

2,5-Di-2-thienylthiazolo[4,5-*d*]-
thiazolePaweł Wagner^{a†} and Maciej Kubicki^{b*}^aInstitute of Organic Chemistry and Technology, Silesian University of Technology, Krzywoustego 4, 44-100 Gliwice, Poland, and ^bDepartment of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
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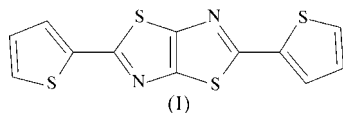
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The molecules of the title compound, $C_{12}H_6N_2S_4$, lie on centres of symmetry. The thiophene and thiazole rings are almost planar and their planes make a dihedral angle of $1.68(8)^\circ$. In the crystal structure, there is a relatively short intermolecular S...S contact distance of $3.5786(9) \text{ \AA}$.

Comment

The strong need for new ecological energy sources has resulted in a growing interest in new organic semiconducting materials, for example, those based on thiophene derivatives (for a review, see Nalva, 1997). Electrical conductivity and the band-gap (E_g) are strongly dependent on some structural parameters, including the geometry of a monomer molecule. Therefore, a detailed knowledge of the geometrical parameters (such as the planarity of the molecules, their mutual arrangement, and any intra- and intermolecular interactions) and electronic properties (*e.g.* the charge-density distribution) is crucial for the rational design of new materials. We performed an X-ray structural analysis of 2,5-di-2-thienylthiazolo[4,5-*d*]thiazole, (I) (Fig. 1), a simple model compound that could be used in electro-optically active materials. The X-ray data could then be used as the starting model for semi-empirical or *ab initio* calculations in molecular engineering.



There is a surprisingly small number of similar compounds in the Cambridge Structural Database (CSD; Allen, 2002); in the May 2002 release, we found only three thiazolo[4,5-*d*]thiazoles and just one compound containing the thieno-thiazole moiety. These findings further emphasize the need for more detailed structural data.

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The molecule of (I) lies on the centre of symmetry in the space group $P2_1/n$. Crystals of all three thiazolo[4,5-*d*]thiazoles found in the CSD belong to crystal class C_{2h} and contain two molecules per unit cell. All of these molecules lie on centres of symmetry in their crystals (Bossio *et al.*, 1987; Bolognesi *et al.*, 1987).

Both symmetry-independent rings in (I) are almost planar [the maximum deviation is $0.0044(8) \text{ \AA}$ for the thiophene ring and $0.0008(7) \text{ \AA}$ for the thiazole ring], and the dihedral angle between the least-squares planes of these rings is $1.68(8)^\circ$. The bond lengths and angles (Table 1) in the thiazole ring are similar to those found in thiazolo[5,4-*d*]thiazole (Bolognesi *et al.*, 1987). The asymmetry of the S—C bond lengths observed in the thiazole ring in (I) is also observed in other thiazole derivatives, especially in cases where there is another ring condensed at the $C4=C5$ double bond. The $S1'-C2'$ bond length of $1.7605(14) \text{ \AA}$ is typical of a single S—C bond, while the $S1'-C4'(1-x, 1-y, -z)$ bond has considerable double-bond character and may therefore be involved in resonance (*cf.* Smith, 1969; Ekstrand & van der Helm, 1977; Bolognesi *et al.*, 1987).

In the crystal structure of (I), relatively short intermolecular $S1' \cdots S1'(-x, 1-y, -z)$ contacts [$3.5786(9) \text{ \AA}$] are observed and these link the molecules into infinite chains along the [100] direction. The angle between a vector connecting the S atoms and a normal to the plane of the thiazole ring is $35.8(2)^\circ$. Such short contacts are quite common in divalent sulfur compounds. However, they are less frequently observed in thiazole derivatives. For all divalent sulfur compounds, intermolecular S...S contacts shorter than 3.6 \AA are observed

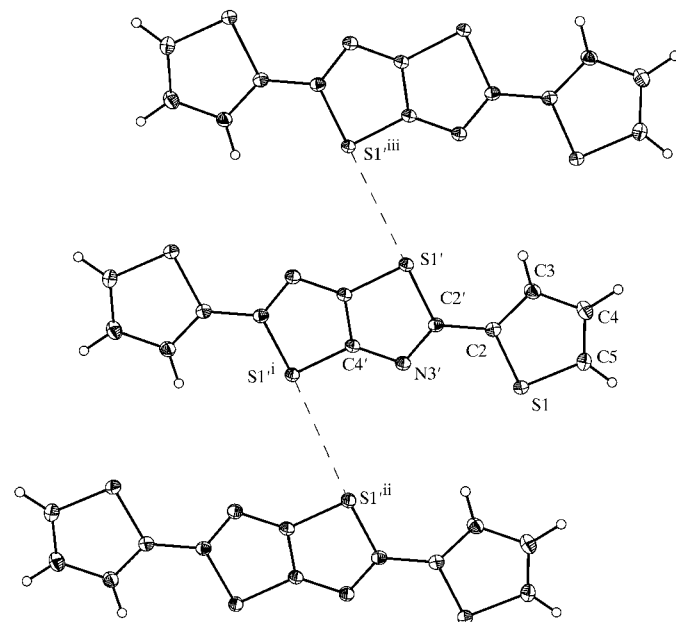


Figure 1

View (Siemens, 1989) of the chain of molecules of (I) connected by S...S contacts (dashed lines), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii. [Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $-1+x, y, z$; (iii) $-x, 1-y, -z$.]

in 11.4% of cases, contacts shorter than 3.65 Å are observed in 13.4% of cases and contacts shorter than 3.7 Å are observed in 16.4% of cases. For compounds with sulfur in a cyclic environment, these values are even higher, the respective values being 12.2, 15.3 and 18.3%. For thiazole derivatives, the fraction of compounds possessing short S··S contacts is much smaller, viz. 4.2% for a 3.6 Å separation, 5.9% for a 3.65 Å separation and 8.2% for a 3.7 Å separation. Such short contacts are not found in any of the three thiazolo[4,5-*d*]-thiazole derivatives for which the crystal structures have been reported.

The crystal packing is determined by the partial overlap of planar molecules (the distance between the mean planes of two molecules related by the center of symmetry is *ca* 3.6 Å) and, to some extent, by S··S contacts and weak C—H··S interactions (*cf.* Table 2).

Experimental

The title compound was synthesized according to the procedure of Thomas (1970) by condensation of dithiooxodiamide with 2-formylthiophene. Colourless prismatic crystals were grown from a methanol solution by slow evaporation.

Crystal data

C ₁₂ H ₆ N ₂ S ₄	$D_x = 1.655 \text{ Mg m}^{-3}$
$M_r = 306.47$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4325 reflections
$a = 6.0040 (12) \text{ \AA}$	$\theta = 4\text{--}22^\circ$
$b = 8.3580 (17) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$c = 12.270 (3) \text{ \AA}$	$T = 100 (1) \text{ K}$
$\beta = 92.72 (3)^\circ$	Prism, yellow
$V = 615.0 (2) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 2$	

Data collection

Kuma KM-4 CCD four-circle diffractometer	$R_{\text{int}} = 0.024$
ω scans	$\theta_{\text{max}} = 29.0^\circ$
5376 measured reflections	$h = -8 \rightarrow 6$
1574 independent reflections	$k = -11 \rightarrow 11$
1475 reflections with $I > 2\sigma(I)$	$l = -16 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.3939P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
1574 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
94 parameters	
All H-atom parameters refined	

Table 1

Selected geometric parameters (Å, °).

S1—C5	1.7187 (15)	S1'—C4 ⁱⁱ	1.7324 (14)
S1—C2	1.7287 (14)	S1'—C2'	1.7605 (14)
C5—S1—C2	91.70 (7)	C2'—N3'—C4'	108.40 (12)
C4 ⁱⁱ —S1'—C2'	88.38 (7)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3··S1 ⁱⁱ	0.94 (2)	3.14 (2)	3.7298 (17)	122.9 (15)
C4—H4··S1 ⁱⁱⁱ	0.97 (2)	3.15 (2)	3.8523 (17)	130.7 (15)
C4—H4··S1 ^{iv}	0.97 (2)	3.18 (2)	4.0704 (17)	153.4 (16)
C5—H5··S1 ^v	0.94 (2)	3.10 (2)	3.9434 (17)	148.9 (16)

Symmetry codes: (ii) $x - 1, y, z$; (iii) $-x, -y, -z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection: *CrysAlisCCD* (Kuma, 1999); cell refinement: *CrysAlisCCD*; data reduction: *CrysAlisRed* (Kuma, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1128). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bolognesi, A., Catellani, M., Destri, S. & Porzio, W. (1987). *Acta Cryst.* **C43**, 2106–2108.
- Bossio, R., Marcaccini, S., Pepino, R., Torroba, T. & Valle, G. (1987). *Synthesis*, pp. 1138–1139.
- Ekstrand, J. D. & van der Helm, D. (1977). *Acta Cryst.* **B33**, 1012–1016.
- Kuma (1999). *CrysAlisCCD* (Version 168) and *CrysAlisRed*. Kuma Diffraction, Wrocław, Poland.
- Nalva, H. S. (1997). *Handbook of Organic Conductive Molecules and Polymers*, Vols. 1–4. Chichester: Wiley and Sons.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Smith, D. L. (1969). *Acta Cryst.* **B25**, 625–632.
- Thomas, D. A. (1970). *J. Heterocycl. Chem.* **7**, 457–462.