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Two bis(ammonium) 1,5-naphthalenedisulfonate salts

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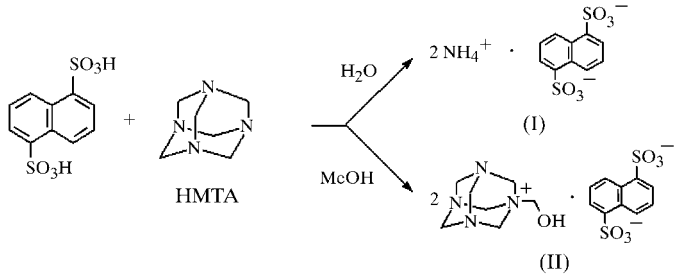
The title compounds, bis(ammonium) naphthalene-1,5-disulfonate, $2NH_4^+\cdot C_{10}H_6O_6S_2^{2-}$, and bis[1-(hydroxymethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane] 1,5-naphthalenedisulfonate, $2C_7H_{15}N_4O^+\cdot C_{10}H_6O_6S_2^{2-}$, were prepared from the acid-promoted reaction of hexamethylenetetramine. In both structures, the disulfonate anion is positioned on an inversion center, with each sulfonate group contributing to the supramolecular assemblies *via* hydrogen bonds. The ammonium cations are linked to sulfonate groups by four distinct $N^+—H\cdots{}^-O—S$ contacts [$N\cdots O$ = 2.846 (2)–2.898 (2) Å and $N—H\cdots O$ = 160 (2)–175 (2)°], whereas the 1-(hydroxymethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane cations form one $O—H\cdots{}^-O—S$ [$O\cdots O$ = 2.628 (2) Å and $O—H\cdots O$ = 176°] and three $C—H\cdots{}^-O—S$ [$C\cdots O$ = 3.359 (2)–3.380 (2) Å and $C—H\cdots O$ = 148–155°] interactions to neighboring sulfonate groups.

Comment

The 1,5-naphthalenedisulfonate moiety has been shown to be a versatile building block in the construction of supramolecular arrays (Russell *et al.*, 1997). Because of the high affinity of the sulfonate group to form hydrogen bonds and the inflexible nature of the naphthyl fragment, patterns of association to neighboring moieties often follow predictable sets of intermolecular contacts. The focus of this investigation was to understand the crystal chemistry of a two-component system composed of 1,5-naphthalenedisulfonic acid and hexamethylenetetramine (HMTA). Similar to previous reports on the donor ability of disulfonates and various acceptor molecules, we anticipated that cocrystallization of the disulfonate and HMTA molecules would form motifs linked *via* strong *D*—H$\cdots$*A* interactions (Holman *et al.*, 2001). Our crystallographic experiments, however, revealed chemical products from the reaction of HMTA and the disulfonic acid. We observed that slow evaporation of HMTA and 1,5-naphthalenedisulfonic acid from aqueous and methanolic solutions gave the ammonium, (I), and *N*-(hydroxymethyl)HMTA, (II), salts, respectively. The acid-promoted degradation of HMTA to formaldehyde and ammonia has been known for some time (Baur & Ruetschi, 1941), with recent reports detailing its influence on the construction of HMTA cocrystalline frameworks (Duraisamy *et al.*, 2000; Lough *et al.*, 2000). The structures of (I) and (II) support such a chemical process by providing structural evidence of chemical species [*i.e.* ammonium and *N*-(hydroxymethyl)HMTA] along the HMTA reaction coordinate.



From inspection of Figs. 1 and 2, it can be seen that the asymmetric units of both title compounds contain a 1,5-naphthalenedisulfonate anion positioned on an inversion center, and either two ammonium [for (I)] or *N*-(hydroxymethyl)HMTA [for (II)] cations. Each of the three sulfonate $S—O^-$ acceptors and the four $N^+—H$ donor groups in compound (I) are utilized in the construction of hydrogen bonds. The disulfonate groups are linked to four adjacent ammonium molecules *via* $N^+—H\cdots{}^-O—S$ contacts (Table 1). The collection of these hydrogen bonds forms a complex network of sulfonate and ammonium associations, as shown in Fig. 3. These intermolecular associations generate molecular alignment with alternating hydrophobic (disulfonate and ammonium ions) and hydrophilic (naphthyl) regions extending in the *bc* plane. In the structure of (II), the disulfonate moiety is hydrogen bonded to two neighboring *N*-(hydroxymethyl)HMTA cations *via* $O—H\cdots{}^-O—S$ close contacts (Table 2). From inspection of Fig. 4, it can be seen that this set of interactions forms a discrete centrosymmetric

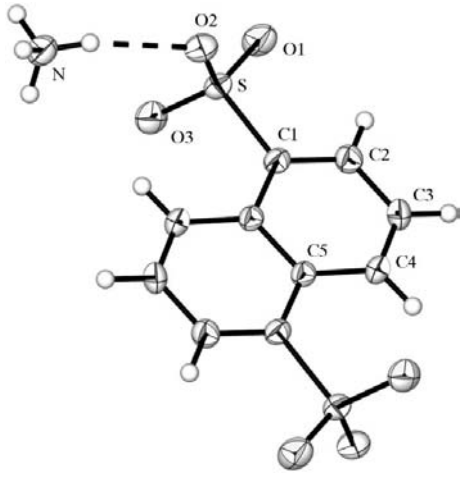


Figure 1
The molecular structure of bis(ammonium) 1,5-naphthalenedisulfonate, (I), showing the atom-labeling scheme and displacement ellipsoids at the 60% probability level.

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trimeric pattern with graph set $D_2^2(10)$ (Bernstein *et al.*, 1995). Molecular alignment in complex (II) is further influenced by additional C—H···$^{-}$O$_3$S interactions between the HMTA and sulfonate moieties. Although such C—H···O interactions are weak compared with conventional hydrogen bonds, recent reports suggest their contribution to crystal packing may play a significant role in the overall construction of molecular assemblies (Desiraju, 2002; Steiner, 2002; Desiraju & Steiner, 1999).

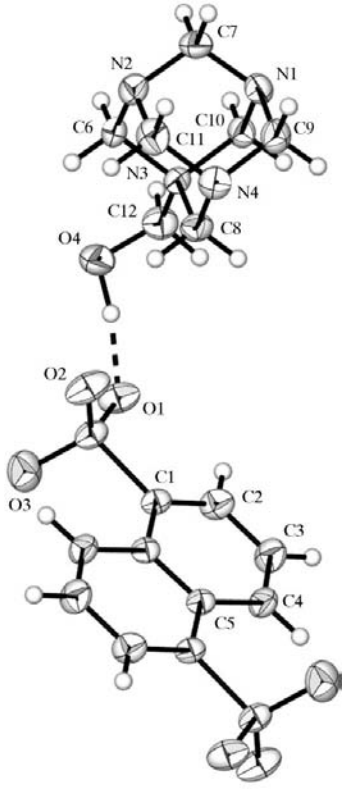

Figure 2
The molecular structure of bis[*N*-(hydroxymethyl)HMTA] 1,5-naphthalenedisulfonate, (II), showing the atom-labeling scheme and displacement ellipsoids at the 60% probability level.

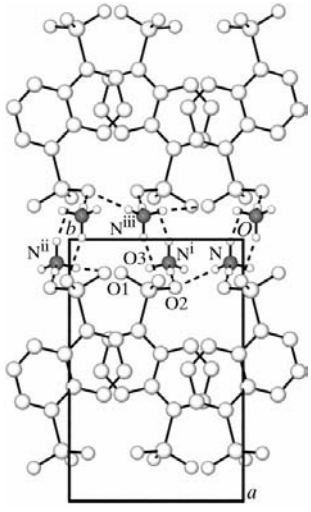

Figure 3
The crystal structure of bis(ammonium) 1,5-naphthalenedisulfonate, (I), showing the N^{+}—H···$^{-}$O—S interactions. Aryl H atoms have been omitted for clarity. [Symmetry codes: (i) $x, \frac{1}{2}-y, z+\frac{1}{2}$; (ii) $x, 1+y, z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

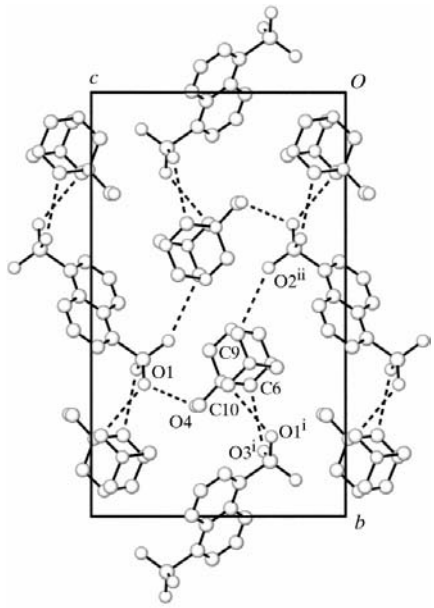

Figure 4
The crystal structure of bis[*N*-(hydroxymethyl)HMTA] 1,5-naphthalenedisulfonate, (II), showing the O—H···$^{-}$O—S and C—H···O contacts. H atoms have been omitted for clarity. [Symmetry codes: (i) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x-1, y, z$.]

Experimental

Compounds (I) and (II) were obtained by the addition of equimolar quantities of 1,5-naphthalenedisulfonic acid and hexamethylenetetraamine to water and a 2:1 methanol–water solution, respectively. The resulting heterogeneous mixtures were stirred at 333 K for ∼30 min until completely dissolved and the resulting solutions were allowed to recrystallize by slow evaporation at room temperature. After 5 d, crystals of both compounds were retrieved and the sample quality assessed by polarized microscopy.

Compound (I)

Crystal data

$2NH_4^+\cdot C_{10}H_6O_6S_2^{2-}$
$M_r = 322.36$
Monoclinic, $P2_1/c$
$a = 11.3771\ (7)$ Å
$b = 7.3386\ (4)$ Å
$c = 7.9974\ (7)$ Å
$\beta = 103.431\ (6)^\circ$
$V = 649.46\ (8)$ Å^3
$Z = 2$
$D_x = 1.648$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 29 reflections
$\theta = 19.3$–24.9°
$\mu = 0.44$ mm^{-1}
$T = 298\ (2)$ K
Transparent plate, colorless
0.56 × 0.44 × 0.08 mm

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (*SHELXTL*; Bruker, 1998)
$T_{min} = 0.844$, $T_{max} = 0.963$
2078 measured reflections
1495 independent reflections
1334 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.5^\circ$
$h = -14 \rightarrow 14$
$k = -9 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections
every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.2958P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.086$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
$S = 1.09$	$\Delta\rho_{min} = -0.37$ e Å^{-3}
1495 reflections	
107 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O2	0.88 (3)	2.04 (3)	2.898 (2)	166 (2)
N—H2N···O2^{i}	0.88 (3)	1.98 (3)	2.846 (2)	175 (2)
N—H3N···O1^{ii}	0.88 (3)	2.01 (3)	2.889 (2)	172 (3)
N—H4N···O3^{iii}	0.92 (3)	1.98 (3)	2.868 (2)	160 (2)

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

Compound (II)

Crystal data

$2C_7H_{15}N_4O^+\cdot C_{10}H_6O_6S_2^{2-}$	$D_x = 1.548$ Mg m^{-3}
$M_r = 628.73$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 52 reflections
$a = 6.0625$ (4) Å	$\theta = 20.7$–$25.9°$
$b = 19.2820$ (10) Å	$\mu = 0.26$ mm^{-1}
$c = 11.6207$ (7) Å	$T = 298$ (2) K
$\beta = 96.72$ (4)°	Transparent rhomboid, colorless
$V = 1349.09$ (14) Å^3	0.68 × 0.32 × 0.20 mm
$Z = 2$	

Data collection

Siemens $P4$ diffractometer	$h = -1 \rightarrow 7$
$\theta/2\theta$ scans	$k = -1 \rightarrow 25$
4192 measured reflections	$l = -15 \rightarrow 15$
3101 independent reflections	3 standard reflections every 97 reflections
2669 reflections with $I > 2\sigma(I)$	intensity decay: <3%
$R_{int} = 0.012$	
$\theta_{max} = 27.5°$	

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4O···O1	0.84	1.79	2.628 (2)	176
C6—H6A···O3^{i}	0.99	2.47	3.380 (2)	153
C9—H9A···O2^{ii}	0.99	2.44	3.359 (2)	155
C10—H10B···O1^{i}	0.99	2.50	3.376 (2)	148

Symmetry codes: (i) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x - 1, y, z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.6708P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.108$	$\Delta\rho_{max} = 0.45$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.33$ e Å^{-3}
3101 reflections	
194 parameters	
H atoms treated by a mixture of independent and constrained refinement	

The H-atom positions for (I) and (II) were located from difference density maps or calculated using C/O—H distance criteria (methylene C—H = 0.99 Å, aryl C—H = 0.95 Å and O—H = 0.84 Å). H atoms were refined isotropically or using a riding model with fixed displacement parameters [U_{iso}(H) = 1.2U_{eq} for the atom to which they are bonded]. The ammonium H atoms in (I) were located in difference maps and refined isotropically.

For both compounds, data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1418). Services for accessing these data are described at the back of the journal.

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