

4,5-Bis(furoylsulfanyl)-1,3-dithiole-2-thione

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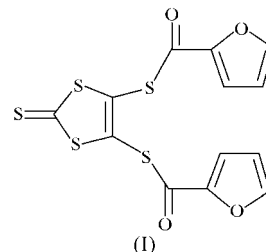
The title compound, $C_{13}H_6O_4S_5$, possesses crystallographically imposed mirror symmetry, with the atoms of the $C=S$ group lying on the mirror plane. It is an example of the general formula $[RCO]_2(dmit)$, where R is a furan ring and dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate. The components exhibit some polarization of their molecular–electronic structure. The dmit and furan moieties exhibit a high degree of conjugation, as the introduction of $C=O$ connecting the conjugated furan (donor) and dmit (acceptor) rings forms a good conjugated system with high delocalization. A polar three-dimensional framework is built from a combination of intermolecular contacts, namely $S \cdots S$ interactions and $C-H \cdots O$ hydrogen bonding. The structural characteristics lead to good second-order non-linear optical properties.

Comment

During the past two decades, organic non-linear optical (NLO) materials have been the subject of extensive theoretical and experimental investigations due to their potentially high non-linearities and rapid electro-optic response compared with their inorganic counterparts (Bosshard *et al.*, 2000). Organic NLO materials play an important role in second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability, *etc.* Many of these materials owe their NLO properties to the possession of delocalized π -electron systems linking donor and acceptor groups which enhance the asymmetric polarizability. Since the NLO effect is electronic in origin at optical frequencies, higher speeds and greater intrinsic non-linearity are possible with conjugated organic molecules.

Since 1979 (Steimeck & Kirmse, 1979), 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) and related ligands have been intensely investigated because they can be used in the assembly of highly electrically conducting radical anion salts and charge-transfer complexes as special π -electron delocalization conjugated systems. They are generally used as

important building blocks for organic, organometallic and coordination complexes which act as electrical conductors and superconductors (Svenstrup & Becher, 1995; Cassoux, 1999; Pullen & Olk, 1999; Robertson & Cronin, 2002), especially bis(ethylenedithio)tetrathiafulvalene and its derivatives (Ishiguro *et al.*, 1998).



The π -electron delocalization in these conjugated systems can also contribute to their ultrafast response capability and large optical non-linearity, just like other organics. Recently, many of these complexes have been reported as possessing good second- (Fang *et al.*, 1994; Zhai *et al.*, 1999) and third-order (Huggard & Blau, 1987; Winter *et al.*, 1992; Zuo *et al.*, 1996; Wang *et al.*, 1999; Bai *et al.*, 1999; Dai *et al.*, 2000; Liu *et al.*, 2002) NLO properties. The title compound, (I), has been prepared as a continuation of this line of research.

Compound (I) has a novel chemical structure with the general formula $[RCO]_2(dmit)$. To date, only three crystal structure determinations of compounds with this general formula have been reported. The first is 4,5-bis(benzoylthio)-4,5-didehydro-1,3-dithiolane-2-thione, (II) (Solans *et al.*, 1987), the second is 4,5-bis(pivaloylsulfanyl)-1,3-dithiole-2-thione, (III) (Wang *et al.*, 2005), and the third is a redetermination of (II) at 120 K (Cox & Doidge-Harrison, 1996).

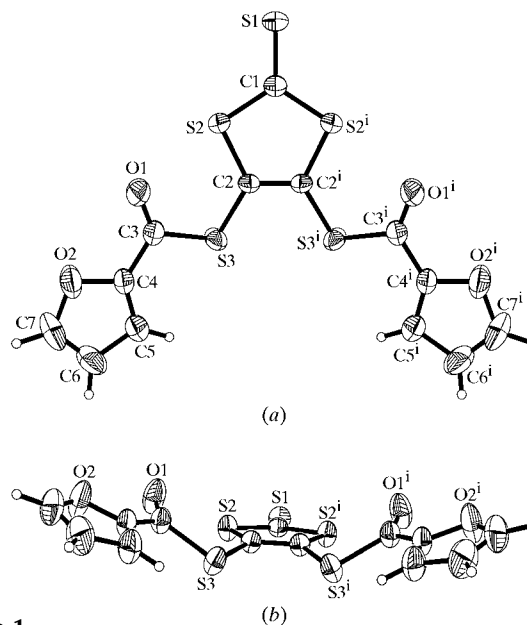


Figure 1

(a) The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. (b) An orthogonal view showing the non-planarity of the molecule. [Symmetry code: (i) $x, 1 - y, z$.]

Generally speaking, such compounds possess very small third-order NLO properties in the absence of a transition metal ion. Since the dmit moiety has a relatively high degree of conjugation, we can investigate crystals containing it for second-order NLO properties. Both (II) and (III) were found to crystallize in centrosymmetric space groups, which leads to a loss of macroscopic second-order NLO properties. However, we found that (I) crystallizes in a non-centrosymmetric space group, a necessary condition for a material to exhibit a second-order NLO effect.

The molecule of (I) has mirror symmetry (C_s), with atoms C1 and S1 situated on the mirror plane (Fig. 1*a*). The length of the C=S double bond [1.643 (5) Å] lies between those in (II) [1.650 (5) Å] and (III) [1.627 (6) Å], and is much longer than the typical C=S bond length (1.599 Å; Allen *et al.*, 1987). The other C—S bonds (Table 1) span the range 1.725 (3)–1.751 (3) Å. All of them are shorter than the typical C—S single bond (1.819 Å; Allen *et al.*, 1987) and are essentially single bonds with some double-bond character. The C2=C2ⁱ bond length [1.362 (6) Å; symmetry code: (i) $x, 1 - y, z$] is larger than those of (II) and (III), but all of them are in the range from 1.33 (1) Å (in an ethenetetrathiol; Broadhurst *et al.*, 1982) to 1.46 (2) Å (in a tetrathiooxalate; Lund *et al.*, 1982). Therefore, the dmit moiety has a rather high degree of conjugation. The C4—O2, C7—O2 and C5—C6 bond lengths in the furan ring are very close to the corresponding typical single-bond lengths. However, since the introduction of C=O, although one C=C double bond in the furan ring [C4=C5 = 1.345 (6) Å] is normal, the other [C6=C7 = 1.318 (8) Å] appears shorter than the typical $Csp^2=Csp^2$ bond length of 1.341 Å (Allen *et al.*, 1987). Moreover, the bond angles in the five-membered rings of the dmit and furan moieties deviate somewhat from those of a regular pentagon (Table 1). The overall molecular conformation of (I) can be defined in terms of the torsion angles. The molecule is significantly non-planar, as shown in Fig. 1(*b*). The dihedral angle between the dmit ring (C1/S2/C2/C2ⁱ/S2ⁱ) and furan ring (O2/C4/C5/C6/C7) is 23.4 (3)°. Two torsion angles indicate this non-planarity: C2ⁱ—C2—S3—C3 and S2—C2—S3—C3, with values of 151.2 (4) and -38.3 (3)°, respectively.

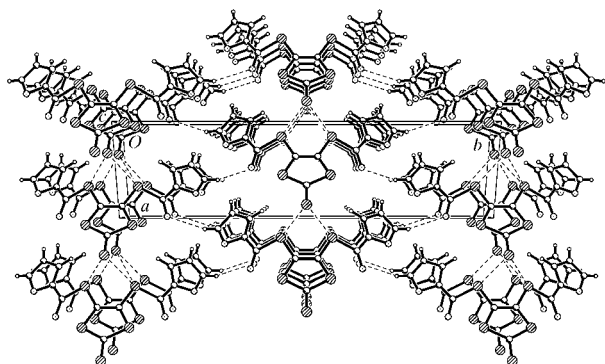


Figure 2
The unit cell of (I), viewed along the c axis, showing the intermolecular S...S interactions and C—H...O hydrogen bonds (dashed lines).

The packing of the molecules in (I) is shown in Fig. 2. The structure of (I) consists of discrete molecules linked by intermolecular S...S interactions (Spek, 2003) and C—H...O hydrogen bonds. S...S interactions play the major part in controlling the supramolecular assembly of the molecules. The shortest contacts, *i.e.* the shortest intermolecular distances between non-H atoms, are S1...S3ⁱⁱ of 3.5741 (18) Å and S1...S3ⁱⁱⁱ of 3.6599 (13) Å [symmetry codes: (ii) $1 + x, y, 1 + z$; (iii) $1 + x, y, 2 + z$]. The O atom of the carbonyl group is involved in an intermolecular hydrogen bond with one CH group of the furan ring (Table 2). The result is a polar three-dimensional framework constructed *via* several kinds of intermolecular interactions.

Overall, both the dmit and furan moieties exhibit a high degree of conjugation. Additionally, the introduction of C=O, which connects the conjugated furan (donor) and dmit (acceptor) rings, forms (I) into a conjugated system with high delocalization. These structural characteristics lead to good second-order NLO properties for (I). The SHG effect of the crystal of (I) was studied by the powder SHG method (Kurtz & Perry, 1968). It was found that the crystal of (I) is obviously superior to crystalline urea in its SHG effect.

Experimental

2-Furoyl chloride (10 ml) was added at room temperature to a solution of $(n\text{-Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ (10 mmol, 9.43 g) in acetone (60 ml) and the mixture was stirred for about 1 h. The resulting yellow precipitate was filtered off, and the yellow filtrate was then left to stand for several hours at *ca* 273 K, after which transparent yellow plate-shaped single crystals of (I) suitable for X-ray structure determination were obtained.

Crystal data

$\text{C}_{13}\text{H}_6\text{O}_4\text{S}_5$	$D_x = 1.672 \text{ Mg m}^{-3}$
$M_r = 386.48$	Mo $K\alpha$ radiation
Monoclinic, Cm	Cell parameters from 40 reflections
$a = 7.2228$ (11) Å	$\theta = 4.8\text{--}12.5^\circ$
$b = 24.518$ (3) Å	$\mu = 0.77 \text{ mm}^{-1}$
$c = 5.0330$ (7) Å	$T = 293$ (2) K
$\beta = 120.521$ (10)°	Plate, yellow
$V = 767.79$ (19) Å ³	$0.39 \times 0.32 \times 0.12 \text{ mm}$
$Z = 2$	

Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.026$
ω scans	$\theta_{\text{max}} = 31.5^\circ$
Absorption correction: ψ scan (XSCANS; Siemens, 1996)	$h = -10 \rightarrow 1$
$T_{\text{min}} = 0.73, T_{\text{max}} = 0.88$	$k = -36 \rightarrow 1$
1644 measured reflections	$l = -6 \rightarrow 7$
1316 independent reflections	3 standard reflections
1064 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
$wR(F^2) = 0.091$	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
$S = 1.02$	Extinction correction: SHELXTL (Bruker, 1997)
1316 reflections	Extinction coefficient: 0.018 (3)
104 parameters	Absolute structure: Flack (1983), with 263 Friedel pairs
H-atom parameters constrained	Flack parameter: -0.11 (13)
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.0399P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

C1—S1	1.643 (5)	C3—S3	1.799 (4)
C1—S2	1.725 (3)	C4—C5	1.345 (6)
C2—C2 ⁱ	1.362 (6)	C4—O2	1.355 (5)
C2—S2	1.737 (3)	C5—C6	1.403 (6)
C2—S3	1.751 (3)	C6—C7	1.318 (8)
C3—O1	1.201 (5)	C7—O2	1.354 (6)
C3—C4	1.447 (5)		
S1—C1—S2	123.22 (13)	C5—C4—C3	132.9 (3)
S2—C1—S2 ⁱ	113.5 (3)	O2—C4—C3	117.6 (3)
C2 ⁱ —C2—S2	115.99 (10)	C4—C5—C6	107.2 (4)
C2 ⁱ —C2—S3	120.31 (10)	C7—C6—C5	105.7 (4)
S2—C2—S3	123.07 (17)	C6—C7—O2	111.8 (4)
O1—C3—C4	125.8 (3)	C4—O2—C7	105.7 (4)
O1—C3—S3	123.7 (3)	C1—S2—C2	97.15 (16)
C4—C3—S3	110.5 (3)	C2—S3—C3	102.70 (17)
C5—C4—O2	109.5 (3)		
C2 ⁱ —C2—S3—C3	151.2 (4)	S2—C2—S3—C3	−38.3 (3)

Symmetry code: (i) $x, 1 - y, z$.**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 [⋯] —O1 ⁱⁱ	0.93	2.55	3.407 (6)	153

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

The absolute structure parameter (Flack, 1983) refined to a value of -0.11 (13) with 263 Friedel pairs. As this does not represent a very reliable determination, Friedel pairs were merged in the final cycles of refinement. All H atoms were placed in geometrically calculated positions and refined riding at a distance of 0.93 Å from their parent C atoms and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1613). Services for accessing these data are described at the back of the journal.

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