Dimethyl 2,2'-[ethane-1,2-diylbis-(sulfanediyl)]dibenzoate

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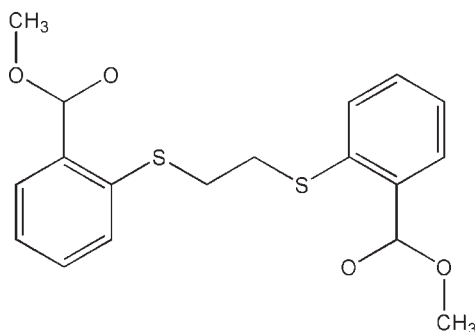Correspondence e-mail: xiaominghu10@163.com

The title compound, $C_{18}H_{18}O_4S_2$, was synthesized by the reaction of 1,2-dibromoethane with methyl thiosalicylate. The complete molecule is generated by crystallographic twofold symmetry: two methyl benzoate units are linked by an –S–(CH$_2$)$_2$–S– bridging chain with a *gauche* S—CH$_2$—CH$_2$—S torsion angle [72.88 (16)°]. The two aromatic rings form a dihedral angle of 79.99 (6)°. In the crystal, adjacent molecules are linked into a three-dimensional network by non-classical C—H⋯O hydrogen bonds.

Related literature

For the potential use of dithiodibenzoates in the construction of diverse frameworks with tailored properties and functions, see: Humphrey *et al.* (2004); Li *et al.* (2007); Murugavel *et al.* (2001); Wang *et al.* (2004); Zhou *et al.* (2009).

Experimental

Crystal data

$C_{18}H_{18}O_4S_2$	V = 873.6 (3) Å^3
M_r = 362.44	Z = 2
Monoclinic, $C2$	Mo $K\alpha$ radiation
a = 15.077 (3) Å	μ = 0.32 mm^{-1}
b = 5.3913 (10) Å	T = 296 K
c = 12.495 (2) Å	0.52 × 0.32 × 0.22 mm
β = 120.662 (2)°	

Data collection

Bruker SMART APEXII diffractometer	3836 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	1948 independent reflections
	1864 reflections with $I > 2\sigma(I)$
T_{min} = 0.850, T_{max} = 0.932	R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032	H-atom parameters constrained
$wR(F^2)$ = 0.082	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
S = 1.08	$\Delta\rho_{min}$ = −0.15 e Å^{-3}
1948 reflections	Absolute structure: Flack (1983), 834 Friedel pairs
110 parameters	
1 restraint	Flack parameter: −0.02 (7)

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯O2^i	0.93	2.51	3.435 (2)	171

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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supporting information

Dimethyl 2,2′-[ethane-1,2-diylbis(sulfanediyl)]dibenzoate

Xiaoming Hu, Jianghua Yu and Limin Yuan

S1. Comment

The flexibility and conformational freedom of the disulfide derivatives of the benzoate – dithiodibenzoates - provides a possibility for the construction of diverse frameworks with tailored properties and functions (Murugavel *et al.*, 2001; Humphrey *et al.*, 2004; Wang *et al.* 2004; Li *et al.*, 2007; Zhou *et al.*, 2009). The flexible bridging ligands adopt unusually twisted structures with different C—S—S—C torsion angles in constructing complexes.
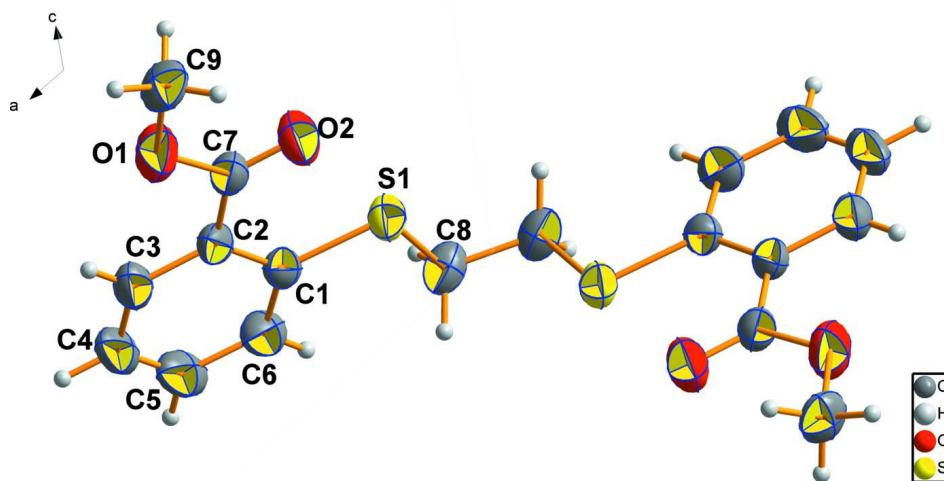
The title compound described here is a longer analogue of 2,2′-dithiodibenzoate with the two methyl benzoate units interconnected by a flexible –S-$(CH_2)_2$-S– bridge (Fig. 1). The torsion angle S—CH_2—CH_2—S is 72.88 (16)°. The two aromatic rings form a dihedral angle of 79.99 (6)°. The C1(sp^2)-S bond length [1.769 (2) Å] is significantly shorter than the C8(sp^3)-S [1.814 (2) Å] bond length due to *p-π* conjugation. There are no significant S⋯S nor S⋯O contacts present in the structure and C—H⋯*π* (arene) hydrogen bonds and aromatic *π*⋯*π* stacking interactions are also absent. In the crystal, intermolecular C—H⋯O hydrogen bonds (Table 1) link the molecules into a three-dimensional supramolecular structure (Fig. 2).

S2. Experimental

The title compound was synthesized as follows: a solution of 1,2-dibromoethane (0.94 g, 5 mmol) in methanol (10 ml) was added dropwise to a mixture of methyl thiosalicylate (1.85 g, 11 mmol), KOH (0.617 g, 11 mmol) and ethanol (10 ml). The reaction mixture was stirred and heated for 12 h. The precipitate was filtered off, washed with water.Yield 72%; Colourless block crystals suitable for single-crystals X-ray analysis were obtained by recrystallization from an aceto-nitrile solution.

S3. Refinement

Hydrogen atoms were placed in calculated positions [C—H = 0.93–0.97 Å] and refined as riding [U_{iso}(H) = 1.2Ueq(C) or 1.5Ueq(C_{methyl})].

Figure 1

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids. Unlabeled atoms are related to labeled atoms by the symmetry code (-*x*, *y*, -*z*).
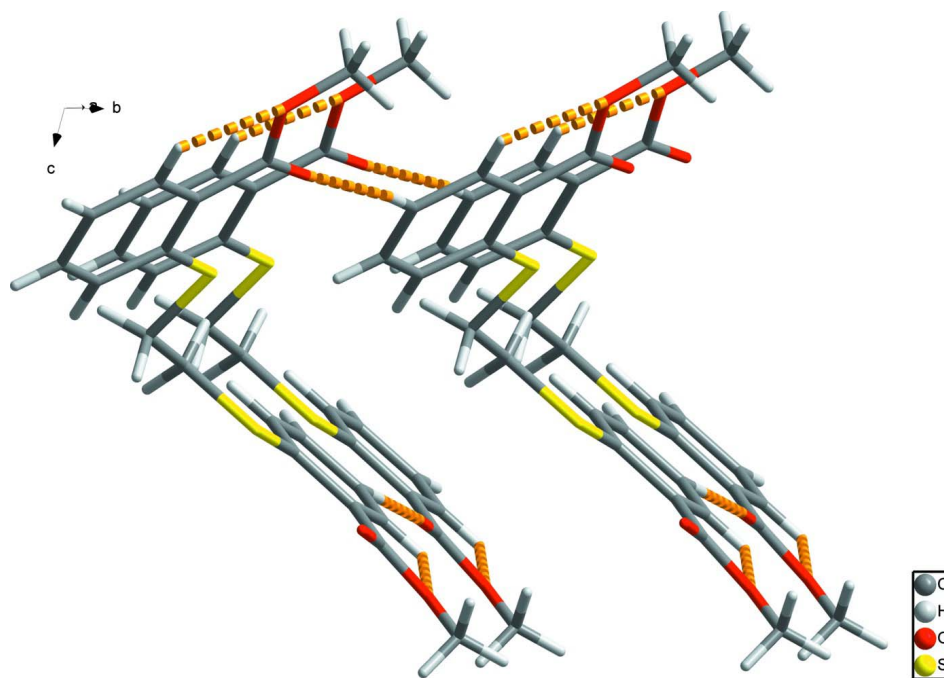
Figure 2

View of the connections inter- and intramolecules in (I) with the C—H···O interactions shown as orange dashed lines.

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Crystal data

$C_{18}H_{18}O_4S_2$	$F(000) = 380$
$M_r = 362.44$	$D_x = 1.378$ Mg m^{-3}
Monoclinic, $C2$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: C 2y	Cell parameters from 2178 reflections
$a = 15.077$ (3) Å	$\theta = 2.7–27.4°$
$b = 5.3913$ (10) Å	$\mu = 0.32$ mm^{-1}
$c = 12.495$ (2) Å	$T = 296$ K
$\beta = 120.662$ (2)°	Block, colourless
$V = 873.6$ (3) Å^3	$0.52 \times 0.32 \times 0.22$ mm
$Z = 2$	

Data collection

Bruker SMART APEXII diffractometer	3836 measured reflections
Radiation source: fine-focus sealed tube	1948 independent reflections
Graphite monochromator	1864 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
	$h = -19 \rightarrow 18$
	$k = -6 \rightarrow 6$
$T_{min} = 0.850$, $T_{max} = 0.932$	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.1272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	
1948 reflections	$(\Delta/\sigma)_{max} < 0.001$
110 parameters	$\Delta\rho_{max} = 0.23$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.15$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 834 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: −0.02 (7)

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 (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.24609 (11)	0.0317 (4)	0.17607 (14)	0.0440 (3)
C2	0.31876 (12)	0.1986 (4)	0.26461 (15)	0.0455 (4)
C3	0.42223 (14)	0.1865 (5)	0.29514 (18)	0.0590 (5)
H3	0.4700	0.2970	0.3530	0.071*
C4	0.45387 (16)	0.0121 (6)	0.2402 (2)	0.0689 (7)
H4	0.5224	0.0062	0.2606	0.083*
C5	0.38363 (18)	−0.1516 (5)	0.1556 (2)	0.0694 (7)
H5	0.4051	−0.2695	0.1192	0.083*
C6	0.28109 (16)	−0.1440 (4)	0.12343 (19)	0.0577 (5)
H6	0.2348	−0.2574	0.0660	0.069*
C7	0.28831 (13)	0.3846 (4)	0.32683 (16)	0.0478 (4)
C8	0.05804 (14)	−0.2095 (4)	0.02558 (17)	0.0525 (4)
H8A	0.0717	−0.1916	−0.0420	0.063*
H8B	0.0879	−0.3649	0.0679	0.063*
C9	0.3458 (2)	0.6901 (7)	0.4813 (3)	0.0898 (8)
H9A	0.2859	0.7821	0.4230	0.135*
H9B	0.4035	0.8008	0.5233	0.135*
H9C	0.3330	0.6119	0.5411	0.135*
O1	0.36822 (11)	0.5052 (4)	0.41658 (15)	0.0793 (5)
O2	0.20111 (11)	0.4248 (3)	0.30111 (15)	0.0675 (4)
S1	0.11495 (3)	0.04719 (7)	0.13359 (4)	0.04790 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0394 (7)	0.0510 (9)	0.0398 (7)	0.0110 (9)	0.0188 (6)	0.0069 (9)
C2	0.0355 (8)	0.0578 (11)	0.0388 (8)	0.0087 (7)	0.0157 (7)	0.0098 (7)
C3	0.0380 (9)	0.0805 (14)	0.0535 (10)	0.0051 (9)	0.0198 (8)	0.0137 (10)
C4	0.0461 (10)	0.100 (2)	0.0675 (12)	0.0304 (14)	0.0340 (9)	0.0303 (14)
C5	0.0659 (14)	0.0845 (17)	0.0697 (14)	0.0365 (12)	0.0433 (12)	0.0199 (12)
C6	0.0567 (11)	0.0623 (12)	0.0551 (11)	0.0187 (10)	0.0292 (9)	0.0041 (9)
C7	0.0387 (9)	0.0555 (11)	0.0409 (8)	−0.0024 (8)	0.0143 (7)	0.0010 (8)
C8	0.0529 (10)	0.0413 (9)	0.0474 (10)	0.0051 (8)	0.0141 (8)	−0.0028 (7)
C9	0.0861 (18)	0.0898 (19)	0.0753 (16)	−0.0203 (16)	0.0279 (14)	−0.0349 (16)
O1	0.0477 (7)	0.1046 (15)	0.0671 (8)	−0.0113 (9)	0.0159 (6)	−0.0323 (10)
O2	0.0418 (7)	0.0789 (10)	0.0765 (9)	−0.0027 (7)	0.0264 (7)	−0.0284 (8)
S1	0.03542 (19)	0.0520 (2)	0.0488 (2)	0.0033 (2)	0.01601 (15)	−0.0082 (2)

Geometric parameters (Å, º)

C1—C6	1.401 (3)	C6—H6	0.9300
C1—C2	1.413 (3)	C7—O2	1.203 (2)
C1—S1	1.7685 (15)	C7—O1	1.324 (2)
C2—C3	1.406 (2)	C8—C8ⁱ	1.527 (4)
C2—C7	1.478 (3)	C8—S1	1.8143 (19)

C3—C4	1.384 (4)	C8—H8A	0.9700
C3—H3	0.9300	C8—H8B	0.9700
C4—C5	1.370 (4)	C9—O1	1.429 (3)
C4—H4	0.9300	C9—H9A	0.9600
C5—C6	1.386 (3)	C9—H9B	0.9600
C5—H5	0.9300	C9—H9C	0.9600
C6—C1—C2	118.08 (15)	O2—C7—O1	122.42 (19)
C6—C1—S1	121.47 (16)	O2—C7—C2	124.88 (16)
C2—C1—S1	120.44 (14)	O1—C7—C2	112.71 (16)
C3—C2—C1	119.52 (18)	C8i—C8—S1	108.52 (12)
C3—C2—C7	119.22 (18)	C8i—C8—H8A	110.0
C1—C2—C7	121.26 (14)	S1—C8—H8A	110.0
C4—C3—C2	120.8 (2)	C8i—C8—H8B	110.0
C4—C3—H3	119.6	S1—C8—H8B	110.0
C2—C3—H3	119.6	H8A—C8—H8B	108.4
C5—C4—C3	119.61 (18)	O1—C9—H9A	109.5
C5—C4—H4	120.2	O1—C9—H9B	109.5
C3—C4—H4	120.2	H9A—C9—H9B	109.5
C4—C5—C6	120.9 (2)	O1—C9—H9C	109.5
C4—C5—H5	119.5	H9A—C9—H9C	109.5
C6—C5—H5	119.5	H9B—C9—H9C	109.5
C5—C6—C1	121.0 (2)	C7—O1—C9	116.51 (17)
C5—C6—H6	119.5	C1—S1—C8	102.68 (10)
C1—C6—H6	119.5		
C6—C1—C2—C3	1.1 (3)	S1—C1—C6—C5	178.76 (16)
S1—C1—C2—C3	−178.69 (15)	C3—C2—C7—O2	173.83 (19)
C6—C1—C2—C7	−178.26 (18)	C1—C2—C7—O2	−6.8 (3)
S1—C1—C2—C7	1.9 (2)	C3—C2—C7—O1	−6.6 (3)
C1—C2—C3—C4	−0.4 (3)	C1—C2—C7—O1	172.80 (18)
C7—C2—C3—C4	178.97 (18)	O2—C7—O1—C9	−0.9 (3)
C2—C3—C4—C5	−0.4 (3)	C2—C7—O1—C9	179.6 (2)
C3—C4—C5—C6	0.5 (3)	C6—C1—S1—C8	2.60 (18)
C4—C5—C6—C1	0.3 (3)	C2—C1—S1—C8	−177.58 (15)
C2—C1—C6—C5	−1.1 (3)	C8i—C8—S1—C1	−176.60 (15)

Symmetry code: (i) −x, y, −z.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯O1	0.93	2.34	2.679 (3)	101
C4—H4⋯O2ii	0.93	2.51	3.435 (2)	171

Symmetry code: (ii) x+1/2, y−1/2, z.