

# Synthesis and crystal structure of ((*E*)-{2-[(*E*)-(4-hydroxynaphthalen-1-yl)methylidene]hydrazin-1-yl}(methylsulfanyl)methylidene)azanum hydrogen sulfate monohydrate

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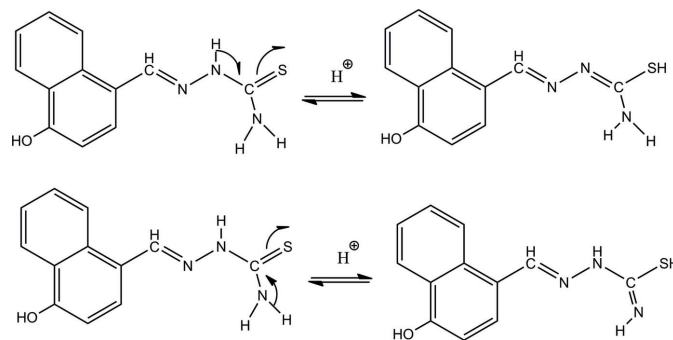
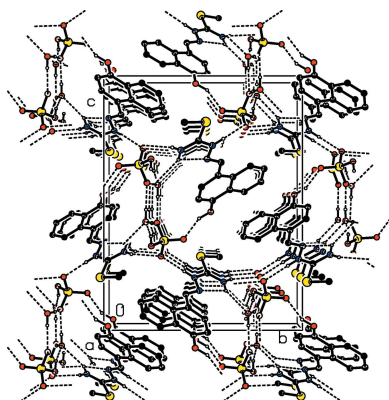
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In the title hydrated molecular salt,  $C_{13}H_{14}N_3S^+ \cdot HSO_4^- \cdot H_2O$ , the protonation of the azomethine N atom in sulfuric acid medium involves the formation of the bisulfate anion. The molecular structure of the cation is obtained from the thiol tautomer of thiosemicarbazone wherein the naphthalene moiety and the conjugation of the bonds contribute to the planarity of the molecular skeleton. In the crystal, the cation, anion and water molecule of crystallization are linked by a series of  $O-H \cdots O$  and  $N-H \cdots O$  hydrogen bonds, forming a three-dimensional network. Within this network, there are also  $C-H \cdots \pi$  interactions present involving symmetry-related naphthalene rings.

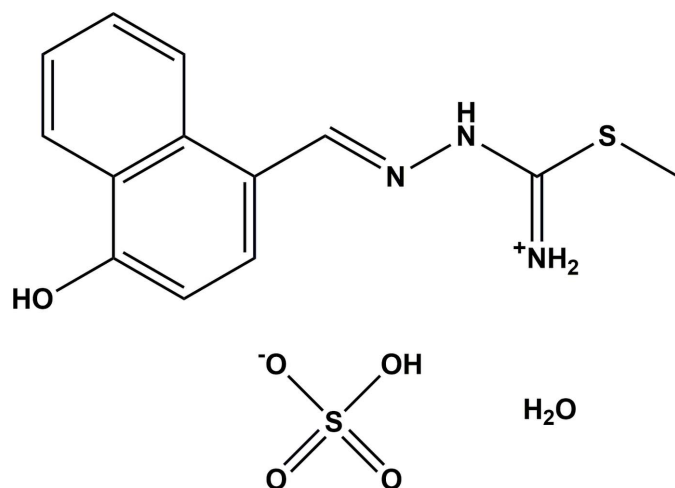
## 1. Chemical context

Thiosemicarbazones and their metal complexes have been widely explored because of their pharmaceutical properties (Klayman *et al.*, 1983). These compounds present a wide variety of biological activities, such as antitumoral, fungicidal and antiviral (Tarasconi *et al.*, 2000), and bactericidal (Abram *et al.*, 1998). The ability of thiosemicarbazone molecules to chelate with traces of metals in biological systems is believed to be a reason for their activity (Teoh *et al.*, 1999). The nature of the aldehyde and ketone from which the thiosemicarbazone is obtained and the nature of the substituents attached at the  $^+NH_2$  N atom influence the biological activity (Beraldo & Gambinob, 2004). Thiosemicarbazones can exist as *E* and *Z* isomers and they exhibit thione–thiol tautomerism, as illustrated for the title compound in Fig. 1. Complexation usually



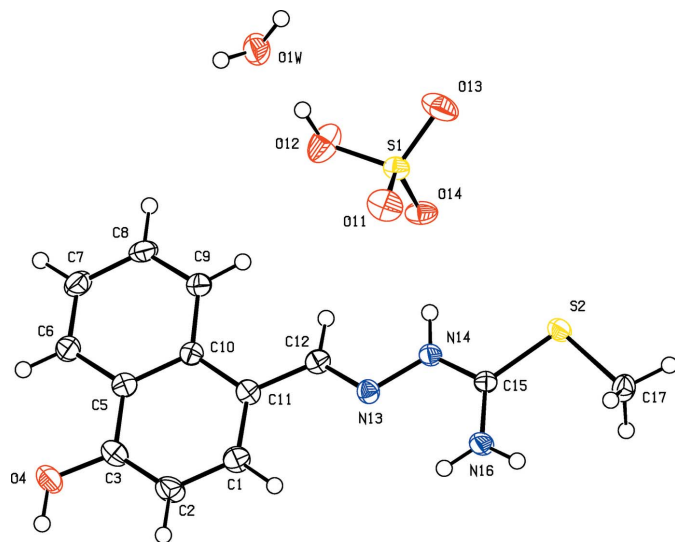
**Figure 1**  
Thiosemicarbazones can exist as *E* and *Z* isomers and they exhibit thione–thiol tautomerism.

takes place *via* dissociation of the acidic proton, resulting in the formation of a five-membered chelate ring (Pal *et al.*, 2002). The crystal structure of the title compound was determined in order to investigate the extent of electron delocalization, the ligand conformation and to explore its biological implications.



## 2. Structural commentary

The molecular structure of the title molecular salt is illustrated in Fig. 2. It is composed of three entities: a bisulfate anion, a thiosemicarbazone cation and a water molecule of crystallization. The cationic entity shows an *E* conformation with respect to the C12=N13 bond and is approximately planar, the maximum deviation from the mean plane through the 18 non-hydrogen atoms being 0.118 (2) Å for atom C12. This planarity is due to electron delocalization along the cationic entity backbone. Bond lengths and angles are close to those



**Figure 2**

A view of the molecular structure of the title molecular salt, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

**Table 1**

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of rings C1–C3/C5/C10/C11 and C5–C10, respectively.

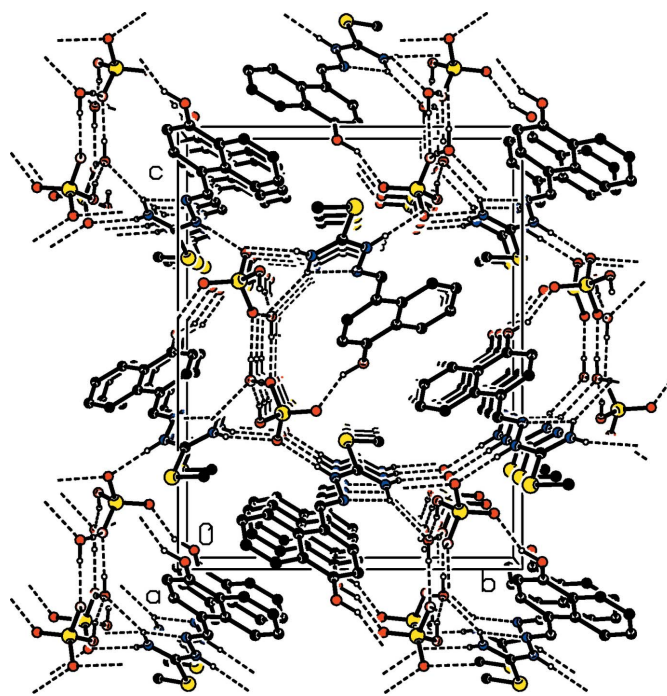
| <i>D</i> —H... <i>A</i>      | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| O1W—H1WA...O13 <sup>i</sup>  | 0.89 (3)    | 1.96 (3)      | 2.791 (4)             | 155 (5)                 |
| O1W—H1WB...O13 <sup>ii</sup> | 0.86 (2)    | 1.88 (3)      | 2.732 (3)             | 172 (5)                 |
| O4—H4O...O11 <sup>iii</sup>  | 0.96 (6)    | 1.84 (6)      | 2.719 (3)             | 153 (6)                 |
| O12—H12O...O1W               | 0.94 (5)    | 1.61 (5)      | 2.543 (4)             | 168 (5)                 |
| N14—H14...O14                | 0.86 (2)    | 2.00 (2)      | 2.860 (3)             | 176 (4)                 |
| N16—H16A...O1W <sup>iv</sup> | 0.86 (2)    | 2.32 (3)      | 3.046 (4)             | 142 (4)                 |
| N16—H16B...O14 <sup>v</sup>  | 0.84 (2)    | 2.20 (3)      | 2.937 (3)             | 147 (4)                 |
| C6—H6...Cg2 <sup>vi</sup>    | 0.95        | 2.67          | 3.451 (3)             | 140                     |
| C7—H7...Cg1 <sup>vi</sup>    | 0.95        | 2.94          | 3.622 (3)             | 130                     |

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

observed for similar (methylidene)hydrazinecarbothioamide derivatives (Gangadharan *et al.*, 2015; Joseph *et al.*, 2004; Houari *et al.*, 2013.)

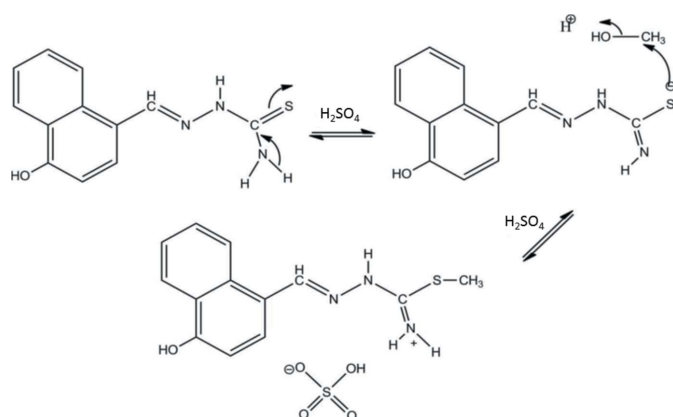
## 3. Supramolecular features

In the crystal, there is an extensive hydrogen-bonding network present. The cation, anion and water molecule of crystallization are linked by a series of O—H...O and N—H...O hydrogen bonds, forming a three-dimensional network (Table 1 and Fig. 3). Within this network there are also C—H... $\pi$  interactions present involving symmetry-related naphthalene rings (Table 1).



**Figure 3**

A view along the *a* axis of the crystal packing of the title molecular salt. The hydrogen bonds are drawn as dashed lines (see Table 1) and the C-bound H atoms have been omitted for clarity.



**Figure 4**  
The synthesis of the title molecular salt.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.37, update May 2016; Groom *et al.*, 2016) for the S-methyl (methylidene)thiosemicarbazidium cation substructure gave two hits, *viz.* S-methyl-*N'*-(pyrrolyl-2'-methylene)isothiosemicarbazidium iodide monohydrate (JIHZUV; Bourosh *et al.*, 1990) and 8-quinolinealdehyde S-methylthiosemicarbazone hydrochloride dihydrate (RUJXOK; Botoshansky *et al.*, 2009). Only the coordinates for the latter structure were available. The cation in RUJXOK, is relatively planar and the bond lengths and angles in the S-methyl (methylidene)thiosemicarbazidium moiety are similar to those observed for the title compound.

#### 5. Synthesis and crystallization

The synthesis of the title molecular salt is illustrated in Fig. 4. An equimolar amount of thiosemicarbazide 10 mmol (0.91 g) and 3-hydroxy-2-naphthaldehyde 10 mmol (1.72 g) were dissolved in a mixture of methanol and water (30 ml, 50%) and refluxed for 5 h in the presence of a catalytic amount of glacial sulfuric acid. Brown crystals suitable for X-ray diffraction analysis were obtained after slow evaporation of the solution.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy H atom was located in a difference Fourier map and freely refined. The water and N-bound H atoms were located in difference Fourier maps and refined with distance restraints O–H = 0.84 (2) Å and N–H = 0.88 (2) Å. The C-bound H atoms were included in calculated positions and treated as riding atoms, with C–H = 0.95–0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  otherwise.

**Table 2**  
Experimental details.

|  |  |
|--|--|
| Crystal data   |  |
| Chemical formula   | $\text{C}_{13}\text{H}_{14}\text{N}_3\text{OS}^+\cdot\text{HO}_4\text{S}^-\cdot\text{H}_2\text{O}$           |
| $M_r$  | 375.41   |
| Crystal system, space group  | Orthorhombic, $P2_12_12_1$   |
| Temperature (K)  | 150  |
| $a, b, c$ (Å)  | 6.3726 (5), 14.2549 (11),<br>18.2817 (12)  |
| $V$ (Å <sup>3</sup> )  | 1660.7 (2)   |
| $Z$  | 4  |
| Radiation type   | Mo $K\alpha$   |
| $\mu$ (mm <sup>-1</sup> )  | 0.36   |
| Crystal size (mm)  | 0.42 × 0.33 × 0.19   |
| Data collection  |  |
| Diffractometer   | Bruker D8 VENTURE  |
| Absorption correction  | Multi-scan (SADABS; Bruker, 2015)  |
| $T_{\text{min}}, T_{\text{max}}$   | 0.752, 0.935   |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections | 19123, 3786, 3586  |
| $R_{\text{int}}$   | 0.073  |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )                    | 0.649  |
| Refinement   |  |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$  | 0.039, 0.103, 1.07   |
| No. of reflections   | 3786   |
| No. of parameters  | 247  |
| No. of restraints  | 5  |
| H-atom treatment   | H atoms treated by a mixture of independent and constrained refinement                                       |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )    | 0.36, -0.33  |
| Absolute structure   | Flack $x$ determined using 1477 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013) |
| Absolute structure parameter   | 0.03 (5)   |

Computer programs: APEX3 and SAINT (Bruker, 2015), SIR97 (Altomare *et al.*, 1999), SHELXL2014 (Sheldrick, 2015) and PLATON (Spek, 2009).

#### Acknowledgements

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## supporting information

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## Synthesis and crystal structure of ((*E*)-{2-[(*E*)-(4-hydroxynaphthalen-1-yl)methylidene]hydrazin-1-yl}(methylsulfonyl)methylidene)azanum hydrogen sulfate monohydrate

**Oussama Nehar, Samira Louhibi, Leila Boukli-Hacene and Thierry Roisnel**

### Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *S SAINT* (Bruker, 2015); data reduction: *S SAINT* (Bruker, 2015); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

((*E*)-{2-[(*E*)-(4-Hydroxynaphthalen-1-yl)methylidene]hydrazin-1-yl}(methylsulfonyl)methylidene)azanum hydrogen sulfate monohydrate

### Crystal data

$C_{13}H_{14}N_3OS^+ \cdot HO_4S^- \cdot H_2O$

$M_r = 375.41$

Orthorhombic,  $P2_12_12_1$

$a = 6.3726$  (5) Å

$b = 14.2549$  (11) Å

$c = 18.2817$  (12) Å

$V = 1660.7$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 784$

$D_x = 1.501$  Mg m<sup>-3</sup>

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

Cell parameters from 9907 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 0.36$  mm<sup>-1</sup>

$T = 150$  K

Block, brown

$0.42 \times 0.33 \times 0.19$  mm

### Data collection

Bruker D8 VENTURE  
diffractometer

Multilayer monochromator  
rotation images scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2015)

$T_{\min} = 0.752$ ,  $T_{\max} = 0.935$

19123 measured reflections

3786 independent reflections

3586 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.073$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.4^\circ$

$h = -8 \rightarrow 8$

$k = -18 \rightarrow 18$

$l = -23 \rightarrow 23$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.103$

$S = 1.07$

3786 reflections

247 parameters

5 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.4752P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2014

(Sheldrick, 2015),

$$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.027 (5)

Absolute structure: Flack  $x$  determined using

1477 quotients  $[(I^+)-(I^-)]/[(I^+)+(I^-)]$  (Parsons *et al.*, 2013)

Absolute structure parameter: 0.03 (5)

### Special details

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

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

|      | $x$          | $y$          | $z$           | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|---------------|----------------------------------|
| S1   | 0.33252 (11) | 0.30710 (5)  | 0.35547 (4)   | 0.0214 (2)                       |
| C1   | 0.6277 (5)   | 0.5080 (2)   | 0.06062 (17)  | 0.0274 (6)                       |
| H1   | 0.5211       | 0.5545       | 0.0624        | 0.033*                           |
| C2   | 0.8011 (5)   | 0.5215 (2)   | 0.01485 (18)  | 0.0302 (7)                       |
| H2   | 0.8125       | 0.5775       | -0.0130       | 0.036*                           |
| C3   | 0.9553 (5)   | 0.4542 (2)   | 0.00993 (16)  | 0.0244 (6)                       |
| O4   | 1.1258 (4)   | 0.46247 (17) | -0.03340 (14) | 0.0334 (6)                       |
| H4O  | 1.141 (10)   | 0.520 (5)    | -0.059 (3)    | 0.09 (2)*                        |
| C5   | 0.9393 (5)   | 0.3697 (2)   | 0.05103 (15)  | 0.0210 (6)                       |
| C6   | 1.0925 (5)   | 0.2980 (2)   | 0.04354 (16)  | 0.0256 (6)                       |
| H6   | 1.2085       | 0.3069       | 0.0117        | 0.031*                           |
| C7   | 1.0739 (5)   | 0.2162 (2)   | 0.08197 (17)  | 0.0308 (7)                       |
| H7   | 1.1746       | 0.1678       | 0.0755        | 0.037*                           |
| C8   | 0.9071 (6)   | 0.2033 (2)   | 0.13084 (17)  | 0.0299 (7)                       |
| H8   | 0.8977       | 0.1467       | 0.1581        | 0.036*                           |
| C9   | 0.7567 (5)   | 0.2716 (2)   | 0.13989 (16)  | 0.0246 (6)                       |
| H9   | 0.6458       | 0.2620       | 0.1738        | 0.029*                           |
| C10  | 0.7656 (4)   | 0.3566 (2)   | 0.09897 (14)  | 0.0192 (5)                       |
| C11  | 0.6085 (5)   | 0.4279 (2)   | 0.10353 (16)  | 0.0215 (6)                       |
| C12  | 0.4268 (5)   | 0.4151 (2)   | 0.15100 (15)  | 0.0220 (6)                       |
| H12A | 0.4066       | 0.3563       | 0.1744        | 0.026*                           |
| N13  | 0.2939 (4)   | 0.48088 (17) | 0.16192 (12)  | 0.0205 (5)                       |
| N14  | 0.1329 (4)   | 0.45700 (16) | 0.20919 (13)  | 0.0202 (5)                       |
| H14  | 0.144 (7)    | 0.406 (2)    | 0.234 (2)     | 0.040 (11)*                      |
| C15  | -0.0120 (4)  | 0.5212 (2)   | 0.22410 (14)  | 0.0182 (5)                       |
| N16  | -0.0075 (4)  | 0.60276 (18) | 0.19085 (14)  | 0.0249 (5)                       |
| H16B | -0.103 (5)   | 0.641 (2)    | 0.199 (2)     | 0.032 (10)*                      |
| H16A | 0.084 (5)    | 0.614 (3)    | 0.1575 (18)   | 0.036 (11)*                      |
| C17  | -0.3802 (5)  | 0.5843 (2)   | 0.28398 (18)  | 0.0253 (6)                       |
| H17A | -0.4311      | 0.5911       | 0.2337        | 0.038*                           |
| H17B | -0.3101      | 0.6423       | 0.2992        | 0.038*                           |

|      |               |              |              |             |
|------|---------------|--------------|--------------|-------------|
| H17C | -0.4990       | 0.5718       | 0.3166       | 0.038*      |
| S2   | -0.19735 (11) | 0.48825 (5)  | 0.28856 (4)  | 0.0245 (2)  |
| O11  | 0.3992 (4)    | 0.40352 (16) | 0.36112 (13) | 0.0348 (6)  |
| O12  | 0.5287 (4)    | 0.2471 (2)   | 0.33653 (15) | 0.0442 (7)  |
| H12O | 0.631 (8)     | 0.246 (4)    | 0.374 (3)    | 0.059 (14)* |
| O13  | 0.2455 (5)    | 0.2712 (2)   | 0.42322 (13) | 0.0433 (7)  |
| O14  | 0.1937 (4)    | 0.29015 (14) | 0.29348 (11) | 0.0278 (5)  |
| O1W  | 0.8206 (4)    | 0.2244 (2)   | 0.42969 (13) | 0.0385 (6)  |
| H1WA | 0.939 (6)     | 0.256 (4)    | 0.426 (3)    | 0.060 (16)* |
| H1WB | 0.784 (8)     | 0.225 (3)    | 0.4750 (15)  | 0.061 (15)* |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| S1  | 0.0240 (3)  | 0.0184 (3)  | 0.0220 (3)  | -0.0050 (3)  | -0.0028 (3)  | 0.0010 (2)   |
| C1  | 0.0309 (15) | 0.0164 (14) | 0.0349 (15) | 0.0031 (12)  | 0.0053 (12)  | 0.0021 (11)  |
| C2  | 0.0386 (17) | 0.0186 (13) | 0.0333 (15) | 0.0000 (14)  | 0.0083 (14)  | 0.0045 (12)  |
| C3  | 0.0286 (15) | 0.0232 (14) | 0.0215 (13) | -0.0062 (11) | 0.0019 (12)  | -0.0019 (11) |
| O4  | 0.0336 (13) | 0.0323 (13) | 0.0344 (12) | 0.0011 (10)  | 0.0136 (10)  | 0.0079 (10)  |
| C5  | 0.0226 (14) | 0.0217 (14) | 0.0186 (12) | -0.0016 (11) | -0.0032 (11) | -0.0032 (10) |
| C6  | 0.0250 (14) | 0.0321 (17) | 0.0196 (13) | 0.0047 (13)  | 0.0002 (11)  | -0.0013 (12) |
| C7  | 0.0324 (17) | 0.0351 (18) | 0.0248 (14) | 0.0145 (14)  | 0.0001 (13)  | 0.0014 (13)  |
| C8  | 0.0347 (16) | 0.0299 (16) | 0.0253 (14) | 0.0108 (14)  | 0.0001 (13)  | 0.0084 (12)  |
| C9  | 0.0254 (14) | 0.0265 (14) | 0.0218 (13) | 0.0037 (11)  | 0.0008 (11)  | 0.0031 (11)  |
| C10 | 0.0202 (13) | 0.0207 (13) | 0.0166 (12) | -0.0004 (10) | -0.0020 (10) | -0.0027 (10) |
| C11 | 0.0244 (14) | 0.0176 (13) | 0.0226 (13) | -0.0011 (11) | 0.0024 (11)  | -0.0026 (10) |
| C12 | 0.0234 (14) | 0.0192 (13) | 0.0233 (13) | -0.0003 (11) | -0.0012 (11) | -0.0009 (11) |
| N13 | 0.0204 (11) | 0.0196 (11) | 0.0215 (11) | 0.0001 (10)  | 0.0021 (9)   | -0.0011 (9)  |
| N14 | 0.0212 (11) | 0.0160 (11) | 0.0233 (11) | 0.0010 (8)   | 0.0028 (10)  | 0.0028 (9)   |
| C15 | 0.0198 (12) | 0.0182 (12) | 0.0166 (11) | -0.0002 (10) | -0.0008 (9)  | -0.0006 (10) |
| N16 | 0.0287 (13) | 0.0187 (12) | 0.0273 (12) | 0.0058 (10)  | 0.0084 (11)  | 0.0056 (10)  |
| C17 | 0.0218 (13) | 0.0214 (13) | 0.0326 (15) | 0.0023 (11)  | 0.0030 (12)  | -0.0007 (12) |
| S2  | 0.0264 (4)  | 0.0209 (3)  | 0.0263 (3)  | 0.0027 (3)   | 0.0080 (3)   | 0.0056 (3)   |
| O11 | 0.0456 (14) | 0.0215 (11) | 0.0372 (12) | -0.0120 (10) | -0.0030 (11) | -0.0060 (10) |
| O12 | 0.0395 (14) | 0.0493 (17) | 0.0437 (14) | 0.0146 (13)  | -0.0118 (12) | -0.0185 (13) |
| O13 | 0.0443 (15) | 0.0602 (17) | 0.0254 (11) | -0.0204 (13) | -0.0057 (10) | 0.0137 (11)  |
| O14 | 0.0353 (12) | 0.0209 (10) | 0.0271 (10) | -0.0059 (9)  | -0.0089 (10) | 0.0040 (8)   |
| O1W | 0.0277 (12) | 0.0604 (17) | 0.0274 (11) | 0.0027 (12)  | 0.0015 (10)  | 0.0012 (11)  |

*Geometric parameters (Å, °)*

|        |           |          |           |
|--------|-----------|----------|-----------|
| S1—O11 | 1.442 (2) | C9—C10   | 1.425 (4) |
| S1—O13 | 1.450 (2) | C9—H9    | 0.9500    |
| S1—O14 | 1.458 (2) | C10—C11  | 1.429 (4) |
| S1—O12 | 1.554 (3) | C11—C12  | 1.459 (4) |
| C1—C11 | 1.391 (4) | C12—N13  | 1.279 (4) |
| C1—C2  | 1.399 (4) | C12—H12A | 0.9500    |
| C1—H1  | 0.9500    | N13—N14  | 1.384 (3) |

|              |             |               |             |
|--------------|-------------|---------------|-------------|
| C2—C3        | 1.375 (4)   | N14—C15       | 1.328 (4)   |
| C2—H2        | 0.9500      | N14—H14       | 0.86 (2)    |
| C3—O4        | 1.350 (4)   | C15—N16       | 1.313 (4)   |
| C3—C5        | 1.424 (4)   | C15—S2        | 1.733 (3)   |
| O4—H4O       | 0.96 (6)    | N16—H16B      | 0.84 (2)    |
| C5—C6        | 1.420 (4)   | N16—H16A      | 0.86 (2)    |
| C5—C10       | 1.424 (4)   | C17—S2        | 1.800 (3)   |
| C6—C7        | 1.366 (5)   | C17—H17A      | 0.9800      |
| C6—H6        | 0.9500      | C17—H17B      | 0.9800      |
| C7—C8        | 1.400 (5)   | C17—H17C      | 0.9800      |
| C7—H7        | 0.9500      | O12—H12O      | 0.94 (5)    |
| C8—C9        | 1.376 (4)   | O1W—H1WA      | 0.89 (3)    |
| C8—H8        | 0.9500      | O1W—H1WB      | 0.86 (2)    |
| O11—S1—O13   | 112.83 (16) | C10—C9—H9     | 119.6       |
| O11—S1—O14   | 113.10 (14) | C5—C10—C9     | 117.7 (3)   |
| O13—S1—O14   | 111.92 (14) | C5—C10—C11    | 119.2 (3)   |
| O11—S1—O12   | 107.66 (17) | C9—C10—C11    | 123.1 (3)   |
| O13—S1—O12   | 107.67 (18) | C1—C11—C10    | 119.3 (3)   |
| O14—S1—O12   | 102.94 (13) | C1—C11—C12    | 120.5 (3)   |
| C11—C1—C2    | 121.3 (3)   | C10—C11—C12   | 120.1 (3)   |
| C11—C1—H1    | 119.4       | N13—C12—C11   | 121.8 (3)   |
| C2—C1—H1     | 119.4       | N13—C12—H12A  | 119.1       |
| C3—C2—C1     | 120.5 (3)   | C11—C12—H12A  | 119.1       |
| C3—C2—H2     | 119.7       | C12—N13—N14   | 114.1 (2)   |
| C1—C2—H2     | 119.7       | C15—N14—N13   | 118.3 (2)   |
| O4—C3—C2     | 123.5 (3)   | C15—N14—H14   | 122 (3)     |
| O4—C3—C5     | 116.2 (3)   | N13—N14—H14   | 118 (3)     |
| C2—C3—C5     | 120.3 (3)   | N16—C15—N14   | 120.0 (3)   |
| C3—O4—H4O    | 117 (4)     | N16—C15—S2    | 124.7 (2)   |
| C6—C5—C10    | 120.0 (3)   | N14—C15—S2    | 115.3 (2)   |
| C6—C5—C3     | 120.6 (3)   | C15—N16—H16B  | 119 (3)     |
| C10—C5—C3    | 119.4 (3)   | C15—N16—H16A  | 120 (3)     |
| C7—C6—C5     | 120.3 (3)   | H16B—N16—H16A | 120 (4)     |
| C7—C6—H6     | 119.9       | S2—C17—H17A   | 109.5       |
| C5—C6—H6     | 119.9       | S2—C17—H17B   | 109.5       |
| C6—C7—C8     | 120.4 (3)   | H17A—C17—H17B | 109.5       |
| C6—C7—H7     | 119.8       | S2—C17—H17C   | 109.5       |
| C8—C7—H7     | 119.8       | H17A—C17—H17C | 109.5       |
| C9—C8—C7     | 120.8 (3)   | H17B—C17—H17C | 109.5       |
| C9—C8—H8     | 119.6       | C15—S2—C17    | 101.74 (14) |
| C7—C8—H8     | 119.6       | S1—O12—H12O   | 114 (3)     |
| C8—C9—C10    | 120.7 (3)   | H1WA—O1W—H1WB | 108 (5)     |
| C8—C9—H9     | 119.6       |               |             |
| C11—C1—C2—C3 | 1.5 (5)     | C8—C9—C10—C5  | -2.5 (4)    |
| C1—C2—C3—O4  | 179.6 (3)   | C8—C9—C10—C11 | 176.9 (3)   |
| C1—C2—C3—C5  | 0.5 (5)     | C2—C1—C11—C10 | -2.0 (5)    |



|               |            |                 |              |
|---------------|------------|-----------------|--------------|
| O4—C3—C5—C6   | -2.3 (4)   | C2—C1—C11—C12   | 179.9 (3)    |
| C2—C3—C5—C6   | 176.9 (3)  | C5—C10—C11—C1   | 0.6 (4)      |
| O4—C3—C5—C10  | 178.9 (3)  | C9—C10—C11—C1   | -178.9 (3)   |
| C2—C3—C5—C10  | -1.9 (4)   | C5—C10—C11—C12  | 178.6 (3)    |
| C10—C5—C6—C7  | 0.2 (4)    | C9—C10—C11—C12  | -0.8 (4)     |
| C3—C5—C6—C7   | -178.6 (3) | C1—C11—C12—N13  | -8.9 (4)     |
| C5—C6—C7—C8   | -2.0 (5)   | C10—C11—C12—N13 | 173.1 (3)    |
| C6—C7—C8—C9   | 1.5 (5)    | C11—C12—N13—N14 | -179.2 (2)   |
| C7—C8—C9—C10  | 0.9 (5)    | C12—N13—N14—C15 | 179.6 (2)    |
| C6—C5—C10—C9  | 2.0 (4)    | N13—N14—C15—N16 | 4.2 (4)      |
| C3—C5—C10—C9  | -179.2 (3) | N13—N14—C15—S2  | -175.70 (19) |
| C6—C5—C10—C11 | -177.5 (3) | N16—C15—S2—C17  | 7.7 (3)      |
| C3—C5—C10—C11 | 1.4 (4)    | N14—C15—S2—C17  | -172.4 (2)   |

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 and Cg2 are the centroids of rings C1—C3/C5/C10/C11 and C5—C10, respectively.

| $D-H\cdots A$  | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| O1 <i>W</i> —H1 <i>WA</i> $\cdots$ O13 <sup>i</sup>  | 0.89 (3) | 1.96 (3)    | 2.791 (4)   | 155 (5)       |
| O1 <i>W</i> —H1 <i>WB</i> $\cdots$ O13 <sup>ii</sup> | 0.86 (2) | 1.88 (3)    | 2.732 (3)   | 172 (5)       |
| O4—H4 <i>O</i> $\cdots$ O11 <sup>iii</sup>           | 0.96 (6) | 1.84 (6)    | 2.719 (3)   | 153 (6)       |
| O12—H12 <i>O</i> $\cdots$ O1 <i>W</i>                | 0.94 (5) | 1.61 (5)    | 2.543 (4)   | 168 (5)       |
| N14—H14 $\cdots$ O14                                 | 0.86 (2) | 2.00 (2)    | 2.860 (3)   | 176 (4)       |
| N16—H16 <i>A</i> $\cdots$ O1 <i>W</i> <sup>iv</sup>  | 0.86 (2) | 2.32 (3)    | 3.046 (4)   | 142 (4)       |
| N16—H16 <i>B</i> $\cdots$ O14 <sup>v</sup>           | 0.84 (2) | 2.20 (3)    | 2.937 (3)   | 147 (4)       |
| C6—H6 $\cdots$ Cg2 <sup>vi</sup>                     | 0.95     | 2.67        | 3.451 (3)   | 140           |
| C7—H7 $\cdots$ Cg1 <sup>vi</sup>                     | 0.95     | 2.94        | 3.622 (3)   | 130           |

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