

Crystal Structure of 3-(1,3-Dithiolan-2-ylidene)pentane-2,4-dione

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This compound with molecular formula C₈H₁₀O₂S₂ crystallized in the orthorhombic space group *Pca*2₁ (*Z* = 4) with unit-cell parameters *a* = 7.3576(9)Å, *b* = 14.2238(11)Å, *c* = 8.714(2)Å. The structure was solved by direct methods and refined to *R* = 0.0309. This compound approximates the rare *ZZ* conformation in which both the ketenedithioacetal group and the oxygen atoms are on the same plane with the sulfur atoms close to the respective oxygen atoms.

(Received July 30, 2007; Accepted September 14, 2007; Published on web November 13, 2007)

Spectroscopic studies on push-pull ethylenes have shown that the coplanarity for such compounds, though favorable on energetic grounds, becomes problematic when steric interactions are present.¹ In 1,1-diacetyl ethylenes, three conformations (*EE*, *EZ* and *ZZ*) must be taken into account. In 1,1-bis-methylthio-2,2-diacetyl ethylene and 1,1-bis-methylthio-2,2-dicarbomethoxy ethylene, the *S-cis-S-trans* arrangement of the carbonyl groups with respect to the C-C double bond approximates the *EZ* conformation.² However, in 3-bis(methylthio)methylene-pentane-2,4-dione, which is closely related to the title compound (Fig. 1), it approximates the *EE* conformation.³

The title compound was obtained by the reaction of acetyl acetone with carbon disulfide in the presence of a base, followed by alkylation with 1,2-dibromoethane. To a suspension of KOH (5.6 g, 0.1 mol) in acetonitrile (30 ml) a mixture of acetyl acetone (10 ml, 0.1 mol) and carbon disulfide (0.1 mol, 6.5 ml) was added and stirred for 2 h at room temperature. A solution of 1,2-dibromoethane (8.5 ml, 0.1 ml) in 10 ml acetonitrile was added to this, and stirred for another 24 h. The obtained crude solid was washed with water, evaporated in a vacuum and recrystallized from dichloromethane.

Colorless prismatic crystals used for data collection were obtained by slow evaporation from an acetone solution. X-ray intensity data were collected on a Enraf-Nonius CAD-4 diffractometer with Cu *K*_α radiation ($\lambda = 1.5418$ Å) in the ω -2 θ scan mode. Then, 868 reflections were measured ($h_{\max} = 0$; k_{\max}

= 17; $l_{\max} = 9$), of which 849 were treated while being observed with $I > 2\sigma(I)$. Data were corrected for Lorentz, polarization and extinction effects. Crystal data, intensity collection conditions and refinement parameters are given in Table 1.

The structure was solved by direct methods using SHELXS97. Isotropic refinements of the hydrogen atoms and anisotropic refinements of the non-hydrogen atoms lowered the *R*-factor to 0.0309. All hydrogen atoms were fixed by the program. The absolute structure of this crystal was determined by Flack's parameters—0.02(3). The maximum and minimum electron densities in the final difference Fourier map were at 0.49 e Å⁻³

Table 1 Crystal and experimental data

CCDC No. 273751	
Empirical formula	C ₈ H ₁₀ O ₂ S ₂
Formula weight	202.28
Temperature (K)	293(2)
Wavelength (Cu <i>K</i> _α) (Å)	1.5418
Crystal system, space group	orthorhombic, <i>Pca</i> 2 ₁
Unit cell dimensions (Å)	<i>a</i> = 7.3576(9), <i>b</i> = 14.2238(11), <i>c</i> = 8.714(2)
Volume (Å ³)	911.9(2)
<i>Z</i> , Calculated density (Mg/m ³)	4, 1.473
Absorption coefficient (mm ⁻¹)	4.945
Crystal size (mm)	0.2 × 0.1 × 0.1
<i>F</i> (0 0 0)	424
θ range for data collection (°)	3.11 to 69.86
Index ranges	-8 ≤ <i>h</i> ≤ 0, 0 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 9
Reflections collected / unique	868 / 868
Completeness to 2 θ = 69.86	93.7%
Refinement method	full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.159
Data / parameters	868/140
Final <i>R</i> indices ($I > 2\sigma(I)$)	<i>R</i> 1 = 0.0309, <i>wR</i> 2 = 0.0787
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0315, <i>wR</i> 2 = 0.0801
Extinction coefficient	0.0172(15)
Largest diff. peak and hole (e. Å ⁻³)	0.491 and -0.345

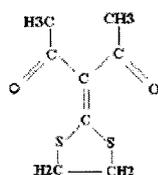


Fig. 1 *ZZ* conformation in the title compound.

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Table 2 Atomic coordinates and equivalent isotropic displacement parameters

Atom	x	y	z	U_{eq}
S1	0.9731(1)	0.0989(1)	0.3232(1)	0.0347(3)
S2	0.9963(1)	0.2445(1)	0.0886(2)	0.0328(3)
O1	1.0215(3)	0.1749(2)	0.5959(4)	0.0448(6)
O2	1.0006(3)	0.4098(2)	0.2209(5)	0.0478(8)
C1	0.9675(5)	0.3287(3)	0.6812(5)	0.0458(9)
C2	1.0085(3)	0.2584(2)	0.5591(5)	0.0308(11)
C3	1.0211(3)	0.2856(2)	0.3964(4)	0.0249(6)
C4	1.0533(4)	0.3841(2)	0.3465(4)	0.0275(6)
C5	1.1630(5)	0.4505(2)	0.4417(5)	0.0414(7)
C6	0.9994(3)	0.2181(2)	0.2831(4)	0.0255(8)
C7	0.9131(4)	0.0641(2)	0.1303(4)	0.0393(7)
C8	1.0189(4)	0.1238(3)	0.0211(6)	0.0423(9)

Table 3 Bond lengths (Å) and angles (deg.) for $C_8H_{10}O_2S_2$

Bond length (Å)		Angle (deg.)	
S(1)-C(6)	1.741(3)	C(6)-S(1)-C(7)	96.2(2)
S(1)-C(7)	1.807(4)	C(6)-S(2)-C(8)	96.3(2)
S(2)-C(6)	1.736(4)	O(1)-C(2)-C(3)	119.9(4)
S(2)-C(8)	1.822(4)	O(1)-C(2)-C(1)	118.4(4)
O(1)-C(2)	1.235(4)	C(3)-C(2)-C(1)	121.6(3)
O(2)-C(4)	1.218(6)	C(6)-C(3)-C(2)	119.7(3)
C(1)-C(2)	1.491(6)	C(6)-C(3)-C(4)	117.6(3)
C(2)-C(3)	1.473(6)	C(2)-C(3)-C(4)	122.7(3)
C(3)-C(6)	1.387(5)	O(2)-C(4)-C(5)	119.7(3)
C(3)-C(4)	1.485(4)	O(2)-C(4)-C(3)	118.7(2)
C(4)-C(5)	1.494(4)	C(5)-C(4)-C(3)	121.3(3)
C(7)-C(8)	1.495(6)	C(3)-C(6)-S(1)	123.2(3)
		C(3)-C(6)-S(2)	123.0(3)
		S(1)-C(6)-S(2)	113.9(2)
		C(8)-C(7)-S(1)	108.0(2)
		C(7)-C(8)-S(2)	106.4(3)

and $-0.35 e \text{ \AA}^{-3}$, respectively.

The final atomic coordinates and the equivalent thermal parameters for all non-hydrogen atoms are given in Table 2. The C(2)-O(1), C(4)-O(2) and C(3)-C(6) bond lengths (Table 3) are comparable to the respective bonds in diisopropyl(1,3-dithiolan-2-ylidene)malonate, a compound having a similar dithiolan ring substitution and showing fungicidal activity.⁴ The C-O bonds are shorter when compared to other pentane 2,4 dione structures having phenyl substitution at the C(3) position.⁵ The five-member ring C(7)-S(1)-C(6)-S(2)-C(8) is in a distorted half-chair conformation that is twisted on C(7)-C(8).

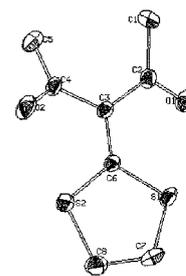


Fig. 2 Molecular structure showing 50% probability ellipsoids (H atoms are omitted for clarity).

The C(2)-O(1) and C(4)-O(2) bonds are *cis* to the double bond C(3)-C(6) (Fig.2), as seen from the torsion angles: O(1)-C(2)-C(3)-C(6) [$17.0(4)^\circ$] and O(2)-C(4)-C(3)-C(6) [$24.9(4)^\circ$]. As a result, the oxygen atoms and the sulfur atoms come closer. Thus, the compound approximates the *ZZ* conformation in which both the ketenedithioacetal group and the oxygen atoms are on the same plane with the sulfur atoms close to the respective oxygen atoms. This conformation is relatively stable due to the push-pull nature of the ketenedithioacetal moiety. Due to the electron-releasing nature of the ketene dithioacetal, oxygen atoms of the carbonyl groups act as strong acceptors, while the sulfur atoms act as strong donors. Thus, the sulfur atoms come closer to the oxygen atoms and the ketenedithioacetal group and the carbonyl groups are on the same plane, giving more stability to the conformation. The shortest intermolecular contacts are the C-H...O bonding along the *c*-direction between the carbonyl oxygen and the hydrogen atom of the methyl carbon at $-x, 1 - y, 1/2 + z$ and the hydrogen bonding along the *b*-direction between the carbonyl oxygen O(2) and carbon atom C(7) of the five-member ring.

D-H ...A	symm	H ...A	D ...A	D-H ...A
C(5)-H(5C)-O(2)	$-x, -y + 1, z + 1/2$	2.5760 Å	3.3627 Å	139.31°
C(7)-H(7A)-O(1)	$-x, -y, z - 1/2$	2.4845 Å	3.4474 Å	171.91°

Acknowledgements

The authors are indebted to (late) Dr. C. V. Asokan, School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, for all the help received, especially in the synthesis of this compound.

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