organic compounds

Bis[diaquahydrogen(1+)] naphthalene-1,5-disulfonate

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In the structure of the title compound, $2H_5O_2^+ \cdot C_{10}H_6O_6S_2^{2-}$, the naphthalene-1,5-disulfonate anion is located on an inversion centre. Two independent water molecules share a proton *via* a strong hydrogen bond, giving rise to a diaquahydrogen(1+) (dihydronium) cation. Strong hydrogen bonds between the diaquahydrogen(1+) cations and the sulfonate groups of the naphthalene-1,5-disulfonate anions produce a three-dimensional network.

Related literature

For related literature, see: Cai *et al.* (2001); Gilli *et al.* (2004); Lundgren & Tellgren (1974); Skakle & Wardell (2006); Swift *et al.* (1998); Zhang *et al.* (2005).
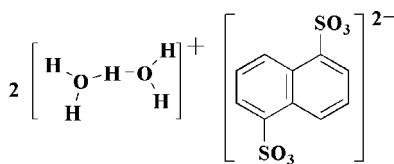
Experimental

Crystal data

$2H_5O_2^+ \cdot C_{10}H_6O_6S_2^{2-}$
M_r = 360.35
Monoclinic, $P2_1/c$
a = 11.4131 (3) Å
b = 9.0543 (2) Å
c = 7.1957 (1) Å
β = 100.3616 (8)°

V = 731.46 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 298 (1) K
$0.38 \times 0.28 \times 0.20$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.868, T_{max} = 0.921

2955 measured reflections
1663 independent reflections
1508 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.139
S = 1.23
1663 reflections
116 parameters
4 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1W—H2$\cdots$O3^i	0.850 (18)	1.793 (19)	2.634 (2)	170 (4)
O1W—H1$\cdots$O2	0.816 (18)	1.84 (2)	2.642 (2)	166 (4)
O1W—H5$\cdots$O2W	1.07 (4)	1.36 (4)	2.419 (3)	173 (3)
O2W—H4$\cdots$O1^{ii}	0.805 (18)	1.87 (2)	2.656 (2)	166 (4)
O2W—H3$\cdots$O2^{iii}	0.788 (18)	1.96 (2)	2.730 (2)	163 (4)

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

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supplementary materials

Bis[diaquahydrogen(1+)] naphthalene-1,5-disulfonate

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Comment

Bifunctional organosulfonates are versatile building blocks for supramolecular assembly and functional materials (Swift *et al.*, 1998). A number of organic and metal-organic networks based on naphthalene-1,5-disulfonic acid have been documented (Cai *et al.*, 2001; Zhang *et al.*, 2005), however, its structure of itself has not been reported. We here describe the crystal structure of a $(H_5O_2^+)_2 \cdot C_{10}H_6O_6S_2^{2-}$ (I), whose molecular structure is illustrated in Figure 1.

In the structure of (I), each naphthalene-1,5-disulfonate anion lies on an inversion center and crystallizes with four water molecules. The sulfonic acid groups are deprotonated with the H atoms transferred to the water molecules. In the current study, despite being run at room temperature, the data quality was sufficient to locate the hydrogen atoms on the water molcules in the difference density Fourier map, and the position of the proton found to be shared between O1W and O2W was allowed to refine freely. The two independent water molecules are strongly hydrogen bonded, forming a diaquahydrogen(1+) $(H_5O_2^+)$ cation. The O···O distance of the hydrogen bonded atoms O1W and O2W is about 2.419 (3) Å, which is very strong and falls into the range of very short hydrogen bonds (< 2.50 Å) (Gilli *et al.*, 2004). The geometry of the $H_5O_2^+$ cation is in agreement with that found in other X-ray and neutron studies (*e.g.* Lundgren & Tellgren, 1974; Skakle & Wardell, 2006): the O—H distances O2W—H5 and O1W—H5 for the shared hydrogen atom (see the hydrogen bonding table) are tentatively in agreement with those found in neutron studies, and the associated hydrogen bond between the water molecules is nearly linear, with the O—H—O angle equal to 173 (3)°. One diaquahydrogen(1+) O atom is pyramidial, with O1W 0.26 (3)Å out of the plane formed by atoms H1, H2 and H5, while the other O atom is almost coplanar, with O2W deviating 0.058 (3)Å from the plane formed by H3, H4 and H5.

Each sulfonic acid group of naphthalene-1,5-disulfonate is involved in four additional hydrogen bonds with four adjacent $H_5O_2^+$ cations. O1 and O3 form a single hydrogen bond with O1W and O2W, respectively, and O2 participates in hydrogen bonds with both O1W and O2W. In this way, the diaquahydrogen(1+) cations are connected into a three-dimensional network (Fig. 2). There are also π-π interactions between the adjacent C2—C3 edges of naphthalene rings with an interplanar distance of 3.41 (3) Å.

Experimental

naphthalene-1,5-disulfonic acid tetrahydrate was obtained from Aldrich. The crystal of 1 was obtained by recrystallizing naphthalene-1,5-disulfonic acid tetrahydrate from water.

Refinement

All non-H atoms were refined anisotropically. The H atoms on naphthalene are visible on difference maps. All hydrogen atoms on carbon were treated as riding atoms with C—H distances of 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$, while hydrogen atom on water were located from difference Fourier electron maps. The position of the shared hydrogen has been refined freely,

supplementary materials

while the other water hydrogen atoms have been restrained to have an O—H distance of 0.82Å within a standard deviation of 0.02 Å (*DFIX* command in *SHELXTL*). All water hydrogen atoms have been set to have an isotropic displacement parameter $U_{iso}(H) = 1.5\ U_{eq}(O)$ of the adjacent oxygen atom.
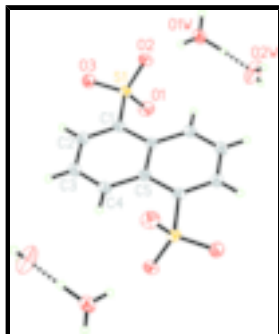
Figures

Fig. 1. A view of compound (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. Unlabeled atoms are generated by the symmetry operator $-x + 2, -y + 1, -z + 1$.
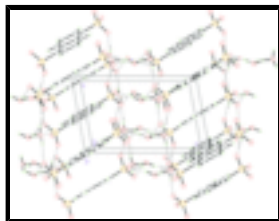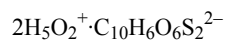

Fig. 2. The three-dimensional network of compound (I) showing the hydrogen bonding interactions (indicated by dashed lines).

Bis[diaquahydrogen(1+)] naphthalene-1,5-disulfonate

Crystal data

$2H_5O_2^+ \cdot C_{10}H_6O_6S_2^{2-}$	$F_{000} = 376$
$M_r = 360.35$	$D_x = 1.636$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2955 reflections
$a = 11.4131$ (3) Å	$\theta = 1.8–27.5°$
$b = 9.0543$ (2) Å	$\mu = 0.41$ mm^{-1}
$c = 7.19570$ (10) Å	$T = 298$ (1) K
$\beta = 100.3616$ (8)°	Block, colourless
$V = 731.46$ (3) Å^3	$0.38 \times 0.28 \times 0.20$ mm
$Z = 2$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	1663 independent reflections
Radiation source: fine-focus sealed tube	1508 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.014$
$T = 293(2)$ K	$\theta_{max} = 27.5°$
φ and ω scans	$\theta_{min} = 1.8°$

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -14 \rightarrow 14$
$T_{min} = 0.868$, $T_{max} = 0.921$	$k = -11 \rightarrow 9$
2955 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.139$	$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 0.1778P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.23$	$(\Delta/\sigma)_{max} = 0.001$
1663 reflections	$\Delta\rho_{max} = 0.89$ e Å^{-3}
116 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
4 restraints	Extinction correction: SHELXTL (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.157 (17)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.72534 (4)	0.40836 (5)	0.24522 (6)	0.0265 (3)
O3	0.67842 (12)	0.26056 (17)	0.2033 (2)	0.0377 (4)
O2	0.65410 (12)	0.48997 (16)	0.3626 (2)	0.0326 (4)
C1	0.87082 (15)	0.3872 (2)	0.3797 (3)	0.0247 (4)
O1	0.73865 (14)	0.49259 (19)	0.0794 (2)	0.0399 (4)
C2	0.91527 (17)	0.2467 (2)	0.4037 (3)	0.0292 (4)
H2B	0.8683	0.1666	0.3558	0.035*
C3	1.03252 (17)	0.2237 (2)	0.5012 (3)	0.0324 (4)
H3B	1.0625	0.1281	0.5174	0.039*
C5	1.05931 (15)	0.4870 (2)	0.5490 (2)	0.0249 (4)
C4	1.10203 (16)	0.3395 (2)	0.5716 (3)	0.0295 (4)

H4A	1.1790	0.3221	0.6358	0.035*
O2W	0.6544 (3)	0.9245 (2)	0.2265 (3)	0.0685 (7)
O1W	0.52651 (15)	0.70960 (19)	0.1890 (3)	0.0448 (4)
H4	0.669 (3)	0.958 (4)	0.332 (3)	0.067*
H1	0.563 (3)	0.635 (3)	0.225 (5)	0.067*
H5	0.583 (3)	0.804 (4)	0.216 (5)	0.067*
H3	0.665 (3)	0.961 (4)	0.131 (3)	0.067*
H2	0.463 (2)	0.720 (4)	0.235 (5)	0.067*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0220 (3)	0.0290 (3)	0.0268 (3)	−0.00021 (15)	−0.0001 (2)	−0.00117 (15)
O3	0.0284 (7)	0.0333 (8)	0.0484 (9)	−0.0033 (6)	−0.0016 (6)	−0.0084 (6)
O2	0.0260 (7)	0.0362 (8)	0.0353 (7)	0.0056 (5)	0.0045 (5)	−0.0002 (6)
C1	0.0198 (8)	0.0283 (9)	0.0250 (9)	0.0001 (7)	0.0017 (7)	−0.0008 (6)
O1	0.0374 (9)	0.0514 (9)	0.0290 (8)	−0.0007 (7)	0.0008 (6)	0.0068 (6)
C2	0.0270 (9)	0.0269 (9)	0.0332 (10)	−0.0015 (7)	0.0037 (7)	−0.0011 (7)
C3	0.0304 (10)	0.0261 (9)	0.0395 (10)	0.0040 (7)	0.0032 (8)	0.0019 (7)
C5	0.0216 (9)	0.0267 (9)	0.0257 (9)	0.0012 (7)	0.0025 (7)	0.0013 (6)
C4	0.0232 (9)	0.0284 (9)	0.0352 (10)	0.0036 (7)	0.0008 (7)	0.0019 (7)
O2W	0.1107 (19)	0.0603 (13)	0.0304 (10)	−0.0399 (12)	0.0014 (11)	0.0016 (8)
O1W	0.0365 (9)	0.0366 (9)	0.0593 (10)	0.0078 (7)	0.0034 (7)	0.0024 (8)

Geometric parameters (Å, °)

S1—O1	1.4472 (15)	C5—C4	1.421 (2)
S1—O3	1.4527 (15)	C5—C5[i]	1.429 (3)
S1—O2	1.4722 (14)	C5—C1[i]	1.431 (2)
S1—C1	1.7755 (18)	C4—H4A	0.9300
C1—C2	1.369 (3)	O2W—H4	0.805 (18)
C1—C5[i]	1.431 (2)	O2W—H5	1.36 (4)
C2—C3	1.410 (3)	O2W—H3	0.788 (18)
C2—H2B	0.9300	O1W—H1	0.816 (18)
C3—C4	1.357 (3)	O1W—H5	1.07 (4)
C3—H3B	0.9300	O1W—H2	0.850 (18)
O1—S1—O3	113.81 (9)	C2—C3—H3B	119.7
O1—S1—O2	111.06 (9)	C4—C5—C5[i]	119.1 (2)
O3—S1—O2	111.13 (9)	C4—C5—C1[i]	123.33 (16)
O1—S1—C1	106.25 (9)	C5[i]—C5—C1[i]	117.6 (2)
O3—S1—C1	106.70 (8)	C3—C4—C5	121.22 (17)
O2—S1—C1	107.47 (8)	C3—C4—H4A	119.4
C2—C1—C5[i]	121.64 (16)	C5—C4—H4A	119.4
C2—C1—S1	117.25 (14)	H4—O2W—H5	112 (3)
C5[i]—C1—S1	121.02 (13)	H4—O2W—H3	129 (4)
C1—C2—C3	119.79 (17)	H5—O2W—H3	118 (3)
C1—C2—H2B	120.1	H1—O1W—H5	110 (3)

C3—C2—H2B	120.1	H1—O1W—H2	113 (4)
C4—C3—C2	120.68 (18)	H5—O1W—H2	112 (3)
C4—C3—H3B	119.7		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H2···O3[ii]	0.850 (18)	1.793 (19)	2.634 (2)	170 (4)
O1W—H1···O2	0.816 (18)	1.84 (2)	2.642 (2)	166 (4)
O1W—H5···O2W	1.07 (4)	1.36 (4)	2.419 (3)	173 (3)
O2W—H4···O1[iii]	0.805 (18)	1.87 (2)	2.656 (2)	166 (4)
O2W—H3···O2[iv]	0.788 (18)	1.96 (2)	2.730 (2)	163 (4)

Symmetry codes: (ii) $-x+1, y+1/2, -z+1/2$; (iii) $x, -y+3/2, z+1/2$; (iv) $x, -y+3/2, z-1/2$.
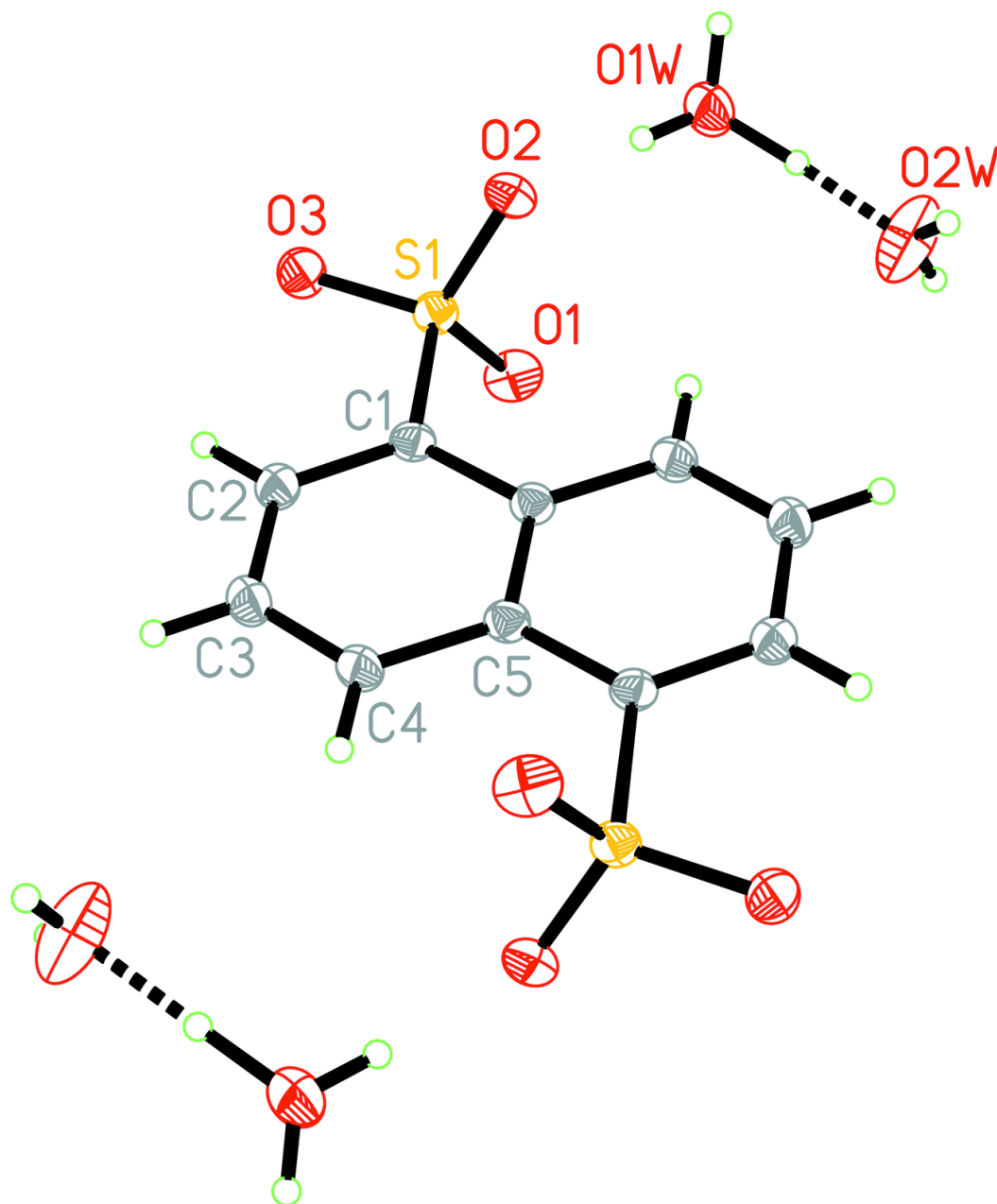
Fig. 1

Fig. 2