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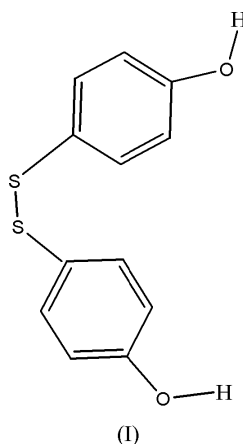
## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.033  
 $wR$  factor = 0.094  
Data-to-parameter ratio = 13.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.4,4'-Dithiodiphenol: a chain of rings generated  
by two pairs of O—H...O hydrogen bonds

In the title compound,  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}_2$ , molecules are linked into chains by two pairs of O—H...O hydrogen bonds [ $\text{H}\cdots\text{O} = 1.99(2)$  Å,  $\text{O}\cdots\text{O} = 2.759(2)$  and  $2.783(2)$  Å and  $\text{O}-\text{H}\cdots\text{O} = 162$  and  $165(2)^\circ$ ]. Four hydroxy groups are linked together *via* hydrogen bonds to form a four-membered ring, which acts as a supramolecular synthon in the construction of one-dimensional chains of rings.

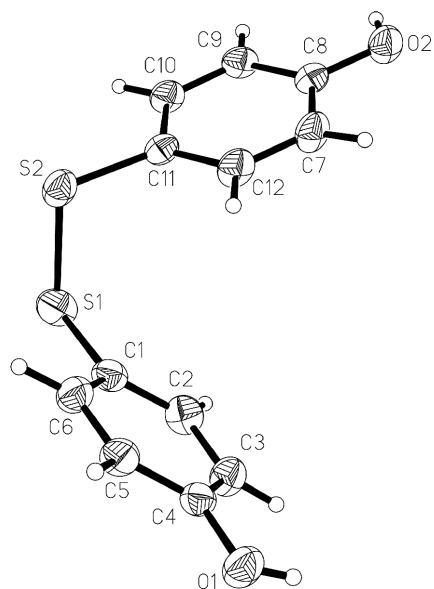
## Comment

Hydrogen bonding, which is a powerful organizing force in designing various supramolecules and solid-state architectures (Subramanian & Zaworotko, 1994), is extensively used not only for networking numerous organic and organometallic compounds (Desiraju, 2000), but also for generating interesting supramolecular properties, such as electrical, optical and magnetic (Létard *et al.*, 1998). The molecule of the title compound, 4,4'-dithiodiphenol, (I), with hydroxy groups and a flexible S—S bond, easily affords hydrogen bonding (Sugiura *et al.*, 1992) in crystal engineering to generate a supramolecular synthon or spacer.

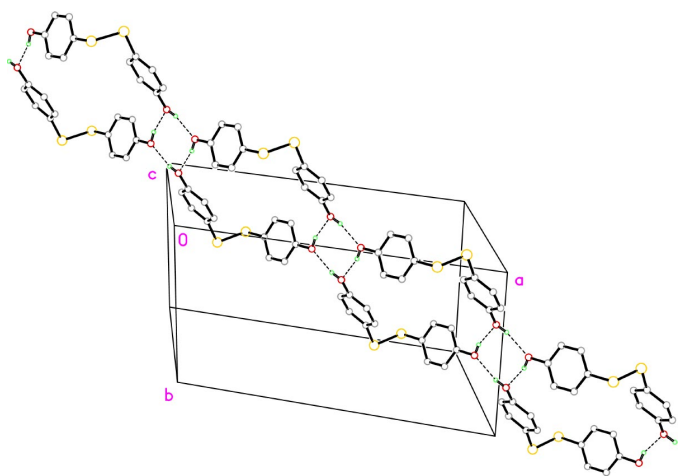


In a previous paper (Wang *et al.*, 1999), the compound bis(2-hydroxyphenyl) disulfide or 2,2'-dithiodiphenol, (II), which was oxidized from 2-mercaptophenol, acts as a spacer to link anions together to form one-dimensional chains through hydrogen bonding. In order to explore extensively the hydrogen-bond effect on the formation of three-dimensional networks in the solid state and the influence of these on the properties of compounds, we prepared compound (I). As with compound (II), (I) was oxidized in air from 4-mercaptophenol, and was intended to act as a building block to construct a three-dimensional organic-inorganic hybrid supramolecule through hydrogen bonding. Unfortunately, only the organic species (I) crystallized from the methanol solution.

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**Figure 1**  
A view of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
A hydrogen-bonded chain of rings in (I). H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonds are indicated by dashed lines.

The structure of (I) (Fig. 1) is similar to that of (II) (Wang *et al.*, 1999). Selected bond lengths and angles are listed in Table 1. The C—S bonds [average 1.773 Å], the S—S—C angles [average 104.5°] and the torsion angle C1—S1—S2—C11 [82.5 (1)°] in (I) are similar to corresponding values in (II). However, the S—S bond length [2.0524 (11) Å] in (I) is significantly longer than the average S—S bond length value of 2.017 (6) Å in (II). According to Hordvik's (1996) observation (Desiraju, 2000), a relationship exists between the S—S bond length and the C—S—S—C torsion angle in organic disulfides, probably caused by lone-pair repulsion which will be minimized when the dihedral angle is 90°. The greater deviation of this angle [82.5 (1)° in (I) compared with 84.3° in (II)] from the ideal value could be caused by the restriction of the rotation of the S—S bond by the hydrogen bonds, which

cannot release the molecular strain. The two benzene rings in the title compound form a dihedral angle of 48.1 (2)°.

The hydroxy groups in the title compound form O—H...O hydrogen bonds which link molecules head-to-tail, forming one-dimensional chains. In addition, adjacent one-dimensional chains are linked together through further hydrogen bonding to form a chain of rings (Fig. 2 and Table 2).

## Experimental

To a solution (15 ml) of MeOH containing (Bu<sub>4</sub>N)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] (0.55 g, 0.25 mmol), a solution of 4-mercaptophenol (0.252 g, 2.0 mmol) in 4 ml of MeOH was added with stirring at room temperature. The solution turned yellow immediately. After stirring for 4 h, the reaction solution was concentrated to 5 ml under reduced pressure. Addition of diethyl ether gave yellow crystals which were suitable for X-ray diffraction.

### Crystal data

C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> S <sub>2</sub>	<i>D</i> <sub>x</sub> = 1.424 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 250.32	Mo <i>K</i> α radiation
Monoclinic, C <sub>2</sub> /c	Cell parameters from 3841 reflections
<i>a</i> = 20.886 (4) Å	<i>θ</i> = 2.2–27.0°
<i>b</i> = 10.959 (2) Å	<i>μ</i> = 0.44 mm <sup>-1</sup>
<i>c</i> = 11.263 (2) Å	<i>T</i> = 293 (2) K
<i>β</i> = 115.09 (3)°	Block, yellow
<i>V</i> = 2334.7 (9) Å <sup>3</sup>	0.11 × 0.11 × 0.08 mm
<i>Z</i> = 8	

### Data collection

Bruker SMART CCD area-detector diffractometer	2547 independent reflections
<i>ω</i> scans	2071 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Bruker, 1998)	<i>R</i> <sub>int</sub> = 0.015
<i>T</i> <sub>min</sub> = 0.953, <i>T</i> <sub>max</sub> = 0.966	<i>θ</i> <sub>max</sub> = 27.0°
6726 measured reflections	<i>h</i> = -26 → 23
	<i>k</i> = -13 → 11
	<i>l</i> = -14 → 13

### Refinement

Refinement on <i>F</i> <sup>2</sup>	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0496 <i>P</i> ) <sup>2</sup> + 0.722 <i>P</i> ]
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.033	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.094	(Δ/σ) <sub>max</sub> = 0.014
<i>S</i> = 1.05	Δρ <sub>max</sub> = 0.24 e Å <sup>-3</sup>
2547 reflections	Δρ <sub>min</sub> = -0.19 e Å <sup>-3</sup>
185 parameters	
All H-atom parameters refined	

**Table 1**

Selected geometric parameters (Å, °).

S1—C1	1.7787 (17)	O1—C4	1.3738 (19)
S1—S2	2.0524 (11)	O2—C8	1.377 (2)
S2—C11	1.7672 (17)		
C1—S1—S2	103.77 (6)	C6—C1—S1	121.49 (14)
C11—S2—S1	105.17 (6)	C5—C4—O1	118.08 (15)
C2—C1—S1	119.12 (14)	C9—C8—O2	121.94 (15)

**Table 2**

Hydrogen-bonding 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>	0.79 (2)	1.99 (2)	2.759 (2)	162 (2)
O2—H11...O1 <sup>ii</sup>	0.81 (2)	1.99 (2)	2.7829 (19)	165 (2)

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

All H atoms were located in a difference Fourier map and refined independently with isotropic displacement parameters. The refined O—H distances are 0.79 (2) and 0.81 (2) Å, while the C—H distances are in the range 0.92 (2)–0.98 (2) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL97*.

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## References

- Bruker (1998). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. (2000). *Stimulating Concepts in Chemistry*, edited by F. Vögtle, J. F. Stoddart & M. Shibasaki, pp. 293–302. Weinheim: Wiley VCH.
- Hordvik, A. (1996). *Acta Chem. Scand.* **20**, 1885–1895.
- Létard, J. F., Guionneau, P., Rabardel, L., Howard, J. A. K., Goeta, A. E., Chasseau, D. & Kahn, O. (1998). *Inorg. Chem.* **37**, 4432–4441.
- Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Subramanian, S. & Zaworotko, M. J. (1994). *Coord. Chem. Rev.* **137**, 357–401.
- Sugiura, K., Toyoda, J., Okamoto, H., Okaniwa, K., Mitani, T., Kawamoto, A., Tanaka, J. & Nakasuji, K. (1992). *Angew. Chem. Int. Engl.* **31**, 852–854.
- Wang, X.-J., Chen, Z.-F., Kang, B.-S., Liang, H., Liu, H.-Q., Yu, K.-B., Su, C.-Y. & Chen, Z.-N. (1999). *Polyhedron*, **18**, 647–655.