

Dihydroxonium 1,5-naphthalenedisulfonate
N,N-dimethylformamide disolvateZhao-Peng Deng, Shan Gao,*
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Key indicators

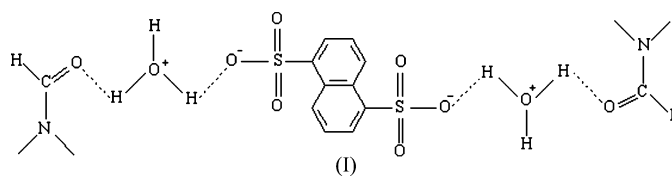
Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.038
 wR factor = 0.111
Data-to-parameter ratio = 17.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title salt adduct, $2\text{H}_3\text{O}^+ \cdot \text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-} \cdot 2\text{C}_3\text{H}_7\text{NO}$, the 1,5-naphthalenedisulfonate dianion lies on an inversion center. Intermolecular interactions link two hydroxonium cations, one 1,5-naphthalenedisulfonate dianion and two *N,N*-dimethylformamide molecules into a short hydrogen-bonded chain. A supramolecular hydrogen-bonding network structure is formed *via* further intermolecular hydrogen bonds.

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Comment

Naphthalene-1,5-disulfonic acid, (1,5- H_2nds), with its rigid structure and two functionally active SO_3 groups in two well separated positions, is known as a good candidate for the construction of supramolecular complexes (Cai, 2004), particularly as the sulfonate unit has a high propensity to form strong hydrogen bonds (Huo *et al.*, 2005). To date, a large number of metal complexes containing 1,5- H_2nds have been reported (Cai *et al.*, 2001; Gao *et al.*, 2005). However, there is no report of the structure of 1,5- H_2nds itself. Recently, we accidentally obtained the title complex by the reaction of naphthalene-1,5-disulfonyl dichloride and glycine in *N,N*-dimethylformamide solution; its crystal structure is reported here.



As illustrated in Fig. 1, the molecular structure of (I) consists of two hydroxonium cations, one 1,5- nds^{2-} dianion and two *N,N*-dimethylformamide molecules, with the 1,5- nds^{2-} dianion lying on an inversion center. One 1,5- nds^{2-} dianion and two *N,N*-dimethylformamide molecules are linked by two hydroxonium cations through intermolecular interactions, forming a short hydrogen-bonded chain. These short chains are further linked by intermolecular hydrogen bonds involving the hydroxonium cations and sulfonate O atoms into a supramolecular hydrogen-bonding network structure (Table 2 and Fig. 2).

Experimental

Naphthalene-1,5-disulfonyl dichloride (10 mmol) was added dropwise to an *N,N*-dimethylformamide solution (15 ml) containing glycine (20 mmol). The mixture was stirred for 1.5 h at room temperature, and then filtered. Colorless prismatic crystals were obtained from the solution after several days. Analysis calculated for

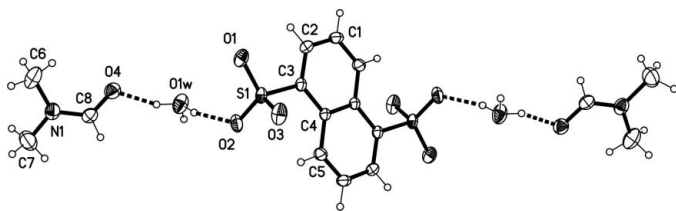


Figure 1
ORTEP plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. Hydrogen bonds are denoted by dashed lines. Unlabeled atoms are related to labeled atoms by $-x, 1 - y, 1 - z$.

$C_{16}H_{26}N_2O_{10}S_2$: C 40.85, H 5.57, N 5.95%. Found: C 40.81, H 5.54, N 5.93%.

Crystal data

$2H_3O^+ \cdot C_{10}H_6O_6S_2 \cdot 2C_3H_7NO$
 $M_r = 470.51$
 Monoclinic, $P2_1/n$
 $a = 9.1614$ (18) Å
 $b = 12.101$ (2) Å
 $c = 10.053$ (2) Å
 $\beta = 100.10$ (3)°
 $V = 1097.2$ (4) Å³
 $Z = 2$

$D_x = 1.424$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9318 reflections
 $\theta = 3.3$ – 27.5°
 $\mu = 0.30$ mm⁻¹
 $T = 295$ (2) K
 Prism, colorless
 $0.32 \times 0.27 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{min} = 0.911, T_{max} = 0.943$
 10588 measured reflections

2507 independent reflections
 2193 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.015$
 $\theta_{max} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -15 \rightarrow 15$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.111$
 $S = 1.05$
 2507 reflections
 147 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.3282P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.52$ e Å⁻³
 $\Delta\rho_{min} = -0.27$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–O1	1.4415 (14)	C1–C5 ⁱ	1.356 (2)
S1–O2	1.4564 (13)	C1–C2	1.404 (2)
S1–O3	1.4579 (14)	C2–C3	1.368 (2)
S1–C3	1.7769 (15)	C3–C4	1.425 (2)
O4–C8	1.270 (2)	C4–C5	1.418 (2)
N1–C8	1.288 (2)	C4–C4 ⁱ	1.432 (3)
N1–C6	1.455 (3)	C5–C1 ⁱ	1.356 (2)
N1–C7	1.471 (3)		
O1–S1–C3	106.86 (8)	C3–C2–C1	120.06 (14)
O1–S1–O2	113.17 (8)	C3–C4–C4 ⁱ	118.04 (16)
O1–S1–O3	113.16 (9)	C4–C3–S1	120.94 (11)
O2–S1–C3	106.59 (7)	C5 ⁱ –C1–C2	120.79 (15)
O2–S1–O3	111.05 (9)	C5–C4–C3	123.25 (13)
O3–S1–C3	105.39 (7)	C5–C4–C4 ⁱ	118.71 (16)
O4–C8–N1	122.66 (19)	C6–N1–C7	118.7 (2)
C1 ⁱ –C5–C4	121.19 (14)	C8–N1–C6	121.1 (2)
C2–C3–C4	121.22 (13)	C8–N1–C7	120.2 (2)
C2–C3–S1	117.84 (11)		

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

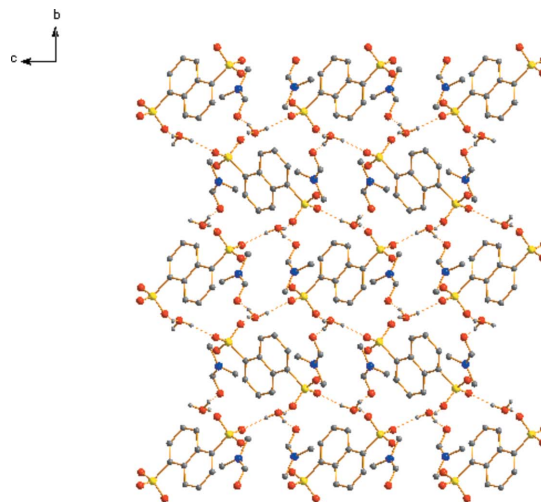


Figure 2
Packing diagram of the title complex, viewed along the a axis, with the O–H...O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W–H1W1...O4	0.87 (2)	1.60 (1)	2.435 (2)	161 (3)
O1W–H1W2...O2	0.87 (2)	1.82 (1)	2.652 (2)	161 (3)
O1W–H1W3...O3 ⁱⁱ	0.87 (2)	1.79 (1)	2.653 (2)	173 (2)

Symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

C-bound H atoms were placed in calculated positions [C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and methine H atoms; C–H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms] and were refined in the riding-model approximation. The H atoms of hydroxonium were located in a difference map and refined with O–H restraints of 0.85 (1) Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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