



Crystal structure of 2-[bis(benzylsulfanyl)methyl]-6-methoxyphenol

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[†] Current address: Discipline of Chemistry, Indian Institute of Technology Indore, Khandwa Road, Simrol Indore 453552, MP, India.**Keywords:** crystal structure; *ortho*-vanillin; thioacetal; dithioether; supramolecular network.**CCDC reference:** 1983985**Supporting information:** this article has supporting information at journals.iucr.org/e^aInstitut UTINAM UMR 6213 CNRS, Université Bourgogne Franche-Comté, 16, Route de Gray, 25030 Besançon Cedex, France, and ^bAnorganische Chemie, TU Dortmund University, Otto-Hahn-Str. 6/6a, D-44227 Dortmund, Germany.

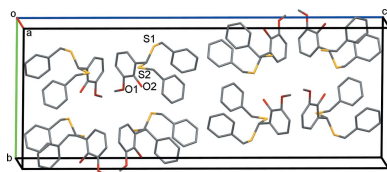
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The title compound, C₂₂H₂₂O₂S₂, **1**, represents an example of an *ortho*-vanillin-based functionalized dithioether, which could be useful as a potential chelating ligand or bridging ligand for coordination chemistry. This dithioacetal **1** crystallizes in the orthorhombic space group *Pbca*. The phenyl rings of the benzyl groups and that of the vanillin unit form dihedral angles of 35.38 (6) and 79.77 (6)°, respectively. The crystal structure, recorded at 100 K, displays both weak intramolecular O—H···O and intermolecular O—H···S hydrogen bonding.

1. Chemical context

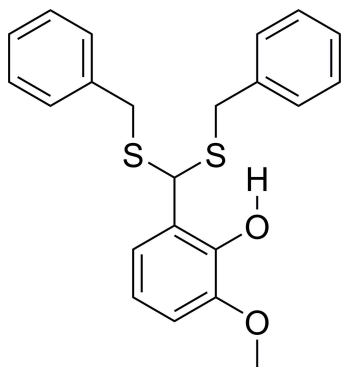
Acyclic and cyclic dithioether compounds containing the —S—C(R)(H)—S— (*R* = H, alkyl, aryl) motif are synthesized by nucleophilic substitution of geminal dihalides X—C(R)(H)—X in the presence of thiolate RS[−] (Murray *et al.*, 1981). Alternatively, they are readily accessible by treatment of aldehydes and ketones with thiols RSH and dithiols HS(CH₂)_{*n*}SH (*n* = 2, 3), yielding geminal dithio ethers, also called acyclic and cyclic thioacetals (1,3-dithiolanes, 1,3-dithianes) (Shaterian *et al.*, 2011). This type of organosulfur compound is commonly used for Corey–Seebach umpolung reactions and the Mzingo reduction of dithioacetals to hydrocarbons (Seebach & Corey, 1975; Zhao *et al.*, 2017), but there are also numerous other transformations in organic chemistry such as their oxidation to sulfoxides and sulfones (Gasparrini *et al.*, 1984). They have also been used in the past as monodentate, chelating or bridging ligands to construct both simple mono- and dinuclear coordination compounds or to assemble coordination networks of varying dimensionality ranging from 1D to 3D. Selected examples are [(C₅H₅)Fe(CO)₂(κ¹-BzSCH₂SBz)]⁺, the 1:1 adduct [Hg₂(NO₃)₂·BzSCH₂SBz], the dinuclear Pd^I complex [ClPd(μ₂-BzSCH₂SBz)₂PdCl], and the monodimensional coordination polymer [Ag₂(BzSCH₂SBz)₂](ClO₄)₂ built upon dinuclear [Ag(μ₂-BzSCH₂SBz)₂Ag]²⁺ units (Brodersen & Rölz, 1977; Fuchita *et al.*, 1991; Kuhn & Schumann, 1986; Li *et al.*, 2005).

In the context of our research interest in the assembly of molecular cluster compounds and coordination polymers by complexation of ArSCH₂SAr or dithiolane- and dithiane-based thiaheterocycles (Chaabéne *et al.*, 2016; Knauer *et al.*, 2020; Knorr *et al.*, 2014; Raghuvanshi *et al.*, 2017, 2019; Schlachter *et al.*, 2018), we have developed novel functionalized dithio ether compounds such as ferrocenyl thioethers



bearing a substituent at the α -carbon atom linking the two $-SR$ groups. With the idea of designing a functionalized thioacetal ligand bearing additional harder O-donor sites along with the two soft S-donor sites, we chose 2-hydroxy-3-methoxybenzaldehyde (*ortho*-vanillin) as the starting material. This hydroxylated aldehyde is present in the extracts and essential oils of many plants. Several papers describe also its use (in its deprotonated vanillinato form or as a Schiff base-derived ligand) in coordination chemistry (Andruh, 2015; Kırpık *et al.*, 2019; Yu *et al.*, 2011). Its reaction with 2 equivalents of benzyl mercaptan affords the targeted dithioacetal 2-hydroxy-3-methoxyphenyl[bis(benzylthio)]methane, **1**, which was isolated in high yield as a crystalline solid.

This acyclic thioacetal contains, in addition to the benzylic thio ether groups and the methoxy group prone to ligate metal centres, a phenolic hydroxyl group, which may allow additional interactions through hydrogen bonding.



2. Structural commentary

Compound **1** crystallizes from CH_2Cl_2 /hexane in the orthorhombic crystal system, space group *Pbca*. The C1–S1 and

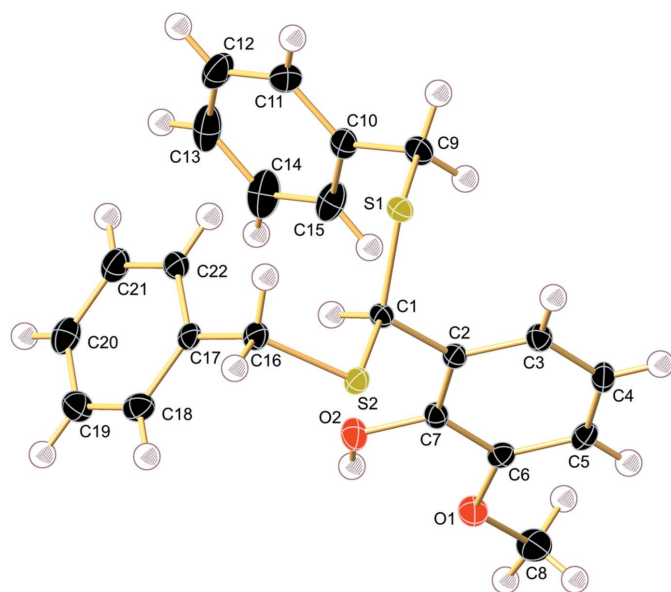


Figure 1
The molecular structure of **1** with displacement ellipsoids drawn at the 50% probability level.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$Cg1$ is the centroid of the C2–C7 ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|----------|-------------|-------------|---------------|
| $O2-H2\cdots S1^i$ | 0.85 (2) | 2.44 (2) | 3.1315 (13) | 139.0 (17) |
| $O2-H2\cdots O1$ | 0.85 (2) | 2.17 (2) | 2.6469 (16) | 115.4 (16) |
| $C9-H9A\cdots C20^{ii}$ | 0.99 | 2.86 | 3.528 (2) | 125 |
| $C5-H5\cdots Cg1^{iii}$ | 0.95 | 2.84 | 3.7487 (15) | 160 |
| $C16-H16A\cdots Cg1^{iv}$ | 0.99 | 2.71 | 3.6316 (15) | 154 |

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

C1–S2 bond lengths of 1.8132 (12) and 1.8189 (12) \AA are comparable with those of [BzSC(H)(C₆H₄NO₂-*p*)SBz] [1.823 (3) and 1.8262 (19) \AA], but are elongated compared with those of bis(benzylsulfanyl)methane (CSD TUQPAX) [1.7988 (13) and 1.8013 (13) \AA ; Yang *et al.*, 2010). The angle S1–C1–S2 is almost identical with that of 4-nitrophenyl-bis(benzylsulfanyl)methane [107.26 (6) *versus* 107.76 $^\circ$], but considerably more acute than in [BzSCH₂SBz] [117.33 (7) $^\circ$]. There is a weak intramolecular O1 \cdots H2 contact of 2.17 (2) \AA between the H atom of the phenolic hydroxyl group and the O-atom of the methoxy group (Table 1). For the starting material, 2-hydroxy-3-methoxybenzaldehyde, a similar intramolecular hydrogen bond seems to be absent; instead, a rather strong intramolecular hydrogen bond between the O–H group and the carbonyl oxygen was found (Iwasaki *et al.*, 1976). The phenyl rings of the benzyl groups (C10–C15) and (C17–C22) and the phenyl ring of the vanillin unit (C2–C7) form dihedral angles of 35.38 (6) and 79.77 (6) $^\circ$, respectively. Compared to the structurally very closely related compound 4-nitrophenyl-bis(benzylsulfanyl)methane [BzSC(H)(C₆H₄NO₂-*p*)SBz] (SUNMAQ; Binkowska *et al.*, 2009), the coplanar and perpendicular arrangement of the phenyl rings is thus lost in **1** (Figs. 1 and 2).

3. Supramolecular features

In the crystal, there is an O–H \cdots S hydrogen bond between the H2 atom of the phenolic hydroxyl group and the S1 atom of a neighbouring molecule with distances [H2 \cdots S1 = 2.44 (2),

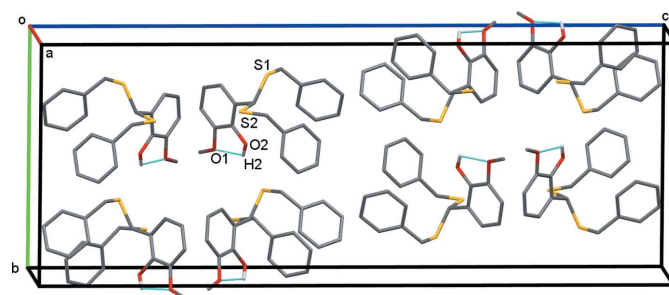


Figure 2
A view of the crystal packing of the title compound. For clarity, H atoms have been omitted. The intramolecular O1 \cdots H2 contacts are shown as dashed lines. For clarity, only H atoms involved in these interactions are presented. The intermolecular contacts are shown in Fig. 3.

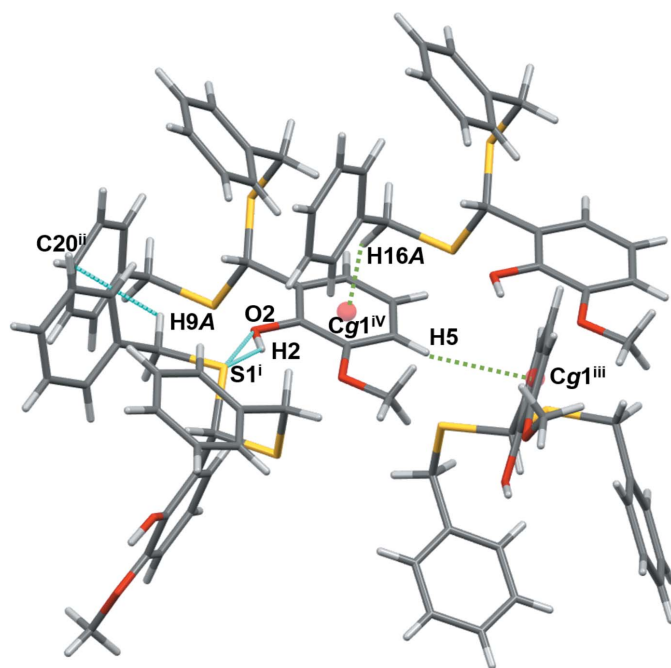


Figure 3
Intermolecular contacts for compound **1**. Symmetry codes as in Table 1.

$O2 \cdots S1 = 3.1315(13) \text{ \AA}$] similar to those reported for 4-(1,3-dithian-2-yl)-1,2-benzenediol [$H \cdots S = 2.44$, $O \cdots S = 3.2417(13) \text{ \AA}$], while the $O-H \cdots S$ angle is more acute [$139.0(17) \text{ versus } 159.2^\circ$] (Fig. 3 and Table 1). This $O2-H2 \cdots S1$ interaction results in the formation of chains running along the b -axis direction.

The benzylic methylene group on sulfur atom S2 interacts with the π -cloud of the phenyl part of the vanillin unit through a $C-H \cdots \pi$ interaction (Table 1). The second phenyl ring of the dithiane unit also exhibits a $C-H \cdots \pi$ interaction: the second methylene group on sulfur atom S1 interacts with a phenyl carbon. The third $C-H \cdots \pi$ contact is between adjacent vanillin units.

4. Database survey

There are several other examples of structurally characterized related dithioethers bearing hydroxy substituents that give rise to the formation of supramolecular networks. Selected examples found in the Cambridge Structural Database (CSD, version 5.40, update August 2019; Groom *et al.*, 2016) include 2-(2-hydroxyphenyl)-1,3-dithiane (WADROJ; Usman *et al.*, 2003), 2-(3-hydroxyphenyl)-1,3-dithiane (KALJUD; Gan-

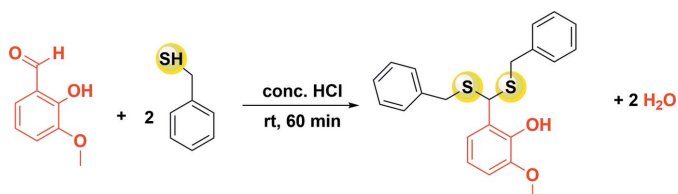


Figure 4
Synthesis of **1**.

Table 2
Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | $C_{22}H_{22}O_2S_2$ |
| M_r | 382.51 |
| Crystal system, space group | Orthorhombic, $Pbca$ |
| Temperature (K) | 100 |
| a, b, c (Å) | 7.7418 (8), 13.856 (3), 36.197 (5) |
| V (Å ³) | 3882.9 (10) |
| Z | 8 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 0.29 |
| Crystal size (mm) | $0.49 \times 0.42 \times 0.25$ |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE area detector |
| Absorption correction | Multi-scan (SADABS; Bruker, 2016) |
| T_{min}, T_{max} | 0.713, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 107706, 5005, 4510 |
| R_{int} | 0.033 |
| $(\sin \theta/\lambda)_{max}$ (Å ⁻¹) | 0.684 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.034, 0.079, 1.09 |
| No. of reflections | 5005 |
| No. of parameters | 241 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³) | 0.34, -0.23 |

Computer programs: APEX2 and SAINT (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

guly *et al.*, 2005), 4,6-bis(1,3-dithian-2-yl)benzene-1,3-diol (DITFIX; Datta *et al.*, 2013), 4-(1,3-dithian-2-yl)benzene-1,3-diol (DITFOD; Datta *et al.*, 2013), 2-phenyl-1,3-dithiepane-5,6-diol (FIBTOC; Liu *et al.*, 2018) and 2,2'-[[4-methoxyphenyl)methylene]disulfanediy]diethanol (YISVUT; Laskar *et al.*, 2013). It is notable that in most of these examples, the intermolecular contacts are noticeably stronger than those of **1**.

Note that in dithioether compounds with phenolic aryl groups as encountered in **1**, the relative position of the phenolic OH substituent seems to play a crucial role, whether the intermolecular contacts are dominated by $O-H \cdots H$ or $O-H \cdots S$ hydrogen bonds. This is nicely illustrated by the series of three isomeric hydroxyphenyl-1,3-dithianes, *ortho*-, *meta*- and *para*- $HO-C_6H_4-C_4H_7S_2$. Whereas 2-(2-hydroxyphenyl)-1,3-dithiane (WADROY) and 2-(3-hydroxyphenyl)-1,3-dithiane (KALJUD) exhibit, like **1**, only intermolecular $O-H \cdots S$ hydrogen bonding, the *para*-derivative 2-(4-hydroxyphenyl)-1,3-dithiane (KALKAK) features solely intermolecular phenolic $O-H \cdots H$ bonding (Ganguly *et al.*, 2005).

5. Synthesis and crystallization

The reaction scheme for the synthesis of the title compound is illustrated in Fig. 4.

3-Methoxysalicylaldehyde (1 mmol, 152 mg), benzyl mercaptan (2.5 mmol, 310 mg), and conc. HCl (2 mL) were

added to a flask at 273 K. The mixture was stirred for 60 min at room temperature. After the reaction was complete, the resulting mixture was neutralized with 10% aq NaHCO₃ (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined extracts were washed with H₂O (3 × 20 mL) and dried over Na₂SO₄. Evaporation of the solvent *in vacuo* gave a solid product, which was further purified by column chromatography. The product was obtained as a white solid, Yield: 83% (430 mg). X-ray quality crystals were obtained by keeping a dichloromethane:hexane (1:1) mixture of **1** at 278 K for 3–4 d. ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.19 (*m*, 11H, Ph), 6.86 (*t*, *J* = 7.8 Hz, 1H, CH), 6.78 (*d*, *J* = 7.8 Hz, 1H, CH), 5.83 (*s*, 1H, OH), 5.13 (*s*, 1H CHS₂), 3.88 (*s*, 3H, OCH₃), 3.79 (*d*, *J* = 13.1 Hz, 2H, CH₂), 3.64 (*d*, *J* = 13.1 Hz, 2H, CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.5 (C_qOH), 142.8 (C_qOCH₃), 137.8 (SCH₂C_q), 129.1 (SCH₂CCH), 128.4 (SCH₂CCHCH), 126.9 (SCH₂CCHCHCH), 125.3 (S₂CHC_q), 120.9 (S₂CHC_qCH), 119.9 (S₂CHC_qCHCH), 110.0 (CHC_qOCH₃), 56.1 (OCH₃), 44.8 (S₂CH), 36.7 (S₂CH₂). IR (ATR) cm⁻¹: 3419 (O–H), 1430–1612 (C=C). 1054 and 1264 (C–O), 766 (C–S). HRMS: (ESI) *m/z* calculated for C₂₂H₂₂O₂S₂Na [*M* + Na]⁺ 405.0953, found 405.0965.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically (C–H = 0.95–1.00 Å) and refined using a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(C) for CH₂ and CH hydrogen atoms and *U*_{iso}(H) = 1.5*U*_{eq}(C-methyl). The phenolic proton H2 was refined independently.

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supporting information

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Crystal structure of 2-[bis(benzylsulfanyl)methyl]-6-methoxyphenol

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Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

2-[Bis(benzylsulfanyl)methyl]-6-methoxyphenol

Crystal data

$C_{22}H_{22}O_2S_2$

$M_r = 382.51$

Orthorhombic, *Pbca*

$a = 7.7418$ (8) Å

$b = 13.856$ (3) Å

$c = 36.197$ (5) Å

$V = 3882.9$ (10) Å³

$Z = 8$

$F(000) = 1616$

$D_x = 1.309$ Mg m⁻³

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

Cell parameters from 9791 reflections

$\theta = 2.3$ – 28.2°

$\mu = 0.29$ mm⁻¹

$T = 100$ K

Block, colourless

$0.49 \times 0.42 \times 0.25$ mm

Data collection

Bruker D8 VENTURE area detector
diffractometer

Radiation source: microfocus sealed X-ray tube,
Incoatec μ s

HELIOS mirror optics monochromator

Detector resolution: 10.4167 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

$T_{\min} = 0.713$, $T_{\max} = 0.746$

107706 measured reflections

5005 independent reflections

4510 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -9 \rightarrow 10$

$k = -18 \rightarrow 18$

$l = -49 \rightarrow 45$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.079$

$S = 1.09$

5005 reflections

241 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 2.6399P]$

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

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.34$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

Extinction correction: SHELXL-2018/3

(Sheldrick 2015b),

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

Extinction coefficient: 0.0017 (2)

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|-------------|----------------------------------|
| S1 | 0.61115 (4) | 0.82824 (2) | 0.63211 (2) | 0.01667 (8) |
| S2 | 0.42202 (4) | 0.68918 (2) | 0.67748 (2) | 0.01772 (8) |
| O1 | 1.02466 (13) | 0.48649 (7) | 0.70693 (3) | 0.0234 (2) |
| O2 | 0.76523 (13) | 0.52864 (7) | 0.66212 (3) | 0.0228 (2) |
| H2 | 0.826 (3) | 0.4778 (15) | 0.6649 (5) | 0.043 (5)* |
| C1 | 0.62315 (15) | 0.70907 (8) | 0.65265 (3) | 0.0146 (2) |
| H1 | 0.631957 | 0.660278 | 0.632378 | 0.017* |
| C2 | 0.77100 (15) | 0.69329 (8) | 0.67929 (3) | 0.0147 (2) |
| C3 | 0.84314 (17) | 0.76632 (9) | 0.70092 (3) | 0.0179 (2) |
| H3 | 0.799141 | 0.830165 | 0.699171 | 0.022* |
| C4 | 0.97814 (17) | 0.74678 (10) | 0.72490 (3) | 0.0202 (3) |
| H4 | 1.025853 | 0.797416 | 0.739354 | 0.024* |
| C5 | 1.04472 (16) | 0.65382 (9) | 0.72807 (3) | 0.0185 (2) |
| H5 | 1.137719 | 0.640764 | 0.744446 | 0.022* |
| C6 | 0.97346 (16) | 0.58102 (9) | 0.70704 (3) | 0.0172 (2) |
| C7 | 0.83624 (16) | 0.60032 (9) | 0.68273 (3) | 0.0157 (2) |
| C8 | 1.17946 (19) | 0.46331 (11) | 0.72664 (5) | 0.0311 (3) |
| H8A | 1.274327 | 0.503799 | 0.717632 | 0.047* |
| H8B | 1.208119 | 0.395191 | 0.722705 | 0.047* |
| H8C | 1.161929 | 0.475073 | 0.753070 | 0.047* |
| C9 | 0.81405 (17) | 0.83571 (10) | 0.60670 (4) | 0.0222 (3) |
| H9A | 0.828248 | 0.902523 | 0.597491 | 0.027* |
| H9B | 0.910248 | 0.822557 | 0.623999 | 0.027* |
| C10 | 0.82841 (17) | 0.76755 (10) | 0.57454 (4) | 0.0216 (3) |
| C11 | 0.7673 (2) | 0.79298 (12) | 0.53965 (4) | 0.0294 (3) |
| H11 | 0.712651 | 0.853694 | 0.536144 | 0.035* |
| C12 | 0.7855 (2) | 0.73040 (14) | 0.51001 (4) | 0.0354 (4) |
| H12 | 0.742688 | 0.748223 | 0.486385 | 0.043* |
| C13 | 0.8656 (2) | 0.64242 (14) | 0.51472 (4) | 0.0367 (4) |
| H13 | 0.880248 | 0.600256 | 0.494264 | 0.044* |
| C14 | 0.9247 (2) | 0.61563 (13) | 0.54931 (5) | 0.0360 (4) |
| H14 | 0.978548 | 0.554677 | 0.552712 | 0.043* |
| C15 | 0.90510 (18) | 0.67790 (11) | 0.57899 (4) | 0.0275 (3) |
| H15 | 0.944821 | 0.658858 | 0.602728 | 0.033* |
| C16 | 0.26715 (16) | 0.68531 (9) | 0.63950 (3) | 0.0188 (2) |
| H16A | 0.150774 | 0.672722 | 0.649760 | 0.023* |
| H16B | 0.264227 | 0.749436 | 0.627453 | 0.023* |
| C17 | 0.30595 (16) | 0.61034 (9) | 0.61075 (3) | 0.0176 (2) |
| C18 | 0.25087 (18) | 0.51529 (10) | 0.61502 (4) | 0.0231 (3) |

| | | | | |
|-----|--------------|--------------|-------------|------------|
| H18 | 0.188646 | 0.497061 | 0.636537 | 0.028* |
| C19 | 0.2863 (2) | 0.44732 (10) | 0.58807 (4) | 0.0274 (3) |
| H19 | 0.246189 | 0.382978 | 0.590983 | 0.033* |
| C20 | 0.37995 (19) | 0.47228 (11) | 0.55688 (4) | 0.0264 (3) |
| H20 | 0.406356 | 0.424957 | 0.538749 | 0.032* |
| C21 | 0.43459 (18) | 0.56639 (12) | 0.55233 (4) | 0.0269 (3) |
| H21 | 0.498143 | 0.584070 | 0.530921 | 0.032* |
| C22 | 0.39681 (17) | 0.63509 (10) | 0.57896 (4) | 0.0223 (3) |
| H22 | 0.433413 | 0.699893 | 0.575465 | 0.027* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|---------------|--------------|
| S1 | 0.01657 (15) | 0.01393 (14) | 0.01952 (15) | −0.00028 (11) | −0.00002 (11) | 0.00077 (10) |
| S2 | 0.01469 (15) | 0.02377 (16) | 0.01471 (14) | −0.00302 (11) | −0.00020 (11) | 0.00089 (11) |
| O1 | 0.0226 (5) | 0.0196 (4) | 0.0279 (5) | 0.0043 (4) | −0.0075 (4) | 0.0010 (4) |
| O2 | 0.0254 (5) | 0.0145 (4) | 0.0285 (5) | 0.0022 (4) | −0.0092 (4) | −0.0048 (4) |
| C1 | 0.0133 (5) | 0.0145 (5) | 0.0159 (5) | −0.0009 (4) | −0.0003 (4) | 0.0000 (4) |
| C2 | 0.0129 (5) | 0.0164 (5) | 0.0147 (5) | −0.0011 (4) | 0.0002 (4) | −0.0002 (4) |
| C3 | 0.0184 (6) | 0.0174 (6) | 0.0180 (6) | −0.0009 (5) | −0.0005 (5) | −0.0022 (4) |
| C4 | 0.0207 (6) | 0.0231 (6) | 0.0169 (6) | −0.0049 (5) | −0.0014 (5) | −0.0035 (5) |
| C5 | 0.0147 (6) | 0.0266 (6) | 0.0141 (5) | −0.0014 (5) | −0.0013 (4) | 0.0017 (5) |
| C6 | 0.0166 (6) | 0.0193 (6) | 0.0158 (5) | 0.0013 (5) | 0.0007 (4) | 0.0022 (4) |
| C7 | 0.0146 (6) | 0.0172 (5) | 0.0154 (5) | −0.0018 (4) | 0.0003 (4) | −0.0012 (4) |
| C8 | 0.0235 (7) | 0.0270 (7) | 0.0428 (9) | 0.0027 (6) | −0.0105 (6) | 0.0110 (6) |
| C9 | 0.0189 (6) | 0.0261 (6) | 0.0217 (6) | −0.0069 (5) | 0.0026 (5) | 0.0003 (5) |
| C10 | 0.0148 (6) | 0.0315 (7) | 0.0186 (6) | −0.0065 (5) | 0.0025 (5) | −0.0010 (5) |
| C11 | 0.0307 (8) | 0.0356 (8) | 0.0221 (6) | −0.0084 (6) | −0.0008 (6) | 0.0060 (6) |
| C12 | 0.0323 (8) | 0.0572 (10) | 0.0168 (6) | −0.0122 (8) | −0.0003 (6) | 0.0013 (6) |
| C13 | 0.0223 (7) | 0.0615 (11) | 0.0264 (7) | −0.0047 (7) | 0.0033 (6) | −0.0175 (7) |
| C14 | 0.0210 (7) | 0.0494 (10) | 0.0376 (8) | 0.0090 (7) | −0.0038 (6) | −0.0153 (7) |
| C15 | 0.0167 (6) | 0.0423 (8) | 0.0236 (7) | 0.0046 (6) | −0.0036 (5) | −0.0051 (6) |
| C16 | 0.0131 (6) | 0.0258 (6) | 0.0175 (6) | −0.0020 (5) | −0.0024 (5) | 0.0022 (5) |
| C17 | 0.0121 (5) | 0.0250 (6) | 0.0157 (5) | −0.0019 (5) | −0.0037 (4) | 0.0027 (5) |
| C18 | 0.0216 (6) | 0.0254 (6) | 0.0222 (6) | −0.0030 (5) | −0.0006 (5) | 0.0061 (5) |
| C19 | 0.0304 (8) | 0.0213 (6) | 0.0306 (7) | −0.0009 (6) | −0.0054 (6) | 0.0034 (5) |
| C20 | 0.0227 (7) | 0.0319 (7) | 0.0247 (7) | 0.0049 (6) | −0.0067 (5) | −0.0060 (6) |
| C21 | 0.0219 (7) | 0.0411 (8) | 0.0177 (6) | −0.0061 (6) | 0.0007 (5) | −0.0017 (6) |
| C22 | 0.0205 (6) | 0.0282 (7) | 0.0182 (6) | −0.0083 (5) | −0.0017 (5) | 0.0022 (5) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|---------|-------------|
| S1—C1 | 1.8132 (12) | C10—C11 | 1.3940 (19) |
| S1—C9 | 1.8232 (14) | C10—C15 | 1.386 (2) |
| S2—C1 | 1.8189 (12) | C11—H11 | 0.9500 |
| S2—C16 | 1.8250 (13) | C11—C12 | 1.387 (2) |
| O1—C6 | 1.3685 (15) | C12—H12 | 0.9500 |
| O1—C8 | 1.4312 (17) | C12—C13 | 1.378 (3) |

| | | | |
|-----------|-------------|---------------|-------------|
| O2—H2 | 0.85 (2) | C13—H13 | 0.9500 |
| O2—C7 | 1.3584 (15) | C13—C14 | 1.383 (2) |
| C1—H1 | 1.0000 | C14—H14 | 0.9500 |
| C1—C2 | 1.5126 (16) | C14—C15 | 1.386 (2) |
| C2—C3 | 1.3960 (17) | C15—H15 | 0.9500 |
| C2—C7 | 1.3893 (17) | C16—H16A | 0.9900 |
| C3—H3 | 0.9500 | C16—H16B | 0.9900 |
| C3—C4 | 1.3854 (18) | C16—C17 | 1.5007 (18) |
| C4—H4 | 0.9500 | C17—C18 | 1.3929 (18) |
| C4—C5 | 1.3920 (19) | C17—C22 | 1.3917 (17) |
| C5—H5 | 0.9500 | C18—H18 | 0.9500 |
| C5—C6 | 1.3789 (18) | C18—C19 | 1.383 (2) |
| C6—C7 | 1.4051 (17) | C19—H19 | 0.9500 |
| C8—H8A | 0.9800 | C19—C20 | 1.385 (2) |
| C8—H8B | 0.9800 | C20—H20 | 0.9500 |
| C8—H8C | 0.9800 | C20—C21 | 1.381 (2) |
| C9—H9A | 0.9900 | C21—H21 | 0.9500 |
| C9—H9B | 0.9900 | C21—C22 | 1.386 (2) |
| C9—C10 | 1.5031 (19) | C22—H22 | 0.9500 |
| | | | |
| C1—S1—C9 | 102.38 (6) | C15—C10—C9 | 120.31 (12) |
| C1—S2—C16 | 101.22 (6) | C15—C10—C11 | 118.51 (13) |
| C6—O1—C8 | 117.12 (11) | C10—C11—H11 | 119.7 |
| C7—O2—H2 | 108.5 (14) | C12—C11—C10 | 120.54 (15) |
| S1—C1—S2 | 107.26 (6) | C12—C11—H11 | 119.7 |
| S1—C1—H1 | 108.6 | C11—C12—H12 | 119.9 |
| S2—C1—H1 | 108.6 | C13—C12—C11 | 120.22 (14) |
| C2—C1—S1 | 115.59 (8) | C13—C12—H12 | 119.9 |
| C2—C1—S2 | 108.11 (8) | C12—C13—H13 | 120.1 |
| C2—C1—H1 | 108.6 | C12—C13—C14 | 119.86 (15) |
| C3—C2—C1 | 123.74 (11) | C14—C13—H13 | 120.1 |
| C7—C2—C1 | 117.80 (10) | C13—C14—H14 | 120.1 |
| C7—C2—C3 | 118.45 (11) | C13—C14—C15 | 119.88 (16) |
| C2—C3—H3 | 119.6 | C15—C14—H14 | 120.1 |
| C4—C3—C2 | 120.77 (12) | C10—C15—H15 | 119.5 |
| C4—C3—H3 | 119.6 | C14—C15—C10 | 120.96 (14) |
| C3—C4—H4 | 119.6 | C14—C15—H15 | 119.5 |
| C3—C4—C5 | 120.79 (12) | S2—C16—H16A | 108.7 |
| C5—C4—H4 | 119.6 | S2—C16—H16B | 108.7 |
| C4—C5—H5 | 120.6 | H16A—C16—H16B | 107.6 |
| C6—C5—C4 | 118.90 (12) | C17—C16—S2 | 114.28 (9) |
| C6—C5—H5 | 120.6 | C17—C16—H16A | 108.7 |
| O1—C6—C5 | 125.87 (12) | C17—C16—H16B | 108.7 |
| O1—C6—C7 | 113.53 (11) | C18—C17—C16 | 121.08 (11) |
| C5—C6—C7 | 120.59 (12) | C22—C17—C16 | 120.27 (12) |
| O2—C7—C2 | 118.79 (11) | C22—C17—C18 | 118.65 (12) |
| O2—C7—C6 | 120.71 (11) | C17—C18—H18 | 119.8 |
| C2—C7—C6 | 120.50 (11) | C19—C18—C17 | 120.31 (13) |

| | | | |
|----------------|--------------|-----------------|--------------|
| O1—C8—H8A | 109.5 | C19—C18—H18 | 119.8 |
| O1—C8—H8B | 109.5 | C18—C19—H19 | 119.7 |
| O1—C8—H8C | 109.5 | C18—C19—C20 | 120.56 (13) |
| H8A—C8—H8B | 109.5 | C20—C19—H19 | 119.7 |
| H8A—C8—H8C | 109.5 | C19—C20—H20 | 120.2 |
| H8B—C8—H8C | 109.5 | C21—C20—C19 | 119.55 (13) |
| S1—C9—H9A | 108.6 | C21—C20—H20 | 120.2 |
| S1—C9—H9B | 108.6 | C20—C21—H21 | 120.0 |
| H9A—C9—H9B | 107.6 | C20—C21—C22 | 120.06 (13) |
| C10—C9—S1 | 114.75 (9) | C22—C21—H21 | 120.0 |
| C10—C9—H9A | 108.6 | C17—C22—H22 | 119.6 |
| C10—C9—H9B | 108.6 | C21—C22—C17 | 120.83 (13) |
| C11—C10—C9 | 121.18 (13) | C21—C22—H22 | 119.6 |
| | | | |
| S1—C1—C2—C3 | 30.00 (15) | C7—C2—C3—C4 | 0.84 (18) |
| S1—C1—C2—C7 | -151.09 (9) | C8—O1—C6—C5 | -8.60 (19) |
| S1—C9—C10—C11 | 87.20 (15) | C8—O1—C6—C7 | 170.97 (12) |
| S1—C9—C10—C15 | -93.52 (14) | C9—S1—C1—S2 | -177.44 (6) |
| S2—C1—C2—C3 | -90.18 (13) | C9—S1—C1—C2 | 61.92 (10) |
| S2—C1—C2—C7 | 88.73 (12) | C9—C10—C11—C12 | 178.27 (13) |
| S2—C16—C17—C18 | 85.08 (14) | C9—C10—C15—C14 | -177.74 (14) |
| S2—C16—C17—C22 | -95.56 (13) | C10—C11—C12—C13 | -0.4 (2) |
| O1—C6—C7—O2 | 0.73 (17) | C11—C10—C15—C14 | 1.6 (2) |
| O1—C6—C7—C2 | -179.12 (11) | C11—C12—C13—C14 | 1.4 (2) |
| C1—S1—C9—C10 | 66.89 (11) | C12—C13—C14—C15 | -0.8 (2) |
| C1—S2—C16—C17 | 56.83 (10) | C13—C14—C15—C10 | -0.6 (2) |
| C1—C2—C3—C4 | 179.74 (11) | C15—C10—C11—C12 | -1.0 (2) |
| C1—C2—C7—O2 | 0.19 (17) | C16—S2—C1—S1 | 66.50 (7) |
| C1—C2—C7—C6 | -179.95 (11) | C16—S2—C1—C2 | -168.23 (8) |
| C2—C3—C4—C5 | -0.18 (19) | C16—C17—C18—C19 | 179.38 (12) |
| C3—C2—C7—O2 | 179.17 (11) | C16—C17—C22—C21 | 179.52 (12) |
| C3—C2—C7—C6 | -0.98 (18) | C17—C18—C19—C20 | 1.3 (2) |
| C3—C4—C5—C6 | -0.34 (19) | C18—C17—C22—C21 | -1.1 (2) |
| C4—C5—C6—O1 | 179.74 (12) | C18—C19—C20—C21 | -1.5 (2) |
| C4—C5—C6—C7 | 0.19 (19) | C19—C20—C21—C22 | 0.4 (2) |
| C5—C6—C7—O2 | -179.67 (11) | C20—C21—C22—C17 | 0.9 (2) |
| C5—C6—C7—C2 | 0.48 (19) | C22—C17—C18—C19 | 0.0 (2) |

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C2—C7 ring.

| <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> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2—H2...S1 ⁱ | 0.85 (2) | 2.44 (2) | 3.1315 (13) | 139.0 (17) |
| O2—H2...O1 | 0.85 (2) | 2.17 (2) | 2.6469 (16) | 115.4 (16) |
| C9—H9A...C20 ⁱⁱ | 0.99 | 2.86 | 3.528 (2) | 125 |

| | | | | |
|-------------------------------------|------|------|-------------|-----|
| C5—H5 \cdots Cg1 ⁱⁱⁱ | 0.95 | 2.84 | 3.7487 (15) | 160 |
| C16—H16A \cdots Cg1 ^{iv} | 0.99 | 2.71 | 3.6316 (15) | 154 |

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