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Crystal structure of 2-Hydroxy-3-methoxyphenyl-(bis(benzylthio))methane

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Keywords

crystal structure; *ortho*-vanillin, thioacetal, dithioether; supramolecular network

Synopsis

The crystal structure of 2-hydroxy-3-methoxyphenyl-(bis(benzylthio))methane (C₂₂H₂₂O₂S₂) was determined at 100 K. Both weak intramolecular O—H···O and intermolecular O—H···S hydrogen bonding can be observed.

Abstract

The title compound **1**, 2-hydroxy-3-methoxyphenyl-(bis(benzylthio))methane (C₂₂H₂₂O₂S₂), represents an example of an *ortho*-vanillin-based functionalized dithioether, which could be useful as potential chelating ligand or bridging ligand for coordination chemistry. This dithioacetal **1**, crystallizes in the orthorhombic space group *Pbca*. 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 synthesised 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)_nSH (n = 2, 3) yielding geminal dithioethers, also called acyclic and cyclic thioacetals (1,3-dithiolanes, 1,3-dithianes) (Shaterian *et al.*, 2011). This type of organosulfur compounds is commonly used for Corey-Seebach umpolung reactions and the Mozingo reduction of dithioacetals to hydrocarbons (Seebach *et al.*, 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 furthermore 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], or

the monodimensional coordination polymer $[\text{Ag}_2(\text{BzSCH}_2\text{SBz})_2](\text{ClO}_4)_2$ built upon dinuclear $[\text{Ag}(\mu_2\text{-BzSCH}_2\text{SBz})_2\text{Ag}]^{2+}$ units (Brodersen *et al.*, 1977; Fuchita *et al.*, 1991; Kuhn *et al.*, 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 ArSCH_2SAr or dithiolane- and dithiane-based thiaheterocycles, (Chaabéne *et al.*, 2016; Knauer *et al.*, 2020; Knorr *et al.*, 2014; Raghuvanshi *et al.*, 2017; Raghuvanshi *et al.*, 2019; Schlachter *et al.*, 2018), we have developed novel functionalized dithioether compounds such as ferrocenyl thioethers bearing a substituent at the alpha-carbon atom linking the two -SR groups. With the idea to design a functionalized thioacetal ligand bearing along with the two soft S-donor sites additional harder O-donor sites, we have chosen 2-hydroxy-3-methoxybenzaldehyde (ortho-vanillin) as 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 Schiff base-derived ligand) in coordination chemistry (Andruh, 2015; Kirpik *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 crystalline solid (Scheme 1).

This acyclic thioacetal contains, in addition to the benzylic thioether 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 C1–S2 bond lengths of 1.8133 (12) and 1.8192 (12) Å match with those of $[\text{BzSC}(\text{H})(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{SBz}]$ (1.823 (3) and 1.8262 (19) Å), but elongated compared with those of bis(benzylsulfanyl)methane (CSD TUQPAX) (1.7988 (13) and 1.8013 (13) Å) (Yang *et al.*, 2010). The angle S1–C1–S2 is almost identical with that of 4-nitrophenyl-bis(benzylsulfanyl)methane (107.25 (6) *versus* 107.76°), but considerably more acute than that of $[\text{BzSCH}_2\text{SBz}]$ (117.33 (7)°). There is a weak intramolecular O1–H2 contact of 2.166 (19) Å between the H atom of the phenolic hydroxyl group and the O-atom of the methoxy group ($d_{\text{O1-H2}} = 2.6467$ (13) Å; $\text{O2-H2-O1} = 115.2$ (15)°). 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 evidenced (Iwaski *et al.*, 1976). The phenyl rings of the benzyl moieties (C10–C18) and (C17–C21) and the phenyl ring of the vanillin part (C2–C7) form dihedral angles of 35.391° and 100.230° respectively. Compared to the structurally very related compound 4-nitrophenyl-bis(benzylsulfanyl)methane $[\text{BzSC}(\text{H})(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{SBz}]$ (CSD SUNMAQ) (Binkowska *et al.*, 2009), the coplanar and perpendicular arrangement of the phenyl rings is thus lost in **1** (Fig.1 and Fig.2).

3. Supramolecular features

In the network, there is an intermolecular O–H \cdots S hydrogen bond between the H2 atom of the phenolic hydroxyl group and the S1 atom of a neighbored molecule with distances ($d_{\text{H2}\cdots\text{S1}} = 2.434$ (19) Å, $d_{\text{O2}\cdots\text{S1}} = 3.1318$ (10) Å) similar to those reported for 4-

(1,3-dithian-2-yl)-1,2-benzenediol ($d\text{H}\cdots\text{S} = 2.44 \text{ \AA}$, $d\text{O}\cdots\text{S} = 3.2417 (13) \text{ \AA}$), while the O-H-S angle is more acute ($\angle\text{O2-H2-S1} = 139.1 (16) \text{ versus } 159.2^\circ$) (Fig. 3 and Table 2). This O2–H2 \cdots S1 interaction results in chain formation running along the *b* direction.

One of the benzylic methylene group near the sulfur atom S2 interacts with the π -cloud of the phenyl part of the vanillin moiety through C-H $\cdots\pi$ contacts. The geometrical parameters for this interaction are $d(\text{H16A}\cdots\text{Cg}) = 2.715 \text{ \AA}$, $d(\text{C16}\cdots\text{Cg}) = 3.632 \text{ \AA}$, and $\angle\text{C16-H16}\cdots\text{Cg} = 154.21^\circ$. The second phenyl ring of the dithiane moiety also exhibits C-H $\cdots\pi$ interaction: the second methylene group near the sulfur atom S1 interacts with a phenyl carbon ($d(\text{H9A}\cdots\text{C20}) = 2.8630 (14) \text{ \AA}$, $d(\text{C9}\cdots\text{C20}) = 3.5271 (18) \text{ \AA}$ and $\angle\text{C9-H9A}\cdots\text{C20} = 125.15 (8)^\circ$). The third C-H $\cdots\pi$ contact involves H5 of one vanillin ring and the phenyl ring of an adjacent vanillin ring. The geometrical parameters for this interaction are $d(\text{H5}\cdots\text{Cg}) = 2.844 \text{ \AA}$, $d(\text{C5}\cdots\text{Cg}) = 3.750 \text{ \AA}$, and $\angle\text{C5-H5}\cdots\text{Cg} = 159.71^\circ$.

4. Database survey

There are several other examples of structurally characterized related dithioethers bearing hydroxy substituents giving rise to 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 (CSD WADROJ), 2-(3-Hydroxyphenyl)-1,3-dithiane (CSD KALJUD), 4,6-bis(1,3-dithian-2-yl)benzene-1,3-diol (CSD DITFIX), 4-(1,3-Dithian-2-yl)benzene-1,3-diol (CSD DITFOD), 2-phenyl-1,3-dithiepane-5,6-diol (CSD FIBTOC), and 2,2'-(((4-Methoxyphenyl)methylene)disulfanediy)diethanol (CSD YISVUT) (Datta *et al.*, 2013; Ganguly *et al.*, 2005; Laskar *et al.*, 2013; Liu *et al.*, 2018; Usman *et al.*, 2003).

5. Synthesis and crystallization

3-Methoxysalicylaldehyde (1 mmol, 152 mg), benzyl mercaptan (2.5 mmol, 310 mg), and conc. HCl (2mL) were added to a flask at 0 °C. The mixture was stirred for 60 min at room temperature. After the reaction was completed, 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 273K for 3-4 days. 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_{qOCH}), 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 1.

All protons were refined independently.

Table 1 Experimental details

	mo_b0238_0m
Crystal data	
Chemical formula	<u>C₂₂H₂₂O₂S₂</u>
M_r	<u>382.51</u>
Crystal system, space group	<u>Orthorhombic, <i>Pbca</i></u>
Temperature (K)	<u>100</u>
a, b, c (Å)	<u>7.7418 (8), 13.856 (3), 36.197 (5)</u>
V (Å ³)	<u>3882.9 (10)</u>
Z	<u>8</u>
Radiation type	<u>Mo $K\alpha$</u>
μ (mm ⁻¹)	<u>0.29</u>
Crystal size (mm)	<u>0.49 × 0.42 × 0.25</u>
Data collection	
Diffractometer	<u>Bruker D8 VENTURE area detector</u>
Absorption correction	<u>Multi-scan <i>SADABS2016</i> (Bruker, 2016) was used for absorption correction. $wR2(int)$ was 0.1206 before and 0.0488 after correction. The ratio of minimum to maximum transmission is 0.9558. The $\lambda/2$ correction factor is not present.</u>
T_{min}, T_{max}	<u>0.713, 0.746</u>
No. of measured, independent and observed [$I \geq 2\sigma(I)$] reflections	<u>107706, 5005, 4510</u>
R_{int}	<u>0.033</u>

$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.684
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	<u>0.033</u> , <u>0.077</u> , <u>1.09</u>
No. of reflections	<u>5005</u>
No. of parameters	<u>324</u>
H-atom treatment	<u>All H-atom parameters refined</u>
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e \AA^{-3})	<u>0.34</u> , <u>-0.21</u>

Computer programs: *APEX2* (Bruker, 2016), *SAINT V8.35A* (Bruker, 2016), *SHELXT* (Sheldrick, 2015), *XL* (Sheldrick, 2008), *Olex2 1.3* (Dolomanov *et al.*, 2009).

Table 2 Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots S1^i$	0.85 (2)	2.44 (2)	3.1317 (11)	139.5 (17)
$O2-H2\cdots O1$	0.85 (2)	2.17 (2)	2.6469 (14)	115.2 (16)

Symmetry code: (i) $-x+3/2, y-1/2, z$.

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Figures

Figure 1

Synthesis of 2-Hydroxy-3-methoxyphenyl-(bis(benzylthio))methane (**1**).

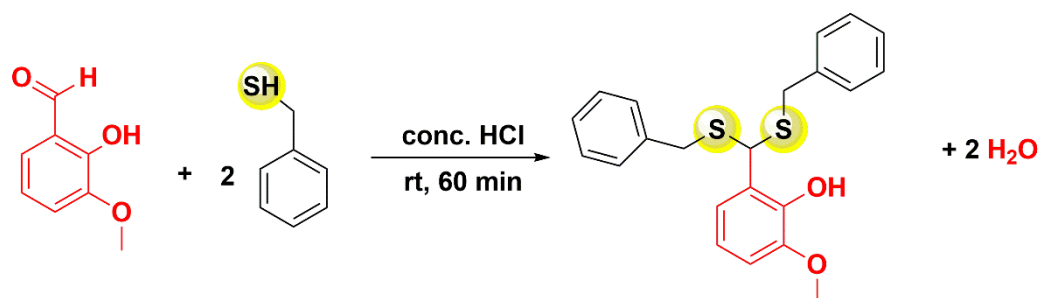


Figure 2

A displacement ellipsoid plot of **1** at the 50% probability level.

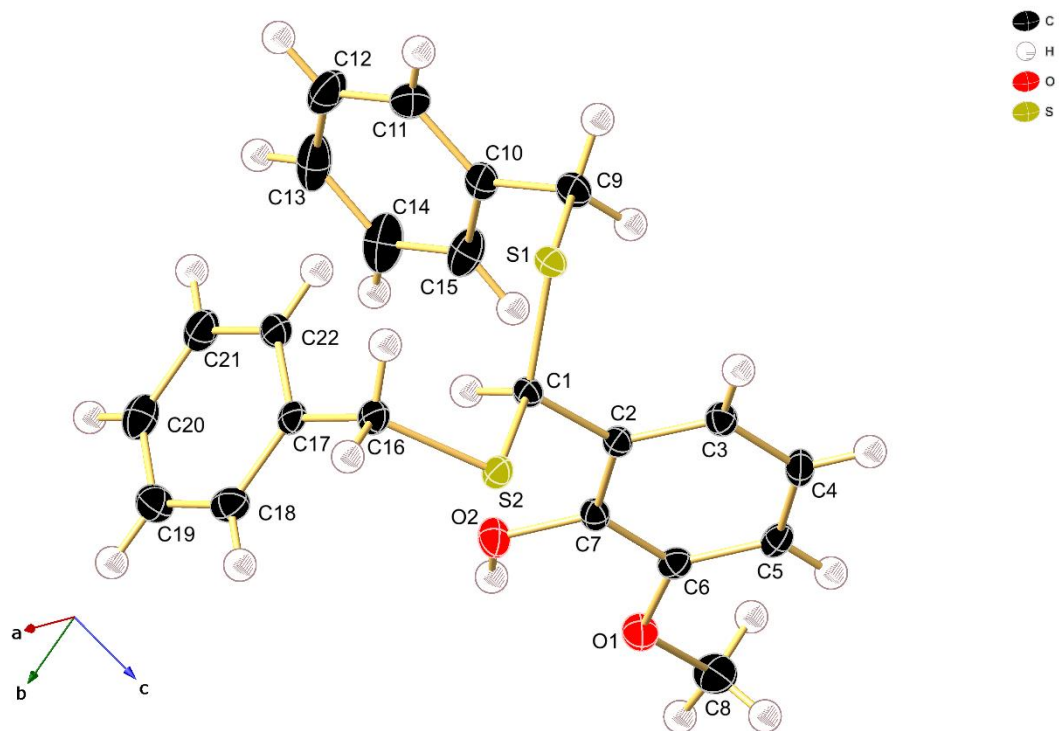


Figure 3

A view of the crystal packing of the title compound. For clarity, the H atoms have been omitted.

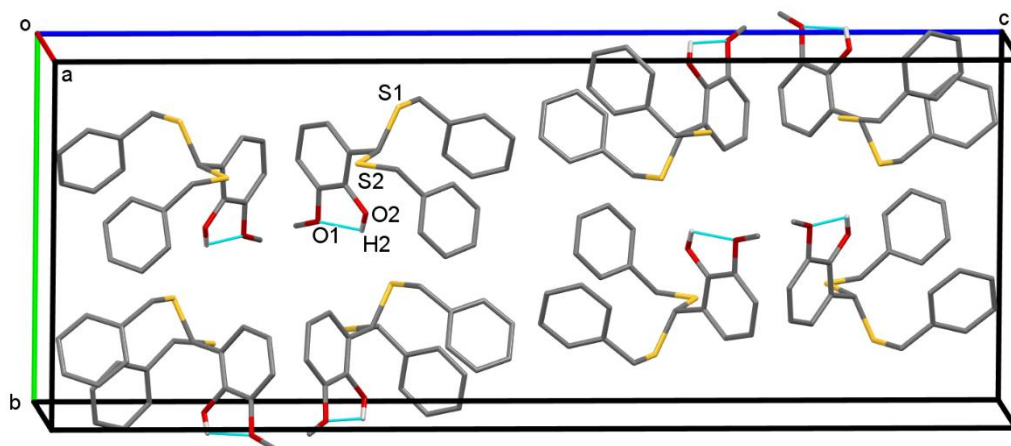


Figure 4

Intermolecular contacts of compound 1.

