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2,2′-Disulfanyldibenzoic acid

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Key indicators

Single-crystal X-ray study
T = 250 K
Mean σ(C–C) = 0.004 Å
R factor = 0.056
wR factor = 0.137
Data-to-parameter ratio = 14.7

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

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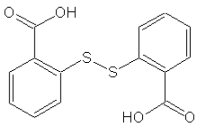
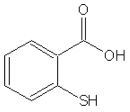
The structure of the title compound, $C_{14}H_{10}O_4S_2$, comprises two 2-benzoic acid thiolate derivatives linked by an S—S disulfide bridge. The compound, which crystallizes in the space group $C2/c$, contains one and a half molecules in the asymmetric unit and 12 molecules in the unit cell. The disulfides are oriented with their rings rotated with respect to one another by dihedral angles of 74.9 (8) and 77.7 (6)°. The material packs in zigzag perpendicular columns whose arrangement is based on an apparent preference for hydrogen bonding between protonated acid moieties, whilst there is also evidence of a ring-stacking arrangement.

Comment

The deprotonated dianion of the title species has been widely used in the synthesis of metal-containing complexes, yet the commonly accepted routes towards its preparation involve ring-opening reactions using mixed starting materials. In an attempt to complex the commercially available organic ligand thiosalicylic acid [2-thiolatobenzoic acid], (II), with stoichiometric amounts of silver from silver acetate starting material under hydrothermal conditions, we were instead successful in preparing large quantities of colourless crystalline 2,2′-disulfanyldibenzoic acid, (I). We therefore present the structural data for (I), as obtained *via* an unexpected route.


(I)


(II)

The asymmetric unit (Fig. 1), consists of one and one-half molecules. There is a twofold rotation axis at the centre of bond S3—S3^{i} (symmetry code as in Table 1). The aryl rings are twisted with respect to one another, the dihedral angles being 74.9 (8)° (S1—S2) and 77.7 (6)° (S3—S3^{i}). The bond lengths in (I) are in agreement with accepted literature values. The disulfide bridges were found to be 2.045 (1) and 2.043 (1) Å for S1—S2 and S3—S3^{i}, respectively, while the average S—C bond distance is 1.781 (3) Å.

The macrostructure of (I) takes the form of a relatively open-packed array of disulfide molecules, arranged in a pseudo-orthogonal manner. The molecules are aligned in planes, the intersections of which are parallel to the c axis, as shown in Fig. 2. This allows for favourable hydrogen-bonding interactions to be formed between carboxylic acid groups on neighbouring molecules, roughly along the ac bisector. Hydrogen-bonding distances were found to be 1.735 (4) and 1.856 (4) Å for the S1—S2-containing molecule, and 1.814 Å

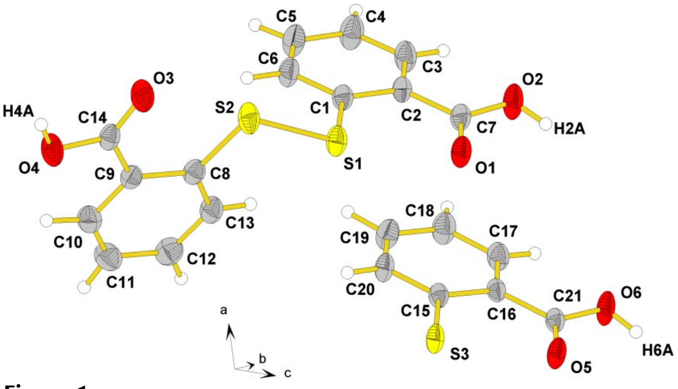


Figure 1
The asymmetric unit of (I), showing one complete molecule and one half molecule drawn as displacement ellipsoids drawn at the 30% probability level.

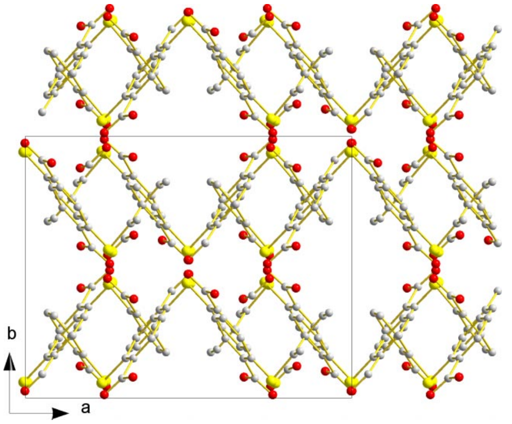


Figure 2
Packing diagram of the unit cell of (I), viewed in the *ab* plane.

in the S3—S3^{i} counterpart. All carboxylic acid groups are coplanar with their attached benzene rings; their network of hydrogen bonding is illustrated in Fig. 3. There is evidence of some alignment of the layers of rings, but π–π-stacking is unlikely since the inter-ring separations are all in excess of 4.4 Å. There are four voids of total volume 117 Å^3 within the unit cell. The difference map has no significant peaks in these regions and the use of the SQUEEZE utility in *PLATON* (Spek, 2003) to account for electron density within the voids yielded a significantly worse refinement than was originally obtained. In addition, any solvent water molecules would be expected to be located near to the carboxylic acid groups so as to maximize their hydrogen bonding. We see no evidence for water molecules in such positions.

Experimental

Miligram quantities of (I) were prepared under hydrothermal conditions using a stainless-steel autoclave purchased from the Parr Corporation, Illinois, and fitted with a 23 ml Teflon liner. Silver acetate (1.0 mmol) was heated with thiosalicylic acid (1.0 mmol) in water (10 ml) at 473 K over 18 h and cooled to room temperature over a further 5 h. Compound (I) was obtained at 72% yield and isolated as large colourless blocks.

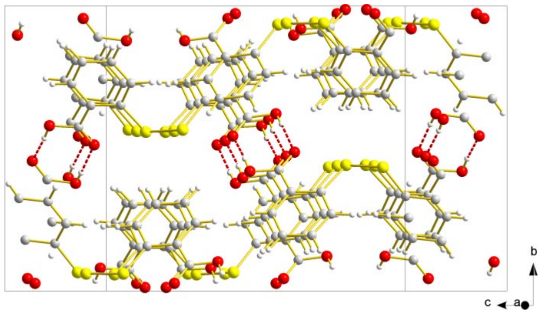


Figure 3
Projection of (I) roughly along the [103] vector, showing hydrogen-bonding contacts as dashed red lines.

Crystal data

$C_{14}H_{10}O_4S_2$
$M_r = 306.34$
Monoclinic, $C2/c$
$a = 16.4457\ (5)$ Å
$b = 12.8087\ (4)$ Å
$c = 20.9540\ (8)$ Å
$\beta = 104.5589\ (13)^\circ$
$V = 4272.2\ (2)$ Å^3
$Z = 12$
$D_x = 1.429$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21148 reflections
$\theta = 1.0$–27.5°
$\mu = 0.38$ mm^{-1}
$T = 250\ (2)$ K
Block, colourless
$0.18 \times 0.18 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.886$, $T_{\max} = 0.955$
14048 measured reflections
4864 independent reflections
2674 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 27.5^\circ$
$h = -21 \rightarrow 20$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.137$
$S = 1.02$
4864 reflections
331 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 3.1475P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.785 (3)	O4—C14	1.312 (3)
S1—S2	2.0449 (10)	O4—H4*A*	0.82 (4)
S2—C8	1.779 (3)	O5—C21	1.215 (3)
S3—C15	1.780 (3)	O6—C21	1.306 (3)
S3—S3^{i}	2.0431 (13)	O6—H6*A*	0.85 (4)
O1—C7	1.219 (3)	C2—C7	1.474 (4)
O2—C7	1.321 (3)	C9—C14	1.479 (4)
O2—H2*A*	0.91 (4)	C16—C21	1.475 (4)
O3—C14	1.212 (3)		
C1—S1—S2	104.85 (9)	C9—C8—S2	120.3 (2)
C8—S2—S1	106.31 (9)	C10—C9—C14	119.6 (3)
C15—S3—S3^{i}	105.72 (9)	C8—C9—C14	120.5 (3)
C7—O2—H2*A*	108 (2)	O3—C14—O4	122.3 (3)
C14—O4—H4*A*	111 (3)	O3—C14—C9	122.8 (2)
C21—O6—H6*A*	107 (2)	O4—C14—C9	114.9 (3)
C6—C1—S1	120.9 (2)	C20—C15—S3	121.5 (2)
C2—C1—S1	120.4 (2)	C16—C15—S3	120.3 (2)
C3—C2—C7	118.9 (3)	C17—C16—C21	119.1 (2)
C1—C2—C7	121.7 (2)	C15—C16—C21	121.4 (2)
O1—C7—O2	122.4 (3)	O5—C21—O6	122.3 (2)
O1—C7—C2	123.3 (2)	O5—C21—C16	123.1 (2)
O2—C7—C2	114.3 (3)	O6—C21—C16	114.6 (3)
C13—C8—S2	121.6 (2)		

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

All H atoms were located in a difference map and allowed to refine freely, giving C—H bond distances ranging from 0.82 (4) Å for O4—H4*A* to 1.01 (3) Å for C19—H19.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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