

4,5-Bis(pivaloylsulfanyl)-1,3-dithiolane-2-thione

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Key indicators

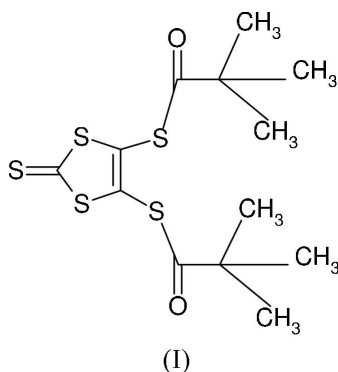
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.061
 wR factor = 0.169
Data-to-parameter ratio = 18.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}_5$, possesses twofold symmetry and is composed of two pivalyl groups lying on opposite sides of the planar 1,3-dithiole-2-thione conjugated moiety. Owing to the introduction of the $\text{C}=\text{O}$ electron-acceptor group the adjacent $\text{C}-\text{S}$ bond length [1.774 (4) Å] is shorter than that of a typical $\text{C}-\text{S}$ single bond. In the crystal structure, there are no significant intermolecular hydrogen bonds.

Received 3 March 2005
Accepted 7 March 2005
Online 18 March 2005

Comment

TTF (tetrathiafulvalene) and BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] derivatives and their charge-transfer salts have attracted much interest because of their high electronic conductivity or superconductivity (Williams *et al.*, 1992). Moreover, these compounds have received some attention in the field of third-order non-linear optics, due to their relatively large conjugated structures (Huggard & Blau, 1987). In order to obtain materials with high optical and/or electrical properties and investigate their structure–property relationships, compounds with various groups bonded to the S atoms in the 4- and 5-positions have been prepared. As part of these studies, the title compound, (I), a precursor of new TTF and BEDT-TTF derivatives, has been prepared and analysed crystallographically.



The molecular structure of (I) is illustrated in Fig. 1 and selected bond distances and angles are given in Table 1. Doubly bonded atom S1 lies in the plane of the five-membered dithiole ring. The molecule possesses C_2 symmetry with the two carbonyl groups located on opposite sides of the five-membered ring. The $\text{C}1-\text{S}1$ distance of 1.627 (6) Å is slightly longer than a typical $\text{C}=\text{S}$ double bond (1.55 Å). The $\text{C}-\text{S}$ bond lengths in the five-membered ring [range 1.721 (3)–1.739 (4) Å] are shorter than for typical $\text{C}-\text{S}$ single bonds (1.82 Å). The $\text{C}2=\text{C}2'$ bond length [1.344 (7) Å; symmetry code: (i) $-x, y, -z + \frac{1}{2}$] in the five-membered ring corresponds to that for a normal $\text{C}=\text{C}$ bond. This shows the high degree of

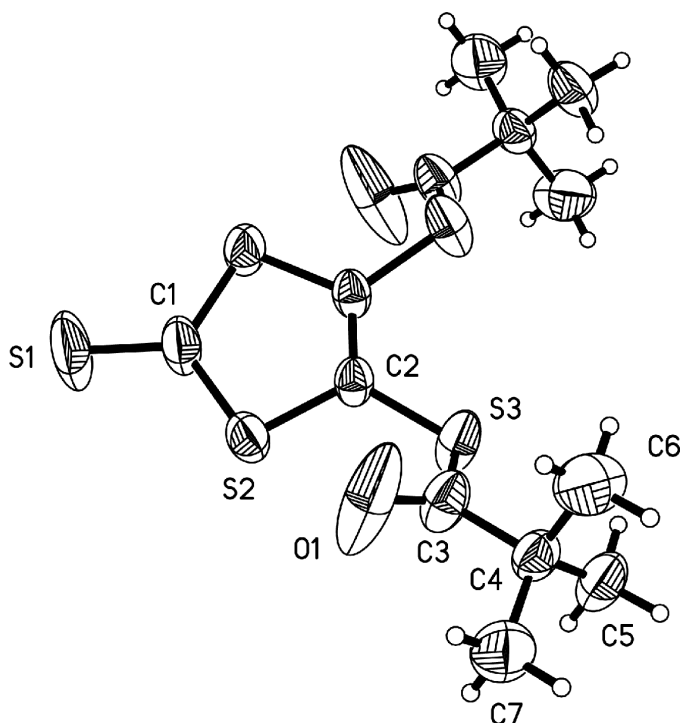


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry code $-x, y, -z + \frac{1}{2}$.

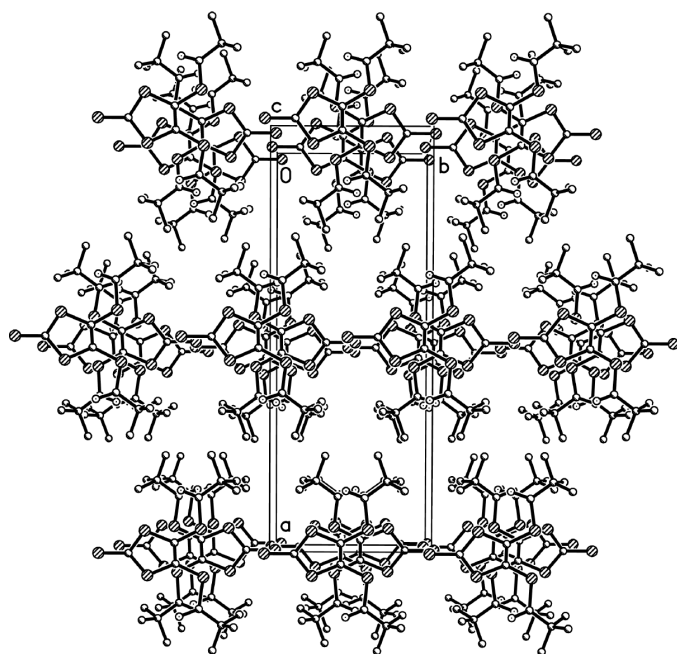


Figure 2
The crystal packing for (I), viewed along the *c* axis.

conjugation of the five-membered ring. The introduction of the C=O electron-acceptor group results in a slight decrease in the C3—S3 bond length [1.774 (4) Å] compared to the same distance in analogous compounds with alkyl substituents (Low *et al.*, 1999; Simonsen *et al.*, 1990; Yu *et al.*, 1995).

In the crystal structure the molecules stack face-to-face along the *c* direction, as shown in Fig. 2. No significant inter-

molecular interactions were detected when the structure was analysed using *PLATON* (Spek, 2003).

Experimental

The title compound was prepared by the reaction of $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ (dmit is the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion, $\text{C}_3\text{S}_5^{2-}$) and pivalyl chloride in acetone. Pivalyl chloride (60 mmol) was added dropwise to a solution of $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ (15 mmol) in acetone (100 ml). The mixture was stirred for 2 h at room temperature and then dissolved in an additional 100 ml of acetone. The resulting orange precipitate that formed was filtered off. The orange filtrate was left to stand for several days, giving pale yellow crystals suitable for X-ray structure analysis.

Crystal data

$\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}_5$	$D_x = 1.372 \text{ Mg m}^{-3}$
$M_r = 366.57$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 57 reflections
$a = 23.469 (3) \text{ \AA}$	$\theta = 4.4\text{--}12.5^\circ$
$b = 8.953 (1) \text{ \AA}$	$\mu = 0.65 \text{ mm}^{-1}$
$c = 8.492 (1) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 95.879 (9)^\circ$	Prism, pale-yellow
$V = 1774.9 (15) \text{ \AA}^3$	$0.40 \times 0.36 \times 0.32 \text{ mm}$
$Z = 4$	

Data collection

Bruker <i>P4</i> diffractometer	$R_{\text{int}} = 0.024$
ω scans	$\theta_{\text{max}} = 26.0^\circ$
Absorption correction: ψ scan (<i>XSCANS</i> ; Bruker, 1997)	$h = -1 \rightarrow 28$
$T_{\text{min}} = 0.762, T_{\text{max}} = 0.843$	$k = -1 \rightarrow 11$
2170 measured reflections	$l = -10 \rightarrow 10$
1746 independent reflections	3 standard reflections
1332 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 4.6825P]$
$R[F^2 > 2\sigma(F^2)] = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.170$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
1746 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
94 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0128 (16)

Table 1

Selected geometric parameters (Å, °).

C1—S1	1.627 (6)	C2—S3	1.748 (4)
C1—S2	1.721 (3)	C3—O1	1.185 (5)
C2—C2 ⁱ	1.344 (7)	C3—S3	1.774 (4)
C2—S2	1.739 (4)		
S1—C1—S2	123.58 (16)	S2—C2—S3	121.2 (2)
S2 ⁱ —C1—S2	112.8 (3)	O1—C3—C4	123.9 (4)
C2 ⁱ —C2—S2	115.99 (12)	O1—C3—S3	120.7 (3)
C2 ⁱ —C2—S3	122.57 (13)	C4—C3—S3	115.4 (3)

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

The H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Bruker, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work is supported by a grant from the High Technology Development Project of China (No. 2002AA313070) and the Natural Science Foundation of China (Nos. 60476020, 60377016 and 50272037).

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