

2-(2-Hydroxyphenyl)-1,3-dithiane

Anwar Usman,^a Hoong-Kun Fun,^{a*} Nemaï C. Ganguly,^b Mrityunjoy Datta^b and Kumares Ghosh^b

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^bDepartment of Chemistry, Faculty of Science, University of Kalyani, Kalyani 741 235, West Bengal, India

Correspondence e-mail: hkfun@usm.my

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.063

wR factor = 0.137

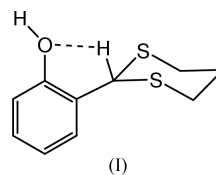
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{10}\text{H}_{12}\text{OS}_2$, the dithiane ring adopts a chair conformation. An intramolecular $\text{C}-\text{H}\cdots\text{O}$ interaction forms an $S(5)$ graph-set ring. Intermolecular $\text{O}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules into sheet-like assemblies parallel to the ab plane.

Comment

Protection of carbonyl compounds as cyclic S-acetals, such as 1,3-dithianes and dithiolanes, and regeneration of the parent carbonyl compounds from these derivatives are of considerable contemporary interest to organic chemists, in view of the central importance of carbonyl compounds in organic synthesis (Greene & Wuts, 1991). Derivatives of 1,3-dithiane are particularly important as versatile intermediates in organic synthesis because they are utilized as acyl anion equivalents *via* temporary inversion of electrophilic carbonyl carbon. This occurs *via* metallation, thereby allowing carbon-carbon bond formation *via* electrophiles (Grobel & Seebeck, 1977). These derivatives are easy to form and display remarkable stability towards acid as well as acidic hydrolysis. The presence of electron-donor and electron-withdrawing groups on the aromatic ring is a crucial factor which determines the ease of cleavage of C-S bonds, using soft electrophiles as reagents (Corey & Erickson, 1971). However, the presence of the dithiane moiety together with another functional group capable of forming hydrogen bonds in the solid state is of special interest, to obtain an insight into the orientation and hydrogen bonding of the dithiane ring (Jeffrey & Saenger, 1991; Desiraju, 1996). In view of this important factor, the crystal structure determination of the title compound, (I), was undertaken, and the results are reported here.



The bond lengths observed in (I) (Fig. 1) have normal values (Allen *et al.*, 1987) and the bond lengths and angles are comparable to those in the related structure 2-(2,6-difluorophenyl)-1,3-dithiane, (II) (Adamson *et al.*, 1995). As observed in (II), the dithiane ring adopts a chair conformation. The conformation about the $\text{C6}-\text{C7}$ bond joining the dithiane and phenyl rings is best described by the torsion angles $\text{C1}-\text{C6}-\text{C7}-\text{S1}$ [$-97.1(2)^\circ$] and $\text{C5}-\text{C6}-\text{C7}-\text{S1}$ [$80.2(3)^\circ$]. An intramolecular $\text{C7}-\text{H7}\cdots\text{O1}$ interaction forms an $S(5)$ graph-set ring (Etter *et al.*, 1990). In the solid state, intermolecular

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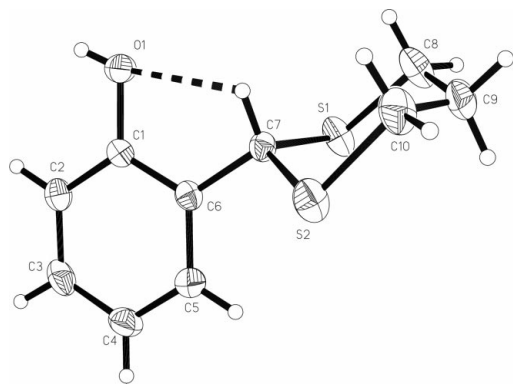


Figure 1
The structure of (I), showing the atom-numbering scheme, with ellipsoids drawn at the 50% probability level.

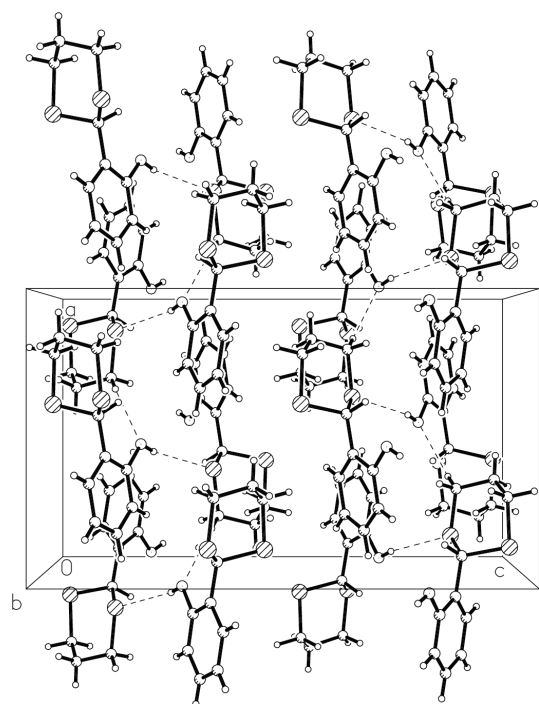


Figure 2
Packing diagram of (I), showing molecular sheets parallel to the *ab* plane.

hydrogen bonds involving the hydroxy group and the dithiane ring, O1—H11 \cdots S2ⁱ and C10—H10A \cdots O1ⁱⁱ, interconnect the molecules into sheet-like assemblies parallel to the *ab* plane (Fig. 2). The symmetry codes are as in Table 2.

Experimental

To a solution of salicylaldehyde (18.7 mmol) in 1,3-propanedithiol (39.9 mmol), boron trifluoride etherate (2 ml) was added with stirring at 273 K for 15 min. After completion of the reaction, the mixture was poured into a saturated aqueous solution of sodium hydrogen carbonate (50 ml) and was extracted three times with ethyl acetate. The organic layer was washed repeatedly with sodium hydrogen carbonate and water. Finally, the organic layer was dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the title compound was isolated by column chromatography, with petroleum ether as eluant. Single crystals suitable for X-ray analysis were obtained from a solution in petroleum ether.

Crystal data

C₁₀H₁₂OS₂
M_r = 212.32
 Orthorhombic, *Pbca*
a = 10.4039 (7) Å
b = 11.0435 (8) Å
c = 17.7471 (12) Å
V = 2039.1 (2) Å³
Z = 8
D_x = 1.383 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 4761 reflections
 θ = 2.3–28.3°
 μ = 0.48 mm⁻¹
T = 293 (2) K
 Block, colorless
 0.46 × 0.40 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.810, *T_{max}* = 0.894
 10961 measured reflections

2524 independent reflections
 2080 reflections with *I* > 2σ(*I*)
R_{int} = 0.034
 θ_{max} = 28.3°
h = -13 → 11
k = -14 → 14
l = -23 → 19

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.063
wR(*F*²) = 0.137
S = 1.24
 2524 reflections
 166 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 2.164P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1—C8	1.814 (3)	S2—C7	1.813 (3)
S1—C7	1.814 (3)	O1—C1	1.364 (3)
S2—C10	1.812 (3)	C6—C7	1.502 (4)
C8—S1—C7	99.4 (2)	C6—C7—S1	109.1 (2)
C10—S2—C7	98.2 (2)	S2—C7—S1	111.8 (1)
C6—C7—S2	111.3 (2)		
C1—C6—C7—S2	139.0 (2)	C1—C6—C7—S1	-97.1 (2)
C5—C6—C7—S2	-43.6 (3)	C5—C6—C7—S1	80.2 (3)

Table 2

Hydrogen-bonding 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>
C7—H7 \cdots O1	0.96 (3)	2.35 (3)	2.769 (3)	105 (2)
O1—H11 \cdots S2 ⁱ	0.73 (3)	2.56 (3)	3.254 (2)	159 (3)
C10—H10A \cdots O1 ⁱⁱ	0.96 (4)	2.54 (4)	3.387 (4)	147 (3)

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

All H atoms were located in a difference Fourier map and were refined isotropically. The C—H distances ranged from 0.89 (4) to 1.00 (4) Å and the O—H distance is 0.73 (3) Å. The highest peak was 0.89 Å from S1.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 2003).

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