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

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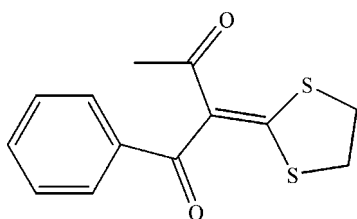
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.029; wR factor = 0.074; data-to-parameter ratio = 12.6.

The title compound, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$, belonging to the group of dioxoketene cyclic S,S -acetals, was prepared from the corresponding dione in high yield. In the structure, the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bonds are not coplanar, with $\text{O}=\text{C}-\text{C}=\text{C}$ 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

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$
 $M_r = 264.35$
 Monoclinic, $P2_1$
 $a = 7.812$ (3) Å
 $b = 5.5115$ (18) Å
 $c = 14.628$ (5) Å
 $\beta = 103.876$ (4)°

$V = 611.4$ (4) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.42$ mm⁻¹
 $T = 298$ (2) K
 $0.14 \times 0.10 \times 0.01$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.956$, $T_{\max} = 0.993$

3073 measured reflections
 1948 independent reflections
 1887 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.073$
 $S = 1.04$
 1948 reflections
 154 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³
 Absolute structure: Flack (1983), with 741 Friedel pairs
 Flack parameter: -0.01 (8)

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.

The authors are grateful to Professor Wan-Shen You and Guang-Ning Zhang for their generous help with this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2371).

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supporting information

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

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S1. 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 $-24.3(4)^\circ$. The dihedral angle between the planes C2_C1_O1 and C2_C3_O2 is $50.7(4)^\circ$, and is $7.6(4)^\circ$ between the C1_C2_C3 and S1_C5_S2 planes.

S2. 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} . 1H -NMR: 2.08(3H,s,CH₃), 3.43(4H,m, 2*SCH₂), 7.70(5H,m, ph)

S3. Refinement

All H atoms were placed in calculated positions (C—H = 0.93 Å, 0.97 Å, 0.96Å of —CH, —CH₂ and —CH₃ respectively) and included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$ ($1.5U_{eq}$ for methyl H atoms).

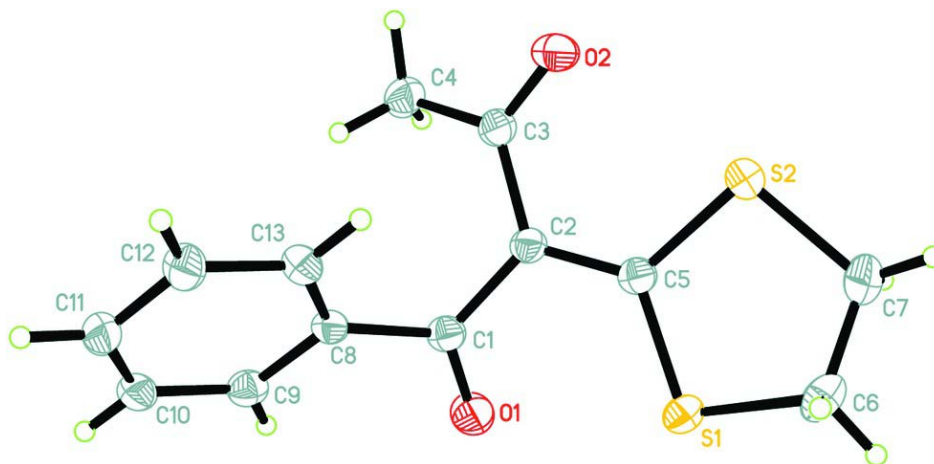


Figure 1

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

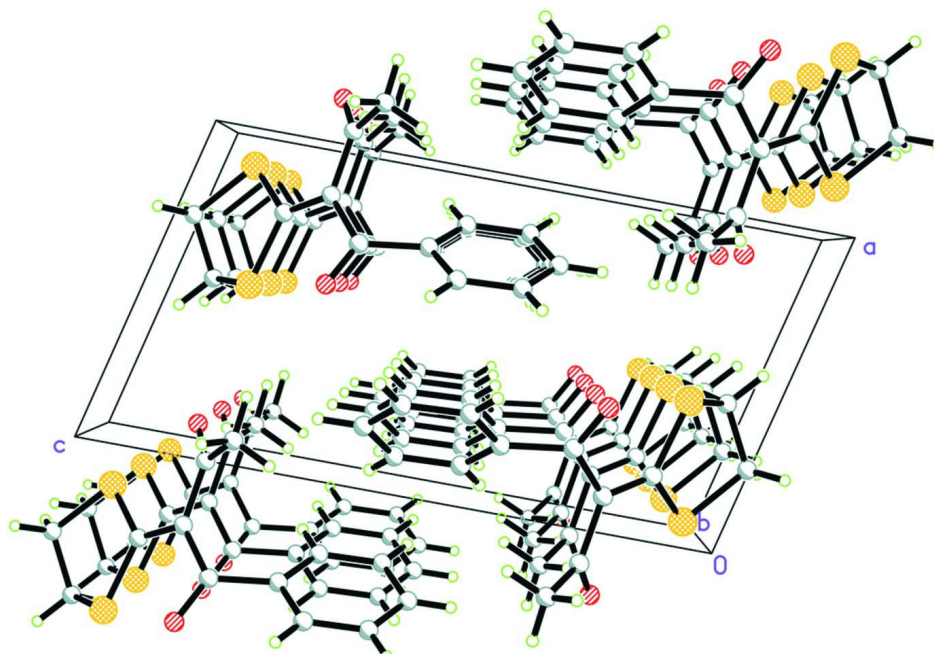


Figure 2

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

$C_{13}H_{12}O_2S_2$

$M_r = 264.35$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_1yb$

$a = 7.812\ (3)\ \text{\AA}$

$b = 5.5115\ (18)\ \text{\AA}$

$c = 14.628\ (5)\ \text{\AA}$

$\beta = 103.876\ (4)^\circ$

$V = 611.4\ (4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 276$

$D_x = 1.436\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3425 reflections

$\theta = 2.7\text{--}27.8^\circ$
 $\mu = 0.42 \text{ mm}^{-1}$
 $T = 298 \text{ K}$

Block, yellow
 $0.14 \times 0.10 \times 0.01 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.956, T_{\max} = 0.993$

3073 measured reflections
 1948 independent reflections
 1887 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.7^\circ$
 $h = -8 \rightarrow 9$
 $k = -6 \rightarrow 6$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.073$
 $S = 1.05$
 1948 reflections
 154 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.1246P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983)
 Absolute structure parameter: $-0.01 (8)$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (Å²)

	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)

supporting information

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)		
