

# Dihydroxonium 1,5-naphthalenedisulfonate *N,N*-dimethylformamide disolvate

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## Key indicators

Single-crystal X-ray study  
 $T = 295\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.038  
 $wR$  factor = 0.111  
Data-to-parameter ratio = 17.1

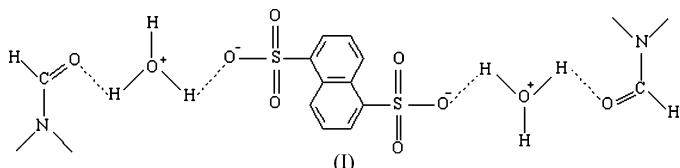
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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

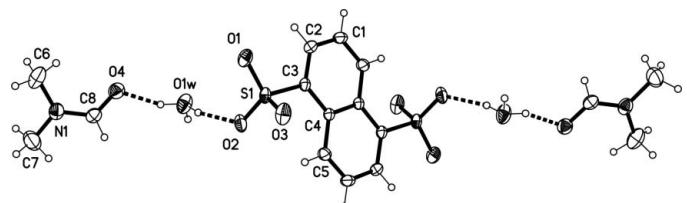
Naphthalene-1,5-disulfonic acid, (1,5-H<sub>2</sub>nds), with its rigid structure and two functionally active SO<sub>3</sub> groups in two well separated positions, is known as a good candidate for the construction of supramolecular complexes (Cai, 2004), particularly as the sulfonate unit has a high propensity to form strong hydrogen bonds (Huo *et al.*, 2005). To date, a large number of metal complexes containing 1,5-H<sub>2</sub>nds have been reported (Cai *et al.*, 2001; Gao *et al.*, 2005). However, there is no report of the structure of 1,5-H<sub>2</sub>nds 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<sup>2-</sup> dianion and two *N,N*-dimethylformamide molecules, with the 1,5-nds<sup>2-</sup> dianion lying on an inversion center. One 1,5-nds<sup>2-</sup> 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**

*ORTEPII* 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  $-x, 1 - y, 1 - z$ .

$\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_{10}\text{S}_2$ : C 40.85, H 5.57, N 5.95%. Found: C 40.81, H 5.54, N 5.93%.

#### Crystal data

$2\text{H}_3\text{O}^+\cdot\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^- \cdot 2\text{C}_3\text{H}_7\text{NO}$

$M_r = 470.51$

Monoclinic,  $P2_1/n$

$a = 9.1614 (18)$  Å

$b = 12.101 (2)$  Å

$c = 10.053 (2)$  Å

$\beta = 100.10 (3)$ °

$V = 1097.2 (4)$  Å<sup>3</sup>

$Z = 2$

#### Data collection

Rigaku R-AXIS RAPID diffractometer

$\omega$  scans

Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.911, T_{\max} = 0.943$

10588 measured reflections

#### 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

$D_x = 1.424$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 9318 reflections

$\theta = 3.3\text{--}27.5$ °

$\mu = 0.30$  mm<sup>-1</sup>

$T = 295$  (2) K

Prism, colorless

0.32 × 0.27 × 0.20 mm

2507 independent reflections

2193 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 27.5$ °

$h = -11 \rightarrow 11$

$k = -15 \rightarrow 15$

$l = -13 \rightarrow 13$

$$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.3282P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

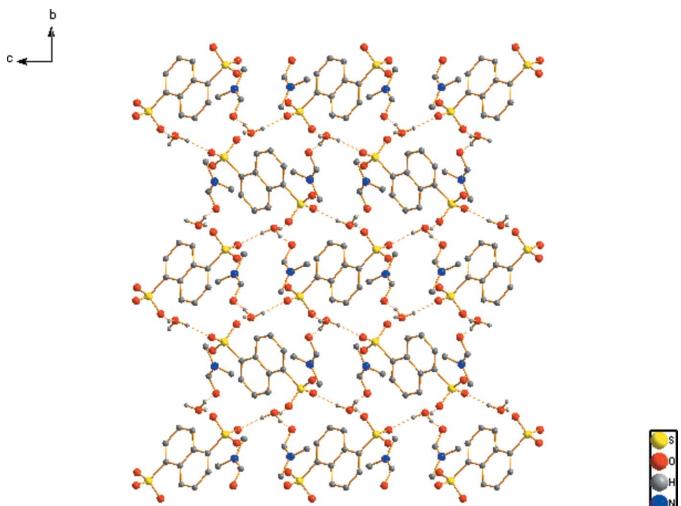
$\Delta\rho_{\max} = 0.52$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.27$  e Å<sup>-3</sup>

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

S1—O1	1.4415 (14)	C1—C5 <sup>i</sup>	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 <sup>i</sup>	1.432 (3)
N1—C6	1.455 (3)	C5—C1 <sup>i</sup>	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 <sup>i</sup>	118.04 (16)
O1—S1—O3	113.16 (9)	C4—C3—S1	120.94 (11)
O2—S1—C3	106.59 (7)	C5 <sup>i</sup> —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 <sup>i</sup>	118.71 (16)
O4—C8—N1	122.66 (19)	C6—N1—C7	118.7 (2)
C1 <sup>i</sup> —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, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
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 <sup>ii</sup>	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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and methine H atoms; C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  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  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

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

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# supporting information

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#### Crystal data



$M_r = 470.51$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 9.1614 (18)$  Å

$b = 12.101 (2)$  Å

$c = 10.053 (2)$  Å

$\beta = 100.10 (3)^\circ$

$V = 1097.2 (4)$  Å<sup>3</sup>

$Z = 2$

$F(000) = 496$

$D_x = 1.424$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9318 reflections

$\theta = 3.3\text{--}27.5^\circ$

$\mu = 0.30$  mm<sup>-1</sup>

$T = 295$  K

Prism, colorless

0.32 × 0.27 × 0.20 mm

#### Data collection

Rigaku R-AXIS RAPID  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.000 pixels mm<sup>-1</sup>  
 $\omega$  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  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.3^\circ$

$h = -11 \rightarrow 11$

$k = -15 \rightarrow 15$

$l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.111$

$S = 1.05$

2507 reflections

147 parameters

6 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from  
neighbouring sites

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<sup>-3</sup>

$\Delta\rho_{\min} = -0.27$  e Å<sup>-3</sup>

#### 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.14585 (4)	0.37380 (3)	0.24652 (4)	0.03585 (15)
O1W	0.48829 (16)	0.24214 (14)	0.42229 (15)	0.0632 (4)
O1	0.25032 (16)	0.42020 (12)	0.17018 (14)	0.0554 (4)
O2	0.20371 (15)	0.27821 (10)	0.32684 (14)	0.0499 (3)
O3	0.00218 (15)	0.34940 (13)	0.16396 (14)	0.0569 (4)
O4	0.66802 (15)	0.15210 (12)	0.30644 (15)	0.0531 (3)
N1	0.81967 (18)	0.00553 (15)	0.31535 (18)	0.0524 (4)
C1	0.15364 (19)	0.66179 (14)	0.44739 (18)	0.0412 (4)
C2	0.17900 (17)	0.57714 (13)	0.35873 (17)	0.0372 (3)
C3	0.11041 (16)	0.47705 (12)	0.36244 (15)	0.0303 (3)
C4	0.01221 (15)	0.45644 (11)	0.45502 (14)	0.0281 (3)
C5	-0.06208 (18)	0.35437 (13)	0.46205 (17)	0.0370 (3)
C6	0.8891 (3)	0.0471 (3)	0.2058 (3)	0.0823 (8)
C7	0.8689 (3)	-0.1014 (2)	0.3770 (4)	0.0849 (9)
C8	0.71438 (19)	0.05935 (16)	0.35600 (19)	0.0449 (4)
H1W1	0.541 (2)	0.1976 (19)	0.382 (2)	0.095*
H1W2	0.3976 (13)	0.240 (2)	0.381 (2)	0.095*
H1W3	0.488 (3)	0.217 (2)	0.5029 (12)	0.095*
H1	0.2002	0.7298	0.4440	0.049*
H2	0.2425	0.5891	0.2974	0.045*
H5	-0.0477	0.2975	0.4035	0.044*
H6A	0.8338	0.1092	0.1642	0.124*
H6B	0.8904	-0.0101	0.1398	0.124*
H6C	0.9889	0.0697	0.2410	0.124*
H7A	0.8227	-0.1140	0.4542	0.127*
H7B	0.9747	-0.1007	0.4046	0.127*
H7C	0.8416	-0.1594	0.3122	0.127*
H8	0.6705	0.0291	0.4244	0.054*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0351 (2)	0.0426 (2)	0.0311 (2)	0.00923 (15)	0.00916 (15)	-0.00635 (14)
O1	0.0612 (8)	0.0647 (9)	0.0484 (8)	0.0068 (7)	0.0323 (7)	-0.0054 (6)
O2	0.0529 (7)	0.0447 (7)	0.0542 (8)	0.0184 (6)	0.0152 (6)	-0.0013 (6)
O3	0.0469 (7)	0.0770 (10)	0.0439 (7)	0.0083 (6)	-0.0001 (6)	-0.0233 (7)
O4	0.0497 (7)	0.0587 (8)	0.0514 (8)	0.0014 (6)	0.0103 (6)	0.0054 (6)
O1W	0.0504 (8)	0.0906 (12)	0.0490 (8)	0.0208 (8)	0.0098 (7)	0.0155 (8)
N1	0.0415 (8)	0.0559 (9)	0.0592 (10)	-0.0036 (7)	0.0070 (7)	-0.0140 (7)
C1	0.0445 (9)	0.0331 (8)	0.0490 (10)	-0.0095 (6)	0.0163 (7)	-0.0006 (7)
C2	0.0359 (8)	0.0410 (8)	0.0378 (8)	-0.0016 (6)	0.0146 (6)	0.0028 (6)
C3	0.0307 (7)	0.0328 (7)	0.0282 (7)	0.0051 (5)	0.0078 (5)	-0.0014 (5)
C4	0.0285 (7)	0.0289 (7)	0.0271 (7)	0.0028 (5)	0.0058 (5)	-0.0010 (5)
C5	0.0425 (8)	0.0306 (7)	0.0396 (8)	-0.0032 (6)	0.0120 (7)	-0.0056 (6)
C6	0.0629 (15)	0.111 (2)	0.0812 (18)	0.0022 (14)	0.0341 (13)	-0.0110 (16)

C7	0.0726 (16)	0.0561 (14)	0.124 (3)	0.0080 (12)	0.0114 (16)	-0.0077 (15)
C8	0.0390 (8)	0.0525 (10)	0.0422 (9)	-0.0097 (7)	0.0043 (7)	-0.0069 (7)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—O1	1.4415 (14)	C5—C1 <sup>i</sup>	1.356 (2)
S1—O2	1.4564 (13)	O1W—H1W1	0.87 (2)
S1—O3	1.4579 (14)	O1W—H1W2	0.87 (2)
S1—C3	1.7769 (15)	O1W—H1W3	0.87 (2)
O4—C8	1.270 (2)	C1—H1	0.9300
N1—C8	1.288 (2)	C2—H2	0.9300
N1—C6	1.455 (3)	C5—H5	0.9300
N1—C7	1.471 (3)	C6—H6A	0.9600
C1—C5 <sup>i</sup>	1.356 (2)	C6—H6B	0.9600
C1—C2	1.404 (2)	C6—H6C	0.9600
C2—C3	1.368 (2)	C7—H7A	0.9600
C3—C4	1.425 (2)	C7—H7B	0.9600
C4—C5	1.418 (2)	C7—H7C	0.9600
C4—C4 <sup>i</sup>	1.432 (3)	C8—H8	0.9300
O1—S1—C3	106.86 (8)	N1—C6—H6B	109.5
O1—S1—O2	113.17 (8)	N1—C6—H6C	109.5
O1—S1—O3	113.16 (9)	N1—C7—H7A	109.5
O2—S1—C3	106.59 (7)	N1—C7—H7B	109.5
O2—S1—O3	111.05 (9)	N1—C7—H7C	109.5
O3—S1—C3	105.39 (7)	N1—C8—H8	118.7
O4—C8—N1	122.66 (19)	C1—C2—H2	120.0
C1 <sup>i</sup> —C5—C4	121.19 (14)	C1 <sup>i</sup> —C5—H5	119.4
C2—C3—C4	121.22 (13)	C2—C1—H1	119.6
C2—C3—S1	117.84 (11)	C3—C2—H2	120.0
C3—C2—C1	120.06 (14)	C4—C5—H5	119.4
C3—C4—C4 <sup>i</sup>	118.04 (16)	C5 <sup>i</sup> —C1—H1	119.6
C4—C3—S1	120.94 (11)	H1W1—O1W—H1W2	109.1 (14)
C5 <sup>i</sup> —C1—C2	120.79 (15)	H1W1—O1W—H1W3	107.8 (14)
C5—C4—C3	123.25 (13)	H1W2—O1W—H1W3	106.1 (13)
C5—C4—C4 <sup>i</sup>	118.71 (16)	H6A—C6—H6B	109.5
C6—N1—C7	118.7 (2)	H6A—C6—H6C	109.5
C8—N1—C6	121.1 (2)	H6B—C6—H6C	109.5
C8—N1—C7	120.2 (2)	H7A—C7—H7B	109.5
O4—C8—H8	118.7	H7A—C7—H7C	109.5
N1—C6—H6A	109.5	H7B—C7—H7C	109.5
S1—C3—C4—C4 <sup>i</sup>	-179.54 (13)	C1—C2—C3—S1	179.43 (13)
S1—C3—C4—C5	0.4 (2)	C2—C3—C4—C4 <sup>i</sup>	-0.3 (2)
O1—S1—C3—C2	1.65 (15)	C2—C3—C4—C5	179.60 (15)
O1—S1—C3—C4	-179.11 (12)	C3—C4—C5—C1 <sup>i</sup>	179.45 (15)
O2—S1—C3—C2	122.94 (13)	C4 <sup>i</sup> —C4—C5—C1 <sup>i</sup>	-0.6 (3)
O2—S1—C3—C4	-57.83 (14)	C5 <sup>i</sup> —C1—C2—C3	0.4 (3)

O3—S1—C3—C2	−118.98 (14)	C6—N1—C8—O4	−2.0 (3)
O3—S1—C3—C4	60.25 (14)	C7—N1—C8—O4	179.8 (2)
C1—C2—C3—C4	0.2 (2)		

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

*Hydrogen-bond geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
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Symmetry code: (ii)  $x+1/2, -y+1/2, z+1/2$ .