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5-(4,5-Diiodo-1,3-dithiol-2-ylidene)-4',5'-bis(methylsulfanyl)-2,2'-bi-1,3-dithiole-4(5H)-thione

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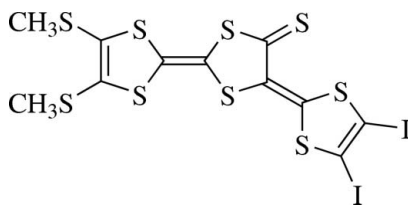
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Key indicators: single-crystal X-ray study; $T = 93$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.038; wR factor = 0.090; data-to-parameter ratio = 21.8.

The molecular skeleton of the title molecule, $\text{C}_{11}\text{H}_6\text{I}_2\text{S}_9$, is nearly planar [maximum deviation 0.052 (3) Å] except for the two methyl groups. In the crystal, molecules related by translation along b axis are associated into columns through π - π interactions between the five-membered rings, with a centroid-centroid distance of 3.593 (5) Å. Interaction between adjacent columns is accomplished by short $\text{S}\cdots\text{I}$ contacts of 3.2099 (4) Å.

Related literature

For background to tetrathiafulvalenothioquinone-1,3-dithiole-emethide derivatives, see: Iwamatsu *et al.* (2000); Wang *et al.* (2005, 2007); Hiraoka *et al.* (2005); Fujiwara *et al.* (2006, 2007). For details of the synthesis, see Iwamatsu *et al.* (1999). For intermolecular $\text{S}\cdots\text{I}$ contacts, see: Ahlsen & Strømme (1974); Herbststein & Schwartz (1984); Freeman *et al.* (1988); Bigoli *et al.* (1996). For van der Waals radii, see: Bondi (1964).



Experimental

Crystal data

$\text{C}_{11}\text{H}_6\text{I}_2\text{S}_9$
 $M_r = 680.50$
 Monoclinic, $C2/c$
 $a = 29.540$ (7) Å

$b = 5.3543$ (13) Å
 $c = 25.163$ (6) Å
 $\beta = 103.544$ (3)°
 $V = 3869.2$ (16) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 4.21$ mm⁻¹

$T = 93$ K
 $0.55 \times 0.18 \times 0.01$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.205$, $T_{\max} = 0.979$
 10568 measured reflections
 4387 independent reflections
 3536 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.090$
 $S = 1.07$
 4387 reflections
 201 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 3.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.31$ e Å⁻³

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: XCIF (Bruker, 2001).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2627).

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5-(4,5-Diiodo-1,3-dithiol-2-ylidene)-4',5'-bis(methylsulfanyl)-2,2'-bi-1,3-dithiole-4(5*H*)-thione

K. Ueda and K. Yoza

Comment

Charge transfer (CT) complexes of new donor molecules featuring a skeleton of tetrathiafulvalenothioquinone-1,3-dithiole-methide with magnetic metal ions are used for the preparation of magnetic molecular conductors, especially ferromagnetic semiconductors and metals (Wang *et al.*, 2005, 2007; Hiraoka *et al.*, 2005; Fujiwara *et al.*, 2006, 2007). In the CT salts of an ethylendithiotetrathiafulvalenothioquinone-1,3-dithiole-methide donor with CuBr₂, the Cu atom (a Lewis acid) of CuBr₂ is bound to the S atom (a Lewis base) of a C=S group in the donor to form a new type of π/d molecular system (Iwamatsu *et al.*, 2000). The introduction of Lewis acids, such as iodine atoms, as substituents in the molecular skeleton is expected to enhance intermolecular interaction through the formation of S \cdots I contacts. These contacts are of special interest in these structures as they may increase the dimensionality of aggregation in the solid-state. In this context, the crystal structure of the title compound, (**I**), was investigated.

The molecular framework of (**I**), Fig. 1, except for two methylthio groups, is almost planar [maximum deviation 0.052 (3) Å]. The displacements of atoms S8, S9, I1 and I2 relative to the plane of the skeleton are -0.164 (3), -0.151 (3), 0.164 (3) and 0.277 (3) Å, respectively. The torsion angles of the two methylthio groups are -136.95° for C10—S8—C8—C9 and 80.97° for C11—S9—C9—C8. In the crystal structure, two different arrangements of the molecules are present. One arrangement has a dihedral angle of 48.41° to the *ac* plane, while the other has a dihedral angle of 131.51° to the *ac* plane. As a result, the molecules are stacked in the same orientations to form one-dimensional columns along the [110] and [1-10] directions (Fig. 2). Although the weak interaction between stacked molecules in the columns is accomplished through contacts between different sulfur atoms [S3 \cdots S5ⁱ = 3.5916 (6) Å; symmetry code: (i) +*x*, 1 + *y*, +*z*] is shorter than the sum of van der Waals radii of two sulfur atoms (3.60 Å), stacked molecules are separated by interplanar distances greater than 3.54 Å and have fairly poor overlap (Bondi, 1964). However, some effective side-by-side contacts are observed between molecules of adjacent columns. The interaction between columns is accomplished by contacts between sulfur and iodine atoms [S3 \cdots I1ⁱⁱ = 3.2099 (4) Å; symmetry code: (ii) 2 - *x*, -1 + *y*, 1/2 - *z*] along the *a* axis (Fig. 3). This distance is shorter than the sum of van der Waals radii of sulfur and iodine atoms (3.78 Å). In the two molecules bound by sulfur-iodine interaction, the C5—S3—I1ⁱⁱ—C1ⁱⁱ moieties are not planar and almost linear S3—I1ⁱⁱ—C1ⁱⁱ fragments lie roughly perpendicular to the molecular skeleton [torsion angle of -81.47° for I1ⁱ—S3—C5—S5 and torsion angle of 97.60° for I1ⁱ—S3—C5—C4], and the dihedral angle of the molecules is 83.11°. Such sulfur-iodine interactions have been observed previously (Ahlsén *et al.*, 1974; Herbststein *et al.*, 1984; Freeman *et al.*, 1988; Bigoli *et al.*, 1996).

Experimental

Compound (**I**) was synthesized by a modification of the method used for the preparation of bis(methylthio)tetrathiafulvalenothioquinone-1,3-dithiole-methide (Iwamatsu *et al.*, 1999). Bis(tetraethylammonium)bis(2,3-bis(methylthio)tetrathiafulvalenyl-6,7-dithiolato)zinc (269 mg, 0.258 mmol) was reacted with 4,5-diiodo-2-methylthio-1,3-dithiole-2,3-dithiolium tetrafluoroborate (535 mg, 1.10 mmol) in THF-DMF (5:1 = *v/v*) at

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room temperature under nitrogen, and stirring was carried out for 12 h. After separation of the reaction mixture by column chromatography on silica gel (eluent: CS₂) followed by recrystallization from CS₂/*n*-hexane, (**I**) was obtained as black needles in 72% yield.

Refinement

The H atoms were geometrically positioned with C—H: 0.98 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The highest residual peak [3.45 e Å⁻³] and deepest hole [-2.31 e Å⁻³] are situated 0.98 Å and 0.69 Å at atom I2, respectively.

Figures

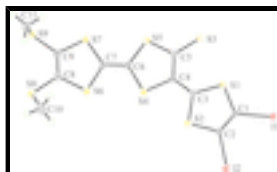


Fig. 1. The molecular structure of (**I**) showing atom labelling and 50% probability displacement ellipsoids for non H-atoms.

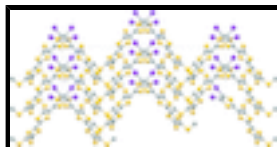


Fig. 2. Projection of the crystal packing in (**I**) down the *ab* plane. The S...S (black) and S...I (blue) contacts are shown with dashed lines. H atoms are omitted for clarity.

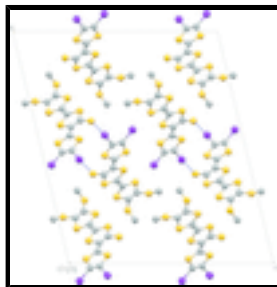


Fig. 3. Projection of the crystal packing in (**I**) down the *ac* plane. The S...I (blue) contacts are shown with dashed lines. H atoms are omitted for clarity.

5-(4,5-Diiodo-1,3-dithiol-2-ylidene)-4',5'-bis(methylsulfanyl)-2,2'-bi-1,3-dithiole-4(5*H*)-thione

Crystal data

C₁₁H₆I₂S₉

$M_r = 680.50$

Monoclinic, *C2/c*

Hall symbol: -*C* 2yc

$a = 29.540$ (7) Å

$b = 5.3543$ (13) Å

$c = 25.163$ (6) Å

$\beta = 103.544$ (3)°

$V = 3869.2$ (16) Å³

$Z = 8$

$F_{000} = 2576$

$D_x = 2.336$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 2871 reflections

$\theta = 2.4$ – 27.5 °

$\mu = 4.21$ mm⁻¹

$T = 93$ K

Needle, black

$0.55 \times 0.18 \times 0.01$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	4387 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode	3536 reflections with $I > 2\sigma(I)$
Monochromator: Bruker Helios multilayer confocal mirror	$R_{\text{int}} = 0.040$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{\text{max}} = 27.5^\circ$
$T = 93 \text{ K}$	$\theta_{\text{min}} = 1.4^\circ$
φ and ω scans	$h = -38 \rightarrow 36$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -6 \rightarrow 6$
$T_{\text{min}} = 0.205$, $T_{\text{max}} = 0.979$	$l = -24 \rightarrow 32$
10568 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
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 20.8292P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
4387 reflections	$(\Delta/\sigma)_{\text{max}} = 0.002$
201 parameters	$\Delta\rho_{\text{max}} = 3.45 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -2.31 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.01287 (15)	1.3727 (9)	0.35298 (19)	0.0158 (10)
C2	1.02057 (16)	1.2692 (10)	0.4024 (2)	0.0198 (11)

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C3	0.94845 (15)	1.0393 (9)	0.34447 (18)	0.0150 (10)
C4	0.91248 (16)	0.8707 (9)	0.32900 (19)	0.0157 (10)
C5	0.88305 (16)	0.8507 (9)	0.27608 (19)	0.0152 (10)
C6	0.85596 (16)	0.5009 (9)	0.3338 (2)	0.0177 (10)
C7	0.83308 (16)	0.3149 (10)	0.35177 (19)	0.0180 (11)
C8	0.80459 (17)	-0.0037 (10)	0.4151 (2)	0.0213 (11)
C9	0.77585 (16)	-0.0346 (10)	0.3660 (2)	0.0197 (11)
C10	0.8099 (2)	0.0697 (12)	0.5245 (2)	0.0345 (14)
H10A	0.8431	0.1096	0.5359	0.052*
H10B	0.7988	0.0128	0.5562	0.052*
H10C	0.7925	0.2190	0.5090	0.052*
C11	0.68641 (17)	-0.0497 (11)	0.3739 (2)	0.0244 (12)
H11A	0.6975	-0.0211	0.4132	0.037*
H11B	0.6563	-0.1358	0.3667	0.037*
H11C	0.6828	0.1110	0.3547	0.037*
I1	1.052758 (10)	1.64937 (6)	0.326836 (12)	0.01695 (10)
I2	1.075939 (14)	1.33621 (9)	0.468614 (15)	0.04003 (14)
S1	0.96539 (4)	1.2618 (2)	0.30265 (5)	0.0163 (2)
S2	0.98132 (4)	1.0369 (3)	0.41150 (5)	0.0202 (3)
S3	0.88601 (4)	1.0394 (2)	0.22343 (5)	0.0186 (3)
S4	0.90284 (4)	0.6524 (2)	0.37793 (5)	0.0196 (3)
S5	0.84272 (4)	0.6130 (2)	0.26660 (5)	0.0194 (3)
S6	0.84983 (4)	0.2173 (3)	0.42068 (5)	0.0217 (3)
S7	0.78627 (4)	0.1484 (3)	0.31171 (5)	0.0200 (3)
S8	0.80104 (5)	-0.1743 (3)	0.47356 (5)	0.0231 (3)
S9	0.72837 (4)	-0.2411 (3)	0.34965 (5)	0.0200 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.013 (2)	0.020 (3)	0.015 (2)	-0.0029 (19)	0.0032 (18)	-0.002 (2)
C2	0.018 (2)	0.023 (3)	0.017 (2)	-0.004 (2)	-0.0002 (19)	0.002 (2)
C3	0.015 (2)	0.017 (3)	0.012 (2)	0.0032 (19)	0.0015 (18)	-0.0001 (19)
C4	0.015 (2)	0.015 (3)	0.017 (2)	0.0032 (19)	0.0038 (18)	0.004 (2)
C5	0.017 (2)	0.016 (3)	0.015 (2)	0.0061 (19)	0.0073 (18)	-0.0025 (19)
C6	0.017 (2)	0.015 (3)	0.020 (3)	-0.0027 (19)	0.0026 (19)	-0.004 (2)
C7	0.017 (2)	0.020 (3)	0.016 (2)	0.000 (2)	0.0033 (19)	-0.003 (2)
C8	0.018 (2)	0.020 (3)	0.026 (3)	-0.004 (2)	0.007 (2)	-0.001 (2)
C9	0.013 (2)	0.020 (3)	0.027 (3)	-0.002 (2)	0.0050 (19)	-0.004 (2)
C10	0.047 (4)	0.035 (4)	0.024 (3)	-0.007 (3)	0.015 (3)	-0.002 (3)
C11	0.018 (2)	0.029 (3)	0.026 (3)	-0.001 (2)	0.005 (2)	-0.004 (2)
I1	0.01587 (16)	0.01857 (18)	0.01695 (17)	-0.00209 (12)	0.00491 (12)	-0.00065 (13)
I2	0.0346 (2)	0.0579 (3)	0.0204 (2)	-0.0239 (2)	-0.00805 (16)	0.01043 (18)
S1	0.0161 (6)	0.0184 (6)	0.0143 (6)	-0.0014 (5)	0.0033 (4)	0.0016 (5)
S2	0.0195 (6)	0.0269 (7)	0.0133 (6)	-0.0053 (5)	0.0019 (5)	0.0029 (5)
S3	0.0198 (6)	0.0193 (7)	0.0160 (6)	0.0023 (5)	0.0027 (5)	0.0014 (5)
S4	0.0223 (6)	0.0212 (7)	0.0153 (6)	-0.0046 (5)	0.0046 (5)	0.0002 (5)
S5	0.0188 (6)	0.0194 (7)	0.0185 (6)	-0.0034 (5)	0.0014 (5)	-0.0020 (5)

S6	0.0208 (6)	0.0254 (8)	0.0182 (6)	-0.0065 (5)	0.0031 (5)	-0.0005 (5)
S7	0.0200 (6)	0.0215 (7)	0.0179 (6)	-0.0040 (5)	0.0033 (5)	-0.0012 (5)
S8	0.0254 (7)	0.0233 (7)	0.0202 (7)	-0.0050 (5)	0.0044 (5)	0.0014 (5)
S9	0.0182 (6)	0.0207 (7)	0.0214 (6)	-0.0037 (5)	0.0052 (5)	-0.0039 (5)

Geometric parameters (Å, °)

C1—C2	1.331 (7)	C7—S7	1.752 (5)
C1—S1	1.758 (5)	C7—S6	1.767 (5)
C1—I1	2.093 (5)	C8—C9	1.336 (7)
C2—S2	1.751 (5)	C8—S8	1.755 (5)
C2—I2	2.074 (5)	C8—S6	1.766 (5)
C3—C4	1.379 (7)	C9—S9	1.758 (5)
C3—S2	1.738 (4)	C9—S7	1.766 (5)
C3—S1	1.739 (5)	C10—S8	1.806 (6)
C4—C5	1.414 (6)	C10—H10A	0.9800
C4—S4	1.769 (5)	C10—H10B	0.9800
C5—S3	1.685 (5)	C10—H10C	0.9800
C5—S5	1.721 (5)	C11—S9	1.820 (5)
C6—C7	1.340 (7)	C11—H11A	0.9800
C6—S5	1.750 (5)	C11—H11B	0.9800
C6—S4	1.758 (5)	C11—H11C	0.9800
C2—C1—S1	117.7 (4)	C8—C9—S9	126.4 (4)
C2—C1—I1	127.1 (4)	C8—C9—S7	117.3 (4)
S1—C1—I1	115.2 (2)	S9—C9—S7	116.2 (3)
C1—C2—S2	116.4 (4)	S8—C10—H10A	109.5
C1—C2—I2	127.5 (4)	S8—C10—H10B	109.5
S2—C2—I2	116.1 (3)	H10A—C10—H10B	109.5
C4—C3—S2	119.2 (4)	S8—C10—H10C	109.5
C4—C3—S1	126.1 (4)	H10A—C10—H10C	109.5
S2—C3—S1	114.7 (3)	H10B—C10—H10C	109.5
C3—C4—C5	125.4 (5)	S9—C11—H11A	109.5
C3—C4—S4	118.4 (4)	S9—C11—H11B	109.5
C5—C4—S4	116.2 (4)	H11A—C11—H11B	109.5
C4—C5—S3	124.2 (4)	S9—C11—H11C	109.5
C4—C5—S5	116.1 (4)	H11A—C11—H11C	109.5
S3—C5—S5	119.8 (3)	H11B—C11—H11C	109.5
C7—C6—S5	124.4 (4)	C3—S1—C1	95.1 (2)
C7—C6—S4	121.0 (4)	C3—S2—C2	96.0 (2)
S5—C6—S4	114.6 (3)	C6—S4—C4	95.5 (2)
C6—C7—S7	125.2 (4)	C5—S5—C6	97.4 (2)
C6—C7—S6	120.2 (4)	C8—S6—C7	95.0 (2)
S7—C7—S6	114.6 (3)	C7—S7—C9	95.4 (2)
C9—C8—S8	124.1 (4)	C8—S8—C10	101.0 (3)
C9—C8—S6	117.5 (4)	C9—S9—C11	97.8 (2)
S8—C8—S6	118.4 (3)		

Fig. 1

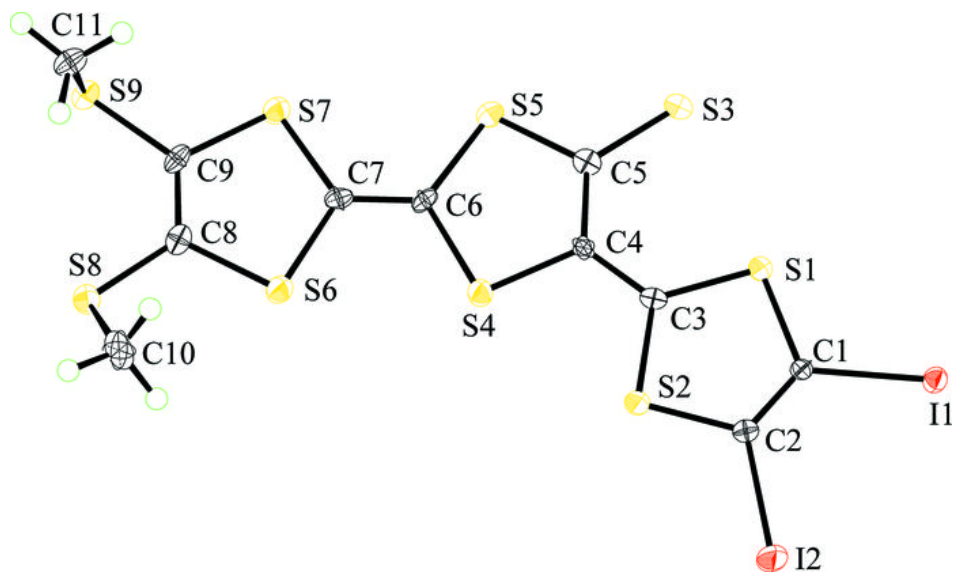


Fig. 2

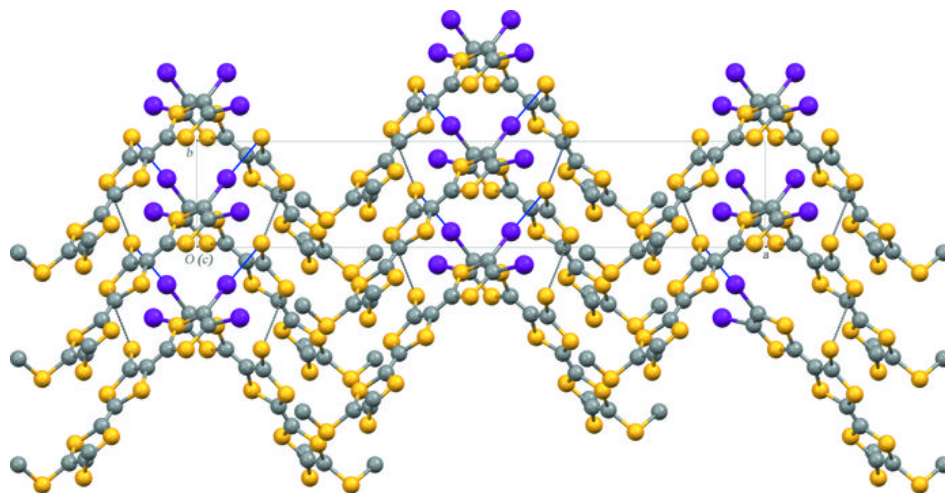


Fig. 3

