Hydrogen bonding and C—H···O interactions in bis(8-dimethylamino-1-dimethylammonionaphthalene) [(DMANH+)2] 4,8-dicarboxynaphthalene-1,5-dicarboxylate dihydrate

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Abstract

The title substance, $2C_{14}H_{19}N_2^+ \cdot C_{14}H_6O_8^{2-} \cdot 2H_2O$, crystallized in the centrosymmetric space group $P\bar{1}$ with one monopositive dimethylamine-dimethylammonio cation, half of a dinegative acid anion and one water molecule in the asymmetric unit, with the anion located on a center of symmetry. There are four intermolecular hydrogen bonds, of which three have $O_{donor}\cdots O_{acceptor}$ distances of 2.577 (1), 2.946 (2) and 2.764 (2) Å, while the fourth has an $N_{donor}\cdots O_{acceptor}$ distance of 3.154 (2) Å. There is a single intramolecular hydrogen bond, in which the $N_{donor}\cdots N_{acceptor}$ distance is 2.620 (2) Å. In each case, the O, or N, and H atoms are ordered. The N_{donor}—H distance in the intramolecular hydrogen bond, 1.06 (1) Å, is among the shortest seen in this cation at room temperature. Moreover, the antiplanar orientation of the H atom in the hydrogen bond between acid anions is noteworthy. There are, in addition, 12 significant intermolecular C—H···O interactions. In these, the C···O distances range from 3.229 (2)–3.671 (2) Å, while the C—H···O angles range from 121–165° for the fixed H atoms involved. A three-dimensional network of hydrogen-bonding interactions is generated.

Comment

This study of the title compound, (I), follows a study of tetrapotassium, tetrarubidium and tetrace-

(I)
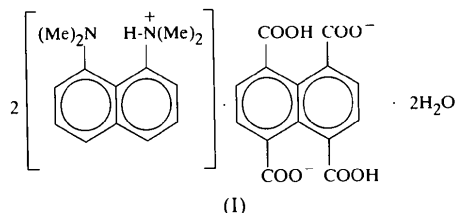
sium naphthalene-1,4,5,8-tetracarboxylate hexahydrates (Fitzgerald *et al.*, 1993), and a study of the compound salt dipotassium naphthalene-1,8-dicarboxylate–

potassium bicarbonate (Fitzgerald & Gerkin, 1999) in a series on hydrogen bonding in organic solids. (I) crystallized in the centrosymmetric space group $P\bar{1}$ with one dimethylamino-dimethylammonio cation (hereafter DMANH+), one half of an acid anion (the anion symmetry is $\bar{1}$) and one water molecule in the asymmetric unit. The refined asymmetric unit (augmented by the symmetry-related half of the tetraacid anion), together with our numbering scheme, is shown in Fig. 1. Three intermolecular O—H···O hydrogen bonds link a central acid anion to two other acid anions and to four water molecules as shown in Fig. 2, while a single weaker N—H···O hydrogen bond links a DMANH+ cation to a water molecule. An intramolecular hydrogen bond, N—H···N, is formed within the DMANH+ cation. In each case, the O, or N, and H atoms are ordered. Geometric parameters of these bonds are given in Table 2. Results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) for basic first- and second-level sets involving these five bonds, labeled *a–e* in the order of their appearance in Table 2, are given in Table 3. Consistent with participation of a water molecule in the hydrogen bonding, finite graphs are a prominent feature. The single chain which appears consists of linked anions and propagates along **a**. A third-level chain, *ade*, which involves anions and water molecules, propagates along **b**. Thus, together they generate a two-dimensional network. We note that this network does not involve the weaker N—H···O bond.

As expected on the basis of the excess of potential hydrogen-bond acceptors (six: O1–O5, N2) over potential donors (four: H3, H10–H12), significant C—H···O interactions occur. 12 such interactions have H···O distances which are less, or only slightly greater, than the corresponding Bondi (1964) van der Waals radius sum. Their geometric parameters are given in Table 2. Eight of these interactions link a DMANH+ cation to three acid anions, three link a DMANH+ cation to one water molecule (the same one involved in the N—H···O hydrogen bond), and one links an acid anion to a water molecule. These interactions, together with the hydrogen bonds, form chains which propagate, *e.g.* along [111] and [101], and with the chains delineated above lead to a three-dimensional network of interactions.

Numerous structures incorporating DMANH+ have been determined with a major goal of characterizing the intramolecular hydrogen bond, N1—H10···N2 in the present nomenclature. Restricting consideration to results of room temperature X-ray studies for purposes of comparison with results for (I), we find that in DMANH+ N—H distances range from ~1.05–1.31 Å, H···N distances range from ~1.30–1.63 Å, N···N distances from ~2.55–2.65 Å and N—H···N angles from ~134–170° (Bartoszak *et al.*, 1993, 1994; Brown *et al.*, 1987; Brzezinski *et al.*, 1994; Glowiak *et al.*, 1987, 1992, 1993; Kanters *et al.*, 1991; López *et al.*, 1996; Malarski *et al.*, 1990; Pyzalska *et al.*, 1983;
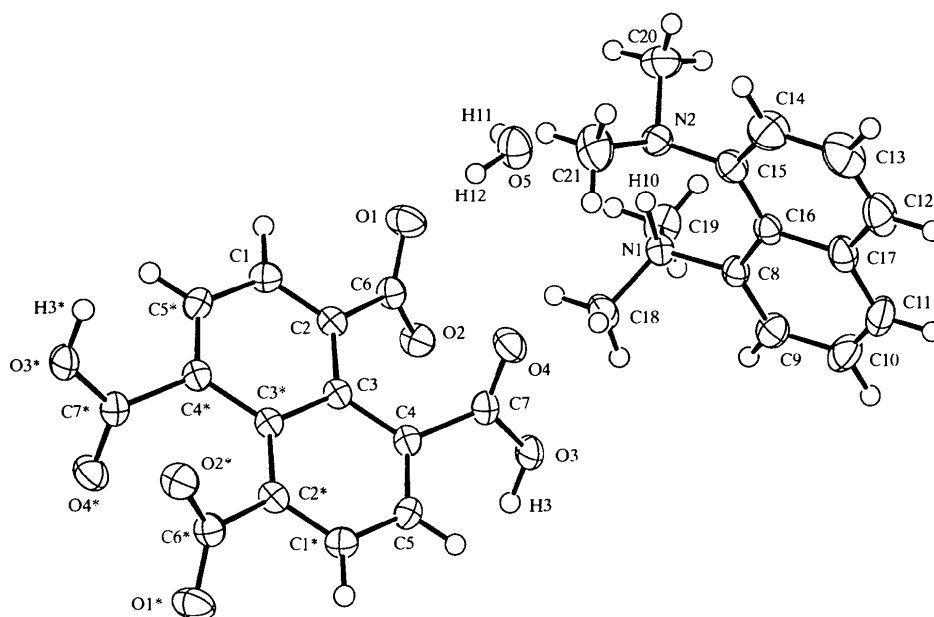
Fig. 1. ORTEPII (Johnson, 1976) drawing of the asymmetric unit of (I) plus the symmetry-related half of the acid anion, showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms.

Truter & Vickery, 1972; Wozniak et al., 1990, 1994, 1996). [A comprehensive tabulation of structural studies of DMANH$^+$ through 1993 is given by Llamas-Saiz et al. (1994).] The values for (I) are, respectively, 1.06 (1), 1.62 (1) and 2.620 (2) Å, and 155 (1)°. These values are notably similar to those reported by Malarski et al. (1990) [1.05 (5), 1.63 (5) and 2.610 (5) Å, and 152 (5)°, respectively] and Glowiak et al. (1993) [1.06 (2), 1.62 (2) and 2.621 (3) Å, and 155 (2)°, respectively], and are quite similar to those of Wozniak et al. (1994) [1.05 (4), 1.57 (4) and 2.573 Å, and 158 (2)°, respectively]. The present case and the three cited for comparison are, by a substantial margin, those exhibiting the greatest asymmetry in the distances between the H atom and the N atoms in the intramolecular DMANH$^+$ hydrogen bond at room temperature.

A second noteworthy feature of the hydrogen bonding in (I) is the orientation of H atom H3, involved in the intermolecular hydrogen bond between acid anions, as shown in Fig. 2. Whereas the magnitude of a C(aromatic ring)—C(carboxyl)—O(carboxyl)—H(carboxyl) torsion angle in an intermolecular hydrogen-bonding carboxyl group is commonly near 180°, here it is only 6 (1)°, thus giving the so-called antiplanar conformation (see, e.g., Leiserowitz, 1976). While analogous torsion angles that are comparably small have been commonly observed for intramolecular hydrogen bonds in aromatic carboxylic acids containing at least one COOH group and one COO$^-$ group (e.g. Barrett et al., 1995; Csoregh et al., 1989; Czugler et al., 1986; Jessen & Küppers, 1991; Jessen et al., 1992; Kozma et al., 1994; Mitchell et al., 1996; Mrvoš-Sermek et al., 1996), oc-
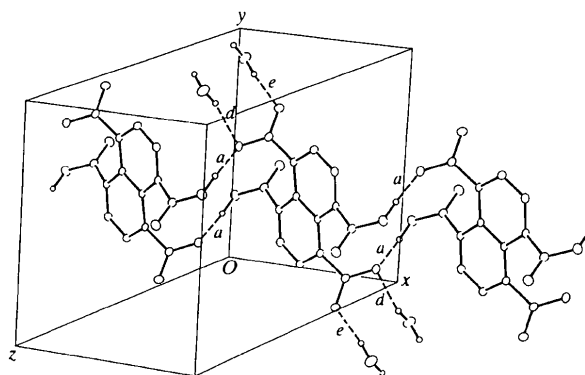

Fig. 2. ORTEPII (Johnson, 1976) drawing of a central acid anion and the neighbors directly hydrogen-bonded to it. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms.

currences of intermolecular hydrogen bonds in the antiplanar conformation, as here, are quite uncommon. Previous examples include antiplanar (and synplanar) hydrogen-bonded catemers in (4-chlorophenyl)propiolic acid (Desiraju et al., 1990) and in (4-bromophenyl)-propiolic acid (Goud & Desiraju, 1993).

The naphthalene core of the acid anion is rather rumpled, with C2 lying 0.046 (1) Å from the best-fit core plane and C4 lying 0.044 (1) Å from it on the opposite side. The dihedral angle between the best-fit core plane and the carboxylate group plane is 48.6 (2)° for the C6/O1/O2 group and 55.4 (1)° for the C7/O3/O4 group. The carboxylate-group C atoms lie −0.286 (1) and 0.408 (1) Å from the core plane. These values are

in good accord with the corresponding values found in tetrapotassium naphthalene-1,4,5,8-tetracarboxylate hexahydrate (Fitzgerald *et al.*, 1993): dihedral angles 52.7 (1) and 52.4 (1)°, and distances from the core plane −0.392 (2) and 0.409 (2) Å.

The naphthalene core of the DMANH$^+$ cation is less rumpled, with its atoms lying at most 0.015 (1) and −0.020 (2) Å from the best-fit core plane. The dihedral angle between the core plane and the dimethylamino group plane is 88.7 (1)° for N1/C18/C19, and 89.1 (1)° for N2/C20/C21. The N atoms lie only −0.002 (1) and 0.043 (1) Å from the cation core plane. The pattern of core angles expected for the cation, regarded as a 1,8-disubstituted naphthalene (see, *e.g.*, Fitzgerald *et al.*, 1991), is partially broken by the formation of the intramolecular hydrogen bond. Thus, while the C8—C16—C15 angle is substantially larger than 120° [125.5 (1)°] as is typical for such disubstitution, the C16—C8—N1 and C16—C15—N2 angles [119.2 (1) and 118.4 (1)°] are not, which is atypical. For bond distance comparisons with the DMANH$^+$ cation of (I), the results of Glowiak *et al.* (1993) are appropriate. For 17 bond distances between non-H atoms, the average difference between corresponding values from these two studies is 0.005 Å, only slightly larger than the typical 0.004 Å s.u. of the previous values.

A packing diagram is presented as Fig. 3 to clarify further the spatial arrangements within and among the cations, anions and water molecules.
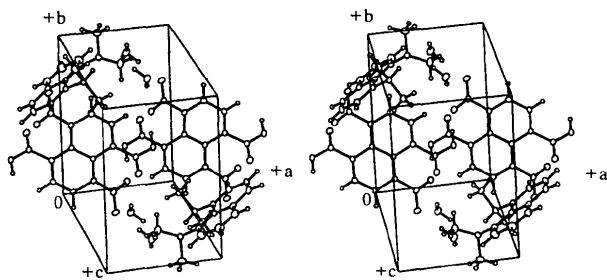

Fig. 3. *ORTEP*II (Johnson, 1976) packing stereodiagram of (I). Displacement ellipsoids are drawn for 20% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms.

Selected bond distances and angles are given in Table 1. All distances and angles fall within normal ranges. The closest intermolecular approaches, excluding pairs of atoms in groups involved in the hydrogen bonds or in the C—H· · ·O interactions discussed above, occur between H5 and H5(−1 − x, 1 − y, −z) and are 0.12 Å less than the corresponding Bondi (1964) van der Waals radius sum.

Experimental

Naphthalene-1,4,5,8-tetracarboxylic acid and 1,8-bis(dimethyl-amino)naphthalene from Aldrich Chemical Company Inc. were ground together, in an approximately 1:3 molar ratio, using a

mortar and pestle. The resulting fine mixture was dissolved in ethanol/water, filtered and evaporated slowly to dryness. A small quantity of water was then added and the container was sealed. One week later the liquid was decanted. Clear, crystalline chunks were present in the solid residue. One of these was cut to provide the experimental sample.

Crystal data

$2C_{14}H_{19}N_2^+ \cdot C_{14}H_6O_8^{2-} \cdot 2H_2O$	Mo $K\alpha$ radiation
$M_r = 768.86$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 7.726 (2)$ Å	$\theta = 14.3–14.9°$
$b = 9.818 (2)$ Å	$\mu = 0.097$ mm^{-1}
$c = 13.169 (2)$ Å	$T = 296$ K
$\alpha = 99.00 (1)°$	Chunk
$\beta = 106.57 (2)°$	$0.32 \times 0.32 \times 0.27$ mm
$\gamma = 91.54 (2)°$	Colorless
$V = 942.9 (3)$ Å^3	
$Z = 1$	
$D_x = 1.354$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5S diffractom-eter	$\theta_{max} = 27.5°$
ω–2θ scans	$h = -10 \rightarrow 9$
Absorption correction: none	$k = 0 \rightarrow 12$
4566 measured reflections	$l = -17 \rightarrow 16$
4316 independent reflections	6 standard reflections
3211 reflections with	every 150 reflections
$I > 2\sigma I$	intensity variation: ±1.4%
$R_{int} = 0.011$	(average maximum relative intensity)

Refinement

Refinement on F^2	$w = 1/[\sigma_{cs}^2 + (0.002I)^2]$
$R(F) = 0.038$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.067$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.86$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
4316 reflections	Extinction correction: none
277 parameters	Scattering factors from
H atoms treated by a	Stewart *et al.* (1965) for
mixture of independent	H and Creagh & McAuley
and constrained refinement	(1992) for C, O, N

Table 1. *Selected geometric parameters (Å, °)*

O1—C6	1.245 (2)	O3—C7	1.324 (2)
O2—C6	1.262 (2)	O4—C7	1.212 (2)
C7—O3—H3	120 (1)	O2—C6—C2	118.4 (1)
H11—O5—H12	107 (1)	O3—C7—O4	120.0 (1)
C3—C2—C6	125.1 (1)	O3—C7—C4	118.4 (1)
C2—C3—C4	122.5 (1)	O4—C7—C4	121.2 (1)
C3—C4—C7	122.9 (1)	N1—C8—C16	119.2 (1)
C5—C4—C7	116.0 (1)	N2—C15—C16	118.4 (1)
O1—C6—O2	124.6 (1)	C8—C16—C15	125.5 (1)
O1—C6—C2	116.8 (1)	C11—C17—C12	120.8 (1)

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

D—H· · ·A	D—H	H· · ·A	D· · ·A	D—H· · ·A
O3—H3· · ·O2^i	0.99 (2)	1.59 (2)	2.577 (1)	173 (2)
N1—H10· · ·N2	1.06 (1)	1.62 (1)	2.620 (2)	155 (1)
N1—H10· · ·O5	1.06 (1)	2.62 (1)	3.154 (2)	111 (1)

O5—H11···O2^{ii}	0.86 (2)	2.13 (2)	2.946 (2)	160 (2)
O5—H12···O1	0.92 (2)	1.86 (2)	2.764 (2)	168 (2)
C12—H7···O3^{iii}	0.98	2.42	3.331 (2)	154
C19—H19A···O1^{iv}	0.98	2.45	3.362 (2)	155
C9—H4···O4^{iv}	0.98	2.49	3.259 (2)	135
C5—H2···O5^{v}	0.96 (1)	2.54 (1)	3.390 (2)	147 (1)
C18—H18B···O4	0.98	2.55	3.418 (2)	148
C21—H21B···O5	0.98	2.56	3.229 (2)	125
C20—H20C···O5	0.98	2.59	3.265 (2)	127
C19—H19C···O5	0.98	2.61	3.259 (2)	124
C18—H18A···O2	0.98	2.65	3.342 (2)	128
C18—H18B···O3	0.98	2.66	3.273 (2)	121
C11—H6···O4^{iii}	0.98	2.71	3.671 (2)	165
C21—H21C···O4	0.98	2.78	3.665 (2)	150

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

Table 3. *Basic first- and second-level graph-set descriptors involving hydrogen bonds labeled a–e in the order of their appearance in Table 2*

	a	b	c	d	e
a	$C(9)[R_2^1(16)]$	–	–	$D_2^1(5)$	$D_2^2(7)$
b		$S(6)$	$D_1^2(4)$	–	–
c			$D(3)$	$D_2^2(5)$	$D_2^2(5)$
d				$D(3)$	$R_4^4(12)$
e					$D(3)$

The amine ring and methyl H atoms were made canonical with C—H = 0.98 Å and $U_{iso} = 1.2 \times U_{eq}$ of the attached C atom. Refined O—H and N—H distances are given in Table 2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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