



Crystal structure of 3,5-dimethylphenyl 2-nitrobenzenesulfonate

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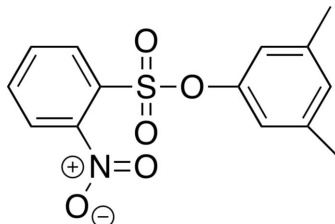
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The title compound, C₁₄H₁₃NO₅S, was synthesized *via* a nucleophilic substitution reaction between 3,5-dimethylphenol and 2-nitrobenzenesulfonyl chloride. The aromatic rings attached to the SO₃ group are oriented in a *gauche* fashion around the ester S—O bond, with a C—S—O—C torsion angle of 84.68 (11)°. The molecules form centrosymmetric dimers *via* π – π stacking interactions between 3,5-dimethylphenyl groups (centroid–centroid distance = 3.709 Å). An intermolecular S=O⋯N interaction between the sulfonyl and nitro groups, with an O⋯N distance of 2.9840 (18) Å, organizes the dimers into columns extending along [011]. These columns are further assembled into (111) layers through C—H⋯O interactions.

1. Chemical context

Microtubules form a major component of the cytoskeleton and have been implicated in a wide variety of cellular functions, such as cell division (Jordan & Wilson, 2004). Microtubules therefore have been targeted in the design of drugs for the treatment of various forms of cancer (Spencer & Faulds, 1994; Teicher, 2008; Trivedi *et al.*, 2008). For example, Combretastatin A-4 (CA-4) has been shown to target tumor vasculature (Griggs *et al.*, 2001). Most known antimicrotubules have poor biopharmaceutical properties, such as chemoresistance and toxicity (Islam *et al.*, 2003; Fortin *et al.*, 2011).



Research in the field for the synthesis of new anti-microtubule compounds has been geared towards compounds with improved biopharmaceutical properties (Fortin *et al.*, 2011). To this end, Fortin and co-workers have designed and synthesized various sulfonate derivatives, which have been

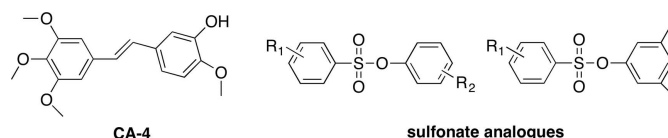


Figure 1
The structures of CA-4 and sulfonate analogues, where R_1 and R_2 are substituents on the sulfonyl and phenoxy benzene rings, respectively.

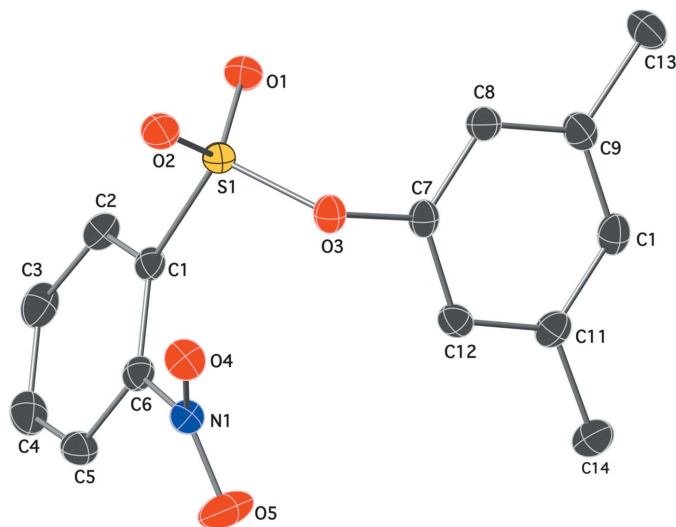


Figure 2

The molecular structure of the title compound, with displacement ellipsoids shown at the 50% probability level. All H atoms have been omitted for clarity. Color codes: black C, blue N, red O and yellow S.

tested as new tubulin inhibitors mimicking Combretastatin A-4 (Fig. 1).

A series of sulfonate derivatives have shown promise as anticancer drugs, with some having lower toxicity than CA-4 (Fortin *et al.*, 2011). We embarked on the synthesis of sulfonate derivatives with the long-term goal of investigating the effect of the benzene-ring substituents on the cytotoxicity of the sulfonate derivatives. To the best of our knowledge, despite the simplicity of the sulfonate derivatives, there has been no relevant previous crystallographic studies. Therefore, we report here the synthesis and crystal structure of 3,5-dimethylphenyl 2-nitrobenzenesulfonate.

2. Structural commentary

In the title molecule (Fig. 2), the $O1=S1=O2$ and $C1-S1-O3$ bond angles of $119.41(7)^\circ$ and $104.16(6)^\circ$ are typical for phenyl benzenesulfonates with a *gauche* conformation around the ester $S-O$ bond. The torsion angle $C1-S1-O3-C7$ around the ester bond is $-84.68(11)^\circ$. Owing to steric hindrance between the *ortho* substituents of the benzene ring, the nitro group is twisted relative to the benzene best plane by

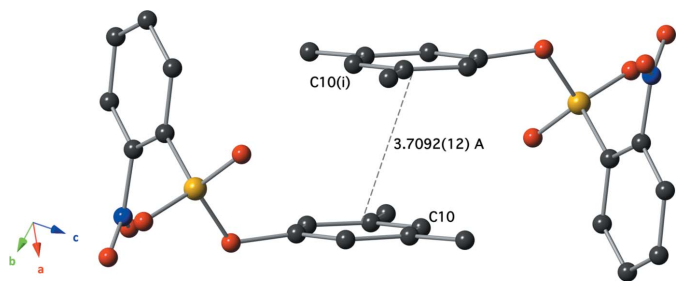


Figure 3

The centrosymmetric dimers formed by intermolecular offset π - π stacking interactions. [Symmetry code: (i) $-x + 1, -y + 2, -z$.]

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5-H5\cdots O1^i$	0.95	2.56	3.4544 (19)	156
$C8-H8\cdots O5^{ii}$	0.95	2.56	3.468 (2)	160

Symmetry codes: (i) $x + 1, y - 1, z$; (ii) $x - 1, y + 1, z$.

$39.91(2)^\circ$, so that the shortest contact of $2.7941(16) \text{\AA}$ between the O atoms of these groups is close to the sum of the van der Waals radii.

3. Supramolecular features

The molecules of the title compound form centrosymmetric dimers *via* intermolecular π - π stacking interactions between the relatively electron-rich C7-C12 benzene rings (Fig. 3), with a plane-to-plane distance of $3.4147(15) \text{\AA}$. The aromatic rings are stacked with an offset, and the distance between the centroids of these rings is $3.709(12) \text{\AA}$. Another centrosymmetric dimer is formed by an $S=O\cdots N$ interaction, with an $N1\cdots O2$ interatomic distance of $2.9840(18) \text{\AA}$. $O\cdots N$ (nitro) interactions between nitro groups have been discussed in the literature (Daszkiewicz, 2013; Caracelli *et al.*, 2014) and we report here the case of sulfonyl and nitro group interactions. Both types of dimers are assembled into a column-type structure extending along $[011]$ (Fig. 4).

There are no classical hydrogen bonds in the crystal structure; however, nonclassical $C-H\cdots O$ interactions between aromatic-ring H atoms and sulfonyl and nitro group O atoms organize the $[011]$ columns into (111) layers. The geometry of these interactions is given in Table 1.

4. Database survey

The Cambridge Structural Database (CSD, Version 5.36 with two updates; Groom & Allen, 2014) contains three structures with an *o*-nitroarylsulfonyl moiety bonded to an aromatic ring through an ester linkage. These are CSD refcodes FEMQUK (Ichikawa *et al.*, 2004), MIBZUT (Pelly *et al.*, 2007), and FEMRIZ (Ichikawa *et al.*, 2004). Like in the title compound, the aromatic substituents of the SO_3 group are oriented *gauche* around the ester $S-O$ bond and the absolute value of the $C-S-O-C$ torsion angle is in the range $85.9(3)$ – $103.43(13)^\circ$. In each of these structures there are either intra- or intermolecular $S=O\cdots N$ interactions between the sulfonate and *o*-nitro groups.

5. Synthesis and crystallization

3,5-Dimethylphenol (2.44 g, 20 mmol) was dissolved in chilled dichloromethane (25 ml). This was followed by the addition of pyridine (3.2 ml, 40 mmol). The resulting solution was cooled in an ice bath under an N_2 atmosphere, followed by the addition of 2-nitrobenzenesulfonyl chloride (4.43 g, 20 mmol) portion-wise. The mixture was stirred at 273 K for 30 mins and then at room temperature for 24 h. The product precipitated

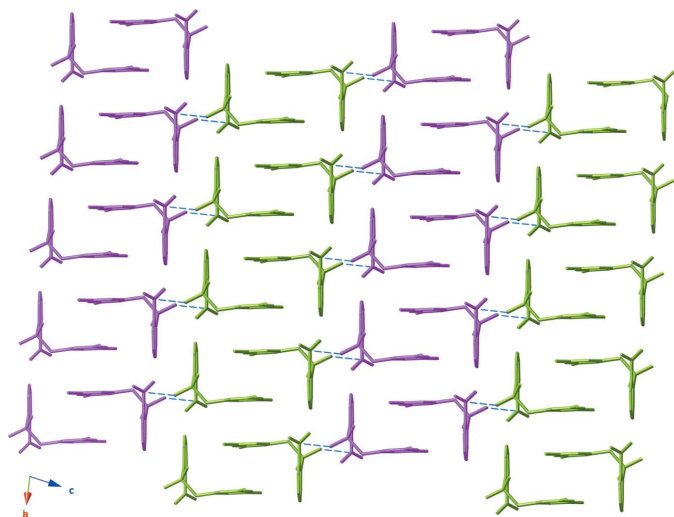


Figure 4

The packing of molecules in the crystal, viewed down the [110] direction. Columns of dimers formed *via* stacking interactions are colored green and pink in an alternating fashion, and potential $\text{N}\cdots\text{O}=\text{S}$ interactions are denoted with blue dashed lines.

from the reaction mixture after sitting at 277 K for two weeks. The product was redissolved in dichloromethane, and the solvent was allowed to evaporate slowly to give large block-shaped crystals that were suitable for analysis by X-ray diffraction (m.p. 374–378 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H 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 $1.5U_{\text{eq}}(\text{C})$ for methyl groups.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{14}\text{H}_{13}\text{NO}_5\text{S}$
M_r	307.31
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	7.9958 (4), 7.9991 (5), 12.0238 (3)
α, β, γ (°)	83.908 (3), 76.286 (3), 63.411 (4)
V (Å ³)	668.10 (6)
Z	2
Radiation type	$\text{Cu K}\alpha$
μ (mm ⁻¹)	2.37
Crystal size (mm)	$0.38 \times 0.34 \times 0.21$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2013)
$T_{\text{min}}, T_{\text{max}}$	0.630, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10317, 2519, 2461
R_{int}	0.022
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.092, 1.05
No. of reflections	2519
No. of parameters	192
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.33, −0.50

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (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 3,5-dimethylphenyl 2-nitrobenzenesulfonate

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *CrystalMaker* (Palmer, 2007); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009; Bourhis *et al.*, 2015).

3,5-Dimethylphenyl 2-nitrobenzenesulfonate

Crystal data

$C_{14}H_{13}NO_5S$

$M_r = 307.31$

Triclinic, $P\bar{1}$

$a = 7.9958$ (4) Å

$b = 7.9991$ (5) Å

$c = 12.0238$ (3) Å

$\alpha = 83.908$ (3)°

$\beta = 76.286$ (3)°

$\gamma = 63.411$ (4)°

$V = 668.10$ (6) Å³

$Z = 2$

$F(000) = 320$

$D_x = 1.528$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 8863 reflections

$\theta = 3.8\text{--}72.3^\circ$

$\mu = 2.37$ mm⁻¹

$T = 173$ K

Block, colourless

$0.38 \times 0.34 \times 0.21$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2013)

$T_{\min} = 0.630$, $T_{\max} = 0.754$

10317 measured reflections

2519 independent reflections

2461 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 72.1^\circ$, $\theta_{\min} = 3.8^\circ$

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.092$

$S = 1.05$

2519 reflections

192 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.3536P]$

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

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

$\Delta\rho_{\max} = 0.33$ e Å⁻³

$\Delta\rho_{\min} = -0.50$ e Å⁻³

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.32156 (5)	0.85859 (5)	0.36621 (3)	0.01694 (13)
O1	0.27175 (16)	1.05073 (15)	0.33973 (10)	0.0239 (3)
O2	0.22079 (15)	0.81004 (16)	0.46826 (9)	0.0240 (3)
O3	0.29830 (15)	0.76150 (15)	0.26599 (9)	0.0193 (2)
O4	0.46725 (16)	0.43665 (16)	0.39045 (10)	0.0240 (3)
O5	0.73130 (19)	0.28883 (18)	0.26840 (12)	0.0375 (3)
N1	0.62367 (18)	0.41785 (18)	0.33520 (11)	0.0201 (3)
C1	0.5719 (2)	0.7475 (2)	0.36177 (12)	0.0171 (3)
C2	0.6508 (2)	0.8662 (2)	0.37453 (13)	0.0216 (3)
H2	0.5728	0.9973	0.3801	0.026*
C3	0.8425 (2)	0.7951 (3)	0.37920 (14)	0.0258 (4)
H3	0.8939	0.8771	0.3902	0.031*
C4	0.9587 (2)	0.6047 (3)	0.36792 (14)	0.0265 (4)
H4	1.0898	0.5564	0.3711	0.032*
C5	0.8841 (2)	0.4845 (2)	0.35195 (13)	0.0227 (3)
H5	0.9643	0.3542	0.3426	0.027*
C6	0.6920 (2)	0.5556 (2)	0.34977 (12)	0.0182 (3)
C7	0.3244 (2)	0.8273 (2)	0.15112 (12)	0.0175 (3)
C8	0.1844 (2)	0.9933 (2)	0.12119 (13)	0.0200 (3)
H8	0.0770	1.0683	0.1773	0.024*
C9	0.2044 (2)	1.0482 (2)	0.00677 (14)	0.0214 (3)
C10	0.3619 (2)	0.9314 (2)	−0.07306 (13)	0.0217 (3)
H10	0.3744	0.9677	−0.1513	0.026*
C11	0.5014 (2)	0.7635 (2)	−0.04207 (13)	0.0198 (3)
C12	0.4822 (2)	0.7111 (2)	0.07297 (13)	0.0186 (3)
H12	0.5755	0.5979	0.0971	0.022*
C13	0.0582 (3)	1.2305 (2)	−0.02968 (16)	0.0294 (4)
H13A	−0.0609	1.2720	0.0288	0.044*
H13B	0.0333	1.2131	−0.1026	0.044*
H13C	0.1069	1.3249	−0.0390	0.044*
C14	0.6690 (2)	0.6430 (2)	−0.13189 (14)	0.0249 (3)
H14A	0.6251	0.6435	−0.2015	0.037*
H14B	0.7263	0.5147	−0.1032	0.037*
H14C	0.7647	0.6923	−0.1494	0.037*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01488 (19)	0.0172 (2)	0.0159 (2)	−0.00464 (15)	−0.00261 (13)	−0.00112 (14)

O1	0.0254 (6)	0.0177 (6)	0.0258 (6)	−0.0055 (4)	−0.0081 (5)	−0.0009 (5)
O2	0.0186 (5)	0.0292 (6)	0.0188 (5)	−0.0075 (5)	−0.0002 (4)	0.0000 (5)
O3	0.0225 (5)	0.0206 (5)	0.0174 (5)	−0.0113 (4)	−0.0061 (4)	0.0026 (4)
O4	0.0227 (6)	0.0257 (6)	0.0254 (6)	−0.0129 (5)	−0.0043 (5)	0.0023 (5)
O5	0.0340 (7)	0.0311 (7)	0.0430 (8)	−0.0111 (6)	0.0021 (6)	−0.0198 (6)
N1	0.0215 (6)	0.0181 (6)	0.0186 (6)	−0.0063 (5)	−0.0052 (5)	0.0000 (5)
C1	0.0157 (7)	0.0211 (7)	0.0126 (6)	−0.0072 (6)	−0.0014 (5)	−0.0007 (6)
C2	0.0236 (7)	0.0231 (8)	0.0179 (7)	−0.0108 (6)	−0.0017 (6)	−0.0027 (6)
C3	0.0258 (8)	0.0362 (9)	0.0219 (8)	−0.0194 (7)	−0.0024 (6)	−0.0044 (7)
C4	0.0170 (7)	0.0397 (10)	0.0227 (8)	−0.0124 (7)	−0.0034 (6)	−0.0006 (7)
C5	0.0183 (7)	0.0240 (8)	0.0195 (7)	−0.0046 (6)	−0.0021 (6)	−0.0001 (6)
C6	0.0187 (7)	0.0212 (7)	0.0137 (7)	−0.0087 (6)	−0.0017 (5)	−0.0006 (6)
C7	0.0210 (7)	0.0189 (7)	0.0169 (7)	−0.0116 (6)	−0.0064 (6)	0.0016 (6)
C8	0.0191 (7)	0.0189 (7)	0.0226 (8)	−0.0074 (6)	−0.0060 (6)	−0.0029 (6)
C9	0.0244 (7)	0.0177 (7)	0.0256 (8)	−0.0098 (6)	−0.0114 (6)	0.0021 (6)
C10	0.0304 (8)	0.0213 (8)	0.0181 (7)	−0.0145 (7)	−0.0086 (6)	0.0030 (6)
C11	0.0238 (7)	0.0188 (7)	0.0208 (7)	−0.0127 (6)	−0.0038 (6)	−0.0023 (6)
C12	0.0196 (7)	0.0146 (7)	0.0233 (8)	−0.0077 (6)	−0.0073 (6)	0.0010 (6)
C13	0.0324 (9)	0.0217 (8)	0.0327 (9)	−0.0074 (7)	−0.0158 (7)	0.0046 (7)
C14	0.0288 (8)	0.0225 (8)	0.0230 (8)	−0.0121 (7)	−0.0017 (6)	−0.0035 (6)

Geometric parameters (Å, °)

S1—O1	1.4249 (12)	C7—C8	1.380 (2)
S1—O2	1.4198 (11)	C7—C12	1.383 (2)
S1—O3	1.5887 (11)	C8—H8	0.9500
S1—C1	1.7797 (15)	C8—C9	1.393 (2)
O3—C7	1.4268 (18)	C9—C10	1.394 (2)
O4—N1	1.2195 (17)	C9—C13	1.505 (2)
O5—N1	1.2263 (18)	C10—H10	0.9500
N1—C6	1.473 (2)	C10—C11	1.392 (2)
C1—C2	1.391 (2)	C11—C12	1.395 (2)
C1—C6	1.400 (2)	C11—C14	1.507 (2)
C2—H2	0.9500	C12—H12	0.9500
C2—C3	1.389 (2)	C13—H13A	0.9800
C3—H3	0.9500	C13—H13B	0.9800
C3—C4	1.385 (3)	C13—H13C	0.9800
C4—H4	0.9500	C14—H14A	0.9800
C4—C5	1.387 (2)	C14—H14B	0.9800
C5—H5	0.9500	C14—H14C	0.9800
C5—C6	1.385 (2)		
O1—S1—O3	109.83 (6)	C8—C7—C12	123.31 (14)
O1—S1—C1	106.85 (7)	C12—C7—O3	117.36 (13)
O2—S1—O1	119.41 (7)	C7—C8—H8	120.8
O2—S1—O3	105.16 (6)	C7—C8—C9	118.42 (14)
O2—S1—C1	110.43 (7)	C9—C8—H8	120.8
O3—S1—C1	104.16 (6)	C8—C9—C10	118.82 (14)

C7—O3—S1	120.43 (9)	C8—C9—C13	120.43 (15)
O4—N1—O5	124.23 (14)	C10—C9—C13	120.75 (15)
O4—N1—C6	118.87 (12)	C9—C10—H10	118.9
O5—N1—C6	116.89 (13)	C11—C10—C9	122.27 (15)
C2—C1—S1	115.24 (12)	C11—C10—H10	118.9
C2—C1—C6	118.36 (14)	C10—C11—C12	118.57 (14)
C6—C1—S1	126.38 (12)	C10—C11—C14	120.02 (14)
C1—C2—H2	119.7	C12—C11—C14	121.41 (14)
C3—C2—C1	120.67 (15)	C7—C12—C11	118.60 (14)
C3—C2—H2	119.7	C7—C12—H12	120.7
C2—C3—H3	119.9	C11—C12—H12	120.7
C4—C3—C2	120.11 (15)	C9—C13—H13A	109.5
C4—C3—H3	119.9	C9—C13—H13B	109.5
C3—C4—H4	119.9	C9—C13—H13C	109.5
C3—C4—C5	120.10 (15)	H13A—C13—H13B	109.5
C5—C4—H4	119.9	H13A—C13—H13C	109.5
C4—C5—H5	120.2	H13B—C13—H13C	109.5
C6—C5—C4	119.59 (15)	C11—C14—H14A	109.5
C6—C5—H5	120.2	C11—C14—H14B	109.5
C1—C6—N1	122.82 (13)	C11—C14—H14C	109.5
C5—C6—N1	116.05 (14)	H14A—C14—H14B	109.5
C5—C6—C1	121.13 (14)	H14A—C14—H14C	109.5
C8—C7—O3	119.06 (13)	H14B—C14—H14C	109.5
S1—O3—C7—C8	−74.03 (15)	C1—S1—O3—C7	−84.68 (11)
S1—O3—C7—C12	111.80 (13)	C1—C2—C3—C4	1.8 (2)
S1—C1—C2—C3	176.26 (12)	C2—C1—C6—N1	−179.70 (14)
S1—C1—C6—N1	2.0 (2)	C2—C1—C6—C5	0.8 (2)
S1—C1—C6—C5	−177.44 (12)	C2—C3—C4—C5	0.0 (2)
O1—S1—O3—C7	29.44 (12)	C3—C4—C5—C6	−1.3 (2)
O1—S1—C1—C2	21.24 (13)	C4—C5—C6—N1	−178.57 (13)
O1—S1—C1—C6	−160.46 (13)	C4—C5—C6—C1	0.9 (2)
O2—S1—O3—C7	159.13 (10)	C6—C1—C2—C3	−2.2 (2)
O2—S1—C1—C2	−110.09 (12)	C7—C8—C9—C10	1.6 (2)
O2—S1—C1—C6	68.21 (15)	C7—C8—C9—C13	−178.43 (14)
O3—S1—C1—C2	137.46 (11)	C8—C7—C12—C11	0.0 (2)
O3—S1—C1—C6	−44.23 (14)	C8—C9—C10—C11	−1.1 (2)
O3—C7—C8—C9	−174.87 (12)	C9—C10—C11—C12	0.0 (2)
O3—C7—C12—C11	173.85 (12)	C9—C10—C11—C14	−179.82 (14)
O4—N1—C6—C1	−39.7 (2)	C10—C11—C12—C7	0.6 (2)
O4—N1—C6—C5	139.82 (14)	C12—C7—C8—C9	−1.1 (2)
O5—N1—C6—C1	141.33 (16)	C13—C9—C10—C11	178.94 (14)
O5—N1—C6—C5	−39.2 (2)	C14—C11—C12—C7	−179.61 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C5—H5 \cdots O1 ⁱ	0.95	2.56	3.4544 (19)	156

C8—H8 \cdots O5 ⁱⁱ	0.95	2.56	3.468 (2)	160
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Symmetry codes: (i) $x+1, y-1, z$; (ii) $x-1, y+1, z$.