)^\circ$
 $V = 3420.9(4)$ Å³
 $Z = 4$
 $D_x = 1.393$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71730$ Å
 Cell parameters from 47 reflections
 $\theta = 4.808\text{--}24.523^\circ$
 $\mu = 0.129$ mm⁻¹
 $T = 120(2)$ K
 Prism
 $0.38 \times 0.15 \times 0.08$ mm
 Colourless

Data collection

Nonius KappaCCD diffractometer
 Area detector θ and ω scans
 Absorption correction: none
 11 065 measured reflections
 3939 independent reflections

2630 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$
 $\theta_{\text{max}} = 27.80^\circ$
 $h = -11 \rightarrow 12$
 $k = -23 \rightarrow 23$
 $l = -24 \rightarrow 21$

Refinement

Refinement on F^2
 $R(F) = 0.058$
 $wR(F^2) = 0.120$
 $S = 1.119$
 3014 reflections
 263 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 4.0310P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O2—C15	1.312(3)	N2—C17	1.319(3)
N1—C8	1.488(3)	N2—C9	1.372(3)
N1—C7	1.482(4)	C17—C18	1.505(4)
N1—C1	1.459(3)		
C15—O2—H2	113(5)	N1—C1—C6	121.2(2)
C1—N1—C8	111.81(19)	N1—C1—C2	118.2(2)
C7—N1—C8	111.6(2)	O2—C15—C16	124.5(2)
C1—N1—C7	112.6(2)	O2—C15—C14	118.7(2)
N1—C1—C6—C5	-179.6(2)	N1—C1—C2—C3	178.8(1)

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...N1'	0.99(7)	1.62(7)	2.555(3)	156(5)
O2—H2...O2''	0.83(7)	1.62(7)	2.447(2)	174(8)
C4—H4...F3'''	0.95(3)	2.53(3)	3.429(3)	158(2)
C8—H8A...O2''	0.99(3)	2.54(3)	3.467(3)	156(2)
C11—H11...F4'''	0.94(3)	2.54(3)	3.395(3)	151(2)

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

The contribution of the disordered solvent to the calculated structure factors was taken into account following the *BYPASS* algorithm (van der Sluis & Spek, 1990), implemented as the *SQUEEZE* option in *PLATON* (Spek, 1990). A total of 92 electrons per unit cell were found in four symmetrically related voids of 109 Å³ each. This amounts to one molecule of acetonitrile (used as a solvent in crystallization). The *SQUEEZE*

routine takes the disordered molecules into account as diffuse electron density and adds this contribution to the F_o^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 excluded) 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: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). 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

BAREND BOUMA,^a HUUB KOOIJMAN,^a JAN KROON,^a EUGENIUSZ GRECH^b AND BOGUMIŁ BRZEZINSKI^c

^a*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.* ^b*Institute of Fundamental Chemistry, Technical University of Szczecin, al. Piastów 42, 71-065 Szczecin, Poland, and* ^c*Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań, Poland. E-mail: h.kooijman@chem.uu.nl*

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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, 2C₁₆H₂₃N₂⁺·C₄O₄²⁻·2H₂O, 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-