



# The first spontaneous resolution of a sulfoxide: Dianin's compound analogue, (*R*)-4-(4-hydroxyphenyl)-2,2,4-trimethylthiachroman-1-oxide

James H. Gall,<sup>a</sup> J. Derek White,<sup>a</sup> David D. MacNicol<sup>a</sup> and Christopher S. Frampton<sup>b\*</sup>

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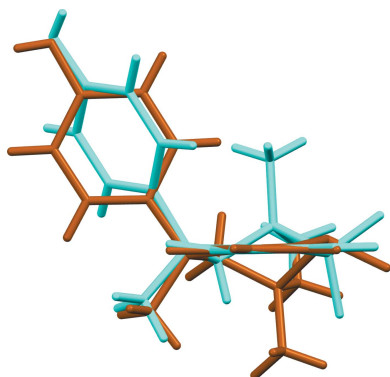
<sup>a</sup>School of Chemistry, Joseph Black Building, University Avenue, University of Glasgow, Glasgow, G12 8QQ, Scotland, and <sup>b</sup>Experimental Techniques Centre, Brunel University London, Kingston Lane, Uxbridge, UB8 3PH, England.

\*Correspondence e-mail: chris.frampton@brunel.ac.uk

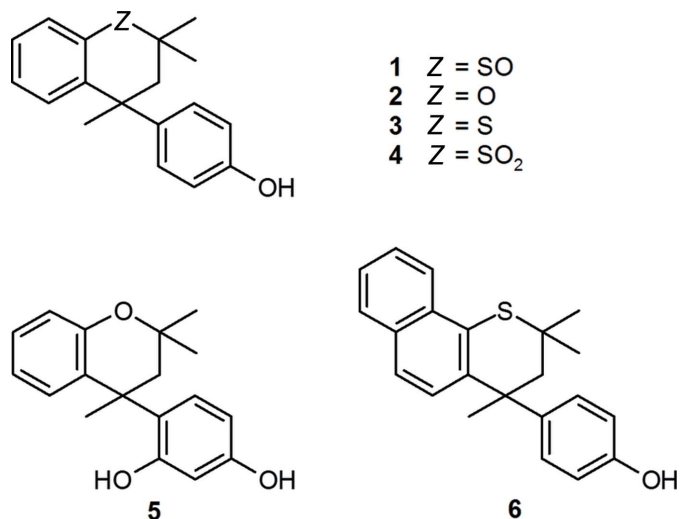
The title sulfoxide, C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S, was prepared by controlled oxidation of *thia*-Dianin's compound using hydrogen peroxide in glacial acetic acid. On recrystallization from glacial acetic acid, it was found to form unsolvated, spontaneously resolved crystals, the initial crystal structure analysis revealing the presence of both sulfoxide epimers in the crystal. On multiple recrystallization a single epimer was observed, with crystallization occurring in the unchanged orthorhombic space group  $P2_12_12_1$ , with  $Z' = 1$ . The molecule possesses a *distal* conformation, referring to the juxtaposition of the *p*-hydroxyphenyl substituent with respect to its *syn*-related methyl group, with the sulfoxide oxygen atom *anti* to the aromatic substituent. The molecular packing features O–H···O hydrogen bond chains running parallel to the *b* axis of the unit cell.

## 1. Chemical context

A significant body of work in the literature relates to specifically targeted structural modification of Dianin's compound, 4-(4-hydroxyphenyl)-2,2,4-trimethylchroman **2**, (MacNicol, 1984; Finocchiaro & Failla, 1996; Collet & Jacques, 1976; Frampton *et al.*, 2017*a,b,c*). Crystallization of the new compounds has normally resulted in one of two outcomes: formation of clathrates in the space group  $R\bar{3}$  (or  $R3$ ) or spontaneous resolution, also a subject of much current interest (Pérez-García & Amabilino, 2007), to form an unsolvated conglomerate in space group  $P2_12_12_1$ , with  $Z' = 1$ , in which the individual crystals are formed by supramolecular assembly of a single enantiomer. A notable departure from the above crystallization modes has, however, been found in the case of Dianin's sulfone **4**, (Frampton *et al.*, 1992), which crystallizes unsolvated in the polar monoclinic space group  $Cc$ , with  $Z' = 1$ , and these crystals exhibited a significant SHG effect. The present work was undertaken to establish if the corresponding sulfoxide **1** would retain the clathrating ability of its immediate progenitor *thia*-Dianin's compound **3**, or would undergo spontaneous resolution, alternative possibilities being the formation of a polar monoclinic crystal or crystallization in a more frequently encountered space group. Interestingly, the achiral bis-sulfoxide *trans*-(*R,S*)- $\alpha,\alpha'$ -di-*tert*-butylsulfanyl-*para*-xylene undergoes conformational spontaneous resolution in the space group  $P2_12_12_1$ ; on dissolution, rapid conformational racemization occurs at room temperature; however, the authors make the point that at 173 K, from calculations, it

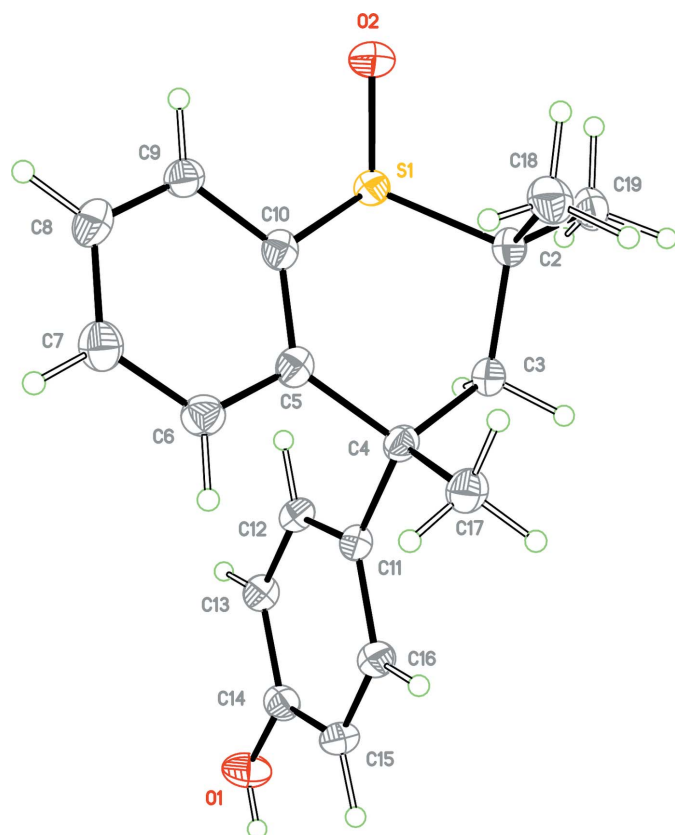


could be possible to obtain one chiral conformation from a single crystal (Xu *et al.*, 2014). Accordingly, the sulfoxide **1** was prepared by controlled oxidation of **3** as described in Section 5, and its crystal structure determined.



## 2. Structural commentary

Initial attempts to determine the crystal structure of **1** revealed the presence of both sulfoxide epimers in the crystal in a ratio of approximately 90:10. It was found that multiple

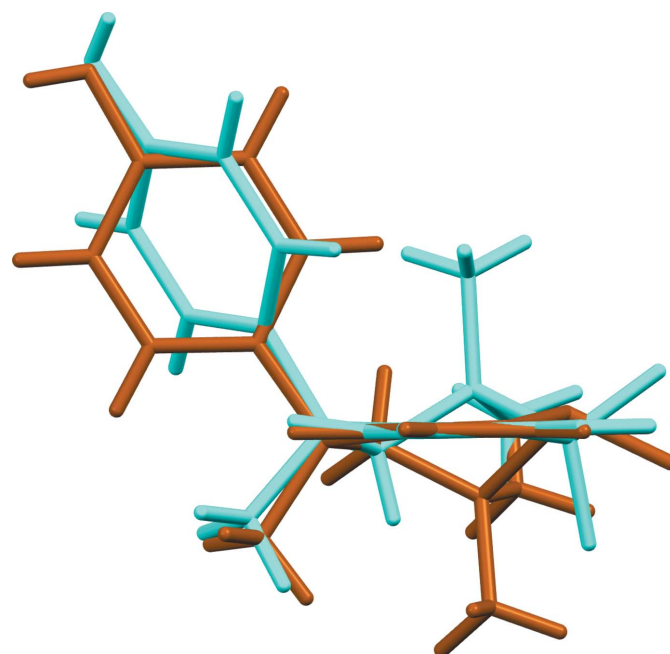


**Figure 1**  
View of molecule **1** with the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level.

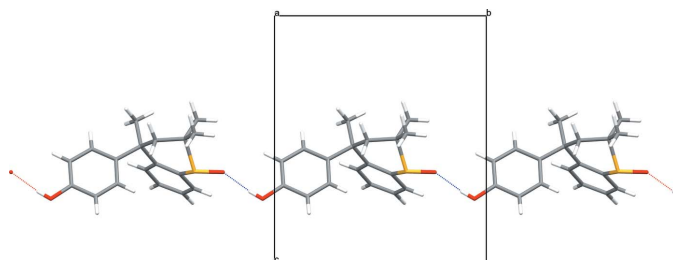
recrystallization of **1** from glacial acetic acid yielded a single epimer, the structure of which is presented here. The crystal structure of **1** is orthorhombic, space group  $P2_12_12_1$  with a single independent molecule in the asymmetric unit, ( $Z' = 1$ ), Fig. 1. The molecule possesses a *distal* conformation, this referring to the juxtaposition of the *p*-hydroxyphenyl substituent with respect to the *syn*-related methyl group. The C2–C3–C4–C11 torsion angle is  $154.0(2)^\circ$ , the corresponding torsion angle for racemic Dianin's compound **2** has a magnitude of  $80.67^\circ$  (Lee *et al.*, 2014) and for 4-(4-hydroxyphenyl)-2,2,4-trimethylchroman-1,1-dioxide **4**, it is  $76.8^\circ$  (Frampton *et al.*, 1992). The expected torsional angle value for a *distal* conformation is  $160^\circ$  whereas that for a *proximal* conformation is  $80^\circ$ . The torsion angle S1–C2–C3–C4, defining the heterocyclic ring chirality, has a value of  $-67.3(2)^\circ$ . Fig. 2 shows an overlay of **1** (brown) with sulfone **4** (cyan). In this figure, the six aromatic atoms of the chroman unit for each structure have been overlaid using the standard molecule overlay routine in *Mercury* (Macrae *et al.*, 2008), resulting in an r.m.s. displacement of  $0.0147 \text{ \AA}$ , and this clearly demonstrates the difference between the *distal* and *proximal* conformations of **1** and **4**, respectively. The absolute configuration of **1**, was determined as being *R* at the chiral centre C4 by anomalous dispersion methods, (Parsons *et al.* 2013), the Flack *x* parameter was determined as  $-0.002(7)$  using 1246 quotients  $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ .

## 3. Supramolecular features

The structure of **1** is isostructural with the enantiomerically pure amine counterparts of Dianin's and *thia*-Dianin's compound, (*R*)-4-(4-aminophenyl)-2,2,4-trimethylchroman and (*S*)-4-(4-aminophenyl)-2,2,4-trimethylthiachroman, both



**Figure 2**  
View of the structure overlay of **1** (brown) and **4** (cyan).

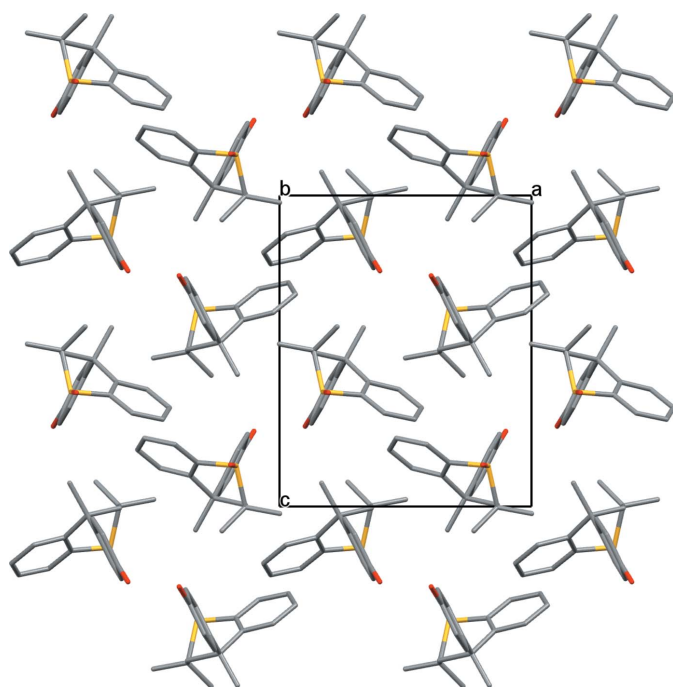


**Figure 3**  
A partial view of the crystal packing down the *a* axis showing the hydrogen-bonded chain. The intermolecular O—H...O hydrogen bond is shown as a dotted line.

of which were obtained by spontaneous resolution (Frampton *et al.*, 2011), and also surprisingly isostructural with the enantiomerically pure forms of 4-(4-hydroxyphenyl)-2,2,4-trimethylchroman, **2** (Lloyd & Bredenkamp, 2005) and 4-(2,4-dihydroxyphenyl)-2,2,4-trimethylchroman, **5** (Beresford *et al.*, 1999). The crystal packing is dominated by the formation of an extended linear hydroxy —OH to sulfoxide O, hydrogen-bonded O—H...O chain along the [010] direction of the unit cell, Figs. 3 and 4, Table 1.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39 update August 2018; Groom *et al.*, 2016) for the *thia*-Dianin's framework, **3**, yielded 15 hits, all of which were genuine examples of analogues of the material under investigation. Although there are no entries for the empty racemic  $R\bar{3}$  host of *thia*-Dianin's compound, there are seven entries for



**Figure 4**  
View of the crystal packing of **1** down the *b* axis.

**Table 1**  
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>
O1—H1...O2 <sup>i</sup>	0.77 (3)	1.92 (3)	2.685 (3)	169 (3)

Symmetry code: (i) *x*, *y* − 1, *z*.

the following host–guest clathrates: ethanol (HPTHCR; MacNicol *et al.*, 1969), 2,5,5-trimethylhex-3-yn-2-ol (TCHHXO; MacNicol & Wilson, 1971), cyclopentane (METCCP; Hardy *et al.*, 1979) and *isopropanol* at four different temperatures demonstrating three commensurate phase changes in the host lattice (VANFOI, 371 K, VANFOI01, 295 K, VANFOI02, 200 K and VANFUO, 90 K; Frampton *et al.*, 2017*a*). *Thia*-Dianin's compound, **3**, was also found in the 1:1 quasi-racemic  $R\bar{3}$  host with Dianin's compound, **2**, in the following three entries: apohost (BIBNAD and BIBNAD01), CCl<sub>4</sub>/H<sub>2</sub>O host–guest clathrate (HIDQAO) (Frampton *et al.*, 2013). The structure and absolute stereochemistry determination of the resolved *S*-enantiomer of *thia*-Dianin's compound used in the formation of the quasi-racemates above (BIBNEH; Frampton *et al.*, 2013). Four further examples demonstrating a slightly modified framework include the 6-methyl analogue (HPMTCM; Hardy *et al.*, 1977), the cyclooctane host–guest clathrate of the 8-methyl analogue (MSOCYO10; Hardy *et al.*, 1979), the oxidized sulfone, **4**, (KUTDUY; Frampton *et al.*, 1992) and 4-(4-hydroxyphenyl)-2,2,4-trimethyl-7,8-benzothiachroman **6**, a fused-ring counterpart of *thia*-Dianin's compound (JELROK; Frampton *et al.*, 2017*c*).

#### 5. Synthesis and crystallization

Preparation of **1**: 4-(4-hydroxyphenyl)-2,2,4-trimethylthia-chroman **3** (MacNicol, 1969) (0.25 g, 0.88 mmol) was dissolved in glacial acetic acid (10 mL) and a 50% excess of 30% hydrogen peroxide (0.15 mL, 1.32 mmol) added. After the reaction was left overnight at *ca* 278 K, the precipitated white solid was filtered off, washed several times with ether, and initially recrystallized from aqueous dimethyl sulfoxide yielding 0.168 g, (63%) of product. A further recrystallization from glacial acetic acid gave colourless crystals which were analysed by X-ray diffraction as described in the text. The crystals were obtained by spontaneous resolution on crystallization, yielding a 50:50 mixture of the pure enantiomers. These crystals also incorporated both spontaneously resolved sulfoxide epimers, four further recrystallizations were performed giving a single epimer of purity greater than 99% [500 MHz <sup>1</sup>H NMR, DMSO-*d*<sub>6</sub> solution analysis gave 99.5 (2)% purity] and the very minor residual second epimer was undetectable in the subsequent X-ray analysis. These crystals melted over a wide range, *ca* 513–536 K, possibly arising from sulfoxide epimerization, along with decomposition, at high temperature. MS [EI<sup>+</sup>]: 300.1178, C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S, calculated 300.1184; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 0.94 (*s*, 3H), 1.31 (*s*, 3H), 1.67 (*s*, 3H), 2.26 (*q*, 2H, δ<sub>AB</sub> = 0.45 ppm, *J*<sub>AB</sub>

= 15.1 Hz), 6.6–7.7 (aromatic, 8H), 9.27(*s*, 1H); FT-IR ( $\nu_{\max}$ , ATR,  $\text{cm}^{-1}$ ): 3176 (*br*), 3197 (minor) [ $\nu(\text{O}-\text{H})$ ]; 1017 [ $\nu(\text{S}-\text{O})$ ].

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

The hydrogen atom of the OH group was localized in the difference-Fourier map and refined isotropically. The other hydrogen atoms were placed in calculated positions and refined within the riding model with  $\text{C}-\text{H} = 0.95\text{--}0.99 \text{ \AA}$  and fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for the other groups].

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**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}$
$M_r$	300.40
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
$a, b, c$ (Å)	10.4311 (3), 11.0892 (3), 12.8868 (3)
$V$ (Å <sup>3</sup> )	1490.65 (7)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.94
Crystal size (mm)	0.18 × 0.12 × 0.10
Data collection	
Diffractometer	Rigaku Oxford Diffraction Super-Nova, Dualflex, AtlasS2
Absorption correction	Gaussian ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)
$T_{\min}, T_{\max}$	0.786, 0.844
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	5735, 3046, 2982
$R_{\text{int}}$	0.016
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.075, 1.03
No. of reflections	3046
No. of parameters	197
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> )	0.27, -0.29
Absolute structure	Flack $x$ determined using 1246 quotients [ $(I^+) - (I^-)$ ]/ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.002 (7)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXD2014/6* (Schneider & Sheldrick, 2002), *SHELXL2014/6* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.  
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## supporting information

*Acta Cryst.* (2018). E74, 1633-1636 [https://doi.org/10.1107/S2056989018014366]

## The first spontaneous resolution of a sulfoxide: Dianin's compound analogue, (R)-4-(4-hydroxyphenyl)-2,2,4-trimethylthiachroman-1-oxide

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### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXD2014/6* (Schneider & Sheldrick, 2002); program(s) used to refine structure: *SHELXL2014/6* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

### (R)-4-(4-Hydroxyphenyl)-2,2,4-trimethyl-3H-1λ<sup>4</sup>-benzothiopyran-1-one

#### Crystal data

C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S

*M<sub>r</sub>* = 300.40

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

*a* = 10.4311 (3) Å

*b* = 11.0892 (3) Å

*c* = 12.8868 (3) Å

*V* = 1490.65 (7) Å<sup>3</sup>

*Z* = 4

*F*(000) = 640

*D<sub>x</sub>* = 1.339 Mg m<sup>-3</sup>

Cu *Kα* radiation, λ = 1.54184 Å

Cell parameters from 3948 reflections

θ = 5.3–74.2°

μ = 1.94 mm<sup>-1</sup>

*T* = 100 K

Block, colourless

0.18 × 0.12 × 0.10 mm

#### Data collection

Rigaku Oxford Diffraction SuperNova,

Dualflex, AtlasS2

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Cu) X-ray Source

Detector resolution: 5.2921 pixels mm<sup>-1</sup>

ω scans

Absorption correction: gaussian

(*CrysAlisPro*; Rigaku OD, 2015)

*T<sub>min</sub>* = 0.786, *T<sub>max</sub>* = 0.844

5735 measured reflections

3046 independent reflections

2982 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.016

θ<sub>max</sub> = 74.5°, θ<sub>min</sub> = 5.3°

*h* = -12→13

*k* = -12→13

*l* = -16→13

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.028

*wR*(*F*<sup>2</sup>) = 0.075

*S* = 1.03

3046 reflections

197 parameters

0 restraints

Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.434P]$$

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

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

$$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using  
1246 quotients  $[(F^+)-(F^-)]/[(F^+)+(F^-)]$  (Parsons *et al.*, 2013)

Absolute structure parameter:  $-0.002$  (7)

### 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	0.17202 (5)	0.62246 (5)	0.63136 (4)	0.01942 (13)
O1	0.10168 (17)	-0.05587 (16)	0.74216 (15)	0.0286 (4)
H1	0.120 (3)	-0.115 (3)	0.713 (2)	0.031 (8)*
O2	0.19457 (17)	0.75661 (14)	0.63392 (14)	0.0290 (4)
C2	0.1359 (2)	0.5775 (2)	0.49805 (16)	0.0213 (5)
C3	0.1350 (2)	0.4390 (2)	0.50523 (16)	0.0203 (4)
H3A	0.1008	0.4077	0.4388	0.024*
H3B	0.0729	0.4164	0.5600	0.024*
C4	0.2625 (2)	0.3703 (2)	0.52807 (15)	0.0183 (4)
C5	0.3535 (2)	0.4405 (2)	0.59971 (15)	0.0191 (4)
C6	0.4737 (2)	0.3919 (2)	0.62341 (17)	0.0229 (4)
H6	0.4947	0.3139	0.5981	0.027*
C7	0.5633 (2)	0.4536 (2)	0.68256 (18)	0.0261 (5)
H7	0.6437	0.4175	0.6977	0.031*
C8	0.5354 (2)	0.5688 (2)	0.71980 (18)	0.0246 (5)
H8	0.5973	0.6126	0.7585	0.030*
C9	0.4163 (2)	0.6183 (2)	0.69968 (15)	0.0211 (4)
H9	0.3956	0.6962	0.7255	0.025*
C10	0.3267 (2)	0.55413 (19)	0.64149 (15)	0.0190 (4)
C11	0.2254 (2)	0.2522 (2)	0.58256 (16)	0.0178 (4)
C12	0.1659 (2)	0.25810 (19)	0.67999 (16)	0.0195 (4)
H12	0.1519	0.3348	0.7109	0.023*
C13	0.1269 (2)	0.1558 (2)	0.73240 (16)	0.0201 (4)
H13	0.0890	0.1629	0.7991	0.024*
C14	0.1431 (2)	0.04203 (19)	0.68765 (17)	0.0206 (4)
C15	0.2012 (2)	0.0339 (2)	0.59057 (18)	0.0224 (4)
H15	0.2127	-0.0427	0.5589	0.027*
C16	0.2426 (2)	0.1379 (2)	0.53978 (16)	0.0207 (4)
H16	0.2836	0.1306	0.4743	0.025*
C17	0.3331 (2)	0.3456 (2)	0.42483 (16)	0.0237 (4)
H17A	0.4110	0.2988	0.4386	0.036*
H17B	0.3563	0.4224	0.3922	0.036*
H17C	0.2769	0.3000	0.3782	0.036*
C18	0.2289 (2)	0.6345 (2)	0.42175 (17)	0.0290 (5)

H18A	0.2208	0.7225	0.4249	0.044*
H18B	0.2091	0.6067	0.3514	0.044*
H18C	0.3167	0.6112	0.4398	0.044*
C19	-0.0004 (2)	0.6226 (2)	0.47748 (17)	0.0261 (5)
H19A	-0.0595	0.5856	0.5273	0.039*
H19B	-0.0261	0.6006	0.4068	0.039*
H19C	-0.0030	0.7105	0.4851	0.039*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0224 (2)	0.0180 (2)	0.0179 (2)	0.0006 (2)	-0.00050 (19)	-0.00088 (18)
O1	0.0335 (9)	0.0175 (8)	0.0347 (9)	-0.0018 (7)	0.0080 (7)	0.0026 (7)
O2	0.0354 (9)	0.0181 (7)	0.0335 (9)	0.0019 (7)	-0.0041 (8)	-0.0025 (7)
C2	0.0268 (11)	0.0212 (11)	0.0159 (9)	0.0007 (8)	-0.0021 (8)	0.0008 (8)
C3	0.0235 (10)	0.0205 (10)	0.0169 (9)	0.0001 (9)	-0.0028 (8)	0.0003 (8)
C4	0.0214 (9)	0.0186 (10)	0.0150 (9)	-0.0011 (9)	0.0001 (7)	-0.0018 (9)
C5	0.0210 (10)	0.0217 (10)	0.0146 (8)	-0.0036 (8)	0.0026 (7)	0.0013 (8)
C6	0.0229 (10)	0.0221 (10)	0.0238 (10)	0.0015 (8)	0.0011 (8)	-0.0022 (9)
C7	0.0215 (10)	0.0308 (12)	0.0261 (11)	0.0015 (9)	0.0001 (9)	0.0005 (10)
C8	0.0215 (10)	0.0292 (12)	0.0231 (10)	-0.0053 (9)	-0.0024 (8)	-0.0021 (9)
C9	0.0263 (10)	0.0194 (10)	0.0177 (9)	-0.0020 (9)	0.0006 (8)	0.0000 (8)
C10	0.0200 (9)	0.0218 (9)	0.0151 (8)	-0.0032 (9)	0.0014 (9)	0.0028 (7)
C11	0.0183 (9)	0.0186 (10)	0.0166 (9)	0.0001 (8)	-0.0020 (8)	-0.0009 (8)
C12	0.0202 (9)	0.0188 (9)	0.0194 (9)	-0.0016 (9)	-0.0008 (9)	-0.0034 (8)
C13	0.0199 (9)	0.0217 (11)	0.0188 (9)	-0.0009 (8)	0.0019 (8)	-0.0003 (8)
C14	0.0187 (10)	0.0184 (10)	0.0247 (10)	-0.0017 (8)	-0.0017 (8)	0.0023 (9)
C15	0.0258 (11)	0.0168 (10)	0.0246 (10)	0.0005 (8)	-0.0016 (9)	-0.0039 (9)
C16	0.0236 (10)	0.0193 (10)	0.0191 (9)	0.0006 (9)	-0.0001 (8)	-0.0016 (9)
C17	0.0296 (11)	0.0253 (11)	0.0161 (9)	0.0002 (9)	0.0033 (9)	-0.0008 (7)
C18	0.0387 (13)	0.0280 (12)	0.0204 (10)	-0.0003 (11)	0.0040 (10)	0.0048 (10)
C19	0.0291 (11)	0.0270 (12)	0.0220 (10)	0.0052 (11)	-0.0055 (8)	0.0010 (10)

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

S1—O2	1.5064 (16)	C9—C10	1.394 (3)
S1—C10	1.788 (2)	C9—H9	0.9500
S1—C2	1.828 (2)	C11—C16	1.394 (3)
O1—C14	1.363 (3)	C11—C12	1.402 (3)
O1—H1	0.77 (3)	C12—C13	1.381 (3)
C2—C18	1.519 (3)	C12—H12	0.9500
C2—C19	1.530 (3)	C13—C14	1.398 (3)
C2—C3	1.539 (3)	C13—H13	0.9500
C3—C4	1.560 (3)	C14—C15	1.393 (3)
C3—H3A	0.9900	C15—C16	1.395 (3)
C3—H3B	0.9900	C15—H15	0.9500
C4—C11	1.535 (3)	C16—H16	0.9500
C4—C5	1.536 (3)	C17—H17A	0.9800

C4—C17	1.545 (3)	C17—H17B	0.9800
C5—C10	1.398 (3)	C17—H17C	0.9800
C5—C6	1.399 (3)	C18—H18A	0.9800
C6—C7	1.387 (3)	C18—H18B	0.9800
C6—H6	0.9500	C18—H18C	0.9800
C7—C8	1.395 (4)	C19—H19A	0.9800
C7—H7	0.9500	C19—H19B	0.9800
C8—C9	1.383 (3)	C19—H19C	0.9800
C8—H8	0.9500		
O2—S1—C10	106.02 (10)	C9—C10—S1	115.34 (17)
O2—S1—C2	108.79 (10)	C5—C10—S1	122.27 (16)
C10—S1—C2	98.01 (10)	C16—C11—C12	117.0 (2)
C14—O1—H1	110 (2)	C16—C11—C4	124.22 (19)
C18—C2—C19	110.19 (19)	C12—C11—C4	118.76 (19)
C18—C2—C3	117.26 (19)	C13—C12—C11	122.0 (2)
C19—C2—C3	109.35 (18)	C13—C12—H12	119.0
C18—C2—S1	111.29 (16)	C11—C12—H12	119.0
C19—C2—S1	105.39 (15)	C12—C13—C14	120.26 (19)
C3—C2—S1	102.53 (14)	C12—C13—H13	119.9
C2—C3—C4	119.60 (18)	C14—C13—H13	119.9
C2—C3—H3A	107.4	O1—C14—C15	123.3 (2)
C4—C3—H3A	107.4	O1—C14—C13	117.9 (2)
C2—C3—H3B	107.4	C15—C14—C13	118.8 (2)
C4—C3—H3B	107.4	C14—C15—C16	120.2 (2)
H3A—C3—H3B	107.0	C14—C15—H15	119.9
C11—C4—C5	108.25 (16)	C16—C15—H15	119.9
C11—C4—C17	111.28 (18)	C11—C16—C15	121.8 (2)
C5—C4—C17	108.20 (17)	C11—C16—H16	119.1
C11—C4—C3	106.76 (17)	C15—C16—H16	119.1
C5—C4—C3	113.09 (18)	C4—C17—H17A	109.5
C17—C4—C3	109.29 (17)	C4—C17—H17B	109.5
C10—C5—C6	116.23 (19)	H17A—C17—H17B	109.5
C10—C5—C4	124.4 (2)	C4—C17—H17C	109.5
C6—C5—C4	119.3 (2)	H17A—C17—H17C	109.5
C7—C6—C5	122.3 (2)	H17B—C17—H17C	109.5
C7—C6—H6	118.9	C2—C18—H18A	109.5
C5—C6—H6	118.9	C2—C18—H18B	109.5
C6—C7—C8	120.0 (2)	H18A—C18—H18B	109.5
C6—C7—H7	120.0	C2—C18—H18C	109.5
C8—C7—H7	120.0	H18A—C18—H18C	109.5
C9—C8—C7	119.2 (2)	H18B—C18—H18C	109.5
C9—C8—H8	120.4	C2—C19—H19A	109.5
C7—C8—H8	120.4	C2—C19—H19B	109.5
C8—C9—C10	120.0 (2)	H19A—C19—H19B	109.5
C8—C9—H9	120.0	C2—C19—H19C	109.5
C10—C9—H9	120.0	H19A—C19—H19C	109.5
C9—C10—C5	122.3 (2)	H19B—C19—H19C	109.5



O2—S1—C2—C18	45.94 (19)	C6—C5—C10—C9	2.8 (3)
C10—S1—C2—C18	-64.08 (18)	C4—C5—C10—C9	-175.00 (19)
O2—S1—C2—C19	-73.49 (17)	C6—C5—C10—S1	-172.93 (15)
C10—S1—C2—C19	176.50 (15)	C4—C5—C10—S1	9.3 (3)
O2—S1—C2—C3	172.10 (14)	O2—S1—C10—C9	31.70 (18)
C10—S1—C2—C3	62.09 (15)	C2—S1—C10—C9	143.96 (16)
C18—C2—C3—C4	54.9 (3)	O2—S1—C10—C5	-152.32 (17)
C19—C2—C3—C4	-178.82 (18)	C2—S1—C10—C5	-40.06 (19)
S1—C2—C3—C4	-67.3 (2)	C5—C4—C11—C16	-124.3 (2)
C2—C3—C4—C11	152.40 (17)	C17—C4—C11—C16	-5.6 (3)
C2—C3—C4—C5	33.5 (2)	C3—C4—C11—C16	113.6 (2)
C2—C3—C4—C17	-87.1 (2)	C5—C4—C11—C12	58.2 (2)
C11—C4—C5—C10	-117.8 (2)	C17—C4—C11—C12	176.96 (19)
C17—C4—C5—C10	121.5 (2)	C3—C4—C11—C12	-63.9 (2)
C3—C4—C5—C10	0.3 (3)	C16—C11—C12—C13	0.7 (3)
C11—C4—C5—C6	64.5 (2)	C4—C11—C12—C13	178.3 (2)
C17—C4—C5—C6	-56.2 (2)	C11—C12—C13—C14	-1.7 (3)
C3—C4—C5—C6	-177.41 (19)	C12—C13—C14—O1	-179.3 (2)
C10—C5—C6—C7	-1.7 (3)	C12—C13—C14—C15	1.2 (3)
C4—C5—C6—C7	176.2 (2)	O1—C14—C15—C16	-179.3 (2)
C5—C6—C7—C8	-0.6 (4)	C13—C14—C15—C16	0.3 (3)
C6—C7—C8—C9	2.0 (4)	C12—C11—C16—C15	0.8 (3)
C7—C8—C9—C10	-1.0 (3)	C4—C11—C16—C15	-176.7 (2)
C8—C9—C10—C5	-1.5 (3)	C14—C15—C16—C11	-1.3 (3)
C8—C9—C10—S1	174.49 (17)		

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>
O1—H1...O2 <sup>i</sup>	0.77 (3)	1.92 (3)	2.685 (3)	169 (3)

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