

4,5-Bis{2-[(benzothiazol-2-yl)sulfanyl]ethylsulfanyl}-1,3-dithiole-2-thione

Jun-Qing Chen,^a Pu-Zhou Hu,^b
Jian-Ge Wang,^b Gui-Rong Qu^a
and Bang-Tun Zhao^{b*}^aCollege of Chemistry and Environmental
Science, Henan Normal University, Xinxing
453002, People's Republic of China, and^bDepartment of Chemistry, Luoyang Normal
University, Luoyang 471022, People's Republic
of China

Correspondence e-mail: zbt@lynu.edu.cn

Key indicators

Single-crystal X-ray study

T = 291 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.037

wR factor = 0.092

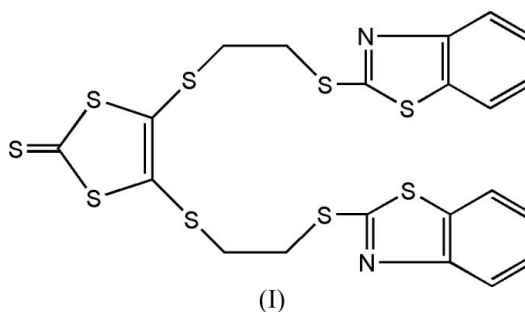
Data-to-parameter ratio = 19.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal packing of the title compound, $\text{C}_{21}\text{H}_{16}\text{N}_2\text{S}_9$, involves weak intermolecular $\text{C}-\text{H}\cdots\text{S}$ interactions and interplanar $\pi-\pi$ stacking, generating a three-dimensional supramolecular structure.

Comment

Tetrathiafulvalene (TTF) and its derivatives are the subject of intense interest in materials chemistry, crystal engineering and supramolecular chemistry (Nielsen *et al.*, 2000; Segura & Martin, 2001; Jeppesen *et al.*, 2004). 1,3-Dithiole-2-thiones, important precursors of TTF derivatives, have also attracted attention (Chen *et al.*, 2005; Fabre, 2004). Considering the potential applications of thiazole compounds in the area of pesticides, medicinal and coordination chemistry (Huang *et al.*, 2004; Zheng *et al.*, 2005), we have aimed to prepare a new family of TTF derivatives bearing thiazole groups. The title compound, (I), (Fig. 1), an important precursor to TTF derivatives, was prepared by the reaction of 4,5-bis(2-bromoethylsulfanyl)-1,3-dithiole-2-thione and 2-mercaptobenzothiazole in the presence of NaOH.



Both the benzothiazole ring systems are almost planar, making a dihedral angle of $69.19 (8)^\circ$ with each other. The N2 benzothiazole ring mean plane is almost coplanar with the central 1,3-dithiole-2-thione mean plane [dihedral angle = $2.25 (9)^\circ$], but the N1 mean plane is substantially twisted with respect to the central ring [dihedral angle = $67.00 (9)^\circ$].

In the crystal structure, molecules of (I) form chains by way of weak intermolecular $\text{C}-\text{H}\cdots\text{S}$ interactions (Jia *et al.*, 2006) with the methylene groups (Fig. 2, Table 1). In addition, $\pi-\pi$ stacking interactions involving adjacent benzothiazole ring planes occur, with centroid-centroid distances of 3.673 and 3.919 \AA (Hunter & Sanders, 1990) (Fig. 3).

Experimental

A sample of 4,5-bis(2-bromoethylsulfanyl)-1,3-dithiole-2-thione (1.05 g, 2.5 mmol) was added to a solution of 2-mercaptobenzothia-

Received 17 October 2006

Accepted 30 October 2006

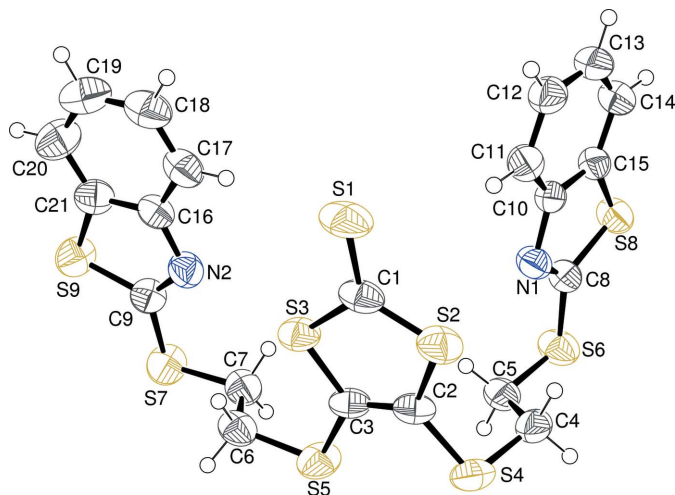


Figure 1
The molecular structure of (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

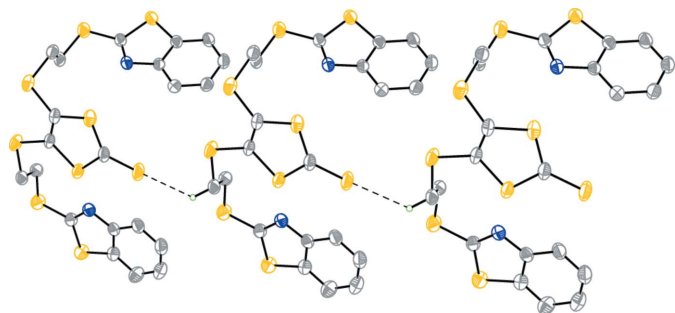


Figure 2
Detail of (I), showing the connectivity of molecules into a chain by way of C–H...S interactions (dashed lines). H atoms have been omitted.

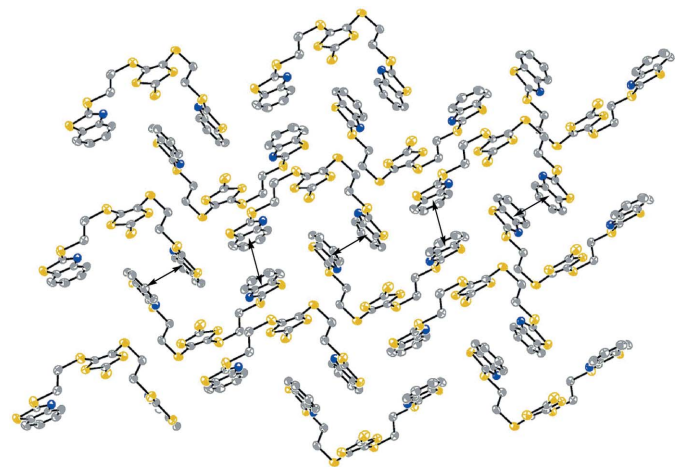


Figure 3
Detail of (I), with interplanar π – π stacking interactions drawn as double arrows. H atoms have been omitted.

zole (1.72 g, 10 mmol) and sodium hydroxide (0.41 g, 10 mmol) in tetrahydrofuran solution (100 ml). The resulting solution was heated under reflux for 24 h under an N_2 atmosphere. After cooling, the solvent was removed *in vacuo* and the residue was recrystallized from $CHCl_3/CH_3OH$ (5:1) to obtain the title compound. Yellow plate-like

crystals of (I) suitable for X-ray measurements were obtained by slow evaporation of an ethanol solution at room temperature over a period of one week (yield: 81%; m.p. 357 K).

Crystal data

$C_{21}H_{16}N_2S_9$
 $M_r = 584.90$
Triclinic, $P\bar{1}$
 $a = 9.4940$ (11) Å
 $b = 10.7870$ (13) Å
 $c = 13.8470$ (17) Å
 $\alpha = 110.536$ (1)°
 $\beta = 105.588$ (1)°
 $\gamma = 93.947$ (1)°

$V = 1258.0$ (3) Å³
 $Z = 2$
 $D_x = 1.544$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.81$ mm⁻¹
 $T = 291$ (2) K
Plate, yellow
 $0.34 \times 0.23 \times 0.11$ mm

Data collection

Bruker APEX2 CCD
diffractometer
 ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.769$, $T_{max} = 0.915$

10333 measured reflections
5510 independent reflections
3908 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.017$
 $\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.092$
 $S = 1.01$
5510 reflections
289 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.384P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.43$ e Å⁻³
 $\Delta\rho_{min} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C6-H6A\cdots S1^i$	0.97	2.83	3.482 (3)	125

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

All H atoms were positioned geometrically ($C-H = 0.93-0.97$ Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker 2004); software used to prepare material for publication: *SHELXTL*.

The support of this work by the Natural Science Foundation of Henan Province (grant Nos. 2004601012 and 0511020100) is gratefully acknowledged.

References

- Bruker (2004). *APEX2* (Version 1.027), *SAINT* (Version 7.12a) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, T., Liu, W.-J., Cong, Z.-Q. & Yin, B.-Z. (2005). *Chin. J. Org. Chem.* **25**, 570–575.
Fabre, J. M. (2004). *Chem. Rev.* **104**, 5133–5150.
Huang, Z., Du, M., Song, H. B. & Bu, X. H. (2004). *Cryst. Growth Des.* **4**, 71–78.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Jeppesen, J. O., Nielsen, M. B. & Becher, J. (2004). *Chem. Rev.* **104**, 5115–5131.
Jia, C., Liu, S. X., Ambrus, C., Neels, A., Labat, G. & Decurtins, S. (2006). *Inorg. Chem.* **45**, 3152–3154.

Nielsen, M. B., Lomholt, C. & Becher, J. (2000). *Chem. Soc. Rev.* **29**, 153–164.

Segura, J. L. & Martin, N. (2001). *Angew. Chem. Int. Ed.* **40**, 1372–1409.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Zheng, Y., Li, J. R., Du, M., Zou, R. Q. & Bu, X. H. (2005). *Cryst. Growth Des.* **5**, 215–222.