

(8-Dimethylamino-1-naphthyl)- dimethylammonium 3-carboxy-1,4,5,- 6,7,7-hexachlorobicyclo[2.2.1]hept- 5-ene-2-carboxylate hydrate

Daphne E. Keller,^a Huub Kooijman,^{a*} Antoine M. M. Scheurs,^a Jan Kroon^a and Eugeniusz Grech^b

^aDepartment of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Universiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands, and

^bInstitute of Fundamental Chemistry, University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland

Correspondence e-mail: h.kooijman@chem.uu.nl

Received 7 July 1999

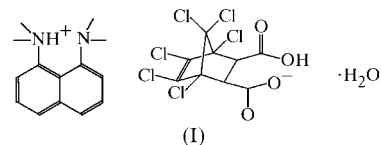
Accepted 17 January 2000

The structure of the title compound, $C_{14}H_{19}N_2^{+} \cdot C_9H_3Cl_6O_4^{-} \cdot H_2O$, consists of singly ionized 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anions and protonated 1,8-bis(dimethylamino)naphthalene cations. In the (8-dimethylamino-1-naphthyl)dimethylammonium cation, a strong disordered intramolecular hydrogen bond is formed with $N \cdots N = 2.589(3) \text{ \AA}$. The geometry and occupancy obtained in the final restrained refinement suggest that the disordered hydrogen bond may be asymmetric. Water molecules link the anion dimers into infinite chains *via* hydrogen bonding.

Comment

The term 'proton sponges' describes a class of compounds which combine an unusually high basicity with a low nucleophilic character. Most of these compounds are diamines (Llamas-Saiz *et al.*, 1994). The $[N-H \cdots N]^+$ hydrogen bonds play an important role in these proton sponges. In a complex of 1,8-bis(dimethylamino)naphthalene (DMAN) with a (slightly) acidic compound, DMAN will absorb a proton from the acidic compound and an intramolecular hydrogen bond will be formed. These hydrogen bonds can be symmetric or asymmetric. When the bridge is asymmetric this will be reflected in the other bond distances of the $DMAN \cdot H^+$ cation (Kanters, Schouten, Duisenberg *et al.*, 1991). It is remarkable that the $N-H$ distance in proton sponges is found to be well out of the range usually observed for $N-H \cdots N$ hydrogen bonds in other molecules (Kanters, Schouten, Kroon & Grech, 1991). For protonated proton sponges the $N \cdots N$ distances are in the range 2.553–2.654 Å (Llamas-Saiz *et al.*, 1994; Kanters, Schouten, Duisenberg *et al.*, 1991). The H atom seems to be located on a rather flat potential energy surface, the nature of which is influenced by the crystal field environment (Jeffrey, 1997). The subject of the present study, (I), is the mono-

hydrated complex of DMAN with 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (1:1), in which DMAN accepts one proton from the carboxylic acid molecule.



The asymmetric unit of (I) (Fig. 1, Table 1) consists of one $DMAN \cdot H^+$ cation, one singly deprotonated (3-carboxy-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2-carboxylate) anion and one water molecule.

The DMAN ring system in (I) is planar ($\sigma_{\text{plane}} 0.007 \text{ \AA}$) and N1 and N2 lie within 0.020 and 0.022 Å, respectively, of the least squares mean plane of the ring system. The disordered H atoms (H1N and H2N) are also in the plane of the ring system, being displaced by only 0.040 and -0.038 \AA , respectively. The DMAN residues are ordered in π -stacked columns along the *a* axis and the perpendicular distances between two DMAN molecules alternate between 4.261 and 4.711 Å.

Among the three different residues several types of hydrogen bonds were observed. In the DMAN molecule there is a strong, somewhat bent, intramolecular $[N-H \cdots N]^+$ hydrogen bond with an $N \cdots N$ distance of 2.589 (3) Å. The H atom is disordered over two positions, whose occupancies refined to 0.60 (5) for H1N and 0.40 (5) for H2N. The resulting difference in occupancy of 0.20 (10) suggests a possible asymmetric hydrogen bond, although the evidence is not conclusive.

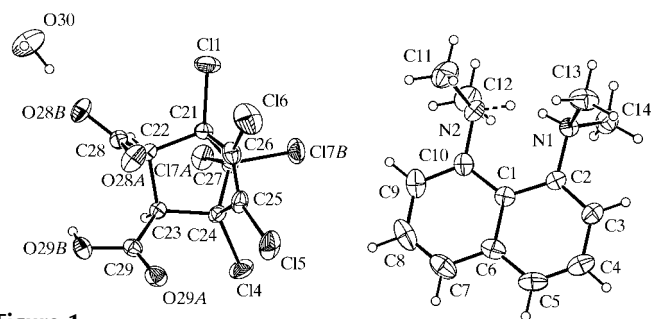


Figure 1

A molecular view of (I) (PLATON; Spek, 1998) showing the cation, anion and water molecule, with the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms are drawn as spheres of arbitrary radii.

The deprotonated acid moiety accepts a hydrogen bond from the still-protonated acid moiety of a symmetry-related molecule, thereby forming a dimer [unitary graph set $R_2^2(14)$] over the inversion centre at $(0,0,\frac{1}{2})$ (Fig. 2). Protonated and deprotonated acid moieties can easily be distinguished on the basis of their $C-O$ bond lengths (Table 1). Intermolecular $O \cdots O$ distances clearly indicate that the water molecules link these rings into infinite chains along [100] by donating hydrogen bonds to both carboxylate O atoms. The water links also form hydrogen-bonded ring systems with the anions [unitary graph set DD , binary graph set $R_4^4(12)$]. There are also weak intermolecular $C-H \cdots A$ interactions present (Table 2).

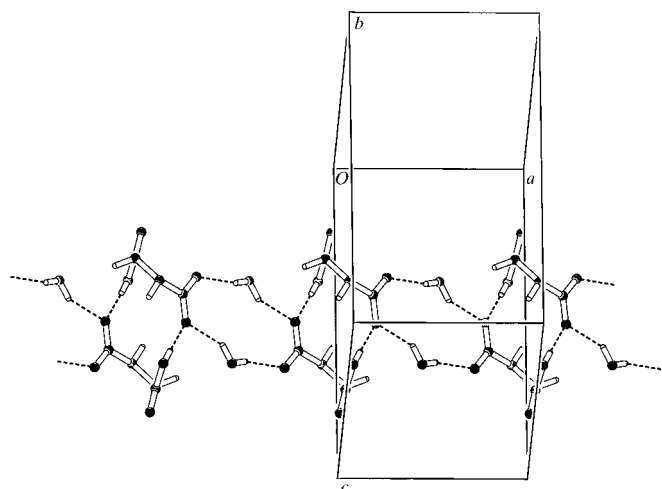


Figure 2
A plot of an infinite chain of hydrogen bonds in (I). The DMAN moieties and the chlorine-substituted rings of the heptene moieties have been omitted for clarity.

Experimental

Crystals of (I) were obtained from a 1:1 solution of DMAN and 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (Aldrich) in a mixture of acetonitrile and water.

Crystal data

$C_{14}H_{19}N_2^+ \cdot C_9H_3Cl_6O_4^- \cdot H_2O$	$Z = 2$
$M_r = 621.17$	$D_x = 1.508 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.7122 (5) \text{ \AA}$	Cell parameters from 25 reflections
$b = 12.8097 (11) \text{ \AA}$	$\theta = 12.65\text{--}19.31^\circ$
$c = 13.7023 (12) \text{ \AA}$	$\mu = 0.665 \text{ mm}^{-1}$
$\alpha = 113.200 (7)^\circ$	$T = 295 (2) \text{ K}$
$\beta = 91.680 (6)^\circ$	Block, colourless
$\gamma = 101.350 (6)^\circ$	$0.6 \times 0.6 \times 0.3 \text{ mm}$
$V = 1368.32 (19) \text{ \AA}^3$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.036$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.47^\circ$
Absorption correction: ψ scan (PLATON; Spek, 1998)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.745$, $T_{\text{max}} = 0.819$	$k = -16 \rightarrow 16$
13 079 measured reflections	$l = -17 \rightarrow 17$
6272 independent reflections	3 standard reflections
4286 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: none

Table 1
Selected geometric parameters (\AA , $^\circ$).

O28A—C28	1.223 (3)	N1—C13	1.482 (3)
O28B—C28	1.253 (2)	N1—C14	1.475 (4)
O29A—C29	1.200 (3)	N2—C10	1.459 (3)
O29B—C29	1.322 (3)	N2—C12	1.479 (4)
N1—C2	1.456 (3)	N2—C11	1.480 (4)
C2—N1—C13	112.0 (2)	N2—C10—C9	120.9 (3)
C2—N1—C14	113.28 (19)	O28A—C28—O28B	125.1 (2)
C14—N1—C13	112.0 (2)	O28A—C28—C22	118.2 (2)
C10—N2—C11	113.2 (2)	O28B—C28—C22	116.73 (18)
C10—N2—C12	111.9 (2)	O29A—C29—O29B	121.5 (2)
C11—N2—C12	111.4 (2)	O29A—C29—C23	123.6 (2)
N1—C2—C1	118.75 (19)	O29B—C29—C23	114.81 (18)
N1—C2—C3	120.2 (2)	H30A—O30—H30B	102 (4)
N2—C10—C1	118.7 (2)		

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.5928P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.998$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
6272 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
335 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 2
Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1N \cdots N2	0.82 (4)	1.82 (3)	2.589 (3)	154 (4)
N2—H2N \cdots N1	0.97 (7)	1.70 (5)	2.589 (3)	152 (4)
O29B—H29B \cdots O28B ⁱ	0.82	1.70	2.520 (2)	173
O30—H30B \cdots O28B ⁱⁱ	0.89 (5)	2.02 (5)	2.783 (3)	143 (4)
O30—H30A \cdots O28A	0.85 (5)	1.95 (5)	2.749 (3)	156 (4)
C9—H9 \cdots C17B ⁱⁱⁱ	0.93	2.78	3.599 (4)	148
C12—H12C \cdots O29B ⁱ	0.96	2.58	3.297 (4)	132
C13—H13A \cdots O30 ⁱ	0.96	2.54	3.220 (3)	128
C14—H14B \cdots O29A ⁱ	0.96	2.46	3.348 (4)	155
C23—H23 \cdots C17A	0.98	2.64	2.994 (2)	102
C23—H23 \cdots O30 ^{iv}	0.98	2.55	3.480 (4)	157

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

The carboxylic H atom was located in a difference Fourier synthesis and subsequently included as part of a rigid rotating group. The water H atoms were placed in hydrogen-bond-forming positions and their coordinates were refined freely. The amino H atoms were introduced at calculated positions and during refinement idealized tetrahedral geometry at the N carrier atom was enforced, with the N—H bond distance and the H atom occupancies allowed to refine. All other H atoms were introduced at calculated positions and refined riding on their carrier atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The authors wish to thank Dr M. Lutz for his helpful comments on the interpretation of the crystallographic data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1360). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Jeffrey, G. A. (1997). *An Introduction to Hydrogen Bonding*, pp. 11–26 and 51–54. New York: Oxford University Press, Inc.
- Kanters, J. A., Schouten, A., Duisenberg, A. J. M., Glowiak, T., Malarski, Z., Sobczyk, L. & Grech, E. (1991). *Acta Cryst.* **C47**, 2148–2151.
- Kanters, J. A., Schouten, A., Kroon, J. & Grech, E. (1991). *Acta Cryst.* **C47**, 807–810.
- Llamas-Saiz, L. A., Foces-Foces, C. & Elguero, J. (1994). *J. Mol. Struct.* **328**, 297–323.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
- Spek, A. L. (1998). *PLATON*. University of Utrecht, The Netherlands.