

## 5-(4-Methylphenylsulfonyl)-1,3-dithiolo[4,5-c]pyrrole-2-thione

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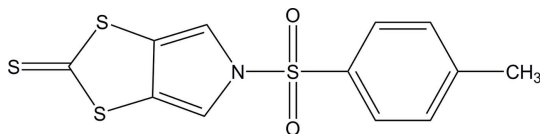
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 Key indicators: single-crystal X-ray study;  $T = 290$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.094; data-to-parameter ratio = 16.5.

The asymmetric unit of the title compound,  $\text{C}_{12}\text{H}_9\text{NO}_2\text{S}_4$ , contains one half-molecule with the N, two S and four C atoms lying on a mirror plane. The molecule exhibits a V-shaped conformation, with a dihedral angle of  $87.00$  ( $7$ )° between the benzene and dithiopyrrole rings. The methyl group was treated as rotationally disordered between two orientations in a 1:1 ratio. In the crystal, weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules into chains in  $[010]$ .

### Related literature

For background to the applications and synthesis of pyrrolo-annulated tetrathiafulvalenes, see: Becher *et al.* (2004); Hou *et al.* (2010). For a related structure, see: Hou *et al.* (2009). For details of the synthesis, see: Jeppesen *et al.* (2000).



### Experimental

#### Crystal data

 $\text{C}_{12}\text{H}_9\text{NO}_2\text{S}_4$ 
 $M_r = 327.44$ 

 Monoclinic,  $C2/m$ 
 $a = 15.687$  (10) Å

 $b = 10.485$  (9) Å

 $c = 8.255$  (4) Å

 $\beta = 96.19$  (3)°

 $V = 1349.9$  (16) Å<sup>3</sup>
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.70$  mm<sup>-1</sup>
 $T = 290$  K  
 $0.46 \times 0.43 \times 0.40$  mm

#### Data collection

 Rigaku R-Axis RAPID  
 diffractometer  
 Absorption correction: multi-scan  
 (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.740$ ,  $T_{\max} = 0.770$ 

 6671 measured reflections  
 1633 independent reflections  
 1467 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.094$   
 $S = 1.19$   
 1633 reflections

 99 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>
**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C3}-\text{H3}\cdots\text{O1}^i$	0.93	2.33	3.243 (3)	166

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS and Rigaku, 2002); 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: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5254).

### References

- Becher, J., Nielsen, K. & Jeppesen, J. O. (2004). *J. Phys. IV Fr.* **114**, 445–448.  
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.  
 Hou, R.-B., Li, B., Yin, B.-Z. & Wu, L.-X. (2009). *Acta Cryst.* **E65**, o1710.  
 Hou, R. B., Su, C., Kang, Y. H., Gu, L. Y. & Yin, B. Z. (2010). *Sens. Lett.* **8**, 309–313.  
 Jeppesen, J. O., Takimiya, K., Jensen, F., Brimert, T., Nielsen, K., Thorup, N. & Becher, J. (2000). *J. Org. Chem.* **65**, 5794–5805.  
 Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.  
 Rigaku/MS & Rigaku (2002). *CrystalStructure*. Rigaku/MS Inc., The Woodlands, Texas, USA.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supplementary materials

*Acta Cryst.* (2012). E68, o1046 [doi:10.1107/S1600536812009622]

**5-(4-Methylphenylsulfonyl)-1,3-dithiolo[4,5-*c*]pyrrole-2-thione****Ning-Juan Zheng and Bing-Zhu Yin****Comment**

Pyrrolo-annulated tetrathiafulvalenes, an important class of electron-donors, are versatile building blocks in supramolecular and materials chemistry (Becher *et al.*, 2004). As a key precursor to the pyrrolo-annulated tetrathiafulvalenes, 5-Tosyl-5*H*-[1,3]dithiolo[4,5-*c*]pyrrole-2-thione, has attracted great attention (Hou *et al.*, 2010). In this paper, we report the crystal structure of the title compound (I).

The asymmetric unit of (I) contains a half of the molecule situated on a mirror plane (Fig. 1). All bond lengths and angles are in the normal ranges and comparable with the reported ones (Hou *et al.* 2009). Atom N1 has a flattened pyramidal environment with the sum of bond angles of 356.9 (2) °. The benzene ring and dithiopyrrole ring form a dihedral angle of 87.00 (7) °. In the crystal, the intermolecular C—H...O hydrogen bonds link the molecules into chains along *b* direction.

**Experimental**

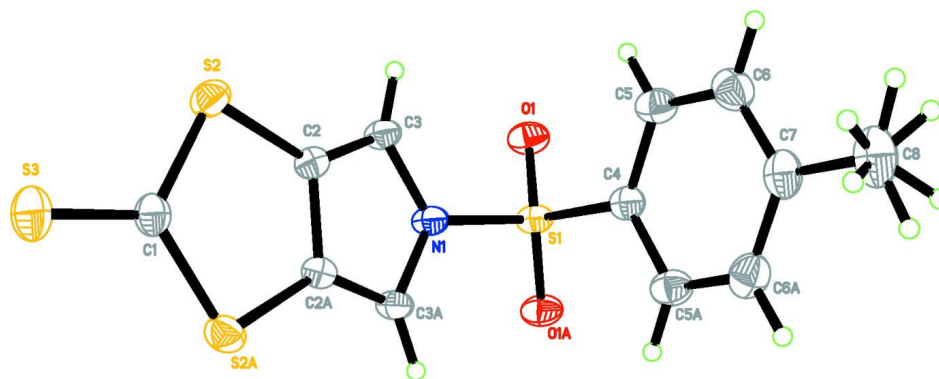
The title compound was prepared according to the literature (Jeppesen *et al.*, 2000). Single crystals suitable for X-ray diffraction were prepared by slow evaporation a mixture of dichloromethane and petroleum (60–90 °C) at room temperature.

**Refinement**

C-bound H-atoms were placed in calculated positions (C—H 0.93 and 0.96 Å) and were included in the refinement in the riding model with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5 U_{\text{eq}}(\text{C})$ . The methyl group was treated as rotationally disordered between two orientations in a ratio 1:1.

**Computing details**

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku, 2002); 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: *SHELXL97* (Sheldrick, 2008).


**Figure 1**

The molecular structure of (I) with the atom numbering. Displacement ellipsoids are drawn at the 30% probability level [symmetry code (A):  $x, -y, z$ ].

### 5-(4-Methylphenylsulfonyl)-1,3-dithiolo[4,5-c]pyrrole-2-thione

#### Crystal data

$C_{12}H_9NO_2S_4$

$M_r = 327.44$

Monoclinic,  $C2/m$

Hall symbol:  $-C\ 2y$

$a = 15.687\ (10)\ \text{\AA}$

$b = 10.485\ (9)\ \text{\AA}$

$c = 8.255\ (4)\ \text{\AA}$

$\beta = 96.19\ (3)^\circ$

$V = 1349.9\ (16)\ \text{\AA}^3$

$Z = 4$

$F(000) = 672$

$D_x = 1.611\ \text{Mg m}^{-3}$

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

Cell parameters from 6182 reflections

$\theta = 3.3\text{--}27.5^\circ$

$\mu = 0.70\ \text{mm}^{-1}$

$T = 290\ \text{K}$

Block, yellow

$0.46 \times 0.43 \times 0.40\ \text{mm}$

#### Data collection

Rigaku R-AXIS RAPID

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.740$ ,  $T_{\max} = 0.770$

6671 measured reflections

1633 independent reflections

1467 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.3^\circ$

$h = -20 \rightarrow 16$

$k = -13 \rightarrow 13$

$l = -10 \rightarrow 10$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.094$

$S = 1.19$

1633 reflections

99 parameters

0 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.4647P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.012$

$\Delta\rho_{\max} = 0.31\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.31\ \text{e \AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0106 (12)

Special details

**Experimental.** (See detailed section in the paper)

**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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.40151 (14)	0.0000	0.3618 (3)	0.0381 (5)	
C2	0.33159 (9)	0.06779 (14)	0.61983 (17)	0.0328 (3)	
C3	0.29981 (10)	0.10896 (15)	0.75702 (18)	0.0360 (3)	
H3	0.2918	0.1931	0.7875	0.043*	
C4	0.11420 (15)	0.0000	0.8848 (2)	0.0352 (4)	
C5	0.07509 (12)	0.11519 (17)	0.8411 (2)	0.0451 (4)	
H5	0.1013	0.1919	0.8736	0.054*	
C6	-0.00330 (12)	0.1139 (2)	0.7486 (2)	0.0509 (4)	
H6	-0.0298	0.1908	0.7179	0.061*	
C7	-0.04379 (16)	0.0000	0.7000 (3)	0.0472 (6)	
C8	-0.12828 (19)	0.0000	0.5964 (3)	0.0635 (8)	
H8A	-0.1210	-0.0344	0.4910	0.095*	0.50
H8B	-0.1495	0.0858	0.5846	0.095*	0.50
H8C	-0.1685	-0.0514	0.6473	0.095*	0.50
N1	0.28154 (13)	0.0000	0.8431 (2)	0.0356 (4)	
O1	0.23189 (8)	0.11804 (11)	1.07477 (13)	0.0442 (3)	
S1	0.21652 (4)	0.0000	0.99190 (6)	0.03409 (18)	
S2	0.37336 (3)	0.14002 (4)	0.45643 (5)	0.04288 (17)	
S3	0.45063 (5)	0.0000	0.19690 (8)	0.0555 (2)	

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0321 (10)	0.0470 (13)	0.0348 (10)	0.000	0.0025 (8)	0.000
C2	0.0351 (7)	0.0290 (8)	0.0338 (7)	-0.0026 (6)	0.0018 (5)	0.0010 (6)
C3	0.0459 (9)	0.0255 (7)	0.0369 (8)	-0.0028 (6)	0.0061 (6)	-0.0007 (6)
C4	0.0448 (12)	0.0348 (11)	0.0273 (9)	0.000	0.0094 (8)	0.000
C5	0.0565 (10)	0.0380 (9)	0.0412 (9)	0.0012 (7)	0.0069 (7)	0.0031 (7)
C6	0.0521 (10)	0.0540 (11)	0.0472 (10)	0.0090 (8)	0.0080 (8)	0.0093 (8)
C7	0.0445 (13)	0.0660 (16)	0.0329 (11)	0.000	0.0123 (9)	0.000
C8	0.0496 (16)	0.095 (2)	0.0456 (14)	0.000	0.0063 (11)	0.000
N1	0.0482 (11)	0.0259 (9)	0.0334 (9)	0.000	0.0073 (7)	0.000
O1	0.0641 (8)	0.0342 (6)	0.0340 (6)	-0.0022 (5)	0.0046 (5)	-0.0071 (4)
S1	0.0498 (3)	0.0270 (3)	0.0257 (3)	0.000	0.0050 (2)	0.000
S2	0.0525 (3)	0.0367 (3)	0.0409 (3)	-0.00501 (17)	0.01189 (18)	0.00431 (15)
S3	0.0545 (4)	0.0717 (5)	0.0429 (4)	0.000	0.0168 (3)	0.000

Geometric parameters (Å, °)

C1—S3	1.635 (2)	C5—H5	0.9300
C1—S2	1.7423 (17)	C6—C7	1.391 (3)
C1—S2 <sup>i</sup>	1.7423 (17)	C6—H6	0.9300
C2—C3	1.356 (2)	C7—C6 <sup>i</sup>	1.391 (3)
C2—C2 <sup>i</sup>	1.422 (3)	C7—C8	1.498 (4)
C2—S2	1.7359 (16)	C8—H8A	0.9600
C3—N1	1.391 (2)	C8—H8B	0.9600
C3—H3	0.9300	C8—H8C	0.9600
C4—C5 <sup>i</sup>	1.385 (2)	N1—C3 <sup>i</sup>	1.391 (2)
C4—C5	1.385 (2)	N1—S1	1.679 (2)
C4—S1	1.747 (3)	O1—S1	1.4221 (14)
C5—C6	1.376 (3)	S1—O1 <sup>i</sup>	1.4221 (14)
S3—C1—S2	122.58 (7)	C6—C7—C8	120.86 (12)
S3—C1—S2 <sup>i</sup>	122.58 (7)	C6 <sup>i</sup> —C7—C8	120.86 (12)
S2—C1—S2 <sup>i</sup>	114.85 (14)	C7—C8—H8A	109.5
C3—C2—C2 <sup>i</sup>	108.56 (9)	C7—C8—H8B	109.5
C3—C2—S2	135.53 (13)	H8A—C8—H8B	109.5
C2 <sup>i</sup> —C2—S2	115.87 (6)	C7—C8—H8C	109.5
C2—C3—N1	106.24 (15)	H8A—C8—H8C	109.5
C2—C3—H3	126.9	H8B—C8—H8C	109.5
N1—C3—H3	126.9	C3—N1—C3 <sup>i</sup>	110.37 (18)
C5 <sup>i</sup> —C4—C5	121.4 (2)	C3—N1—S1	123.26 (10)
C5 <sup>i</sup> —C4—S1	119.27 (11)	C3 <sup>i</sup> —N1—S1	123.26 (10)
C5—C4—S1	119.27 (11)	O1—S1—O1 <sup>i</sup>	120.99 (11)
C6—C5—C4	118.71 (18)	O1—S1—N1	105.49 (7)
C6—C5—H5	120.6	O1 <sup>i</sup> —S1—N1	105.49 (7)
C4—C5—H5	120.6	O1—S1—C4	110.02 (7)
C5—C6—C7	121.42 (19)	O1 <sup>i</sup> —S1—C4	110.02 (7)
C5—C6—H6	119.3	N1—S1—C4	103.14 (10)
C7—C6—H6	119.3	C2—S2—C1	96.66 (9)
C6—C7—C6 <sup>i</sup>	118.3 (2)		

Symmetry code: (i)  $x, -y, z$ .

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 <sup>iii</sup> —O1 <sup>ii</sup>	0.93	2.33	3.243 (3)	166

Symmetry code: (ii)  $-x+1/2, -y+1/2, -z+2$ .