

Diethylenetriammonium oxonium  
naphthalene-1,6-disulfonate 3.5-hydrateZhi-Min Jin,<sup>a\*</sup> Ling He,<sup>b</sup> Li-Zhao  
Chen,<sup>a</sup> Ling-Su Li,<sup>a</sup>  
Zhan-Fei Lai<sup>a</sup> and Li Li<sup>a</sup><sup>a</sup>College of Pharmaceutical Sciences, Zhejiang  
University of Technology, Hangzhou 310014,  
People's Republic of China, and <sup>b</sup>Chemistry  
Department, Zhejiang University, Hangzhou  
310027, People's Republic of China

Correspondence e-mail: zhimin-j@tom.com

## Key indicators

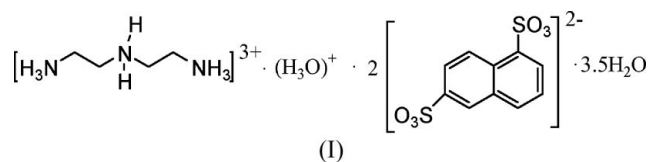
Single-crystal X-ray study  
 $T = 273$  K  
Mean  $\sigma(C-C) = 0.004$  Å  
 $R$  factor = 0.054  
 $wR$  factor = 0.147  
Data-to-parameter ratio = 12.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title complex,  $C_4H_{16}N_3^{3+} \cdot H_3O^+ \cdot 2C_{10}H_6O_6S_2^{2-} \cdot 3.5H_2O$ , comprises one diethylenetriammonium trication, one oxonium cation, two naphthalene-1,6-disulfonate dianions and three-and-a-half water molecules. The oxonium cation donates a proton to each of three acceptors, forming strong hydrogen bonds,  $O-H \cdots O$  [2.476 (4), 2.473 (4) and 2.503 (4) Å].  $O-H \cdots O$  and  $N-H \cdots O$  hydrogen bonds link the title complex into layers parallel to the (010) plane.

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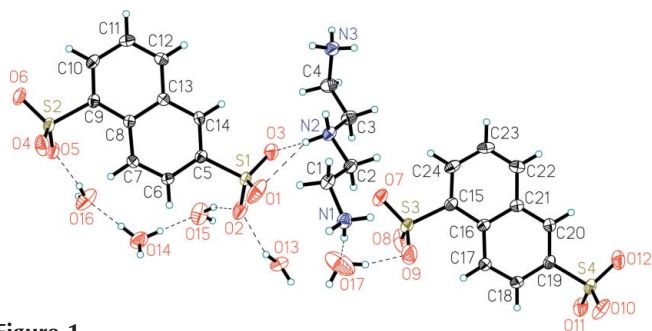
## Comment

Organosulfonates are widely used industrially as surfactants and dyes. Recently, they have been studied as potential liquid crystalline (Huo *et al.*, 1994) and non-linear optical materials (Marder *et al.*, 1994; Russell *et al.*, 1994), and as complexing agents in the form of sulfonated macrocycles (Steed *et al.*, 1995). So far, many crystallographic studies on naphthalene-sulfonate complexes have been reported (Gunderman *et al.*, 1997; Alvarez *et al.*, 1998; Cai, Chen, Feng *et al.*, 2001; Cai, Chen, Liao *et al.*, 2001; Chen *et al.*, 2002, 2004; Chandrasekhar *et al.*, 2003; Sharma *et al.*, 2005), but few investigations into complexes with naphthalene-1,6-disulfonate (1,6-NDS) and organic amines (Shan *et al.*, 2005) have been performed. The title complex, (I), has now been synthesized and the structure is discussed here.



The title complex consists of one diethylenetriammonium trication, one oxonium ion, two 1,6-NDS dianions and three-and-a-half water molecules (Fig. 1). The S—O distances, ranging from 1.422 (3) to 1.453 (2) Å, are slightly shorter than those of previously reported examples of sulfonates (Gunderman *et al.*, 1997; Chen *et al.*, 2004; Shan *et al.*, 2005). The diethylenetriammonium trication, in which all three N atoms are protonated, is linked to one water molecule and one 1,6-NDS dianion by  $N-H \cdots O$  hydrogen bonds (Table 2). This water molecule is linked to another 1,6-NDS dianion by an  $O-H \cdots O$  hydrogen bond.

Oxonium cations are often observed in sulfonates (Arora & Sundaralingam, 1971; Finholt & Williams, 1973; Hanson, 1987; Lundgren, 1979; Sartori *et al.*, 1994). In (I), the oxonium cation is involved in  $O-H \cdots O$  hydrogen bonds, in which two water molecules (O15 and O16) are further connected to two 1,6-NDS dianions *via* two more  $O-H \cdots O$  hydrogen bonds. This is similar to a previous case (Hanson, 1987), in which two



**Figure 1**  
The asymmetric unit of (I), showing the atom labels and 40% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

sulfonate groups were linked through water molecules and an oxonium ion. Some of the hydrogen bonds listed in Table 2 link the complex into layers parallel to the (010) plane (Fig. 2).

### Experimental

Diethylenetriamine and naphthalene-1,6-disulfonic acid (molar ratio 1:2) were mixed and dissolved in sufficient water by heating to 353 K whereupon a clear solution resulted. Crystals of (I) were formed by gradual evaporation of water at 293 K over a period of two weeks.

#### Crystal data

$C_4H_{16}N_3^{3+} \cdot H_3O^{+} \cdot 2C_{10}H_6O_6S_2^{2-} \cdot 3.5H_2O$   
 $M_r = 760.85$   
 Monoclinic,  $C2/c$   
 $a = 25.392$  (2) Å  
 $b = 13.1747$  (11) Å  
 $c = 19.5144$  (16) Å  
 $\beta = 96.011$  (2)°  
 $V = 6492.2$  (9) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.557$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1109 reflections  
 $\theta = 2.2$ – $18.1$ °  
 $\mu = 0.37$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 Block, colourless  
 $0.38 \times 0.32 \times 0.29$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{min} = 0.868$ ,  $T_{max} = 0.898$   
 16963 measured reflections

5848 independent reflections  
 4933 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.023$   
 $\theta_{max} = 25.2$ °  
 $h = -17 \rightarrow 30$   
 $k = -15 \rightarrow 15$   
 $l = -23 \rightarrow 23$

#### Refinement

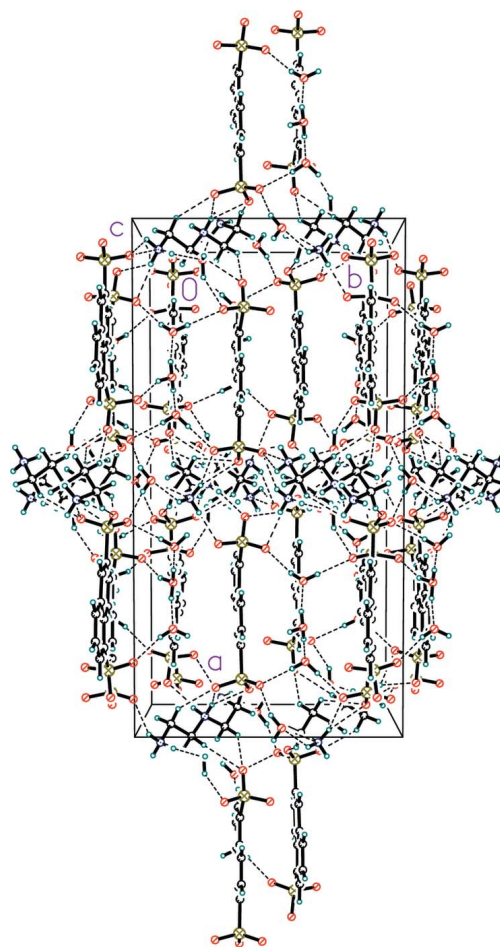
Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.147$   
 $S = 1.05$   
 5848 reflections  
 464 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 13.0061P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.81$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.56$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|          |             |          |             |
|----------|-------------|----------|-------------|
| S1—O3    | 1.422 (3)   | N1—C1    | 1.474 (4)   |
| S1—O2    | 1.431 (2)   | N2—C2    | 1.483 (4)   |
| S1—O1    | 1.445 (3)   | N2—C3    | 1.493 (4)   |
| S1—C5    | 1.768 (3)   | N3—C4    | 1.491 (4)   |
| O3—S1—O2 | 114.2 (2)   | O2—S1—C5 | 106.36 (13) |
| O3—S1—O1 | 110.8 (2)   | O1—S1—C5 | 106.75 (14) |
| O2—S1—O1 | 110.76 (18) | C2—N2—C3 | 114.0 (2)   |
| O3—S1—C5 | 107.56 (14) |          |             |



**Figure 2**  
The packing of (I), viewed along the  $c$  axis. Hydrogen bonds are shown as dashed lines.

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                        | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------------------------|----------|--------------|--------------|----------------|
| N1—H1A $\cdots$ O17                   | 0.89     | 1.83         | 2.706 (5)    | 170            |
| N1—H1B $\cdots$ O11 <sup>i</sup>      | 0.89     | 2.39         | 2.923 (3)    | 119            |
| N1—H1B $\cdots$ O11 <sup>ii</sup>     | 0.89     | 2.21         | 3.025 (4)    | 152            |
| N1—H1C $\cdots$ O5 <sup>iii</sup>     | 0.89     | 2.07         | 2.946 (3)    | 166            |
| N1—H1C $\cdots$ O6 <sup>iii</sup>     | 0.89     | 2.57         | 3.240 (3)    | 132            |
| N2—H2A $\cdots$ O6 <sup>iv</sup>      | 0.90     | 1.94         | 2.774 (4)    | 154            |
| N2—H2B $\cdots$ O1                    | 0.90     | 2.42         | 3.222 (4)    | 149            |
| N2—H2B $\cdots$ O3                    | 0.90     | 2.22         | 2.988 (4)    | 143            |
| N3—H3A $\cdots$ O4 <sup>iv</sup>      | 0.89     | 1.95         | 2.844 (4)    | 179            |
| N3—H3B $\cdots$ O13 <sup>v</sup>      | 0.89     | 2.19         | 2.917 (4)    | 138            |
| N3—H3C $\cdots$ O12 <sup>vi</sup>     | 0.89     | 2.43         | 3.204 (4)    | 145            |
| N3—H3C $\cdots$ O10 <sup>vi</sup>     | 0.89     | 2.25         | 3.071 (4)    | 154            |
| O13—H13A $\cdots$ O2                  | 0.85     | 2.00 (2)     | 2.768 (4)    | 149            |
| O13—H13B $\cdots$ O2 <sup>ii</sup>    | 0.85 (6) | 1.93 (1)     | 2.768 (3)    | 170            |
| O14—H14A $\cdots$ O16                 | 0.85 (2) | 1.64 (2)     | 2.476 (4)    | 172 (3)        |
| O14—H14B $\cdots$ O8 <sup>vii</sup>   | 0.84 (3) | 1.70 (3)     | 2.503 (4)    | 158            |
| O14—H14C $\cdots$ O15                 | 0.85 (2) | 1.62 (2)     | 2.473 (4)    | 180            |
| O15—H15A $\cdots$ O10 <sup>viii</sup> | 0.85 (2) | 1.84 (3)     | 2.687 (4)    | 180            |
| O15—H15B $\cdots$ O2                  | 0.85 (2) | 1.90 (3)     | 2.704 (4)    | 158 (3)        |
| O16—H16A $\cdots$ O9 <sup>viii</sup>  | 0.80 (2) | 2.02 (2)     | 2.813 (5)    | 175            |
| O16—H16B $\cdots$ O5                  | 0.82 (2) | 2.01 (3)     | 2.820 (4)    | 170 (3)        |
| O17—H17A $\cdots$ O9                  | 0.89 (3) | 2.05 (3)     | 2.856 (5)    | 150 (3)        |
| O17—H17B $\cdots$ O1 <sup>vii</sup>   | 0.80 (2) | 2.08 (2)     | 2.821 (5)    | 156            |

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

H atoms of water molecules and oxonium ions were located in difference Fourier maps, and incorporated in the refinement with O—H and H···H distances restrained to 0.82 (2) and 1.39 (1) Å, respectively. Other H atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.89 (NH<sub>3</sub>), 0.90 (NH<sub>2</sub>) and 0.97 Å (methylene), with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent atom})$ .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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