

6,6'-Dihydroxy-3,3'-dithiodibenzoic acid

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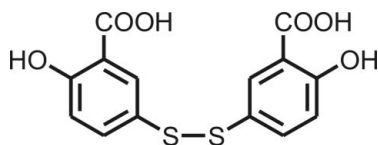
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.045; wR factor = 0.103; data-to-parameter ratio = 11.9.

In the title compound, $\text{C}_{14}\text{H}_{10}\text{O}_6\text{S}_2$, the dihedral angle between the planes of the two phenylene rings is $55.9(1)^\circ$. Both hydroxy groups form intramolecular hydrogen bonds; however, one of them also engages in intermolecular hydrogen bonding. In the crystal, molecules are connected into helical chains by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The crystal studied was an inversion twin with a domain ratio of 0.51 (13):0.49 (13).

Related literature

For hydrogen bonds and $\pi-\pi$ stacking interactions in aromatic compounds, see: Janiak (2000); Hunter & Sanders (1990); Orr *et al.* (1999); Kaafarani *et al.* (2001). For a comparison of bond dimensions for disulfide compounds, see: Kaitner & Pavlovic (1997); Korp & Bernal (1984); Ni *et al.* (2004); Sacerdoti *et al.* (1975).



Experimental

Crystal data

 $\text{C}_{14}\text{H}_{10}\text{O}_6\text{S}_2$ $M_r = 338.34$ Orthorhombic, $P2_12_12_1$ $a = 5.3065(6)$ Å $b = 11.1657(13)$ Å $c = 23.906(2)$ Å $V = 1416.5(3)$ Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.40$ mm⁻¹ $T = 298$ K $0.24 \times 0.15 \times 0.14$ mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.910$, $T_{\max} = 0.946$ 6436 measured reflections
2502 independent reflections
2060 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.103$ $S = 1.09$

2502 reflections

211 parameters

4 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Absolute structure: Flack (1983),

1007 Friedel pairs

Flack parameter: 0.49 (13)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2-\text{H}2\cdots\text{O}5^i$	0.85 (3)	1.90 (3)	2.739 (4)	171 (4)
$\text{O}3-\text{H}3\cdots\text{O}1$	0.84 (4)	1.91 (5)	2.616 (4)	142 (5)
$\text{O}3-\text{H}3\cdots\text{O}6^{ii}$	0.84 (4)	2.52 (4)	3.063 (5)	123 (4)
$\text{O}4-\text{H}4\cdots\text{O}1^{iii}$	0.85 (4)	1.79 (4)	2.636 (4)	175 (4)
$\text{O}6-\text{H}6\cdots\text{O}5$	0.85 (4)	1.90 (4)	2.642 (4)	146 (5)

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

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

We are grateful to Professor Da-QI Wang, Liaocheng University, for the X-ray structure determination.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2599).

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supplementary materials

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6,6'-Dihydroxy-3,3'-dithiodibenzoic acid

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Comment

Hydrogen bonds and π - π stacking interactions play an important role in the self-assembly and recognition of aromatic compounds (Janiak, 2000; Hunter & Sanders, 1990) as an auxiliary stabilizing short contact (Orr *et al.*, 1999; Kaafarani *et al.*, 2001).

The two phenyl rings of the title compound are bonded with two S atoms at a distance of 1.781 (4) Å (S2—C13) and 1.793 (4) Å (S1—C6), and the C—C distances of two phenyl groups range from 1.371 (5) to 1.407 (6) Å (Figure 1 and Table 1). Interestingly, there are intermolecular S \cdots S interactions in the crystal structures, which are not common in diphenyl disulfide derivatives (Korp & Bernal, 1984; Kaitner & Pavlovic 1997; Ni *et al.*, 2004; Sacerdoti *et al.*, 1975). The intermolecular S \cdots S interactions distance is 3.414 (2) Å, whereas the shorter intramolecular S—S distance is 2.051 (2) Å. The dihedral angle of these two phenyl rings is 55.9 (1)°, which is different from other molecules such as 4, 4'-dithiodiphenol (48.1 (2)°) (Ni *et al.*, 2004) and diphenyl disulfide (76.7 (3)°) (Sacerdoti *et al.*, 1975).

The crystal structure of 5, 5'-dithiodisalicylic acid demonstrates the self-assembly of molecules into three dimensional networks *via* hydrogen bonds (Table 2) and intermolecular S \cdots S interactions.

Experimental

The title compound (I) was prepared as follows: To a solution of 5-(chlorosulfonyl)-2-hydroxybenzoic acid (19 mmol, 4.5 g) in conc. HCl (30 ml) cooled to 0 °C in an ice bath, Sn (118 mmol, 14.0 g) was added. The reaction mixture was stirred for 12 h and then refluxed for 6 h. The precipitate was separated and dissolved in Et₂O. After filtration the organic layer was concentrated under reduced pressure to afford a solid that was subsequently purified by recrystallization using a mixture of EtOH and H₂O. Yellow needle crystals of (I) were obtained by slow evaporation from EtOH/acetone/DMSO/DMF(5:1:3:3) after five months. Analysis calculated for C₁₄H₁₀O₆S₂: C 49.70, H 2.98%; found: C 49.18, H 2.75%.

Refinement

All H atoms were placed in calculated positions and treated as riding, with C—H in the range 0.93–0.98 Å and with $U_{\text{iso}}(\text{H})=1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

Figures

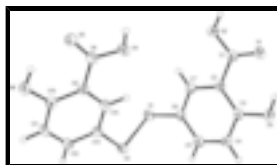


Fig. 1. The molecular structure of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level.

6,6'-Dihydroxy-3,3'-dithiodibenzoic acid

Crystal data

$C_{14}H_{10}O_6S_2$	$D_x = 1.587 \text{ Mg m}^{-3}$
$M_r = 338.34$	Melting point: 523 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: P 2ac 2ab	Cell parameters from 2489 reflections
$a = 5.3065 (6) \text{ \AA}$	$\theta = 2.5\text{--}25.5^\circ$
$b = 11.1657 (13) \text{ \AA}$	$\mu = 0.40 \text{ mm}^{-1}$
$c = 23.906 (2) \text{ \AA}$	$T = 298 \text{ K}$
$V = 1416.5 (3) \text{ \AA}^3$	Needle, yellow
$Z = 4$	$0.24 \times 0.15 \times 0.14 \text{ mm}$
$F_{000} = 696$	

Data collection

Bruker SMART area-detector diffractometer	2502 independent reflections
Radiation source: fine-focus sealed tube	2060 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.043$
$T = 298 \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 1.7^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -6 \rightarrow 6$
$T_{\text{min}} = 0.910$, $T_{\text{max}} = 0.946$	$k = -13 \rightarrow 13$
6436 measured reflections	$l = -28 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.9484P]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2502 reflections	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
211 parameters	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
4 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1007 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.49 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.4934 (6)	0.8216 (2)	0.21892 (11)	0.0439 (7)
O2	-0.6036 (6)	0.6399 (3)	0.18732 (11)	0.0439 (8)
H2	-0.717 (6)	0.643 (4)	0.2123 (14)	0.066*
O3	-0.1299 (6)	0.9391 (3)	0.16941 (13)	0.0519 (8)
H3	-0.254 (6)	0.934 (5)	0.1911 (17)	0.078*
O4	-0.1551 (7)	0.3528 (3)	0.20456 (12)	0.0505 (8)
H4	-0.269 (7)	0.338 (4)	0.2286 (15)	0.076*
O5	-0.0215 (6)	0.1743 (3)	0.23556 (11)	0.0438 (7)
O6	0.3765 (6)	0.0759 (3)	0.18767 (12)	0.0503 (8)
H6	0.252 (6)	0.080 (5)	0.2099 (17)	0.075*
S1	-0.0244 (2)	0.52404 (9)	0.01641 (4)	0.0370 (3)
S2	0.34345 (19)	0.46809 (9)	0.01989 (4)	0.0360 (2)
C1	-0.4622 (8)	0.7376 (4)	0.18627 (14)	0.0343 (9)
C2	-0.2645 (7)	0.7386 (3)	0.14288 (15)	0.0303 (9)
C3	-0.1095 (8)	0.8396 (3)	0.13723 (15)	0.0360 (10)
C4	0.0804 (8)	0.8402 (4)	0.09698 (16)	0.0391 (10)
H4A	0.1880	0.9057	0.0942	0.047*
C5	0.1095 (8)	0.7447 (3)	0.06154 (16)	0.0391 (10)
H5	0.2337	0.7470	0.0341	0.047*
C6	-0.0443 (8)	0.6441 (3)	0.06607 (15)	0.0324 (9)
C7	-0.2280 (8)	0.6406 (3)	0.10693 (15)	0.0339 (9)
H7	-0.3285	0.5729	0.1107	0.041*
C8	-0.0058 (8)	0.2582 (4)	0.20199 (16)	0.0367 (9)
C9	0.1795 (7)	0.2604 (3)	0.15645 (15)	0.0314 (9)
C10	0.3593 (8)	0.1685 (3)	0.15118 (15)	0.0356 (9)
C11	0.5317 (8)	0.1726 (3)	0.10729 (16)	0.0404 (10)
H11	0.6534	0.1130	0.1041	0.048*
C12	0.5236 (8)	0.2640 (3)	0.06854 (16)	0.0387 (9)
H12	0.6396	0.2651	0.0394	0.046*
C13	0.3440 (8)	0.3550 (3)	0.07246 (14)	0.0312 (9)
C14	0.1790 (8)	0.3533 (3)	0.11681 (15)	0.0350 (9)
H14	0.0637	0.4155	0.1207	0.042*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0515 (18)	0.0345 (16)	0.0456 (15)	0.0031 (16)	0.0185 (17)	-0.0067 (13)
O2	0.047 (2)	0.0394 (16)	0.0449 (16)	-0.0082 (15)	0.0179 (15)	-0.0035 (14)
O3	0.057 (2)	0.0356 (16)	0.063 (2)	-0.0068 (15)	0.0226 (17)	-0.0158 (15)
O4	0.0540 (19)	0.0474 (18)	0.0502 (18)	0.0124 (17)	0.0237 (16)	0.0074 (15)
O5	0.0474 (18)	0.0416 (17)	0.0423 (16)	0.0038 (16)	0.0113 (16)	0.0068 (13)
O6	0.050 (2)	0.0404 (17)	0.0605 (19)	0.0127 (16)	0.0138 (17)	0.0138 (16)
S1	0.0372 (6)	0.0428 (5)	0.0311 (5)	0.0055 (5)	-0.0017 (5)	-0.0050 (5)
S2	0.0371 (5)	0.0370 (5)	0.0340 (5)	0.0005 (5)	0.0064 (5)	0.0011 (5)
C1	0.034 (2)	0.040 (2)	0.0291 (19)	0.005 (2)	0.0003 (19)	0.0052 (18)
C2	0.031 (2)	0.0292 (19)	0.031 (2)	0.0008 (18)	-0.0014 (18)	0.0029 (17)
C3	0.040 (2)	0.032 (2)	0.036 (2)	0.0092 (19)	0.002 (2)	-0.0012 (18)
C4	0.036 (3)	0.033 (2)	0.049 (2)	-0.0035 (19)	0.006 (2)	0.004 (2)
C5	0.044 (3)	0.040 (2)	0.033 (2)	0.007 (2)	0.009 (2)	0.009 (2)
C6	0.036 (2)	0.031 (2)	0.0302 (19)	0.0064 (19)	-0.0022 (19)	0.0001 (16)
C7	0.039 (2)	0.031 (2)	0.032 (2)	0.0007 (19)	-0.0032 (19)	0.0034 (17)
C8	0.032 (2)	0.038 (2)	0.040 (2)	0.003 (2)	-0.001 (2)	-0.0059 (19)
C9	0.031 (2)	0.034 (2)	0.0297 (19)	-0.0025 (18)	0.0036 (18)	-0.0039 (17)
C10	0.041 (2)	0.034 (2)	0.032 (2)	0.000 (2)	-0.002 (2)	-0.0023 (17)
C11	0.034 (2)	0.034 (2)	0.052 (2)	0.011 (2)	0.009 (2)	-0.0032 (19)
C12	0.033 (2)	0.045 (2)	0.038 (2)	0.003 (2)	0.008 (2)	-0.0022 (19)
C13	0.031 (2)	0.033 (2)	0.0293 (19)	-0.0027 (19)	0.0005 (19)	-0.0065 (17)
C14	0.035 (2)	0.035 (2)	0.035 (2)	0.0044 (19)	-0.0009 (19)	-0.0021 (18)

Geometric parameters (\AA , $^\circ$)

O1—C1	1.231 (4)	C4—C5	1.371 (5)
O2—C1	1.324 (5)	C4—H4A	0.9300
O2—H2	0.848 (10)	C5—C6	1.393 (5)
O3—C3	1.356 (5)	C5—H5	0.9300
O3—H3	0.842 (10)	C6—C7	1.380 (5)
O4—C8	1.322 (5)	C7—H7	0.9300
O4—H4	0.848 (10)	C8—C9	1.467 (5)
O5—C8	1.236 (5)	C9—C14	1.405 (5)
O6—C10	1.356 (4)	C9—C10	1.407 (6)
O6—H6	0.849 (10)	C10—C11	1.393 (5)
S1—C6	1.793 (4)	C11—C12	1.380 (5)
S1—S2	2.0511 (15)	C11—H11	0.9300
S2—C13	1.781 (4)	C12—C13	1.396 (5)
C1—C2	1.476 (5)	C12—H12	0.9300
C2—C3	1.402 (5)	C13—C14	1.375 (5)
C2—C7	1.404 (5)	C14—H14	0.9300
C3—C4	1.394 (5)		
C1—O2—H2	113 (3)	C6—C7—C2	120.6 (4)
C3—O3—H3	111 (4)	C6—C7—H7	119.7

C8—O4—H4	108 (4)	C2—C7—H7	119.7
C10—O6—H6	108 (4)	O5—C8—O4	122.4 (4)
C6—S1—S2	104.89 (14)	O5—C8—C9	122.7 (4)
C13—S2—S1	104.24 (14)	O4—C8—C9	115.0 (4)
O1—C1—O2	122.6 (4)	C14—C9—C10	118.6 (3)
O1—C1—C2	122.4 (4)	C14—C9—C8	120.8 (4)
O2—C1—C2	115.0 (3)	C10—C9—C8	120.6 (3)
C3—C2—C7	119.1 (3)	O6—C10—C11	117.7 (4)
C3—C2—C1	119.4 (3)	O6—C10—C9	123.0 (3)
C7—C2—C1	121.5 (3)	C11—C10—C9	119.3 (4)
O3—C3—C4	116.4 (4)	C12—C11—C10	120.6 (4)
O3—C3—C2	123.9 (4)	C12—C11—H11	119.7
C4—C3—C2	119.6 (4)	C10—C11—H11	119.7
C5—C4—C3	120.3 (4)	C11—C12—C13	121.0 (4)
C5—C4—H4A	119.9	C11—C12—H12	119.5
C3—C4—H4A	119.9	C13—C12—H12	119.5
C4—C5—C6	120.9 (4)	C14—C13—C12	118.4 (4)
C4—C5—H5	119.6	C14—C13—S2	123.6 (3)
C6—C5—H5	119.6	C12—C13—S2	118.0 (3)
C7—C6—C5	119.4 (3)	C13—C14—C9	121.9 (4)
C7—C6—S1	119.3 (3)	C13—C14—H14	119.0
C5—C6—S1	121.1 (3)	C9—C14—H14	119.0
C6—S1—S2—C13	89.96 (17)	O5—C8—C9—C14	175.4 (4)
O1—C1—C2—C3	-1.7 (5)	O4—C8—C9—C14	-4.7 (5)
O2—C1—C2—C3	178.1 (3)	O5—C8—C9—C10	-3.8 (6)
O1—C1—C2—C7	178.4 (4)	O4—C8—C9—C10	176.1 (4)
O2—C1—C2—C7	-1.7 (5)	C14—C9—C10—O6	179.2 (4)
C7—C2—C3—O3	179.5 (3)	C8—C9—C10—O6	-1.6 (6)
C1—C2—C3—O3	-0.3 (6)	C14—C9—C10—C11	0.4 (6)
C7—C2—C3—C4	-1.3 (6)	C8—C9—C10—C11	179.5 (4)
C1—C2—C3—C4	178.9 (3)	O6—C10—C11—C12	179.7 (4)
O3—C3—C4—C5	-178.1 (4)	C9—C10—C11—C12	-1.4 (6)
C2—C3—C4—C5	2.7 (6)	C10—C11—C12—C13	0.4 (6)
C3—C4—C5—C6	-1.9 (6)	C11—C12—C13—C14	1.8 (6)
C4—C5—C6—C7	-0.2 (6)	C11—C12—C13—S2	-178.8 (3)
C4—C5—C6—S1	174.9 (3)	S1—S2—C13—C14	-29.0 (3)
S2—S1—C6—C7	-127.2 (3)	S1—S2—C13—C12	151.6 (3)
S2—S1—C6—C5	57.7 (3)	C12—C13—C14—C9	-2.9 (6)
C5—C6—C7—C2	1.5 (6)	S2—C13—C14—C9	177.8 (3)
S1—C6—C7—C2	-173.7 (3)	C10—C9—C14—C13	1.8 (6)
C3—C2—C7—C6	-0.8 (6)	C8—C9—C14—C13	-177.4 (4)
C1—C2—C7—C6	179.0 (3)		

Hydrogen-bond 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>
O2—H2 \cdots O5 ⁱ	0.85 (3)	1.90 (3)	2.739 (4)	171 (4)
O3—H3 \cdots O1	0.84 (4)	1.91 (5)	2.616 (4)	142 (5)

supplementary materials

O3—H3···O6 ⁱⁱ	0.84 (4)	2.52 (4)	3.063 (5)	123 (4)
O4—H4···O1 ⁱⁱⁱ	0.85 (4)	1.79 (4)	2.636 (4)	175 (4)
O6—H6···O5	0.85 (4)	1.90 (4)	2.642 (4)	146 (5)

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

Fig. 1

