Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(dihydronium) naphthalene-1,5-disulfonate

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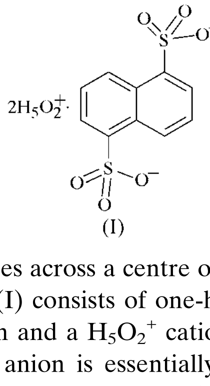
Received 9 November 2007
Accepted 26 November 2007
Online 22 December 2007

The title compound is a salt, $2H_5O_2^+\cdot C_{10}H_6O_6S_2^{2-}$, in which the anion lies across an inversion centre in the space group *C*2/*c*, while the cation contains a short but noncentred O—H···O hydrogen bond. The ionic components are linked by charge-assisted O—H···O hydrogen bonds into a three-dimensional framework structure.

Comment

In solid hydrates of strong acids, the H atom has been found to be hydrated to form a series of cations which have been characterized as H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ depending upon the degree of hydration. A search of the Cambridge Structural Database (Version 5.28; Allen, 2002) for structures containing the naphthalene-1,5-disulfonate anion yielded only seven examples, all salts of the metals of groups 1 and 2 (Cai *et al.*, 2001). The structure of naphthalene-1,5-disulfonic acid itself is not known. We report here the crystal structure of naphthalene-1,5-disulfonic acid tetrahydrate, in which the H atoms of the SO_3H groups are transferred to the water molecules to form the salt $2H_5O_2^+\cdot C_{10}H_6(SO_3)_2^{2-}$, (I).



(I)

The anion in (I) lies across a centre of inversion so that the asymmetric unit of (I) consists of one-half of a naphthalene-1,5-disulfonate anion and a $H_5O_2^+$ cation (Fig. 1). The naphthalene ring of the anion is essentially planar [the greatest deviations of the C atoms from the weighted mean ring plane are smaller than 0.010 (2) Å], but its bond distances exhibit significant differences from those of naphthalene itself (Brock & Dunitz, 1982; Oddershede & Larsen, 2001). The C2—C3, C3—C4 and C3—C3^i bonds [symmetry code: (i) $-x + 1$, $-y$, $-z + 1$; Table 1] are significantly longer than the other C—C bonds within the ring. The distortions are the result of the substitution effect of the SO_3 groups joined to the ring at the 1,5-positions. The *ab initio* gas-phase geometry calculated for an isolated anion shows quite good correlation between the

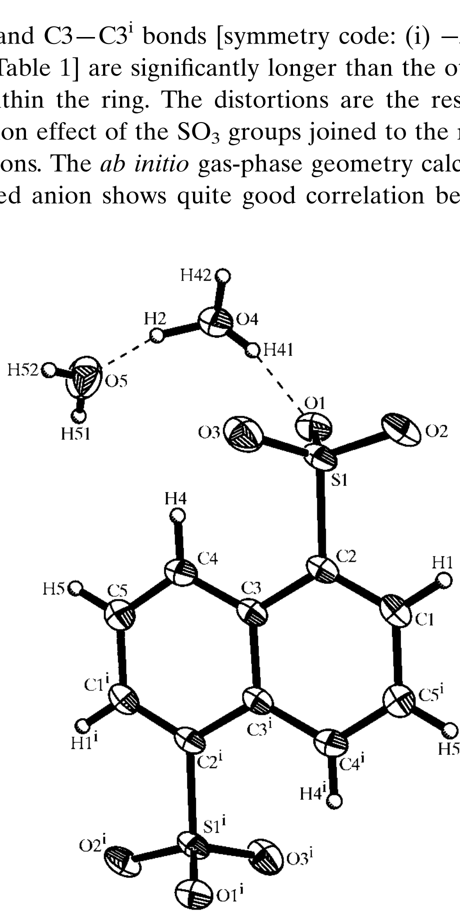


Figure 1
A view of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.

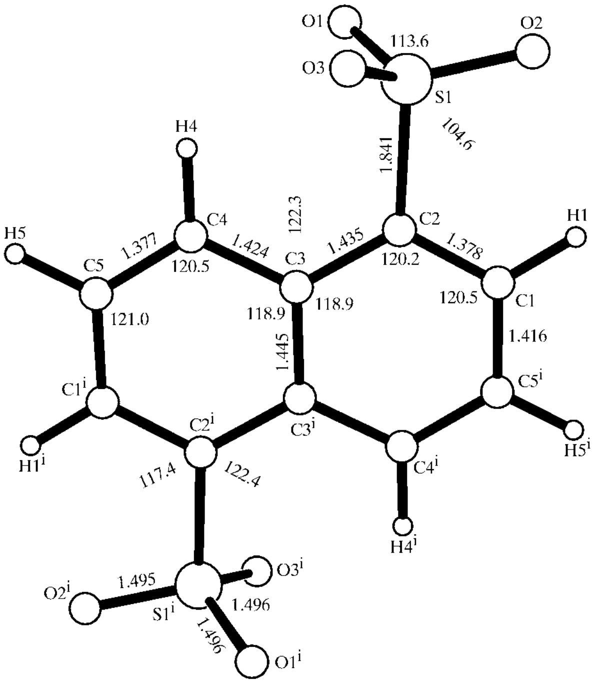


Figure 2
Results of the optimized molecular orbital calculations (B3LYP/6–31+G*) for the naphthalene-1,5-disulfonate anion (Å, °).

DOI: 10.1107/S0108270107063342

C—C bonds and C—C—C angles within the ring (Fig. 2). Thus, the distortions arise mainly from the electronic structure and to a lesser degree from the molecular interaction as well as from the crystal packing forces. The S—O bonds of the SO_3^- group are all intermediate in length between double S=O and single bonds (Allen *et al.*, 1987), indicating charge delocalization on to all O atoms of this group.

The C—S bond length in the crystal structure is shorter than that calculated for the gas-phase structure (1.841 Å), owing to the interactions of negatively charged SO_3^- groups with the π-aromatic ring. In the crystal structure, this interaction decreases as a result of the hydrogen-bonding system, which reduces the charge on the SO_3^- groups. The small differences between the experimental S—O bond lengths result from the strengths of the hydrogen bonds in which the O atoms are involved (Table 2).

The acidic H atom is dihydrated such that pairs of water molecules are joined together *via* a short O—H···O hydrogen bond to form a discrete $H_5O_2^+$ ion. However, the acidic H atom is not located at the centre between the O atoms, but closer to one of the two water molecules (Table 2). This is in contrast to the results of molecular orbital (MO) calculations performed for an isolated $H_5O_2^+$ cation, which is predicted to be symmetric (O···O = 2.42 Å, O—H = 1.21 Å and O—H—O = 177°), although in the crystal structure the cation is nonsymmetrical. *Ab initio* MO calculations indicate that substantial energy is involved in the hydration of the hydronium ion (*e.g.* $H_3O^+ + H_2O = H_5O_2^+$, 37 kcal mol^{-1}). The $H_5O_2^+$ ion has a *gauche* conformation, with a dihedral angle of 99.5°, as defined by the dihedral angle between the O4/H41/H42 and O5/H51/H52 planes. Thus, the bonding arrangement together with the lone pair of electrons around each O atom in $H_5O_2^+$ is tetrahedral. However, because of the hydrogen-bonding system and, especially, the lone pair of electrons on both O atoms, the tetrahedron is significantly distorted, since the lone pair of electrons affords a wider region than the bonding pair, as predicted by the valence-shell electron-pair repulsion model (Gillespie, 1963, 1992).

The molecular arrangement in the crystal structure of (I) is mainly determined by relatively strong and directional hydrogen bonds (Table 2), and to a lesser degree by a π–π interaction between the naphthalene ring systems, where the interplanar spacing is *ca* 3.53 Å (Fig. 3). This value is comparable to the sum of the C-atom van der Waals radii of the π-ring system (Pauling, 1967). However, as a result of the mutual shift of the rings, the π–π interaction is not fully effective. The π–π overlapping between the rings takes place only *via* the outermost C—C bonds (C1—C5^{i} and C5—C1^{i}). The naphthalene-1,5-disulfonate anions are stacked in the crystal structure along the *b* axis at $z = 0$ and $z = \frac{1}{2}$, and they make an angle of 17.7° with the (010) plane, so forming sheets parallel to (001). The $H_5O_2^+$ cations are located between these sheets and join together *via* O—H···O hydrogen bonds into a three-dimensional network. Each $H_5O_2^+$ cation links four anions. Atom O1 of the SO_3^- group is involved in two hydrogen bonds, while the other two O atoms of SO_3^- are each involved in one hydrogen bond (Table 2).

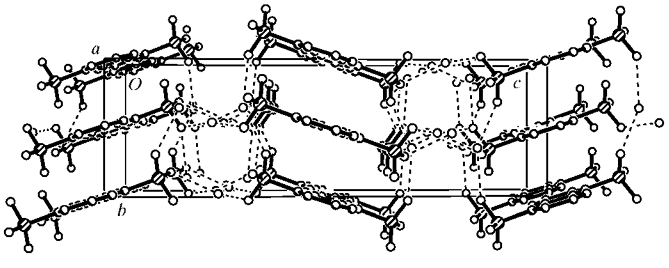


Figure 3
A view of the crystal packing in (I), showing the three-dimensional hydrogen-bonded network. H atoms have been omitted for clarity.

Experimental

Suitable crystals of (I) were obtained by slow evaporation of an aqueous solution of naphthalene-1,5-disulfonic acid. MO calculations were performed using *GAUSSIAN98* (Frisch *et al.*, 1998).

Crystal data

$2H_5O_2^+ \cdot C_{10}H_6O_6S_2^{2-}$
$M_r = 360.37$
Monoclinic, $C2/c$
$a = 9.1183$ (18) Å
$b = 7.1051$ (14) Å
$c = 22.954$ (4) Å
$\beta = 95.08$ (1)°
$V = 1481.3$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.41$ mm^{-1}
$T = 295$ (2) K
0.32 × 0.28 × 0.11 mm

Data collection

Kuma KM-4 diffractometer with CCD area detector
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 1990*b*)
$T_{\min} = 0.884$, $T_{\max} = 0.961$
9288 measured reflections
1835 independent reflections
1575 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.077$
$S = 1.06$
1835 reflections
116 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.4431 (12)	C1—C5^{i}	1.406 (2)
S1—O2	1.4475 (11)	C2—C3	1.4281 (18)
S1—O1	1.4683 (11)	C3—C4	1.411 (2)
S1—C2	1.7703 (13)	C3—C3^{i}	1.431 (2)
C1—C2	1.361 (2)	C4—C5	1.357 (2)
O3—S1—O2	113.54 (7)	O3—S1—C2	107.27 (7)
O3—S1—O1	111.35 (7)	O2—S1—C2	106.80 (7)
O2—S1—O1	111.02 (7)	O1—S1—C2	106.42 (6)

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

H atoms bonded to C atoms were treated as riding in geometrically idealized positions, with C—H distances of 0.93 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). H atoms bonded to O atoms were located in difference maps and their coordinates were refined [with $U_{\rm iso}(H) = 1.5U_{\rm eq}(O)$], giving a range of O—H distances of 0.80 (4)–0.86 (4) Å for the terminal H atoms, and distances of 1.02 (4) and 1.42 (4) Å for the bridging H atom.

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H2···O5	1.02 (4)	1.42 (4)	2.416 (2)	163 (3)
O4—H41···O1	0.86 (3)	1.76 (3)	2.6059 (19)	167 (2)
O4—H42···O2^{ii}	0.82 (3)	1.83 (3)	2.6294 (17)	164 (2)
O5—H51···O3^{iii}	0.80 (4)	1.90 (4)	2.6562 (19)	156 (4)
O5—H52···O1^{iv}	0.86 (4)	1.83 (4)	2.6891 (19)	171 (4)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL97*.

This work was financially supported by the Ministry of Science and Information Society Technologies (project No. 3 T09A 121 28).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3169). Services for accessing these data are described at the back of the journal.

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