

5-Isopropylidene-1,3-dithiolo[4,5-*d*]-[1,3]dithiole-2-thioneMasaaki Tomura^{a*} and Yoshiro Yamashita^b^aInstitute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and^bDepartment of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Correspondence e-mail: tomura@ims.ac.jp

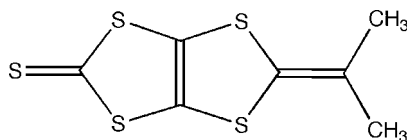
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.011$ Å; R factor = 0.072; wR factor = 0.246; data-to-parameter ratio = 23.6.

The title compound, $\text{C}_7\text{H}_6\text{S}_5$, contains a 5-ylidene-1,3-dithiolo[4,5-*d*][1,3]dithiole-2-thione framework, which is an important synthetic precursor of multi-dimensional organic superconductors and conductors. The molecular framework is planar with an r.m.s. deviation of 0.012 Å for the non-H atoms. In the crystal structure, molecules are linked by short intermolecular $\text{S}\cdots\text{S}$ interactions [3.501 (5) and 3.581 (4) Å], constructing a zigzag molecular tape network along the c axis.

Related literature

For general background, see: Williams *et al.* (1992); Ishiguro *et al.* (1998). For the synthesis of the title compound, see: Misaki *et al.* (1992). For related structures with a 5-ylidene-1,3-dithiolo[4,5-*d*][1,3]dithiole-2-thione framework, see: Bryce *et al.* (2000); Hock *et al.* (2002); Beck *et al.* (2006). For bond-length data, see: Allen *et al.* (1987). For values of van der Waals radii, see: Bondi (1964). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{C}_7\text{H}_6\text{S}_5$	$\gamma = 71.95$ (2)°
$M_r = 250.47$	$V = 502.9$ (8) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.082$ (6) Å	Mo $K\alpha$ radiation
$b = 7.126$ (6) Å	$\mu = 1.09$ mm ⁻¹
$c = 10.534$ (10) Å	$T = 291$ K
$\alpha = 86.12$ (3)°	$0.09 \times 0.02 \times 0.01$ mm
$\beta = 84.77$ (3)°	

Data collection

Rigaku/MSC Mercury CCD diffractometer	2643 independent reflections
Absorption correction: none	785 reflections with $I > 2\sigma(I)$
4550 measured reflections	$R_{\text{int}} = 0.117$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$	112 parameters
$wR(F^2) = 0.246$	H-atom parameters constrained
$S = 0.84$	$\Delta\rho_{\text{max}} = 0.46$ e Å ⁻³
2643 reflections	$\Delta\rho_{\text{min}} = -0.50$ e Å ⁻³

Data collection: *CrystalClear* (Rigaku/MSC, 2006); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); 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: HG2498).

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supplementary materials

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5-Isopropylidene-1,3-dithiolo[4,5-*d*][1,3]dithiole-2-thione

M. Tomura and Y. Yamashita

Comment

Molecules containing an 5-ylidene-[1,3]dithiolo[4,5-*d*][1,3]dithiole-2-thione framework are important synthetic precursors of multi-dimensional organic superconductors and conductors. Intermolecular S⋯S interactions involving peripheral sulfur atoms may increase the dimensionality in solid states and suppress metal-insulator transitions (Williams *et al.*, 1992; Ishiguro *et al.*, 1998). A search for the molecular framework in the Cambridge Structural Database (Version 5.30; Allen, 2002) gave only three examples (Bryce *et al.*, 2000; Hock *et al.*, 2002; Beck *et al.*, 2006). Thus, we report here the molecular and crystal structures of the title compound (I).

The compound (I) crystallizes in the $P\bar{1}$ space group with one molecule in the asymmetric unit. The molecular structure is shown in Fig. 1. The bond lengths are within the normal ranges (Allen *et al.*, 1987). The molecular framework is planar with an r.m.s. deviation of 0.012 Å from the least-squares plane. In the crystal structure, the molecules are linked *via* short intermolecular S⋯S interactions [3.581 (4) for S1—S1(-*x*, -*y* + 3, -*z*) and 3.501 (5) Å for S5—S5(-*x*, -*y* + 3, -*z* - 1)] to construct a zigzag molecular tape network along the *c* axis (Fig. 2). The S⋯S interactions are 0.5–2.8% shorter than the sum of the corresponding van der Waals radii (Bondi, 1964). The molecules also form a π -stacking along the *a* axis with an interplanar distance of 3.54 (1) Å.

Experimental

The title compound (I) was synthesized according to the literature method (Misaki *et al.*, 1992). Brown crystals of (I) suitable for X-ray analysis were grown from a dichloromethane solution.

Refinement

All H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Figures

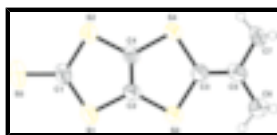


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms and H atoms are shown as small spheres of arbitrary radii.

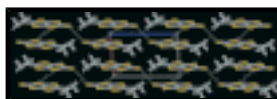


Fig. 2. The packing diagram of (I), viewed along the *b* axis. Dashed lines indicate intermolecular S⋯S interactions.

5-Isopropylidene-1,3-dithiolo[4,5-*d*][1,3]dithiole-2-thione

Crystal data

$C_7H_6S_5$	$Z = 2$
$M_r = 250.47$	$F_{000} = 256$
Triclinic, $P\bar{1}$	$D_x = 1.654 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 7.082 (6) \text{ \AA}$	$\lambda = 0.71070 \text{ \AA}$
$b = 7.126 (6) \text{ \AA}$	Cell parameters from 843 reflections
$c = 10.534 (10) \text{ \AA}$	$\theta = 3.0\text{--}29.7^\circ$
$\alpha = 86.12 (3)^\circ$	$\mu = 1.09 \text{ mm}^{-1}$
$\beta = 84.77 (3)^\circ$	$T = 291 \text{ K}$
$\gamma = 71.95 (2)^\circ$	Needle, brown
$V = 502.9 (8) \text{ \AA}^3$	$0.09 \times 0.02 \times 0.01 \text{ mm}$

Data collection

Rigaku/MSC Mercury CCD diffractometer	2643 independent reflections
Radiation source: Rotating Anode	785 reflections with $I > 2\sigma(I)$
Monochromator: Confocal	$R_{\text{int}} = 0.117$
Detector resolution: $14.63 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 31.1^\circ$
$T = 291 \text{ K}$	$\theta_{\text{min}} = 3.0^\circ$
φ and ω scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -10 \rightarrow 10$
4550 measured reflections	$l = -10 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2]$
$wR(F^2) = 0.246$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.84$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2643 reflections	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
112 parameters	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.003 (3)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.1573 (3)	1.3556 (3)	-0.12379 (19)	0.0502 (6)
S2	0.2864 (3)	0.9827 (3)	-0.25144 (18)	0.0496 (6)
S3	0.1902 (3)	1.1364 (3)	0.13884 (18)	0.0452 (6)
S4	0.3259 (3)	0.7524 (3)	0.00739 (18)	0.0434 (6)
S5	0.1908 (4)	1.3598 (4)	-0.4066 (2)	0.0710 (9)
C1	0.2089 (11)	1.2401 (12)	-0.2662 (7)	0.048 (2)
C2	0.2080 (10)	1.1425 (11)	-0.0257 (7)	0.0427 (19)
C3	0.2706 (10)	0.8745 (11)	0.1547 (7)	0.0407 (18)
C4	0.2678 (9)	0.9729 (12)	-0.0871 (7)	0.0385 (17)
C5	0.2896 (10)	0.7741 (12)	0.2681 (8)	0.045 (2)
C6	0.2430 (11)	0.8811 (12)	0.3900 (7)	0.056 (2)
H6A	0.3602	0.8472	0.4365	0.084*
H6B	0.1395	0.8439	0.4405	0.084*
H6C	0.1994	1.0210	0.3711	0.084*
C7	0.3596 (11)	0.5529 (11)	0.2761 (7)	0.049 (2)
H7A	0.3818	0.5036	0.1917	0.073*
H7B	0.2603	0.5056	0.3239	0.073*
H7C	0.4816	0.5078	0.3179	0.073*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0512 (13)	0.0409 (13)	0.0522 (14)	-0.0080 (10)	-0.0035 (10)	0.0126 (10)
S2	0.0551 (14)	0.0473 (14)	0.0417 (12)	-0.0113 (11)	0.0001 (9)	0.0038 (10)
S3	0.0519 (13)	0.0337 (12)	0.0451 (12)	-0.0077 (10)	0.0010 (9)	-0.0006 (9)
S4	0.0513 (13)	0.0308 (12)	0.0429 (12)	-0.0058 (10)	-0.0014 (9)	0.0009 (9)
S5	0.0751 (18)	0.078 (2)	0.0561 (16)	-0.0221 (15)	-0.0135 (12)	0.0300 (13)
C1	0.049 (5)	0.044 (5)	0.047 (5)	-0.007 (4)	-0.011 (4)	0.012 (4)
C2	0.046 (5)	0.031 (5)	0.047 (5)	-0.008 (4)	-0.002 (4)	-0.003 (4)
C3	0.040 (4)	0.039 (5)	0.040 (4)	-0.010 (4)	0.004 (3)	-0.001 (3)
C4	0.032 (4)	0.038 (4)	0.040 (4)	-0.004 (3)	-0.006 (3)	0.006 (3)
C5	0.039 (4)	0.037 (5)	0.058 (5)	-0.014 (4)	0.013 (4)	-0.001 (4)

supplementary materials

C6	0.066 (6)	0.050 (6)	0.051 (5)	-0.016 (5)	0.002 (4)	-0.005 (4)
C7	0.056 (5)	0.039 (5)	0.049 (5)	-0.016 (4)	0.002 (4)	0.014 (4)

Geometric parameters (Å, °)

S1—C1	1.716 (8)	C3—C5	1.346 (10)
S1—C2	1.738 (8)	C5—C6	1.496 (10)
S2—C4	1.723 (7)	C5—C7	1.497 (10)
S2—C1	1.744 (8)	C6—H6A	0.9600
S3—C2	1.725 (8)	C6—H6B	0.9600
S3—C3	1.775 (8)	C6—H6C	0.9600
S4—C4	1.758 (7)	C7—H7A	0.9600
S4—C3	1.783 (7)	C7—H7B	0.9600
S5—C1	1.652 (7)	C7—H7C	0.9600
C2—C4	1.341 (10)		
S1...S1 ⁱ	3.581 (4)	S5...S5 ⁱⁱ	3.501 (5)
C1—S1—C2	96.7 (4)	C3—C5—C6	120.7 (8)
C4—S2—C1	94.9 (4)	C3—C5—C7	121.2 (7)
C2—S3—C3	94.4 (3)	C6—C5—C7	118.1 (7)
C4—S4—C3	94.3 (4)	C5—C6—H6A	109.5
S5—C1—S1	123.5 (5)	C5—C6—H6B	109.5
S5—C1—S2	122.1 (5)	H6A—C6—H6B	109.5
S1—C1—S2	114.4 (4)	C5—C6—H6C	109.5
C4—C2—S3	119.7 (6)	H6A—C6—H6C	109.5
C4—C2—S1	115.0 (6)	H6B—C6—H6C	109.5
S3—C2—S1	125.3 (5)	C5—C7—H7A	109.5
C5—C3—S3	123.3 (6)	C5—C7—H7B	109.5
C5—C3—S4	122.0 (6)	H7A—C7—H7B	109.5
S3—C3—S4	114.6 (4)	C5—C7—H7C	109.5
C2—C4—S2	118.9 (6)	H7A—C7—H7C	109.5
C2—C4—S4	117.0 (6)	H7B—C7—H7C	109.5
S2—C4—S4	124.1 (5)		
C2—S1—C1—S5	180.0 (5)	S3—C2—C4—S2	-179.5 (4)
C2—S1—C1—S2	-0.9 (5)	S1—C2—C4—S2	-0.4 (8)
C4—S2—C1—S5	179.9 (5)	S3—C2—C4—S4	-0.3 (8)
C4—S2—C1—S1	0.8 (5)	S1—C2—C4—S4	178.8 (3)
C3—S3—C2—C4	0.3 (6)	C1—S2—C4—C2	-0.2 (6)
C3—S3—C2—S1	-178.7 (5)	C1—S2—C4—S4	-179.3 (5)
C1—S1—C2—C4	0.8 (6)	C3—S4—C4—C2	0.1 (6)
C1—S1—C2—S3	179.8 (5)	C3—S4—C4—S2	179.2 (4)
C2—S3—C3—C5	179.6 (7)	S3—C3—C5—C6	-0.2 (10)
C2—S3—C3—S4	-0.2 (4)	S4—C3—C5—C6	179.7 (5)
C4—S4—C3—C5	-179.8 (7)	S3—C3—C5—C7	-179.5 (5)
C4—S4—C3—S3	0.1 (4)	S4—C3—C5—C7	0.3 (10)

Symmetry codes: (i) $-x, -y+3, -z$; (ii) $-x, -y+3, -z-1$.

Fig. 1

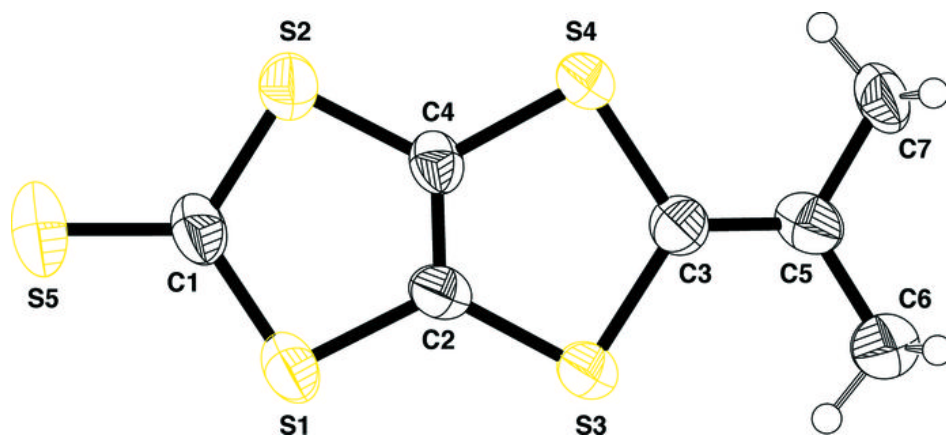


Fig. 2

