organic compounds

2-(1,3-Dithian-2-ylidene)-1-phenyl-butane-1,3-dione

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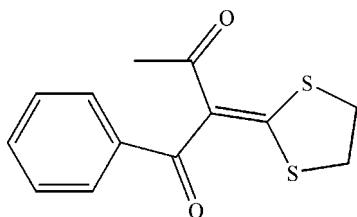Correspondence e-mail: zhanglc_07@sina.com

The title compound, $C_{13}H_{12}O_2S_2$, belonging to the group of dioxoketene cyclic S,S-acetals, was prepared from the corresponding dione in high yield. In the structure, the C=O and C=C bonds are not coplanar, with O=C—C=C torsion angles of −36.8 (4) and −21.0 (4)°. The dithian ring has a twisted conformation.

Related literature

For related literature, see: Choi *et al.* (1988); Lin *et al.* (2005); Zhu *et al.* (1996, 1997).

Experimental

Crystal data

$C_{13}H_{12}O_2S_2$	V = 611.4 (4) Å³
M_r = 264.35	Z = 2
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
a = 7.812 (3) Å	μ = 0.42 mm⁻¹
b = 5.5115 (18) Å	T = 298 (2) K
c = 14.628 (5) Å	0.14 × 0.10 × 0.01 mm
β = 103.876 (4)°	

Data collection

Bruker APEXII CCD diffractometer	3073 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	1948 independent reflections
T_{min} = 0.956, T_{max} = 0.993	1887 reflections with $I > 2\sigma(I)$
	R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029	H-atom parameters constrained
$wR(F^2)$ = 0.073	$\Delta\rho_{max}$ = 0.24 e Å⁻³
S = 1.04	$\Delta\rho_{min}$ = −0.17 e Å⁻³
1948 reflections	Absolute structure: Flack (1983), with 741 Friedel pairs
154 parameters	Flack parameter: −0.01 (8)
1 restraint	

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); 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*.

References

Bruker (2005). *APEX2* (Version 1.27) and *SAINT* (Version 7.12A). Bruker AXS Inc., Madison, Wisconsin, USA.
Choi, E. B., Youn, I. K. & Pak, C. S. (1988). *Synthesis*, **7**, 792–794.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Lin, C., Yu, H. F., Liu, Q. & Hou, D. Y. (2005). *Chin. J. Org. Chem.* **25**, 819–821.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhu, Z. M., Wang, Y., Xu, Y. T. & Mei, Z. M. (1996). *Chin. Chem. Lett.* **7**, 95–96.
Zhu, Z. M., Wang, Y., Xu, Y. T. & Mei, Z. M. (1997). *Chin. Chem. Lett.* **8**, 367–368.

supplementary materials

2-(1,3-Dithian-2-ylidene)-1-phenylbutane-1,3-dione

L.-C. Zhang, N. Li, X.-H. Li, C.-Y. Huang and G.-H. Zhou

Comment

The dioxo ketene cyclic S,S-acetals have been known as a precursor for the synthesis of not only unsaturated ketones and keto esters, but also heterocyclic compounds (Choi *et al.*, 1988; Lin *et al.*, 2005; Zhu *et al.*, 1996; Zhu *et al.*, 1997). We have synthesized the title compound, 1-phenyl-2-(1,3-dithian −2-ylidene)-butane-1,3-dione and determined its molecular structure (Fig. 1). In the structure, the C=O bonds, the benzene ring, and the C2=C5 double bond are not co-planar. The O1—C1—C8—C13 torsion angle is −24.3 (4)°. The dihedral angle between the planes C2_C1_O1 and C2_C3_O2 is 50.7 (4)°, and is 7.6 (4) ° between the C1_C2_C3 and S1_C5_S2 planes.

Experimental

To a suspension of 1-phenyl-butane-1,3-dione(21 mmol) and anhydrous K_2CO_3(60 mmol)in DMF(20 ml was added CS_2(30 mmol) at room temperature. After stirring for about 1 h, 1,2-dibromoethane (22 mmol) was added in full. Stirring was continued another 10 min at room temperature. Water(250 ml) was added to precipitate the yellow block-shaped product, which was recrystallized from ethanol, providing analytically pure compound suitable for single-crystal X-ray diffraction. *M*.p. 404 K°. Analysis: Found: C: 59.15, H: 4.50; calculated: C: 59.06, H: 4.58%. IR spectra: 3083,1647,1615,1418 and 1240 cm$^{-1.}$ ^{1}H-NMR: 2.08(3*H*,s,CH_3), 3.43(4*H*,m, 2*SCH_2), 7.70(5*H*,m, ph)

Refinement

All H atoms were placed in calculated positions (C—H = 0.93 Å, 0.97 Å, 0.96Å of –CH, –CH_2 and-CH_3 respectively) and included in the refinement in the riding-model approximation with U_{iso}(H) = 1.2U_{eq}(carrier atom) (1.5U_{eq} for methyl H atoms).
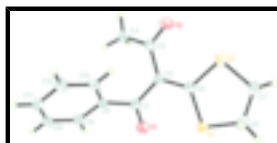
Figures

Fig. 1. The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.
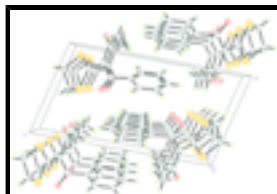

Fig. 2. The packing diagram of the compound. viewed down the *c* axis. H atoms have been omitted for clarity.

2-(1,3-Dithian-2-ylidene)-1-phenylbutane-1,3-dione

Crystal data

$C_{13}H_{12}O_2S_2$	$F_{000} = 276$
$M_r = 264.35$	$D_x = 1.436$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 3425 reflections
$a = 7.812$ (3) Å	$\theta = 2.7–27.8º$
$b = 5.5115$ (18) Å	$\mu = 0.42$ mm^{-1}
$c = 14.628$ (5) Å	$T = 298$ (2) K
$\beta = 103.876$ (4)º	Block, yellow
$V = 611.4$ (4) Å^3	$0.14 \times 0.10 \times 0.01$ mm
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer	1948 independent reflections
Radiation source: fine-focus sealed tube	1887 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.015$
$T = 298(2)$ K	$\theta_{max} = 25.0º$
ω scans	$\theta_{min} = 2.7º$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -8 \rightarrow 9$
$T_{min} = 0.956$, $T_{max} = 0.993$	$k = -6 \rightarrow 6$
3073 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.1246P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
1948 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
154 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983)
Primary atom site location: structure-invariant direct methods	Flack parameter: -0.01 (8)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
S1	0.45599 (7)	0.16653 (13)	0.16380 (4)	0.04320 (18)
S2	0.11323 (8)	0.39993 (14)	0.08953 (4)	0.04637 (18)
O1	0.4104 (2)	−0.2094 (4)	0.27828 (13)	0.0563 (5)
O2	−0.1208 (2)	0.2157 (4)	0.17817 (13)	0.0531 (5)
C1	0.2829 (3)	−0.1090 (5)	0.29623 (15)	0.0361 (5)
C2	0.1629 (3)	0.0454 (5)	0.22544 (15)	0.0342 (5)
C3	−0.0288 (3)	0.0456 (5)	0.21677 (16)	0.0377 (6)
C4	−0.1148 (3)	−0.1726 (6)	0.24704 (18)	0.0482 (7)
H4A	−0.2388	−0.1430	0.2380	0.072*
H4B	−0.0636	−0.2046	0.3124	0.072*
H4C	−0.0971	−0.3102	0.2101	0.072*
C5	0.2343 (3)	0.1860 (5)	0.16689 (14)	0.0348 (5)
C6	0.4601 (4)	0.4458 (6)	0.1000 (2)	0.0532 (7)
H6A	0.4788	0.5824	0.1431	0.064*
H6B	0.5552	0.4423	0.0679	0.064*
C7	0.2864 (4)	0.4705 (7)	0.0300 (2)	0.0614 (9)
H7A	0.2807	0.3597	−0.0222	0.074*
H7B	0.2720	0.6346	0.0055	0.074*
C8	0.2575 (3)	−0.1219 (5)	0.39431 (15)	0.0328 (5)
C9	0.3325 (3)	−0.3133 (5)	0.45259 (16)	0.0390 (5)
H9A	0.3892	−0.4378	0.4286	0.047*
C10	0.3233 (3)	−0.3194 (6)	0.54551 (17)	0.0459 (6)
H10A	0.3714	−0.4495	0.5836	0.055*
C11	0.2424 (3)	−0.1316 (6)	0.58230 (17)	0.0461 (7)
H11A	0.2390	−0.1337	0.6454	0.055*
C12	0.1671 (3)	0.0579 (6)	0.52532 (17)	0.0438 (6)
H12A	0.1111	0.1825	0.5497	0.053*
C13	0.1749 (3)	0.0631 (5)	0.43144 (16)	0.0368 (5)
H13A	0.1243	0.1917	0.3932	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0350 (3)	0.0536 (4)	0.0445 (3)	0.0025 (3)	0.0165 (2)	0.0021 (3)
S2	0.0403 (3)	0.0550 (4)	0.0434 (3)	0.0041 (3)	0.0093 (3)	0.0130 (3)
O1	0.0513 (11)	0.0737 (14)	0.0483 (10)	0.0252 (10)	0.0205 (8)	0.0065 (10)
O2	0.0350 (9)	0.0578 (14)	0.0650 (12)	0.0054 (9)	0.0091 (8)	0.0119 (10)
C1	0.0330 (11)	0.0399 (13)	0.0353 (12)	0.0004 (12)	0.0078 (9)	−0.0035 (12)
C2	0.0309 (11)	0.0423 (15)	0.0298 (11)	0.0007 (10)	0.0082 (9)	−0.0025 (11)
C3	0.0344 (12)	0.0467 (16)	0.0318 (11)	−0.0004 (11)	0.0073 (10)	−0.0018 (12)
C4	0.0393 (13)	0.059 (2)	0.0466 (14)	−0.0102 (12)	0.0099 (12)	0.0019 (13)
C5	0.0331 (11)	0.0413 (14)	0.0294 (10)	−0.0005 (11)	0.0066 (9)	−0.0056 (11)
C6	0.0499 (15)	0.058 (2)	0.0607 (16)	−0.0052 (13)	0.0302 (13)	−0.0006 (15)
C7	0.0612 (17)	0.077 (2)	0.0520 (16)	0.0039 (16)	0.0259 (14)	0.0197 (16)
C8	0.0279 (10)	0.0354 (13)	0.0341 (11)	−0.0003 (10)	0.0052 (8)	0.0013 (11)
C9	0.0346 (11)	0.0368 (14)	0.0460 (13)	0.0028 (12)	0.0103 (10)	0.0009 (12)
C10	0.0345 (11)	0.0525 (16)	0.0487 (13)	0.0018 (13)	0.0062 (10)	0.0188 (15)
C11	0.0402 (12)	0.0626 (19)	0.0346 (12)	−0.0066 (14)	0.0071 (10)	0.0035 (14)
C12	0.0490 (14)	0.0475 (16)	0.0358 (13)	0.0020 (12)	0.0117 (11)	−0.0068 (12)
C13	0.0384 (12)	0.0347 (13)	0.0352 (12)	0.0033 (10)	0.0050 (10)	0.0007 (10)

Geometric parameters (Å, °)

S1—C5	1.746 (2)	C6—H6A	0.9700
S1—C6	1.804 (3)	C6—H6B	0.9700
S2—C5	1.747 (3)	C7—H7A	0.9700
S2—C7	1.817 (3)	C7—H7B	0.9700
O1—C1	1.221 (3)	C8—C13	1.385 (3)
O2—C3	1.233 (3)	C8—C9	1.394 (3)
C1—C2	1.487 (3)	C9—C10	1.378 (3)
C1—C8	1.496 (3)	C9—H9A	0.9300
C2—C5	1.369 (3)	C10—C11	1.387 (4)
C2—C3	1.472 (3)	C10—H10A	0.9300
C3—C4	1.495 (4)	C11—C12	1.377 (4)
C4—H4A	0.9600	C11—H11A	0.9300
C4—H4B	0.9600	C12—C13	1.389 (3)
C4—H4C	0.9600	C12—H12A	0.9300
C6—C7	1.497 (4)	C13—H13A	0.9300
C5—S1—C6	95.83 (12)	H6A—C6—H6B	108.5
C5—S2—C7	96.03 (13)	C6—C7—S2	108.04 (19)
O1—C1—C2	121.3 (2)	C6—C7—H7A	110.1
O1—C1—C8	119.2 (2)	S2—C7—H7A	110.1
C2—C1—C8	119.2 (2)	C6—C7—H7B	110.1
C5—C2—C3	120.3 (2)	S2—C7—H7B	110.1
C5—C2—C1	118.4 (2)	H7A—C7—H7B	108.4
C3—C2—C1	121.3 (2)	C13—C8—C9	119.0 (2)
O2—C3—C2	120.6 (2)	C13—C8—C1	121.5 (2)

O2—C3—C4	119.5 (2)	C9—C8—C1	119.3 (2)
C2—C3—C4	119.6 (2)	C10—C9—C8	120.5 (2)
C3—C4—H4A	109.5	C10—C9—H9A	119.7
C3—C4—H4B	109.5	C8—C9—H9A	119.7
H4A—C4—H4B	109.5	C9—C10—C11	120.1 (3)
C3—C4—H4C	109.5	C9—C10—H10A	120.0
H4A—C4—H4C	109.5	C11—C10—H10A	120.0
H4B—C4—H4C	109.5	C12—C11—C10	120.0 (2)
C2—C5—S1	122.47 (19)	C12—C11—H11A	120.0
C2—C5—S2	123.26 (17)	C10—C11—H11A	120.0
S1—C5—S2	114.27 (14)	C11—C12—C13	120.0 (3)
C7—C6—S1	107.8 (2)	C11—C12—H12A	120.0
C7—C6—H6A	110.1	C13—C12—H12A	120.0
S1—C6—H6A	110.1	C8—C13—C12	120.5 (2)
C7—C6—H6B	110.1	C8—C13—H13A	119.8
S1—C6—H6B	110.1	C12—C13—H13A	119.8
O1—C1—C2—C5	−36.8 (4)	C5—S1—C6—C7	−36.6 (2)
C8—C1—C2—C5	137.1 (2)	S1—C6—C7—S2	45.7 (3)
O1—C1—C2—C3	142.2 (3)	C5—S2—C7—C6	−32.4 (3)
C8—C1—C2—C3	−43.9 (3)	O1—C1—C8—C13	149.8 (3)
C5—C2—C3—O2	−21.0 (4)	C2—C1—C8—C13	−24.2 (3)
C1—C2—C3—O2	160.0 (2)	O1—C1—C8—C9	−24.3 (4)
C5—C2—C3—C4	153.3 (2)	C2—C1—C8—C9	161.7 (2)
C1—C2—C3—C4	−25.7 (3)	C13—C8—C9—C10	0.6 (3)
C3—C2—C5—S1	−172.03 (19)	C1—C8—C9—C10	174.8 (2)
C1—C2—C5—S1	7.0 (3)	C8—C9—C10—C11	−1.4 (4)
C3—C2—C5—S2	8.2 (3)	C9—C10—C11—C12	1.7 (4)
C1—C2—C5—S2	−172.79 (18)	C10—C11—C12—C13	−1.1 (4)
C6—S1—C5—C2	−165.4 (2)	C9—C8—C13—C12	0.0 (3)
C6—S1—C5—S2	14.38 (17)	C1—C8—C13—C12	−174.0 (2)
C7—S2—C5—C2	−172.7 (2)	C11—C12—C13—C8	0.2 (4)
C7—S2—C5—S1	7.48 (18)		

Fig. 1

Fig. 2