

# Crystal structure of 2,4-dinitrophenyl 4-methylbenzenesulfonate: a new polymorph

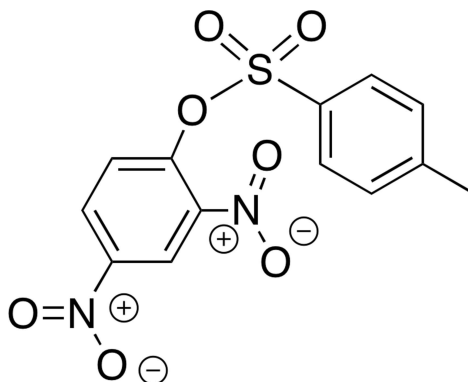
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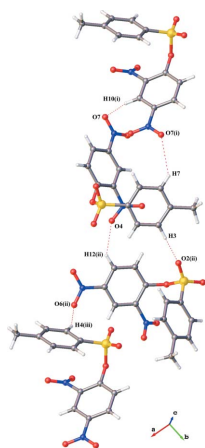
The title compound, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>7</sub>S, was synthesized *via* a nucleophilic substitution reaction between 2,4-dinitrophenol and *p*-toluenesulfonyl chloride. This crystal structure is a polymorph of CSD entry WUVYUH [Vembu *et al.* (2003). *Acta Cryst*, **E59**, o378–380]. The aromatic substituents on the sulfonate group are oriented *gauche* to one another with a C—O—S—C torsion angle of  $-62.0(3)^\circ$ . The supramolecular features that contribute to the crystal stability are offset  $\pi$ - $\pi$  [centroid-centroid distance = 3.729(2) Å] and multiple C—H $\cdots$ O interactions.

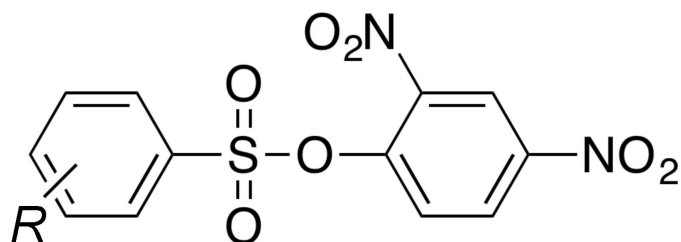
## 1. Chemical context

Nucleophilic substitution reactions at the carbonyl carbon atom are an important class of reactions in biological processes. Analogous to the carbonyl group, nucleophilic substitution reactions of sulfonyl derivatives have also been reported (Castro *et al.*, 2003; Terrier *et al.*, 2003; Um *et al.*, 2004, 2013; Qrareya *et al.*, 2014). The mechanism of nucleophilic substitution reactions at the carbonyl group is well understood (Stefanidis *et al.*, 1993; Lee *et al.*, 2002). However, the mechanism for nucleophilic substitution reactions at the sulfonyl group is not fully understood (Morales-Rojas & Moss, 2002; Um *et al.*, 2013).



A review of the current literature lends credence to both a concerted mechanism and a non-concerted mechanism (Guthrie, 1991; Colthurst & Williams, 1997; Spillane *et al.*, 2001; Um *et al.*, 2003, 2004, 2013). Using primary and secondary amines as nucleophiles, the factors influencing regioselectivity of nucleophilic substitution reactions at the sulfonyl group have been reported (Um *et al.*, 2004). It has been demonstrated that the regioselectivity and S—O bond fission mechanism depends on the basicity of the amine and the electronic nature of the sulfonyl substituent. Based on the





**Figure 1**  
General structure of sulfonate analogues. *R* represents electron-donating and electron-withdrawing substituents.

current state of knowledge in the field, we have sought to capitalize on the chemistry learned on the mechanistic insight of S—O vs C—O bond fission by investigating the effect of different substituents on the reactivity of sulfonates. In our work, we are interested in using various sulfonate analogues (Fig. 1) as electrophilic substrates in nucleophilic aromatic substitution ( $S_NAr$ ) reactions similar to those reported by others (Qrareya *et al.*, 2014). As the title compound is of interest in our ongoing effort on probing the mechanism of  $S_NAr$  reactions with sulfonate derivatives, we report here on the synthesis and crystal structure of a new polymorph of 2,4-dinitrophenyl 4-methylbenzenesulfonate (Fig. 2).

## 2. Structural commentary

The central sulfur atom (S1) is tetrahedral with S=O bond lengths of 1.415 (3) and 1.414 (3) Å, and an S—O bond length of 1.634 (3) Å (Fig. 2*a*). The bond angle between the S=O groups (O1—S1—O2) is 121.20 (17)°, while that of the aromatic substituents (O3—S1—C5) is 103.27 (15)°. The two aromatic rings are in a *gauche* orientation about the O3—S1 bond with a torsion angle (C8—O3—S1—C5) of  $-62.0$  (3)°.

For comparison, the polymorph WUVYUH (Vembu *et al.*, 2003*a*) has S=O bond lengths of 1.4204 (10) and 1.4246 (10) Å, and the S—O bond length is 1.6195 (9) Å (Fig. 2*b*). While the bond lengths of the two polymorphs agree within 0.01 Å of each other, there are some differences between bond angles. The aromatic rings in WUVYUH are in an *anti* orientation along the S—O bond, with a torsion angle of 141.02 (9)°. The bond angle between the S=O groups (O1—S1—O2) is 119.80 (6)°, while that of the aromatic substituents (O3—S1—C5) is 98.17 (5)°.

## 3. Supramolecular features

There are no classical hydrogen-bonding interactions in this crystal. There are, however, several intermolecular C—H...O interactions with  $D\cdots A$  distances less than 3.5 Å and  $D-H\cdots A$  angles greater than 120° (Table 1, Fig. 3). An offset  $\pi$ - $\pi$  stacking interaction is present between the relatively electron-poor ring C8—C13 and the relatively electron-rich ring C2—C7<sup>v</sup> (Fig. 4). The centroid—centroid distance is 3.729 (2) Å, the C2—C7 ring is offset by 1.529 (5) Å and tilted 5.74 (12)° out of the

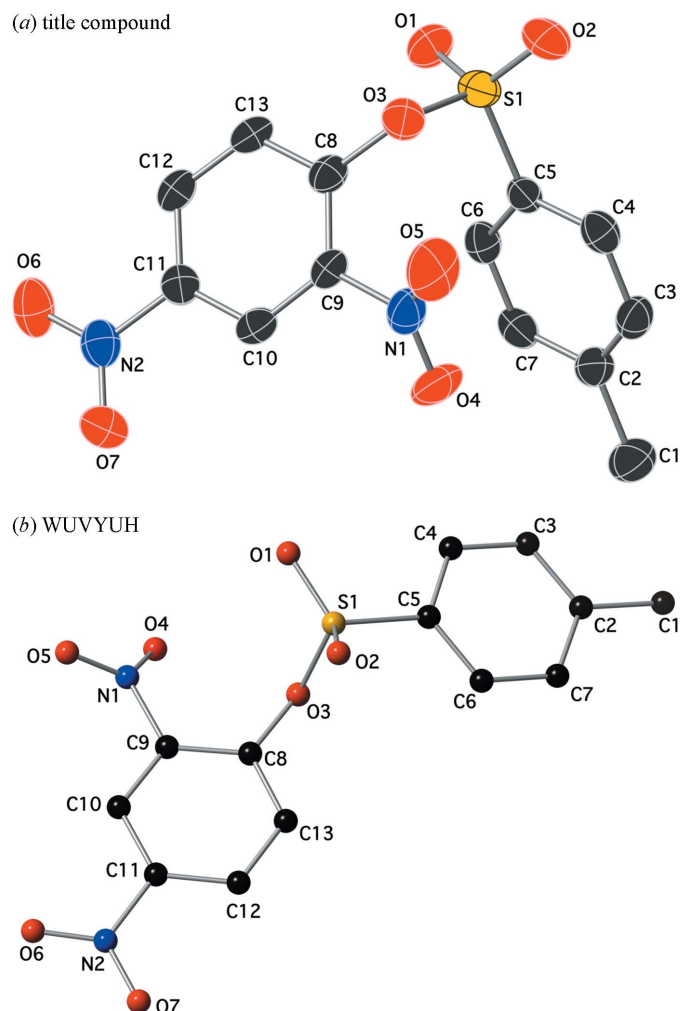
**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3...O2 <sup>i</sup>	0.95	2.42	3.273 (5)	149
C4—H4...O6 <sup>ii</sup>	0.95	2.57	3.486 (5)	162
C7—H7...O7 <sup>iii</sup>	0.95	2.75	3.499 (5)	137
C10—H10...O7 <sup>iv</sup>	0.95	2.51	3.233 (5)	133
C12—H12...O4 <sup>v</sup>	0.95	2.34	3.087 (5)	135

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

plane defined by the C8—C13 ring [symmetry code: (v)  $\frac{3}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$ ].

One nitro group (N2,O6,O7) is in proximity to the sulfonic ester of the C2—C7<sup>v</sup> ring of a nearby  $\pi$ - $\pi$  dimer. Fig. 4 also shows that the atoms of these two functional groups are oriented to align the electron-poor N2(nitro) with the electron-rich O1(sulfonic ester), and the electron-poor S1(sulfonic



**Figure 2**  
(*a*) The asymmetric unit of the title compound along with the atom-numbering scheme, showing displacement ellipsoids at the 50% probability level; (*b*) the structure and atom-numbering scheme of a polymorph of the title compound WUVYUH (Vembu, *et al.*, 2003*a*). All hydrogen atoms have been omitted for clarity.

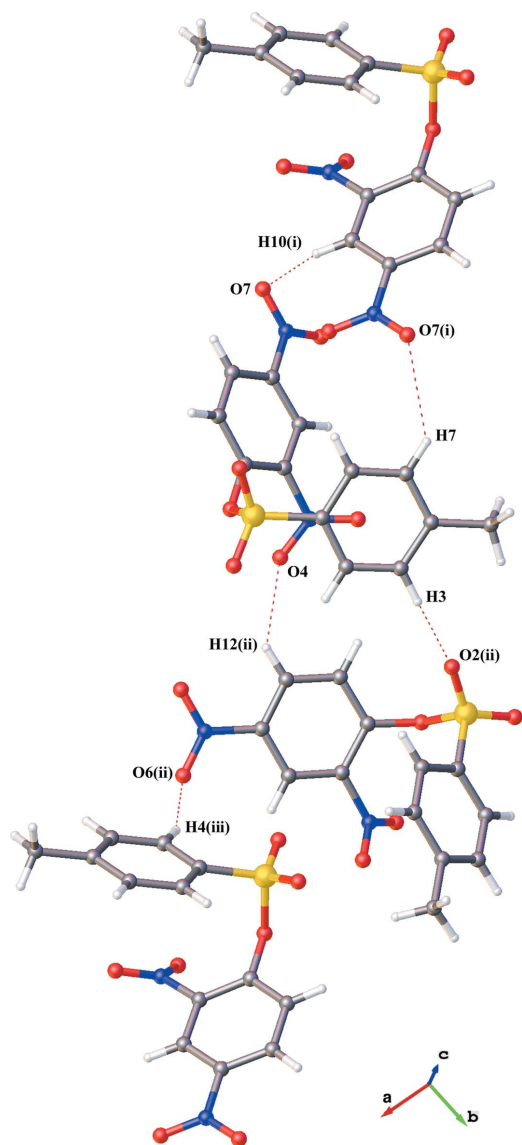


Figure 3

A drawing of a selection of the C–H···O interactions present in the crystal lattice using a ball and stick model. Symmetry codes: (i)  $-x + 1, -y + 1, z + \frac{1}{2}$ ; (ii)  $-x + \frac{3}{2}, y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + 2, -y + 2, z - \frac{1}{2}$ .

ester) with the electron-rich O7(nitro). Interatomic distances are N2(nitro)···O17<sup>v</sup>(sulfonic ester) = 3.379 (4) Å, and O7(nitro)···S1<sup>v</sup>(sulfonic ester) = 3.877 (3) Å. The relatively short intermolecular distance between N2 and O17 suggests the presence of favorable N···O interactions in the crystal (Daszkiewicz, 2013).

#### 4. Database survey

The Cambridge Structural Database (CSD, version 5.36, May 2015; Groom and Allen, 2014) contains 171 aromatic 4-toluenesulfonic esters. Of these, there are 14 structures where the aromatic ring bears substituents at both the 2- and 4-positions. One of these structures is quite similar to the title compound (GOFTIF: Ji *et al.*, 2008) where the *ortho*-substituent is a nitro group and the *para*-position bears a second

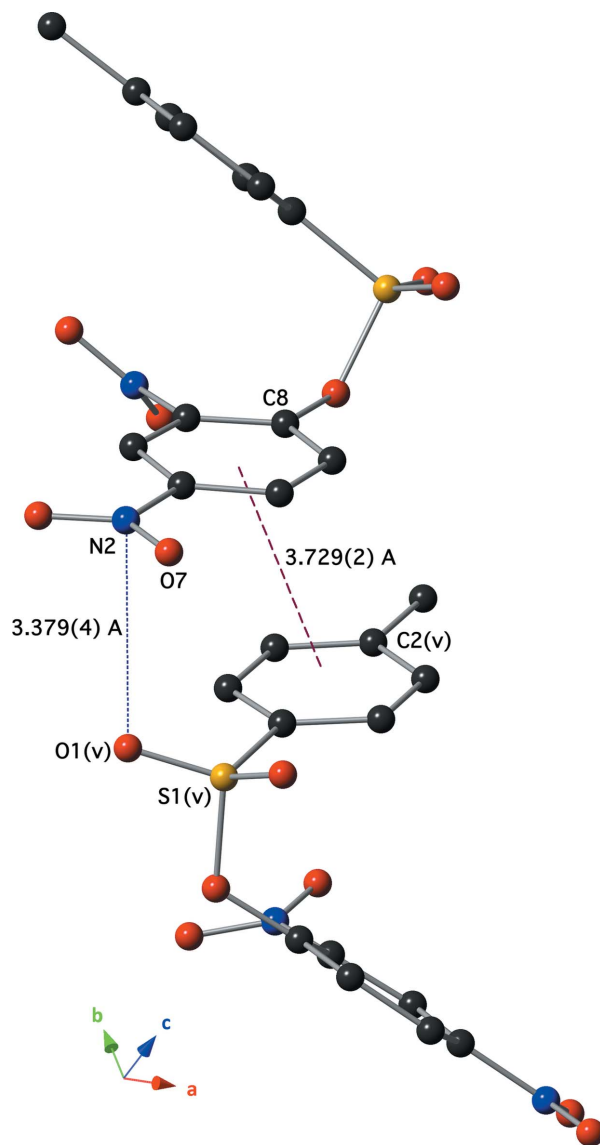


Figure 4

A drawing of the intermolecular  $\pi$ – $\pi$  stacking and nitro–sulfonic ester interactions present in the crystal using a ball and stick model. Symmetry code (v)  $-x + \frac{3}{2}, y - \frac{1}{2}, z + \frac{1}{2}$ .

tosylate group. The remaining entries have various electron-rich groups in the *ortho*-position including methoxy (*e.g.* FEMROF: Ichikawa *et al.*, 2004), ethoxy (*e.g.* HIRHOG: Ramachandran *et al.*, 2007), chlorine (OJENEW: Vembu *et al.*, 2003*b*) and alkyl amine (PERFEZ: Zhao *et al.*, 2013).

The CSD contains three additional structures where the position *ortho* to the sulfonic ester bears a nitro group. In FAYBAJ (Manivannan *et al.*, 2005), this *o*-nitro group is the only substituent. The aromatic ring in XIYZIP is part of a naphthalene system and also bears a 4-nitro group (Ramachandran *et al.*, 2008). The third structure in this set is a polymorph of the title compound (WUVYUH: Vembu *et al.*, 2003*a*) that was solved in the orthorhombic space group *Pbca*. One significant difference between WUVYUH and the title compound is the orientation of the groups around the S–O bond (see the *Structural commentary* section for more details).

## 5. Synthesis and crystallization

The title compound was prepared by stirring 2,4-dinitrophenol (5 mmol), *p*-toluenesulfonyl chloride (5 mmol) and pyridine (3 mmol) in 10 mL of dichloromethane for 30 minutes at room temperature. The reaction was heated to 353 K for 30 minutes in a microwave reactor, then cooled to room temperature and stirred overnight in a fume hood. The reaction mixture was transferred to a scintillation vial where the pale yellow product crystallized upon standing after several days and was filtered from the mother liquor (m.p. 393.4–394.7 K).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for CH groups and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups.

## Acknowledgements

The authors thank the GVSU for financial support (Weldon Fund, CSCE), the NSF for a 300 MHz Jeol FT–NMR (CCLI-0087655) and Pfizer, Inc. for the donation of a Varian Inova 400 FT–NMR. The CCD-based X-ray diffractometers at Michigan State University were upgraded and/or replaced by departmental funds.

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Table 2

Experimental details.

Crystal data	
Chemical formula	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>7</sub> S
$M_r$	338.29
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>
Temperature (K)	173
$a, b, c$ (Å)	14.7716 (12), 12.6403 (11), 7.6734 (6)
$V$ (Å <sup>3</sup> )	1432.8 (2)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.27
Crystal size (mm)	0.27 × 0.21 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2014)
$T_{\text{min}}, T_{\text{max}}$	0.686, 0.745
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	11432, 2624, 2326
$R_{\text{int}}$	0.036
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.088, 1.05
No. of reflections	2624
No. of parameters	209
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.18, -0.18
Absolute structure	Flack $x$ determined using 970 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013).
Absolute structure parameter	-0.02 (4)

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *XS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *CrystalMaker* (Palmer, 2007) and *OLEX2* (Dolomanov *et al.*, 2009; Bourhis *et al.*, 2015).

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## supporting information

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## Crystal structure of 2,4-dinitrophenyl 4-methylbenzenesulfonate: a new polymorph

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### Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *XS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *CrystalMaker* (Palmer, 2007); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009; Bourhis *et al.*, 2015).

### 2,4-Dinitrophenyl 4-methylbenzenesulfonate

#### Crystal data

$C_{13}H_{10}N_2O_7S$

$M_r = 338.29$

Orthorhombic, *Pna*2<sub>1</sub>

$a = 14.7716$  (12) Å

$b = 12.6403$  (11) Å

$c = 7.6734$  (6) Å

$V = 1432.8$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 696$

$D_x = 1.568$  Mg m<sup>-3</sup>

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

Cell parameters from 5781 reflections

$\theta = 2.8$ – $25.4^\circ$

$\mu = 0.27$  mm<sup>-1</sup>

$T = 173$  K

Chunk, yellow

$0.27 \times 0.21 \times 0.20$  mm

#### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2014)

$T_{\min} = 0.686$ ,  $T_{\max} = 0.745$

11432 measured reflections

2624 independent reflections

2326 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 25.4^\circ$ ,  $\theta_{\min} = 2.1^\circ$

$h = -17 \rightarrow 17$

$k = -15 \rightarrow 15$

$l = -9 \rightarrow 9$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.088$

$S = 1.05$

2624 reflections

209 parameters

1 restraint

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.2683P]$

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

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

$\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

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

Absolute structure parameter:  $-0.02$  (4)

*Special details*

**Experimental.** SADABS (Bruker, 2014) was used for absorption correction.  $wR2(\text{int})$  was 0.0928 before and 0.0535 after correction. The Ratio of minimum to maximum transmission is 0.9202. The  $\lambda/2$  correction factor is 0.00150.

**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	0.84591 (5)	0.72917 (7)	0.62435 (14)	0.0377 (2)
O1	0.92559 (18)	0.7834 (2)	0.5749 (4)	0.0520 (8)
O2	0.84576 (18)	0.6573 (2)	0.7657 (4)	0.0480 (8)
O3	0.82059 (18)	0.6622 (2)	0.4489 (3)	0.0393 (6)
O4	0.7331 (2)	0.7555 (3)	0.1741 (4)	0.0698 (10)
O5	0.6041 (2)	0.8003 (2)	0.2866 (5)	0.0622 (9)
O6	0.43774 (19)	0.4573 (2)	0.3474 (4)	0.0569 (8)
O7	0.5026 (2)	0.3344 (2)	0.4987 (4)	0.0552 (8)
N1	0.6675 (2)	0.7407 (3)	0.2684 (5)	0.0447 (8)
N2	0.5033 (2)	0.4212 (3)	0.4265 (4)	0.0409 (7)
C1	0.5319 (3)	1.0307 (3)	0.6779 (6)	0.0526 (11)
H1A	0.4769	0.9950	0.6376	0.079*
H1B	0.5436	1.0927	0.6047	0.079*
H1C	0.5240	1.0531	0.7991	0.079*
C2	0.6109 (2)	0.9555 (3)	0.6659 (5)	0.0383 (9)
C3	0.6881 (3)	0.9821 (3)	0.5730 (5)	0.0391 (9)
H3	0.6911	1.0490	0.5167	0.047*
C4	0.7608 (2)	0.9138 (3)	0.5602 (4)	0.0360 (8)
H4	0.8130	0.9328	0.4950	0.043*
C5	0.7559 (2)	0.8168 (2)	0.6448 (4)	0.0299 (7)
C6	0.6796 (2)	0.7879 (3)	0.7391 (4)	0.0345 (8)
H6	0.6770	0.7214	0.7966	0.041*
C7	0.6077 (2)	0.8575 (3)	0.7480 (5)	0.0373 (8)
H7	0.5551	0.8380	0.8114	0.045*
C8	0.7418 (2)	0.6020 (3)	0.4478 (5)	0.0323 (8)
C9	0.6651 (2)	0.6401 (3)	0.3637 (4)	0.0307 (7)
C10	0.5859 (2)	0.5833 (3)	0.3596 (5)	0.0337 (8)
H10	0.5329	0.6110	0.3061	0.040*
C11	0.5861 (2)	0.4846 (3)	0.4361 (5)	0.0323 (8)
C12	0.6613 (2)	0.4440 (3)	0.5188 (5)	0.0363 (8)
H12	0.6593	0.3754	0.5693	0.044*
C13	0.7395 (2)	0.5035 (3)	0.5279 (5)	0.0362 (8)
H13	0.7911	0.4774	0.5880	0.043*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0284 (4)	0.0403 (4)	0.0443 (5)	0.0001 (4)	-0.0037 (5)	0.0048 (5)
O1	0.0275 (12)	0.0566 (16)	0.072 (2)	-0.0066 (12)	0.0026 (13)	0.0053 (15)
O2	0.0478 (17)	0.0453 (15)	0.0507 (17)	0.0058 (12)	-0.0094 (13)	0.0130 (13)
O3	0.0330 (13)	0.0407 (14)	0.0444 (15)	0.0004 (12)	0.0077 (11)	-0.0014 (12)
O4	0.077 (2)	0.069 (2)	0.063 (2)	-0.0155 (17)	0.0088 (18)	0.0306 (17)
O5	0.073 (2)	0.0364 (14)	0.077 (2)	0.0159 (15)	-0.0244 (17)	0.0065 (15)
O6	0.0387 (16)	0.0549 (17)	0.077 (2)	-0.0012 (14)	-0.0106 (16)	-0.0068 (17)
O7	0.070 (2)	0.0441 (15)	0.0517 (17)	-0.0187 (14)	0.0021 (15)	0.0053 (14)
N1	0.058 (2)	0.0326 (16)	0.044 (2)	-0.0040 (16)	-0.0153 (17)	0.0052 (14)
N2	0.044 (2)	0.0391 (16)	0.0391 (18)	-0.0051 (15)	0.0050 (16)	-0.0065 (15)
C1	0.051 (2)	0.047 (2)	0.059 (3)	0.0125 (18)	-0.009 (2)	-0.011 (2)
C2	0.0358 (19)	0.0371 (18)	0.042 (2)	0.0007 (16)	-0.0077 (16)	-0.0076 (17)
C3	0.050 (2)	0.0285 (17)	0.039 (2)	-0.0011 (16)	-0.0090 (17)	0.0033 (15)
C4	0.0358 (19)	0.0388 (19)	0.0335 (19)	-0.0086 (16)	0.0015 (15)	0.0028 (15)
C5	0.0268 (16)	0.0322 (15)	0.0307 (18)	-0.0046 (13)	-0.0045 (15)	0.0029 (17)
C6	0.037 (2)	0.0323 (18)	0.0342 (19)	-0.0063 (15)	-0.0001 (16)	0.0020 (16)
C7	0.0304 (18)	0.042 (2)	0.039 (2)	-0.0069 (16)	0.0000 (16)	-0.0065 (17)
C8	0.0294 (18)	0.0328 (18)	0.0346 (17)	0.0035 (14)	0.0080 (15)	0.0015 (16)
C9	0.0383 (19)	0.0254 (16)	0.0283 (16)	0.0049 (15)	0.0017 (15)	0.0020 (14)
C10	0.036 (2)	0.0325 (17)	0.0324 (18)	0.0090 (15)	-0.0008 (16)	-0.0015 (15)
C11	0.0328 (19)	0.0326 (17)	0.0315 (18)	-0.0003 (15)	0.0062 (15)	-0.0024 (15)
C12	0.044 (2)	0.0280 (17)	0.0366 (19)	0.0059 (15)	0.0014 (17)	0.0056 (15)
C13	0.0362 (19)	0.0326 (17)	0.0397 (19)	0.0112 (15)	0.0006 (16)	0.0040 (16)

*Geometric parameters (Å, °)*

S1—O1	1.414 (3)	C3—H3	0.9500
S1—O2	1.415 (3)	C3—C4	1.381 (5)
S1—O3	1.634 (3)	C4—H4	0.9500
S1—C5	1.737 (3)	C4—C5	1.390 (4)
O3—C8	1.391 (4)	C5—C6	1.388 (5)
O4—N1	1.224 (4)	C6—H6	0.9500
O5—N1	1.210 (4)	C6—C7	1.381 (5)
O6—N2	1.231 (4)	C7—H7	0.9500
O7—N2	1.228 (4)	C8—C9	1.389 (5)
N1—C9	1.468 (5)	C8—C13	1.389 (5)
N2—C11	1.465 (4)	C9—C10	1.374 (5)
C1—H1A	0.9800	C10—H10	0.9500
C1—H1B	0.9800	C10—C11	1.378 (5)
C1—H1C	0.9800	C11—C12	1.379 (5)
C1—C2	1.507 (5)	C12—H12	0.9500
C2—C3	1.387 (5)	C12—C13	1.379 (5)
C2—C7	1.391 (5)	C13—H13	0.9500
O1—S1—O2	121.20 (17)	C4—C5—S1	118.8 (3)

O1—S1—O3	102.73 (16)	C6—C5—S1	120.0 (2)
O1—S1—C5	110.64 (16)	C6—C5—C4	121.2 (3)
O2—S1—O3	107.40 (14)	C5—C6—H6	120.6
O2—S1—C5	109.80 (17)	C7—C6—C5	118.8 (3)
O3—S1—C5	103.27 (15)	C7—C6—H6	120.6
C8—O3—S1	118.7 (2)	C2—C7—H7	119.4
O4—N1—C9	116.5 (3)	C6—C7—C2	121.3 (3)
O5—N1—O4	125.9 (3)	C6—C7—H7	119.4
O5—N1—C9	117.6 (4)	C9—C8—O3	119.7 (3)
O6—N2—C11	118.6 (3)	C13—C8—O3	120.6 (3)
O7—N2—O6	123.2 (3)	C13—C8—C9	119.8 (3)
O7—N2—C11	118.3 (3)	C8—C9—N1	120.8 (3)
H1A—C1—H1B	109.5	C10—C9—N1	117.5 (3)
H1A—C1—H1C	109.5	C10—C9—C8	121.6 (3)
H1B—C1—H1C	109.5	C9—C10—H10	121.3
C2—C1—H1A	109.5	C9—C10—C11	117.5 (3)
C2—C1—H1B	109.5	C11—C10—H10	121.3
C2—C1—H1C	109.5	C10—C11—N2	118.2 (3)
C3—C2—C1	121.0 (3)	C10—C11—C12	122.3 (3)
C3—C2—C7	118.5 (3)	C12—C11—N2	119.5 (3)
C7—C2—C1	120.5 (3)	C11—C12—H12	120.2
C2—C3—H3	119.2	C11—C12—C13	119.7 (3)
C4—C3—C2	121.6 (3)	C13—C12—H12	120.2
C4—C3—H3	119.2	C8—C13—H13	120.5
C3—C4—H4	120.7	C12—C13—C8	119.1 (3)
C3—C4—C5	118.6 (3)	C12—C13—H13	120.5
C5—C4—H4	120.7		
S1—O3—C8—C9	101.6 (3)	O7—N2—C11—C12	2.6 (5)
S1—O3—C8—C13	-79.5 (4)	N1—C9—C10—C11	174.5 (3)
S1—C5—C6—C7	-177.7 (3)	N2—C11—C12—C13	179.9 (3)
O1—S1—O3—C8	-177.1 (2)	C1—C2—C3—C4	-179.7 (3)
O1—S1—C5—C4	21.1 (3)	C1—C2—C7—C6	-179.7 (4)
O1—S1—C5—C6	-161.2 (3)	C2—C3—C4—C5	-0.7 (5)
O2—S1—O3—C8	54.0 (3)	C3—C2—C7—C6	0.5 (5)
O2—S1—C5—C4	157.5 (3)	C3—C4—C5—S1	178.3 (3)
O2—S1—C5—C6	-24.8 (3)	C3—C4—C5—C6	0.6 (5)
O3—S1—C5—C4	-88.2 (3)	C4—C5—C6—C7	0.0 (5)
O3—S1—C5—C6	89.5 (3)	C5—S1—O3—C8	-62.0 (3)
O3—C8—C9—N1	3.0 (5)	C5—C6—C7—C2	-0.6 (5)
O3—C8—C9—C10	-179.9 (3)	C7—C2—C3—C4	0.2 (5)
O3—C8—C13—C12	-177.6 (3)	C8—C9—C10—C11	-2.7 (5)
O4—N1—C9—C8	44.8 (5)	C9—C8—C13—C12	1.4 (5)
O4—N1—C9—C10	-132.4 (4)	C9—C10—C11—N2	-177.5 (3)
O5—N1—C9—C8	-136.9 (4)	C9—C10—C11—C12	1.9 (5)
O5—N1—C9—C10	46.0 (5)	C10—C11—C12—C13	0.5 (5)
O6—N2—C11—C10	1.6 (5)	C11—C12—C13—C8	-2.2 (5)
O6—N2—C11—C12	-177.8 (3)	C13—C8—C9—N1	-176.0 (3)



O7—N2—C11—C10                      -178.0 (3)                      C13—C8—C9—C10                      1.1 (5)

*Hydrogen-bond geometry (Å, °)*

<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>
C3—H3...O2 <sup>i</sup>	0.95	2.42	3.273 (5)	149
C4—H4...O6 <sup>ii</sup>	0.95	2.57	3.486 (5)	162
C7—H7...O7 <sup>iii</sup>	0.95	2.75	3.499 (5)	137
C10—H10...O7 <sup>iv</sup>	0.95	2.51	3.233 (5)	133
C12—H12...O4 <sup>v</sup>	0.95	2.34	3.087 (5)	135

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