

## 2,5-Bis(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione

Kazumasa Ueda,<sup>a,b\*</sup> Kenta Suzuki,<sup>b</sup> Kei Kunimoto<sup>b</sup> and Kenji Yoza<sup>c</sup>

<sup>a</sup>Division of Basic Engineering, Faculty of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu, Shizuoka 432-8561, Japan, <sup>b</sup>Department of Materials Science and Chemical Engineering, Graduate School of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu, Shizuoka 432-8561, Japan, and <sup>c</sup>Bruker AXS Co. Ltd, Moriya-cho 3-9, Kanagawa-ku, Kanagawa, Kanagawa 221-0022, Japan  
Correspondence e-mail: tkueda@ipc.shizuoka.ac.jp

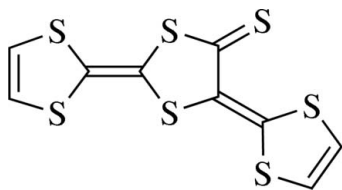
Received 12 October 2011; accepted 30 November 2011

Key indicators: single-crystal X-ray study;  $T = 93$  K; mean  $\sigma(\text{C}-\text{C}) = 0.009$  Å; disorder in main residue;  $R$  factor = 0.061;  $wR$  factor = 0.107; data-to-parameter ratio = 14.5.

The asymmetric unit of the title compound,  $\text{C}_9\text{H}_4\text{S}_7$ , contains two independent molecules, in one of which the central five-membered ring is disordered over two orientations in a 0.924 (3):0.076 (3) ratio. The molecular skeleton is almost planar: the average distance of the atoms from their mean plane is 0.128 (7) Å in the ordered molecule, and 0.088 (5) and 0.123 (2) Å in the major and minor disorder components, respectively. The ordered and disordered molecules form separate columns by stacking along the  $b$  axis. Adjacent columns interact *via* short  $\text{S}\cdots\text{S}$  [3.33 (2), 3.434 (3), 3.444 (2), 3.503 (2), 3.519 (3) and 3.53 (4) Å] and  $\text{S}\cdots\text{H}$  [2.814 (2), 2.87 (7), 2.92 (2), 2.9269 (18), 2.93 (2), 2.94 (2), 2.939 (2), 2.967 (2) and 2.974 (1) Å] contacts.

### Related literature

For background to 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione derivatives, see: Iwamatsu *et al.* (1999, 2000); Wang *et al.* (2005, 2007); Hiraoka *et al.* (2005); Fujiwara *et al.* (2006, 2007); Ueda & Yoza (2009*a,b,c*). For the synthesis, see: Ueda *et al.* (2010). For van der Waals radii, see: Bondi (1964).



### Experimental

#### Crystal data

$\text{C}_9\text{H}_4\text{S}_7$

$M_r = 336.54$

Monoclinic,  $P2_1$   
 $a = 17.669$  (5) Å  
 $b = 3.9110$  (11) Å  
 $c = 18.380$  (5) Å  
 $\beta = 108.177$  (4)°  
 $V = 1206.8$  (6) Å<sup>3</sup>

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 1.27$  mm<sup>-1</sup>  
 $T = 93$  K  
 $0.09 \times 0.02 \times 0.02$  mm

#### Data collection

Bruker APEXII CCD area-detector diffractometer  
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.894$ ,  $T_{\text{max}} = 0.975$   
6965 measured reflections  
4975 independent reflections  
3396 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$   
 $wR(F^2) = 0.107$   
 $S = 0.98$   
4975 reflections  
344 parameters  
421 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.63$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.52$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983), 1849 Friedel pairs  
Flack parameter:  $-0.18$  (18)

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINTE* (Bruker, 2010); data reduction: *SAINTE*; 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: *XCIF* (Bruker, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2030).

### References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
Bruker (2010). *APEX2, SAINT, XCIF*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
Fujiwara, H., Wada, K., Hiraoka, T., Hayashi, T., Sugimoto, T. & Nakazumi, H. (2006). *J. Low Temp. Phys.* **142**, 405–408.  
Fujiwara, H., Wada, K., Hiraoka, T., Hayashi, T., Sugimoto, T., Nakazumi, H., Teramura, M., Yokogawa, K., Yasuzuka, S. & Murata, K. (2007). *Multifunctional Conducting Molecular Materials*, edited by G. Saito, F. Wudl, R. C. Haddon, K. Tanigaki, T. Enoki, H. E. Katz & M. Maesato, pp. 161–164. Cambridge: RSC Publishing.  
Hiraoka, T., Kamada, Y., Matsumoto, T., Fujiwara, H., Sugimoto, T., Noguchi, S., Ishida, T., Nakazumi, H. & Katori, H. A. (2005). *J. Mater. Chem.* **15**, 3479–3487.  
Iwamatsu, M., Kominami, T., Ueda, K., Sugimoto, T., Adachi, T., Fujita, H., Yoshino, H., Mizuno, Y., Murata, K. & Shiro, M. (2000). *Inorg. Chem.* **39**, 3810–3815.  
Iwamatsu, M., Kominami, T., Ueda, K., Sugimoto, T., Fujita, H. & Adachi, T. (1999). *Chem. Lett.* pp. 329–330.  
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Ueda, K., Suzuki, K., Suzuki, K., Yoza, K. & Ishida, T. (2010). *Phys. B (Amsterdam)*, **405**, S69–S74.  
Ueda, K. & Yoza, K. (2009*a*). *Acta Cryst.* **E65**, o2716.  
Ueda, K. & Yoza, K. (2009*b*). *Acta Cryst.* **E65**, o2831.  
Ueda, K. & Yoza, K. (2009*c*). *Acta Cryst.* **E65**, o2920.  
Wang, M., Fujiwara, H., Sugimoto, T., Noguchi, S. & Ishida, T. (2005). *Inorg. Chem.* **44**, 1184–1186.  
Wang, M., Xiao, X., Fujiwara, H., Sugimoto, T., Noguchi, S., Ishida, T., Mori, T. & Katori, H. A. (2007). *Inorg. Chem.* **46**, 3049–3056.

**supplementary materials**

*Acta Cryst.* (2012). E68, o52 [ doi:10.1107/S1600536811051518 ]

## 2,5-Bis(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione

K. Ueda, K. Suzuki, K. Kunimoto and K. Yoza

### Comment

Donor molecules featuring a skeleton of 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-thione (**I**) and 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolane-4-quinone (**II**) are used for the preparation of charge transfer (CT) complexes with magnetic metal anions (Wang *et al.*, 2005, 2007; Hiraoka *et al.*, 2005; Fujiwara *et al.*, 2006, 2007). In CT salts these molecules can form unique crystal structures with channels in addition to the usual layer stacking structures as a result of intermolecular S $\cdots$ S contacts. Through an investigation of the unique molecular arrangements of the derivatives of (**I**) and (**II**) in their crystals, we found that the derivatives of (**I**) are stacked in the same orientation and the derivatives of (**II**) are alternately stacked in opposite directions (Ueda & Yoza, 2009*a*, 2009*b*, 2009*c*; Ueda *et al.*, 2010). This result suggests that the stacking orientation of the derivatives is largely influenced by their molecular skeletons. To identify the stacking orientation of skeleton (**I**), we synthesized (**I**) and investigated its crystal structure.

The asymmetric unit contains two crystallographically independent molecules. One of the two independent molecules shows orientational disorder in the C=S containing five-membered ring with occupancies of 0.924 (3) (molecule A) and 0.076 (3) (molecule B). The other molecule of the asymmetric unit, molecule C, is ordered. The framework of (**I**) is almost planar: the mean deviation of the atoms from their mean plane is 0.088 (5) Å for A, 0.123 (2) Å for B and 0.128 (7) Å for C.

In the crystal structure, two different orientations of the molecules are present. Both orientations enclose a dihedral angle of about 27° with the *ac* plane, but the mean plane of the molecules is nearly parallel either with (011) or with (01-1) (Fig. 2). Molecules with the same orientation form stacks along the *b* axis. The stacked molecules are separated by interplanar distances greater than 3.54 Å and have a fairly poor overlap. However some effective side-by-side contacts are observed between molecules of adjacent columns (Fig. 3). The interaction between adjacent columns is accomplished through contacts between different sulfur atoms: S9 $\cdots$ S3B<sup>i</sup> = 3.33 (2) Å [(i): 1-x, 1/2+y, 1-z]; S8 $\cdots$ S3A<sup>ii</sup> = 3.434 (3) Å [(ii): x, 1+y, 1+z]; S6 $\cdots$ S6<sup>iii</sup> = 3.444 (2) Å [(iii): -x, 1/2+y, -z]; S3C $\cdots$ S10<sup>i</sup> = 3.503 (2) Å; S4 $\cdots$ S9<sup>i</sup> = 3.519 (3) Å; S2B $\cdots$ S3A<sup>iv</sup> = 3.53 (4) Å [(iv): x, 1+y, z]; and through contacts between sulfur and hydrogen atoms: S2C $\cdots$ H9A<sup>i</sup> = 2.814 (2) Å, S1B $\cdots$ H15A = 2.87 (7); S3B $\cdots$ H11A<sup>iv</sup> = 2.92 (2) Å; S5 $\cdots$ H6A<sup>i</sup> = 2.9269 (18) Å; S3B $\cdots$ H11A<sup>v</sup> = 2.93 (2) Å [(v): x, y, z-1]; S3B $\cdots$ H12A<sup>vi</sup> = 2.94 (2) Å [(vi): 1-x, -1/2+y, 1-z]; S2C $\cdots$ H9A<sup>vii</sup> = 2.939 (2) Å [(vii): -x, -1/2+y, 1-z]; S3A $\cdots$ H8A<sup>iii</sup> = 2.967 (2) Å; S3C $\cdots$ H14A<sup>viii</sup> = 2.974 (1) Å [(viii): -x, 1/2+y, 1-z]. These distances are shorter than the sum of corresponding van der Waals radii, *i.e.*, 3.60 Å for S $\cdots$ S and 3.00 Å for S $\cdots$ H (Bondi, 1964).

### Experimental

Compound (**I**) was synthesized by a modification of the method used for the preparation of 2-[4,5-bis(ethylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4,5-diiodo-1,3-dithiol-2-ylidene)-1,3-dithiolan-4-thione (Ueda *et al.*, 2010). Bis(tetra-*n*-butylammonium)bis[2-(1,3-dithiol-2-ylidene)-1,3-dithiole-4,5-bis(thiolate)]zinc (194 mg, 0.170 mmol) reacted with 2-methylsulfanyl-1,3-dithiole-2-ylidene tetrafluoroborate (89.3 mg, 0.378 mmol) in THF-DMF (4:1 = *v/v*) at room temperature under nitrogen, and stirring was carried out for 12 h. After separation of the reaction mixture by column chroma-

## supplementary materials

---

tography on silica gel (eluent CS<sub>2</sub>) followed by recrystallization from 1:10 CS<sub>2</sub>/hexane, (**I**) was obtained as black needles in 79% yield.

### Refinement

The H atoms were geometrically positioned with C—H: 0.98 Å, and refined as riding, with  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ .

The following *SHELX* instructions were applied as restraints during refinement: SADI 0.01 S1C S2C S1A S2A S1B S2B / SADI 0.01 C6C S3C C6A S3A C6B S3B / SADI 0.01 C5C S1C C5A S1A C5B S1B / SADI 0.01 C6C C5C C6A C5A C6B C5B / SADI 0.01 S2C C6C S2A C6A S2B C6B / SADI 0.01 C4C S2C C4A S2A C4B S2B / SADI 0.01 S1C C4C S1A C4A S1B C4B / FLAT S1A S2A S3A C4A C5A C6A / FLAT S1B S2B S3B C4B C5B C6B / FLAT S1C S2C S3C C4C C5C C6C / SIMU 0.01 / ISOR 0.01.

### Figures

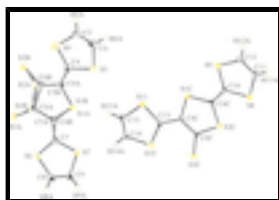


Fig. 1. The molecular structure of (**I**) showing atom labeling and 50% probability displacement ellipsoids for non-H-atoms.

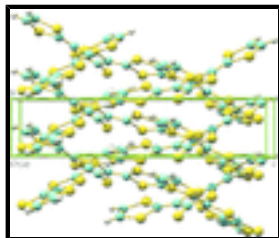


Fig. 2. Projection of the crystal packing of (**I**) down the *bc* plane.

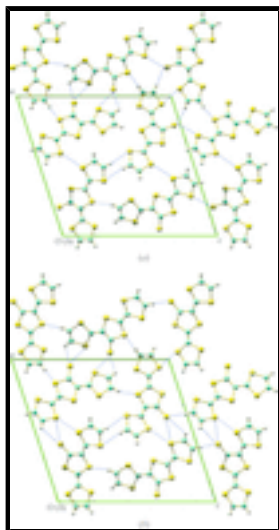


Fig. 3. (a) Projection of the crystal packing of molecules A and C in (**I**) down the *ac* plane. The S...S and S...H contacts are shown with blue solid lines. (b) Projection of the crystal packing of molecules B and C in (**I**) down the *ac* plane. The S...S and S...H contacts are shown with blue solid lines.

(I)

*Crystal data*

|                                |   |
|--------------------------------|---|
| $C_9H_4S_7$                    | $F(000) = 680$  |
| $M_r = 336.54$                 | $D_x = 1.852 \text{ Mg m}^{-3}$                         |
| Monoclinic, $P2_1$             | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 17.669 (5) \text{ \AA}$   | Cell parameters from 794 reflections                    |
| $b = 3.9110 (11) \text{ \AA}$  | $\theta = 2.3\text{--}23.9^\circ$                       |
| $c = 18.380 (5) \text{ \AA}$   | $\mu = 1.27 \text{ mm}^{-1}$                            |
| $\beta = 108.177 (4)^\circ$    | $T = 93 \text{ K}$                                      |
| $V = 1206.8 (6) \text{ \AA}^3$ | Needle, black   |
| $Z = 4$                        | $0.09 \times 0.02 \times 0.02 \text{ mm}$               |

*Data collection*

|   |  |
|---|--|
| Bruker APEXII CCD area-detector diffractometer              | 4975 independent reflections   |
| Radiation source: Bruker TXS fine-focus rotating anode      | 3396 reflections with $I > 2\sigma(I)$                                 |
| Bruker Helios multilayer confocal mirror                    | $R_{\text{int}} = 0.054$   |
| Detector resolution: $8.333 \text{ pixels mm}^{-1}$         | $\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 1.9^\circ$ |
| phi and $\omega$ scans                                      | $h = -22 \rightarrow 15$   |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $k = -5 \rightarrow 4$   |
| $T_{\text{min}} = 0.894$ , $T_{\text{max}} = 0.975$         | $l = -22 \rightarrow 23$   |
| 6965 measured reflections                                   |  |

*Refinement*

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.061$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.107$  | $w = 1/[\sigma^2(F_o^2) + (0.0283P)^2]$                  |
| $S = 0.98$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 4975 reflections   | $(\Delta/\sigma)_{\text{max}} = 0.002$                   |
| 344 parameters   | $\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$      |
| 421 restraints   | $\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$     |
| Primary atom site location: structure-invariant direct methods | Absolute structure: Flack (1983), 1849 Friedel pairs     |
|  | Flack parameter: $-0.18 (18)$                            |

# supplementary materials

---

## Special details

**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) |
|------|--------------|-------------|--------------|----------------------------------|-----------|
| C4   | 0.3976 (4)   | 0.7807 (19) | 0.2942 (4)   | 0.0247 (17)                      |           |
| C5   | 0.5339 (4)   | 1.060 (2)   | 0.3647 (4)   | 0.035 (2)                        |           |
| H5A  | 0.5870       | 1.1430      | 0.3772       | 0.042*                           |           |
| C6   | 0.4937 (4)   | 1.091 (2)   | 0.4121 (5)   | 0.035 (2)                        |           |
| H6A  | 0.5160       | 1.1990      | 0.4604       | 0.043*                           |           |
| C7   | 0.1148 (4)   | 0.3154 (18) | 0.1591 (4)   | 0.0190 (16)                      |           |
| C8   | -0.0317 (4)  | 0.151 (2)   | 0.1023 (4)   | 0.0244 (17)                      |           |
| H8A  | -0.0815      | 0.0767      | 0.0685       | 0.029*                           |           |
| C9   | -0.0268 (4)  | 0.277 (2)   | 0.1707 (4)   | 0.0251 (18)                      |           |
| H9A  | -0.0718      | 0.2915      | 0.1884       | 0.030*                           |           |
| C10  | 0.3122 (4)   | 0.6221 (18) | 0.8314 (3)   | 0.0139 (14)                      |           |
| C11  | 0.3743 (4)   | 0.922 (2)   | 0.9615 (4)   | 0.0238 (17)                      |           |
| H11A | 0.3839       | 1.0134      | 1.0115       | 0.029*                           |           |
| C12  | 0.4298 (4)   | 0.941 (2)   | 0.9257 (4)   | 0.0248 (17)                      |           |
| H12A | 0.4792       | 1.0526      | 0.9490       | 0.030*                           |           |
| C13  | 0.1820 (4)   | 0.1225 (19) | 0.5609 (4)   | 0.0154 (15)                      |           |
| C14  | 0.1298 (4)   | -0.035 (2)  | 0.4192 (4)   | 0.0195 (16)                      |           |
| H14A | 0.0971       | -0.1098     | 0.3703       | 0.023*                           |           |
| C15  | 0.2009 (4)   | 0.085 (2)   | 0.4285 (3)   | 0.0205 (17)                      |           |
| H15A | 0.2218       | 0.1003      | 0.3868       | 0.025*                           |           |
| C4A  | 0.3347 (6)   | 0.633 (2)   | 0.2437 (4)   | 0.0190 (17)                      | 0.924 (3) |
| C5A  | 0.1947 (5)   | 0.384 (2)   | 0.1739 (4)   | 0.0155 (15)                      | 0.924 (3) |
| C6A  | 0.2391 (6)   | 0.323 (3)   | 0.1228 (5)   | 0.021 (2)                        | 0.924 (3) |
| C4B  | 0.191 (4)    | 0.346 (17)  | 0.181 (4)    | 0.018 (4)                        | 0.076 (3) |
| C5B  | 0.335 (6)    | 0.59 (2)    | 0.248 (3)    | 0.023 (4)                        | 0.076 (3) |
| C6B  | 0.331 (2)    | 0.485 (10)  | 0.173 (3)    | 0.023 (3)                        | 0.076 (3) |
| C4C  | 0.2640 (3)   | 0.4578 (17) | 0.7717 (3)   | 0.0170 (15)                      |           |
| C5C  | 0.1960 (3)   | 0.1937 (16) | 0.6374 (3)   | 0.0151 (15)                      |           |
| C6C  | 0.1387 (3)   | 0.1573 (17) | 0.6762 (3)   | 0.0158 (15)                      |           |
| S4   | 0.48789 (12) | 0.8603 (6)  | 0.27620 (13) | 0.0385 (6)                       |           |
| S5   | 0.39615 (10) | 0.9263 (6)  | 0.38449 (10) | 0.0270 (5)                       |           |
| S6   | 0.05349 (11) | 0.1230 (5)  | 0.07570 (9)  | 0.0211 (4)                       |           |
| S7   | 0.06754 (10) | 0.4126 (5)  | 0.22574 (9)  | 0.0201 (4)                       |           |

|     |              |             |              |             |           |
|-----|--------------|-------------|--------------|-------------|-----------|
| S8  | 0.28575 (11) | 0.7290 (5)  | 0.91400 (10) | 0.0219 (5)  |           |
| S9  | 0.40896 (10) | 0.7580 (5)  | 0.83649 (10) | 0.0225 (5)  |           |
| S10 | 0.09618 (10) | -0.0554 (5) | 0.49847 (9)  | 0.0189 (4)  |           |
| S11 | 0.25580 (10) | 0.2146 (5)  | 0.51919 (9)  | 0.0204 (4)  |           |
| S1A | 0.2450 (5)   | 0.5721 (17) | 0.2628 (3)   | 0.0191 (11) | 0.924 (3) |
| S2A | 0.33680 (13) | 0.4760 (6)  | 0.15541 (12) | 0.0277 (6)  | 0.924 (3) |
| S3A | 0.20601 (13) | 0.1459 (6)  | 0.03754 (11) | 0.0275 (6)  | 0.924 (3) |
| S1B | 0.246 (6)    | 0.52 (2)    | 0.268 (3)    | 0.015 (6)   | 0.076 (3) |
| S2B | 0.242 (2)    | 0.312 (11)  | 0.114 (2)    | 0.021 (4)   | 0.076 (3) |
| S3B | 0.4040 (14)  | 0.512 (7)   | 0.1345 (13)  | 0.026 (6)   | 0.076 (3) |
| S1C | 0.28927 (10) | 0.3657 (5)  | 0.68923 (9)  | 0.0193 (4)  |           |
| S2C | 0.16991 (10) | 0.3150 (5)  | 0.76938 (9)  | 0.0193 (4)  |           |
| S3C | 0.04904 (10) | -0.0125 (5) | 0.64141 (10) | 0.0211 (5)  |           |

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

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C4  | 0.025 (3)   | 0.021 (4)   | 0.032 (4)   | -0.001 (3)   | 0.014 (3)   | 0.000 (3)    |
| C5  | 0.021 (4)   | 0.028 (5)   | 0.055 (5)   | -0.001 (3)   | 0.012 (3)   | -0.006 (4)   |
| C6  | 0.024 (4)   | 0.028 (5)   | 0.048 (4)   | -0.006 (3)   | 0.002 (3)   | -0.004 (4)   |
| C7  | 0.026 (3)   | 0.013 (4)   | 0.017 (3)   | 0.005 (3)    | 0.004 (3)   | 0.000 (3)    |
| C8  | 0.027 (4)   | 0.018 (4)   | 0.022 (3)   | -0.004 (3)   | -0.001 (3)  | -0.001 (3)   |
| C9  | 0.026 (3)   | 0.026 (4)   | 0.025 (4)   | 0.000 (3)    | 0.011 (3)   | -0.002 (3)   |
| C10 | 0.016 (3)   | 0.010 (3)   | 0.014 (3)   | 0.002 (3)    | 0.003 (3)   | 0.000 (3)    |
| C11 | 0.028 (4)   | 0.021 (4)   | 0.017 (3)   | 0.003 (3)    | -0.001 (3)  | -0.002 (3)   |
| C12 | 0.022 (3)   | 0.020 (4)   | 0.022 (3)   | -0.002 (3)   | -0.009 (3)  | 0.000 (3)    |
| C13 | 0.017 (3)   | 0.010 (3)   | 0.020 (3)   | -0.002 (3)   | 0.006 (3)   | -0.002 (3)   |
| C14 | 0.020 (3)   | 0.022 (4)   | 0.013 (3)   | -0.001 (3)   | 0.000 (3)   | -0.001 (3)   |
| C15 | 0.026 (4)   | 0.025 (4)   | 0.012 (3)   | 0.004 (3)    | 0.008 (3)   | 0.003 (3)    |
| C4A | 0.020 (3)   | 0.015 (4)   | 0.024 (3)   | 0.000 (3)    | 0.009 (3)   | 0.002 (3)    |
| C5A | 0.022 (3)   | 0.015 (3)   | 0.011 (3)   | 0.003 (3)    | 0.008 (3)   | 0.003 (3)    |
| C6A | 0.033 (3)   | 0.015 (4)   | 0.014 (4)   | 0.008 (3)    | 0.007 (3)   | 0.000 (3)    |
| C4B | 0.025 (5)   | 0.016 (6)   | 0.015 (5)   | 0.004 (5)    | 0.006 (5)   | 0.001 (5)    |
| C5B | 0.024 (6)   | 0.020 (6)   | 0.026 (6)   | 0.000 (5)    | 0.010 (5)   | 0.001 (5)    |
| C6B | 0.027 (5)   | 0.021 (5)   | 0.024 (5)   | 0.002 (5)    | 0.010 (4)   | 0.001 (5)    |
| C4C | 0.012 (3)   | 0.018 (4)   | 0.018 (3)   | -0.002 (3)   | 0.001 (3)   | -0.003 (3)   |
| C5C | 0.012 (3)   | 0.017 (4)   | 0.012 (3)   | -0.001 (3)   | -0.002 (3)  | 0.000 (3)    |
| C6C | 0.019 (3)   | 0.015 (4)   | 0.012 (3)   | -0.002 (3)   | 0.004 (3)   | -0.001 (3)   |
| S4  | 0.0305 (11) | 0.0339 (16) | 0.0588 (14) | -0.0056 (11) | 0.0250 (11) | -0.0026 (12) |
| S5  | 0.0204 (10) | 0.0262 (12) | 0.0319 (11) | 0.0003 (9)   | 0.0046 (9)  | -0.0031 (10) |
| S6  | 0.0292 (11) | 0.0190 (11) | 0.0142 (9)  | -0.0007 (9)  | 0.0053 (8)  | -0.0010 (9)  |
| S7  | 0.0263 (10) | 0.0191 (11) | 0.0157 (9)  | -0.0017 (9)  | 0.0075 (8)  | -0.0033 (9)  |
| S8  | 0.0256 (10) | 0.0229 (12) | 0.0175 (9)  | 0.0008 (9)   | 0.0073 (8)  | -0.0053 (9)  |
| S9  | 0.0188 (10) | 0.0243 (12) | 0.0231 (10) | -0.0012 (9)  | 0.0047 (8)  | -0.0029 (9)  |
| S10 | 0.0190 (9)  | 0.0192 (11) | 0.0162 (9)  | -0.0016 (9)  | 0.0023 (8)  | -0.0002 (9)  |
| S11 | 0.0201 (10) | 0.0231 (12) | 0.0176 (9)  | -0.0038 (9)  | 0.0052 (8)  | -0.0013 (8)  |
| S1A | 0.0212 (12) | 0.020 (3)   | 0.0185 (13) | -0.0022 (18) | 0.0095 (12) | -0.0003 (15) |
| S2A | 0.0320 (12) | 0.0275 (14) | 0.0304 (12) | -0.0002 (11) | 0.0197 (10) | -0.0006 (11) |

## supplementary materials

---

|     |             |             |             |             |             |              |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| S3A | 0.0421 (14) | 0.0252 (14) | 0.0197 (11) | 0.0054 (11) | 0.0162 (10) | -0.0023 (10) |
| S1B | 0.015 (7)   | 0.016 (8)   | 0.017 (8)   | 0.000 (7)   | 0.007 (6)   | -0.002 (7)   |
| S2B | 0.030 (6)   | 0.018 (6)   | 0.016 (6)   | 0.007 (5)   | 0.008 (5)   | 0.004 (5)    |
| S3B | 0.027 (8)   | 0.029 (9)   | 0.025 (8)   | 0.009 (7)   | 0.010 (6)   | -0.002 (7)   |
| S1C | 0.0158 (9)  | 0.0238 (12) | 0.0174 (9)  | -0.0032 (8) | 0.0040 (7)  | -0.0057 (8)  |
| S2C | 0.0171 (9)  | 0.0224 (12) | 0.0178 (9)  | 0.0004 (8)  | 0.0047 (8)  | -0.0012 (8)  |
| S3C | 0.0156 (9)  | 0.0243 (12) | 0.0218 (9)  | -0.0010 (8) | 0.0035 (8)  | 0.0004 (9)   |

### *Geometric parameters (Å, °)*

|           |            |             |            |
|-----------|------------|-------------|------------|
| C4—C4A    | 1.336 (11) | C13—C5C     | 1.378 (8)  |
| C4—C5B    | 1.38 (9)   | C13—S10     | 1.736 (7)  |
| C4—S4     | 1.756 (7)  | C13—S11     | 1.744 (6)  |
| C4—S5     | 1.763 (7)  | C14—C15     | 1.302 (8)  |
| C5—C6     | 1.292 (9)  | C14—S10     | 1.739 (6)  |
| C5—S4     | 1.758 (8)  | C14—H14A    | 0.9500     |
| C5—H5A    | 0.9500     | C15—S11     | 1.723 (7)  |
| C6—S5     | 1.759 (7)  | C15—H15A    | 0.9500     |
| C6—H6A    | 0.9500     | C4A—S1A     | 1.743 (6)  |
| C7—C4B    | 1.28 (6)   | C4A—S2A     | 1.746 (7)  |
| C7—C5A    | 1.377 (9)  | C5A—C6A     | 1.418 (9)  |
| C7—S7     | 1.727 (6)  | C5A—S1A     | 1.761 (6)  |
| C7—S6     | 1.748 (7)  | C6A—S3A     | 1.646 (9)  |
| C8—C9     | 1.327 (9)  | C6A—S2A     | 1.747 (10) |
| C8—S6     | 1.726 (7)  | C4B—S2B     | 1.743 (10) |
| C8—H8A    | 0.9500     | C4B—S1B     | 1.745 (10) |
| C9—S7     | 1.742 (7)  | C5B—C6B     | 1.417 (11) |
| C9—H9A    | 0.9500     | C5B—S1B     | 1.761 (10) |
| C10—C4C   | 1.326 (8)  | C6B—S3B     | 1.649 (11) |
| C10—S9    | 1.765 (6)  | C6B—S2B     | 1.744 (11) |
| C10—S8    | 1.772 (6)  | C4C—S2C     | 1.741 (6)  |
| C11—C12   | 1.343 (8)  | C4C—S1C     | 1.747 (6)  |
| C11—S8    | 1.712 (7)  | C5C—C6C     | 1.415 (7)  |
| C11—H11A  | 0.9500     | C5C—S1C     | 1.760 (6)  |
| C12—S9    | 1.721 (7)  | C6C—S3C     | 1.652 (6)  |
| C12—H12A  | 0.9500     | C6C—S2C     | 1.740 (6)  |
| C4A—C4—S4 | 123.6 (5)  | C4—C4A—S2A  | 122.9 (7)  |
| C5B—C4—S4 | 125 (3)    | S1A—C4A—S2A | 115.1 (5)  |
| C4A—C4—S5 | 122.7 (5)  | C7—C5A—C6A  | 125.6 (7)  |
| C5B—C4—S5 | 121 (3)    | C7—C5A—S1A  | 117.0 (6)  |
| S4—C4—S5  | 113.6 (4)  | C6A—C5A—S1A | 117.4 (5)  |
| C6—C5—S4  | 118.2 (6)  | C5A—C6A—S3A | 126.5 (8)  |
| C6—C5—H5A | 120.9      | C5A—C6A—S2A | 114.1 (6)  |
| S4—C5—H5A | 120.9      | S3A—C6A—S2A | 119.4 (6)  |
| C5—C6—S5  | 117.8 (7)  | C7—C4B—S2B  | 120 (5)    |
| C5—C6—H6A | 121.1      | C7—C4B—S1B  | 123 (5)    |
| S5—C6—H6A | 121.1      | S2B—C4B—S1B | 114.8 (9)  |
| C4B—C7—S7 | 117 (3)    | C4—C5B—C6B  | 123 (7)    |
| C5A—C7—S7 | 120.7 (5)  | C4—C5B—S1B  | 123 (4)    |



|              |           |             |           |
|--------------|-----------|-------------|-----------|
| C4B—C7—S6    | 128 (3)   | C6B—C5B—S1B | 113 (5)   |
| C5A—C7—S6    | 125.0 (5) | C5B—C6B—S3B | 126 (5)   |
| S7—C7—S6     | 114.3 (4) | C5B—C6B—S2B | 118 (5)   |
| C9—C8—S6     | 119.1 (6) | S3B—C6B—S2B | 116 (3)   |
| C9—C8—H8A    | 120.4     | C10—C4C—S2C | 122.5 (4) |
| S6—C8—H8A    | 120.4     | C10—C4C—S1C | 123.1 (4) |
| C8—C9—S7     | 115.5 (5) | S2C—C4C—S1C | 114.4 (3) |
| C8—C9—H9A    | 122.2     | C13—C5C—C6C | 124.4 (5) |
| S7—C9—H9A    | 122.2     | C13—C5C—S1C | 118.0 (4) |
| C4C—C10—S9   | 123.5 (4) | C6C—C5C—S1C | 117.5 (4) |
| C4C—C10—S8   | 123.4 (5) | C5C—C6C—S3C | 126.5 (5) |
| S9—C10—S8    | 113.2 (4) | C5C—C6C—S2C | 113.8 (4) |
| C12—C11—S8   | 117.7 (5) | S3C—C6C—S2C | 119.6 (3) |
| C12—C11—H11A | 121.2     | C4—S4—C5    | 95.2 (4)  |
| S8—C11—H11A  | 121.2     | C6—S5—C4    | 95.2 (4)  |
| C11—C12—S9   | 118.2 (6) | C8—S6—C7    | 94.7 (3)  |
| C11—C12—H12A | 120.9     | C7—S7—C9    | 96.2 (3)  |
| S9—C12—H12A  | 120.9     | C11—S8—C10  | 95.6 (3)  |
| C5C—C13—S10  | 126.7 (5) | C12—S9—C10  | 95.3 (3)  |
| C5C—C13—S11  | 119.1 (5) | C13—S10—C14 | 94.6 (3)  |
| S10—C13—S11  | 114.3 (4) | C15—S11—C13 | 95.3 (3)  |
| C15—C14—S10  | 118.4 (5) | C4A—S1A—C5A | 95.6 (3)  |
| C15—C14—H14A | 120.8     | C6A—S2A—C4A | 97.7 (5)  |
| S10—C14—H14A | 120.8     | C4B—S1B—C5B | 98 (2)    |
| C14—C15—S11  | 117.5 (5) | C6B—S2B—C4B | 96 (3)    |
| C14—C15—H15A | 121.3     | C4C—S1C—C5C | 95.7 (3)  |
| S11—C15—H15A | 121.3     | C6C—S2C—C4C | 98.3 (3)  |
| C4—C4A—S1A   | 122.0 (5) |             |           |

Fig. 1

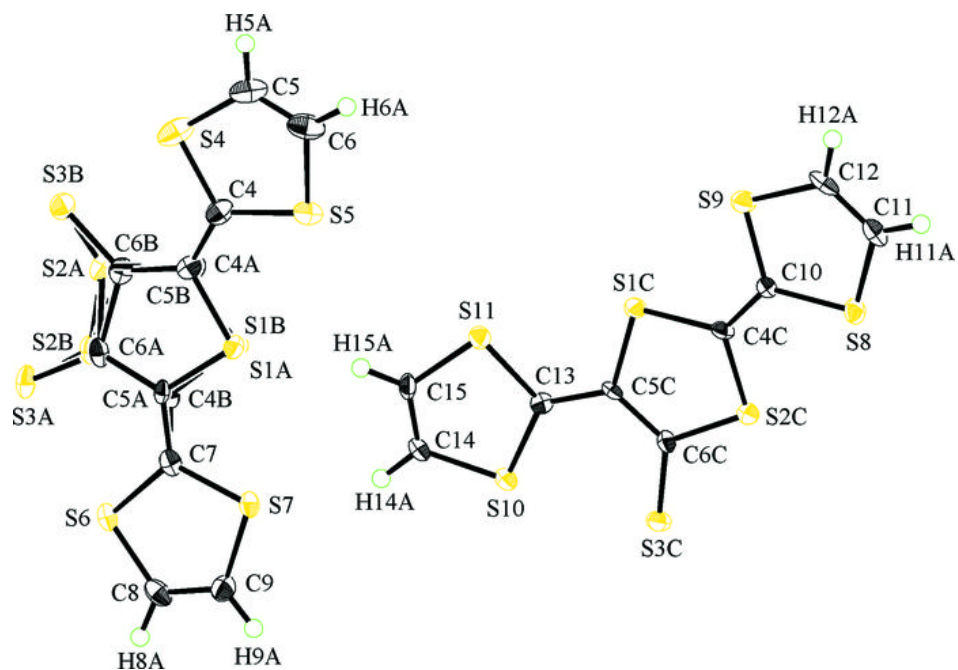


Fig. 2

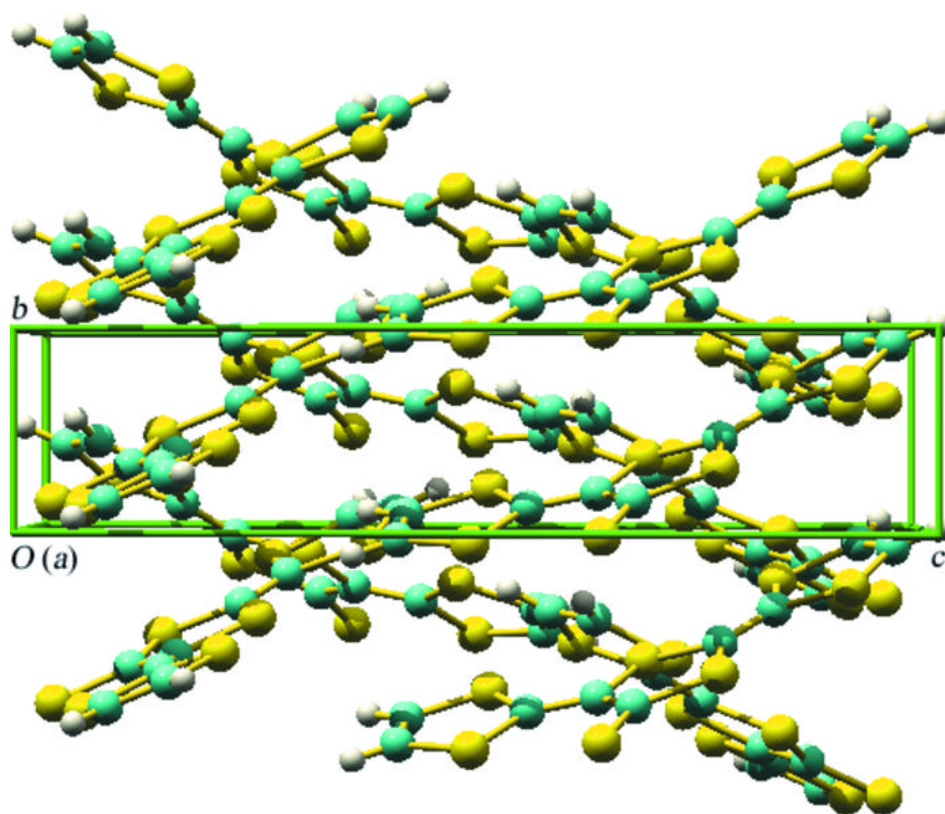


Fig. 3

