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Key indicators

Single-crystal X-ray study
 $T = 150$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.036
 wR factor = 0.094
 Data-to-parameter ratio = 37.3

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

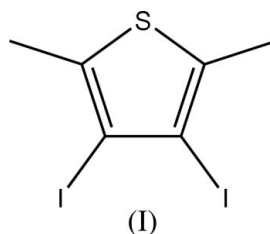
3,4-Diiodo-2,5-dimethylthiophene

In the crystal structure of the title compound, $\text{C}_6\text{H}_6\text{I}_2\text{S}$, the molecules pack to form one-dimensional chains connected by intermolecular $\text{S} \cdots \text{I}$ interactions.

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Comment

The title compound, (I) (Fig. 1), was prepared as part of a study aimed at producing new photochromic materials. Thiophene derivatives are important intermediates in the synthesis of photochromic compounds, organic light emitting diodes (OLED) and organic conductors. For photochromic compounds, potential applications are in the areas of optical recording, full-colour display and photoswitches.



The molecule of compound (I) possesses normal geometric parameters and is essentially planar. Intermolecular $\text{S} \cdots \text{I}$ interactions are observed in the structure with a distance of 3.641 (4) Å (Fig. 2). Such intermolecular interactions are also observed in the structure of tetraiodothiophene cocrystallized with tetrabutylammonium iodide (Bock & Holl, 2002), with $\text{S} \cdots \text{I}$ distances of 3.58 and 3.59 Å, and other work involving I_2 interactions with thioethers suggest the distances are typical *e.g.* 3.70 Å in the formation of extended structural networks (Blake *et al.*, 1997 and 1998). Weak intermolecular $\text{C}-\text{H} \cdots \text{I}$ interactions are not observed in this structure.

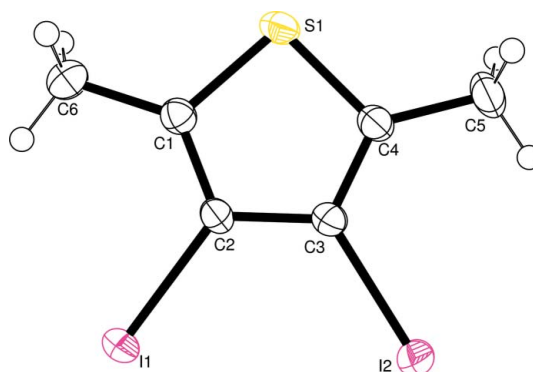


Figure 1
 The molecular structure of (I), showing 50% probability ellipsoids for non-H atoms.

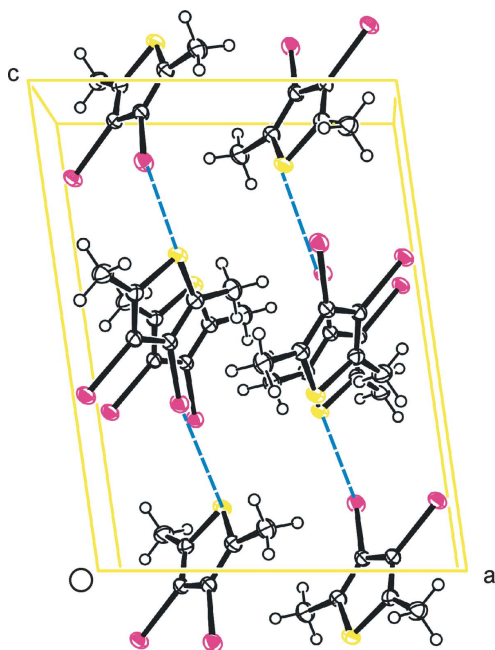


Figure 2
The unit-cell contents of (I), viewed along [010] (50% probability ellipsoids). The dashed lines indicate the closest intermolecular S...I contacts.

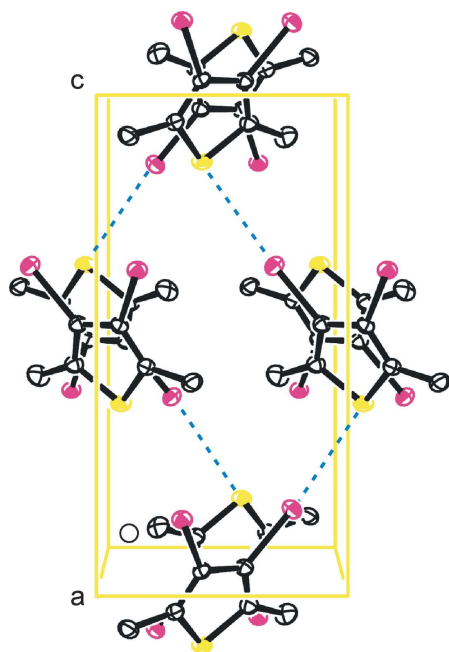


Figure 3
The unit-cell contents of (I), viewed along [100] (50% probability ellipsoids). The dashed lines indicate the closest intermolecular S...I contacts.

Experimental

To a vigorously stirred mixture of iodine (11.5 g, 45 mmol), water (25 ml), iodic acid (3.9 g, 22 mmol), sulfuric acid (3 ml) and glacial acetic acid (75 ml) was added 2,5-dimethylthiophene (5 ml, 44 mmol).

The solution was stirred at 323 K for 3 h and saturated aqueous sodium thiosulfate (150 ml) was added. The organic phase was extracted with diethyl ether (4 × 50 ml), dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane and the solution was passed through a column of silica gel to remove the coloured material (9.15 g, 57%). The compound was recrystallized from dichloromethane at room temperature, giving crystals of (I) suitable for X-ray analysis (yield 9.15 g, 57%).

Crystal data

C ₆ H ₆ I ₂ S	$V = 900.31 (18) \text{ \AA}^3$
$M_r = 363.97$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.0141 (13) \text{ \AA}$	$\mu = 7.14 \text{ mm}^{-1}$
$b = 6.7478 (6) \text{ \AA}$	$T = 150 (2) \text{ K}$
$c = 13.4597 (17) \text{ \AA}$	$0.49 \times 0.45 \times 0.35 \text{ mm}$
$\beta = 98.156 (10)^\circ$	

Data collection

Stoe IPDSII image-plate diffractometer	7570 measured reflections
Absorption correction: numerical (<i>X-RED32</i> ; Stoe & Cie, 2002)	3171 independent reflections
$T_{\min} = 0.073$, $T_{\max} = 0.145$	2876 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	85 parameters
$wR(F^2) = 0.094$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\max} = 1.84 \text{ e \AA}^{-3}$
3171 reflections	$\Delta\rho_{\min} = -1.56 \text{ e \AA}^{-3}$

H atoms were placed in idealized positions (C–H = 0.98 Å) and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The highest residual electron-density peak is located 1.05 Å from atom I1 and the deepest hole is located 0.67 Å from the same atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *WinGX* (Farrugia, 1999).

We thank the EPSRC for funds which enabled the purchase of the Stoe IPDSII diffractometer. We acknowledge the use of the EPSRC's Chemical Database Service at Daresbury (Fletcher *et al.*, 1996).

References

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supporting information

Acta Cryst. (2007). E63, o1393–o1394 [https://doi.org/10.1107/S160053680700760X]

3,4-Diiodo-2,5-dimethylthiophene

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Crystal data

$C_6H_6I_2S$

$M_r = 363.97$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 10.0141$ (13) Å

$b = 6.7478$ (6) Å

$c = 13.4597$ (17) Å

$\beta = 98.156$ (10)°

$V = 900.31$ (18) Å³

$Z = 4$

$F(000) = 656$

$D_x = 2.685$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1487 reflections

$\theta = 3.1$ – 34.8 °

$\mu = 7.14$ mm⁻¹

$T = 150$ K

Block, colourless

$0.49 \times 0.45 \times 0.35$ mm

Data collection

Stoe IPDSII image plate
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans, 125 frames at 1° intervals, exposure
time 1 minute

Absorption correction: numerical
(X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.073$, $T_{\max} = 0.145$

7570 measured reflections

3171 independent reflections

2876 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 32.5$ °, $\theta_{\min} = 3.1$ °

$h = -15 \rightarrow 12$

$k = -10 \rightarrow 8$

$l = -19 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.094$

$S = 1.08$

3171 reflections

85 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 2.0477P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.041$

$\Delta\rho_{\max} = 1.84$ e Å⁻³

$\Delta\rho_{\min} = -1.56$ e Å⁻³

Extinction correction: SHELXL97,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0094 (5)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.95491 (2)	0.33976 (4)	0.148780 (18)	0.02573 (9)
I2	0.72610 (3)	0.78586 (4)	0.149067 (19)	0.02665 (9)
S1	0.65840 (10)	0.41677 (16)	-0.13796 (7)	0.02577 (19)
C1	0.7839 (4)	0.3079 (6)	-0.0553 (3)	0.0224 (6)
C2	0.8076 (3)	0.4170 (6)	0.0308 (3)	0.0208 (6)
C4	0.6355 (4)	0.6116 (6)	-0.0584 (3)	0.0241 (6)
C3	0.7227 (4)	0.5899 (6)	0.0289 (3)	0.0223 (6)
C6	0.8507 (5)	0.1212 (7)	-0.0829 (3)	0.0301 (8)
H2	0.9409	0.1521	-0.0989	0.036*
H3	0.7966	0.0609	-0.1415	0.036*
H1	0.8584	0.0284	-0.0264	0.036*
C5	0.5330 (4)	0.7677 (8)	-0.0880 (4)	0.0336 (9)
H5	0.4744	0.7267	-0.1492	0.040*
H4	0.5783	0.8920	-0.1006	0.040*
H6	0.4785	0.7874	-0.0338	0.040*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02439 (13)	0.02973 (15)	0.02117 (13)	0.00487 (8)	-0.00335 (9)	0.00026 (8)
I2	0.02565 (13)	0.02720 (15)	0.02611 (14)	0.00265 (8)	0.00028 (9)	-0.00559 (8)
S1	0.0258 (4)	0.0318 (5)	0.0183 (4)	0.0018 (3)	-0.0021 (3)	-0.0003 (3)
C1	0.0227 (15)	0.0244 (16)	0.0201 (15)	0.0015 (12)	0.0032 (12)	0.0020 (12)
C2	0.0191 (13)	0.0227 (16)	0.0201 (14)	0.0022 (11)	0.0011 (11)	0.0026 (11)
C4	0.0222 (14)	0.0266 (17)	0.0227 (16)	0.0025 (13)	0.0001 (12)	0.0009 (13)
C3	0.0200 (14)	0.0254 (17)	0.0205 (15)	0.0015 (12)	-0.0003 (12)	-0.0004 (12)
C6	0.0346 (19)	0.031 (2)	0.0253 (18)	0.0046 (16)	0.0065 (15)	-0.0039 (15)
C5	0.0266 (18)	0.039 (2)	0.034 (2)	0.0124 (17)	0.0003 (16)	0.0070 (17)

Geometric parameters (\AA , $^\circ$)

I1—C2	2.074 (4)	C4—C5	1.486 (6)
I2—C3	2.085 (4)	C6—H2	0.9800
S1—C1	1.721 (4)	C6—H3	0.9800
S1—C4	1.731 (4)	C6—H1	0.9800
C1—C2	1.365 (5)	C5—H5	0.9800

C1—C6	1.498 (6)	C5—H4	0.9800
C2—C3	1.442 (5)	C5—H6	0.9800
C4—C3	1.369 (5)		
C1—S1—C4	94.18 (19)	C1—C6—H2	109.5
C2—C1—C6	129.4 (4)	C1—C6—H3	109.5
C2—C1—S1	110.0 (3)	H2—C6—H3	109.5
C6—C1—S1	120.6 (3)	C1—C6—H1	109.5
C1—C2—C3	113.0 (3)	H2—C6—H1	109.5
C1—C2—I1	122.2 (3)	H3—C6—H1	109.5
C3—C2—I1	124.8 (3)	C4—C5—H5	109.5
C3—C4—C5	129.6 (4)	C4—C5—H4	109.5
C3—C4—S1	109.0 (3)	H5—C5—H4	109.5
C5—C4—S1	121.3 (3)	C4—C5—H6	109.5
C4—C3—C2	113.8 (4)	H5—C5—H6	109.5
C4—C3—I2	122.5 (3)	H4—C5—H6	109.5
C2—C3—I2	123.7 (3)		
C4—S1—C1—C2	0.1 (3)	C5—C4—C3—C2	179.5 (4)
C4—S1—C1—C6	-179.4 (3)	S1—C4—C3—C2	0.3 (4)
C6—C1—C2—C3	179.5 (4)	C5—C4—C3—I2	1.4 (6)
S1—C1—C2—C3	0.0 (4)	S1—C4—C3—I2	-177.81 (19)
C6—C1—C2—I1	0.9 (6)	C1—C2—C3—C4	-0.2 (5)
S1—C1—C2—I1	-178.60 (18)	I1—C2—C3—C4	178.4 (3)
C1—S1—C4—C3	-0.2 (3)	C1—C2—C3—I2	177.9 (3)
C1—S1—C4—C5	-179.5 (4)	I1—C2—C3—I2	-3.6 (4)
