organic compounds

(5E)-2-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4-iodo-1,3-dithiol-2-ylidene)-1,3-dithiolan-4-one

Kazumasa Ueda[a]* and Kenji Yoza[b]

[a]Division of Applied Science and Fundamental Engineering, Faculty of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu, Shizuoka, 432-8561, Japan, and [b]Bruker AXS Co Ltd, Moriya-cho 3-9, Kanagawa-ku, Kanagawa, Kanagawa 221-0022, Japan

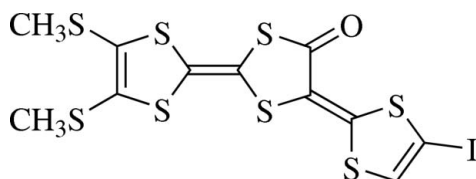Correspondence e-mail: tkueda@ipc.shizuoka.ac.jp

The molecular framework of the title compound, $C_{11}H_7IOS_8$, is almost planar [maximum deviation = 0.040 (4) Å], except for the two methylsulfanyl groups, which are twisted relative to the molecular skeleton, making C—S—C—C torsion angles of 144.1 (8) and −141.3 (8)°. In the crystal, molecules are stacked alternately in opposite orientations, forming a one-dimensional column parallel to [110]. The primary interactions between molecules comprising the columns are of the S···S type [3.554 (1) Å]. Interactions between columns are of the S···S type [3.411 (1) along b and 3.444 (1) Å along c], as well as S···I contacts [3.435 (2) Å].

Related literature

For background to 2,5-di(1,3-dithiole-2-ylidene)-1,3-dithiolan-4-one derivatives, see: Iwamatsu et al. (1999); Matsumoto et al. (2002, 2003); Hiraoka et al. (2007); Ueda & Yoza (2009). For the synthesis, see: Ueda & Yoza (2009). For background to intermolecular S···I contacts, see: Blake et al. (1997, 1998, 1999); Bricklebank et al. (2000); Ouvrard et al. (2003). For van der Waals radii, see: Bondi (1964).

Experimental

Crystal data

$C_{11}H_7IOS_8$	a = 8.309 (3) Å
M_r = 538.55	b = 8.344 (3) Å
Triclinic, $P\bar{1}$	c = 14.618 (7) Å
α = 90.851 (6)°	Mo $K\alpha$ radiation
β = 105.132 (6)°	μ = 2.87 mm^{-1}
γ = 118.510 (4)°	T = 93 K
V = 848.0 (6) Å^3	0.04 × 0.04 × 0.04 mm
Z = 2	

Data collection

Bruker APEXII CCD area-detector diffractometer	9773 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3820 independent reflections
T_{min} = 0.894, T_{max} = 0.894	3065 reflections with $I > 2\sigma(I)$
	R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055	190 parameters
$wR(F^2)$ = 0.161	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 2.34 e Å^{-3}
3820 reflections	$\Delta\rho_{min}$ = −1.13 e Å^{-3}

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); 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., 2008); software used to prepare material for publication: XCIF (Bruker, 2001).

References

Blake, A. J., Cristiani, F., Devillanova, F. A., Garau, A., Gilby, L. M., Gould, R. O., Isaia, F., Lippolis, V., Parsons, S., Radek, C. & Schröder, M. (1997). J. Chem. Soc. Dalton Trans. pp. 1337–1346.

Blake, A. J., Devillanova, F. A., Garau, A., Gilby, L. M., Gould, R. O., Isaia, F., Lippolis, V., Parsons, S., Radek, C. & Schröder, M. (1998). J. Chem. Soc. Dalton Trans. pp. 2037–2046.

Blake, A. J., Devillanova, F. A., Garau, A., Isaia, F., Lippolis, V., Parsons, S. & Schröder, M. (1999). J. Chem. Soc. Dalton Trans. pp. 525–531.

Bondi, A. (1964). J. Phys. Chem. 68, 441–451.

Bricklebank, N., Hargreaves, S. & Spey, S. E. (2000). Polyhedron, 19, 1163–1166.

Bruker (2001). XCIF. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2004). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2006). APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.

Hiraoka, T., Fujiwara, H., Sugimoto, T., Nakazumi, H., Noguchi, S., Kuribayashi, A., Ishida, T., Yokogawa, K., Murata, K., Mori, T., Aruga-Katori, H., Kimura, S. & Hagiwara, M. (2007). J. Mater. Chem. 17, 1664–1673.

Iwamatsu, M., Kominami, T., Ueda, K., Sugimoto, T., Fujita, H. & Adachi, T. (1999). Chem. Lett. pp. 329–330.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). J. Appl. Cryst. 41, 466–470.

Matsumoto, T., Kamada, Y., Sugimoto, T., Tada, T., Nakazumi, H., Kawakami, T. & Yamaguchi, K. (2003). Synth. Met. 135–136, 575–576.

Matsumoto, T., Kominami, T., Ueda, K., Sugimoto, T., Tada, T., Noguchi, S., Yoshino, H., Murata, K., Shiro, M., Negishi, E., Toyota, N., Endo, S. & Takahashi, K. (2002). Inorg. Chem. 41, 4763–4769.

Ouvrard, C., Le Questel, J.-Y., Berthelot, M. & Laurence, C. (2003). Acta Cryst. B59, 512–526.

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

Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

Ueda, K. & Yoza, K. (2009). Acta Cryst. E65, o2716.

supporting information

(5*E*)-2-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4-iodo-1,3-dithiol-2-ylidene)-1,3-dithiolan-4-one

Kazumasa Ueda and Kenji Yoza

S1. Comment

2,5-Di(1,3-dithiol-2-ylidene)-1,3-dithiolan-4-one derivatives are used for the preparation of charge transfer salts with magnetic metal anions (Iwamatsu *et al.*, 1999; Matsumoto *et al.*, 2002*a*, *b*, 2003; Hiraoka *et al.*, 2007). In CT salts these molecules can form unique crystal structures containing channels in addition to the usual stacked layer structures. The control of donor molecule interactions by means of chemical modification of the 2,5-di(1,3-dithiol-2-ylidene)-1,3-dithiolan-4-one skeleton may increase the dimensionality of aggregation in the solid-state. In this context, we have previously synthesized a molecule substituted with two iodide atoms, namely 2-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4,5-diiodo-1,3-dithiol- 2-ylidene)-1,3-dithiolan-4-one, and observed fairly close I⋯O interactions in the crystal (Ueda & Yoza, 2009). As a continuation of these studies, herein, we present the crystal structure of a molecule substituted with one iodide atom, (I).

The molecular framework of (I), Fig. 1, except for two methylsulfanyl groups, is almost planar. The displacements of atoms S6, S9, and I1 relative to the plane of the skeleton are 0.106 (4), 0.236 (5) and 0.013 (4) Å, respectively. The torsion angles of the two methylsulfanyl groups are 144.1 (8)° for C10—S6—C8—C9 and -141.3 (8)° for C11—S9—C9—C8.

In the crystal structure, the molecules are stacked alternately in opposite orientations, forming a one-dimensional column parallel to the [110] direction (Fig. 2). The weak interactions between stacked molecules is accomplished through S⋯S contacts [S4⋯S6^{i} = 3.554 (1) Å; symmetry code (i): 2-x, 2-y, 2-z] which are shorter than the sum of van der Waals radii of two S atoms, i.e. 3.60 Å (Bondi, 1964). It is noted that although the stacked molecules are separated by interplanar distances as short as 3.54 Å, they have fairly poor overlap. Some effective side-by-side contacts are observed between molecules of adjacent columns. These interactions are accomplished through S⋯S contacts [S2⋯S5^{ii} = 3.411 (1) Å; symmetry code (ii): x, 1 + y, z] along the *b* axis. Stability along the c axis are afforded by additional S⋯S contacts [S9⋯S9^{iii} = 3.444 (1) Å; symmetry code (iii): 2 - x, 2 - y, 1 - z] as well as S⋯I contacts [S6⋯I1^{iv} = 3.435 (2) Å; symmetry code (iv): x, 1 + y, -1 + z]. This latter distance is shorter than the sum of corresponding van der Waals radii for S and I, i.e. 3.78 Å (Bondi, 1964). Such S⋯I interactions have been observed previously (Blake *et al.*, 1997, 1998, 1999; Bricklebank *et al.*, 2000). The intermolecular angles, 162.8 (2)° for S6⋯I1^{iv}—C1^{iv} and 105.8 (4)° for C10—S6⋯I1^{iv}, are close to the ideal geometry (180° for C—I⋯S and 109.5° for C—S⋯I) which have been proposed for these types of associations (Ouvrard *et al.*, 2003).

S2. Experimental

Compound (I) was synthesized by a modification of the method used for the preparation of 2-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4,5-diiodo-1,3-dithiol- 2-ylidene)-1,3-dithiolan-4-one (Ueda & Yoza, 2009). Bis(tetramethylammonium)bis[2-[4,5-bis(methylsulfanyl)-1,3-dithiol-2- ylidene]-1,3-dithiole-4,5-bis(thiolato)]zinc (402.4 mg,

0.4322 mmol) was reacted with 4-iodo-2-methylsulfanyl-1,3-dithiole-2-ylium tetrafluoroborate (457.5 mg, 1.2639 mmol) in THF-DMF (5:1 = *v/v*) at room temperature under nitrogen. Stirring was carried out for 12 h. After separation of the reaction mixture by column chromatography on silica gel (eluent CS_2) followed by recrystallization from CS_2/hexane, (5*E*)-2-[4,5-bis(methylsulfanyl)-1,3-dithiole-2-ylidene]-5-(4-iodo- 1,3-dithiole-2-ylidene)-1,3-dithiolan-4-thione (II) was obtained as dark-green needles in 74% yield.

When compound (II) (151.6 mg, 0.2733 mmol) was reacted with mercury(II) acetate (191.6 mg, 0.6012 mmol) in THF-AcOH (50:1 = *v/v*), compound (I) was obtained as dark-red platelets in 58% yield by recrystallization from CS_2/hexane.

S3. Refinement

The H atoms were geometrically placed with C—H = 0.95-0.98 Å, and refined as in the riding model approximation with $U_{iso}(H) = 1.2$-$1.5U_{eq}(C)$.

The maximum and minimum residual electron density peaks of 2.34 and -1.13 eÅ^{-3}, respectively, were located 1.00 Å and 0.83 Å from the I1 atom, respectively.
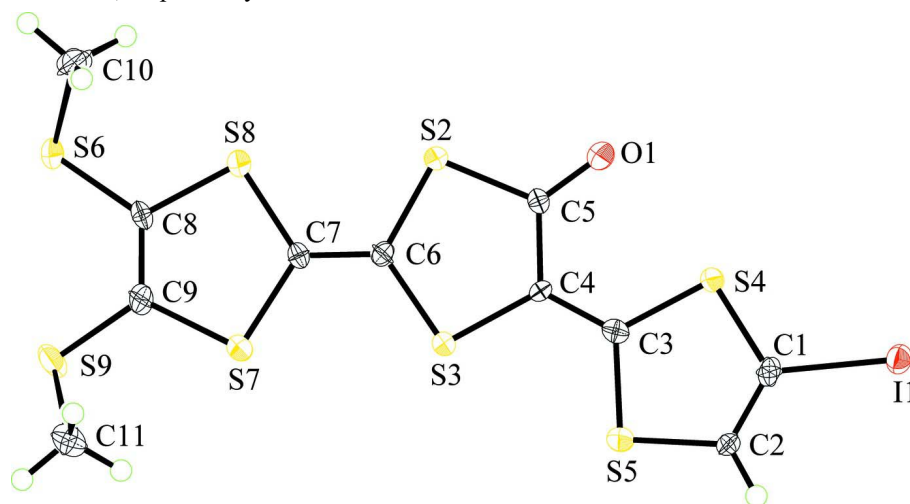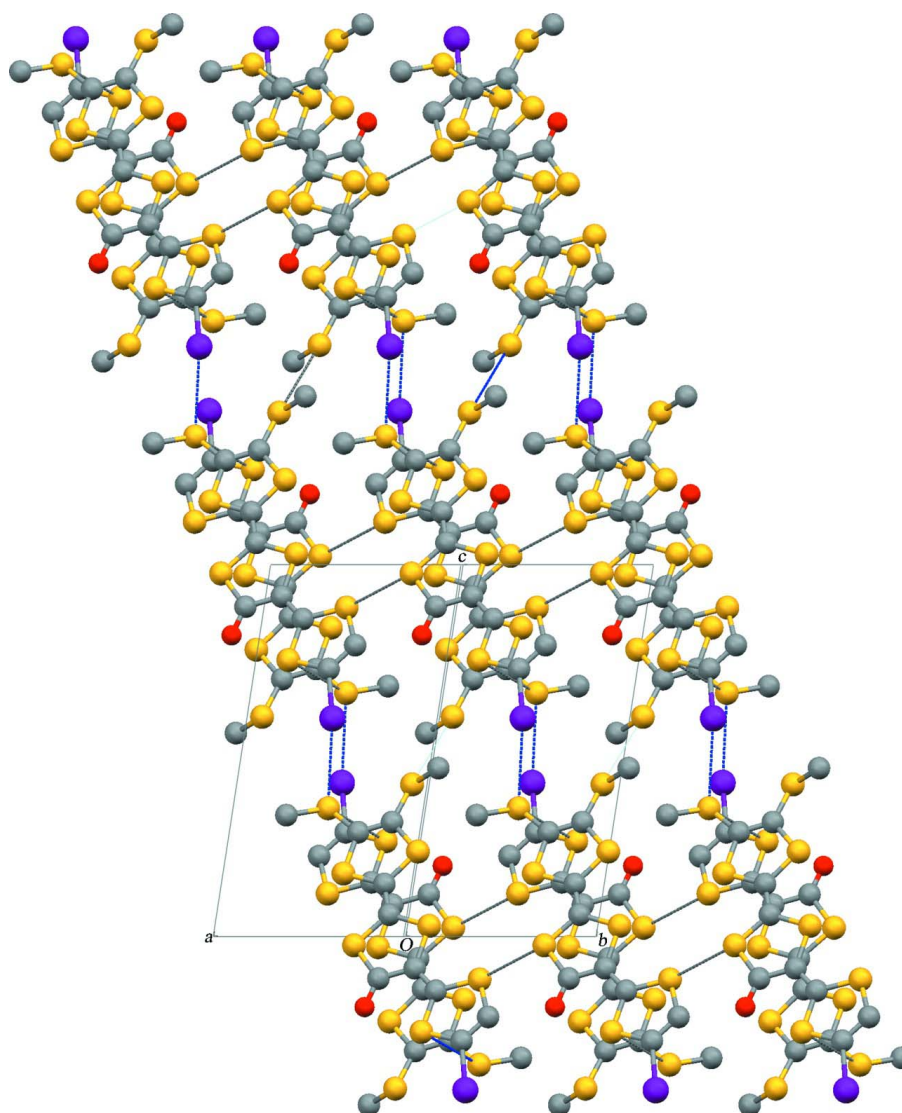

Figure 1

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

Figure 2

Projection of the crystal packing in (I) along the [110] direction. The S···S (gray), and S···I (blue) contacts are shown with dashed lines. H atoms are omitted for clarity.
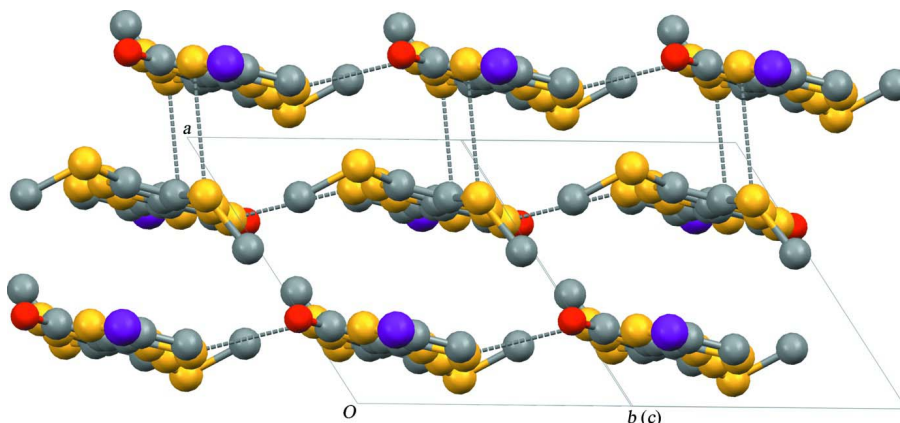
Figure 3

Projection of the crystal packing in (I) along the longer molecular axis. The S⋯S contacts are shown with gray dashed lines. H atoms are omitted for clarity.

(5*E*)-2-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4-iodo-1,3- dithiol-2-ylidene)-1,3-dithiolan-4-one

Crystal data

$C_{11}H_7IOS_8$	$Z = 2$
$M_r = 538.55$	$F(000) = 524$
Triclinic, $P\bar{1}$	$D_x = 2.109$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.309$ (3) Å	Cell parameters from 2153 reflections
$b = 8.344$ (3) Å	$\theta = 2.8–25.3°$
$c = 14.618$ (7) Å	$\mu = 2.87$ mm^{-1}
$\alpha = 90.851$ (6)°	$T = 93$ K
$\beta = 105.132$ (6)°	Block, dark-red
$\gamma = 118.510$ (4)°	$0.04 \times 0.04 \times 0.04$ mm
$V = 848.0$ (6) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	$T_{min} = 0.894$, $T_{max} = 0.894$
Radiation source: Bruker TXS fine-focus rotating anode	9773 measured reflections
	3820 independent reflections
Bruker Helios multilayer confocal mirror monochromator	3065 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.050$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 1.5°$
φ and ω scans	$h = -10\rightarrow10$
	$k = -10\rightarrow10$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$l = -18\rightarrow18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.055$	
$wR(F^2) = 0.161$	
$S = 1.07$	Hydrogen site location: inferred from neighbouring sites
3820 reflections	
190 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0842P)^2 + 3.4063P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 2.34$ e Å^{-3}
$\Delta\rho_{min} = -1.13$ e Å^{-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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.7414 (11)	0.3494 (11)	1.2804 (5)	0.0208 (15)
C2	0.7832 (11)	0.2717 (10)	1.2163 (5)	0.0200 (15)
H2A	0.7957	0.1652	1.2252	0.024*
C3	0.7600 (10)	0.5445 (10)	1.1458 (5)	0.0171 (14)
C4	0.7523 (10)	0.6656 (10)	1.0854 (5)	0.0147 (14)
C5	0.7096 (11)	0.8045 (10)	1.1130 (5)	0.0176 (15)
C6	0.7518 (10)	0.8433 (10)	0.9411 (5)	0.0188 (15)
C7	0.7691 (10)	0.9104 (10)	0.8586 (5)	0.0168 (14)
C8	0.7811 (11)	1.1023 (10)	0.7195 (5)	0.0195 (15)
C9	0.8259 (11)	0.9774 (10)	0.6922 (6)	0.0227 (16)
C10	0.5811 (14)	1.2907 (13)	0.6735 (8)	0.040 (2)
H10A	0.5663	1.3860	0.6401	0.060*
H10B	0.6051	1.3221	0.7424	0.060*
H10C	0.4633	1.1708	0.6481	0.060*
C11	0.7773 (12)	0.7290 (12)	0.5471 (7)	0.0317 (19)
H11A	0.8072	0.7093	0.4888	0.048*
H11B	0.6381	0.6763	0.5324	0.048*
H11C	0.8218	0.6686	0.5964	0.048*
I1	0.72165 (7)	0.26967 (7)	1.41327 (4)	0.02158 (17)
O1	0.6819 (8)	0.8263 (7)	1.1898 (4)	0.0248 (12)
S2	0.6928 (3)	0.9427 (3)	1.02369 (13)	0.0204 (4)
S3	0.7856 (3)	0.6574 (3)	0.97138 (13)	0.0192 (4)
S4	0.7150 (3)	0.5414 (2)	1.25643 (13)	0.0180 (4)
S5	0.8134 (3)	0.3773 (3)	1.11542 (14)	0.0223 (4)
S6	0.7799 (3)	1.2779 (3)	0.65508 (14)	0.0222 (4)
S7	0.8283 (3)	0.8205 (3)	0.77148 (14)	0.0215 (4)
S8	0.7337 (3)	1.0982 (3)	0.83040 (14)	0.0212 (4)
S9	0.8974 (4)	0.9749 (3)	0.59090 (16)	0.0318 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.018 (4)	0.025 (4)	0.019 (4)	0.011 (3)	0.004 (3)	0.005 (3)
C2	0.029 (4)	0.017 (4)	0.018 (4)	0.015 (3)	0.008 (3)	0.006 (3)
C3	0.014 (3)	0.015 (3)	0.021 (4)	0.005 (3)	0.006 (3)	0.001 (3)
C4	0.018 (3)	0.014 (3)	0.016 (3)	0.010 (3)	0.006 (3)	0.004 (3)
C5	0.021 (4)	0.021 (4)	0.014 (3)	0.011 (3)	0.007 (3)	0.004 (3)
C6	0.019 (4)	0.020 (4)	0.018 (4)	0.010 (3)	0.006 (3)	0.003 (3)
C7	0.017 (3)	0.017 (4)	0.014 (3)	0.007 (3)	0.005 (3)	0.002 (3)
C8	0.022 (4)	0.021 (4)	0.014 (4)	0.008 (3)	0.010 (3)	0.005 (3)
C9	0.024 (4)	0.016 (4)	0.027 (4)	0.005 (3)	0.014 (3)	0.007 (3)
C10	0.045 (6)	0.035 (5)	0.062 (7)	0.028 (5)	0.032 (5)	0.027 (5)
C11	0.030 (4)	0.026 (4)	0.038 (5)	0.010 (4)	0.016 (4)	0.002 (4)
I1	0.0234 (3)	0.0216 (3)	0.0216 (3)	0.0115 (2)	0.0088 (2)	0.00788 (19)
O1	0.034 (3)	0.022 (3)	0.026 (3)	0.017 (3)	0.014 (3)	0.010 (2)
S2	0.0297 (10)	0.0244 (10)	0.0164 (9)	0.0194 (8)	0.0092 (8)	0.0063 (7)
S3	0.0267 (10)	0.0213 (9)	0.0160 (9)	0.0154 (8)	0.0094 (8)	0.0053 (7)
S4	0.0220 (9)	0.0180 (9)	0.0191 (9)	0.0113 (7)	0.0111 (7)	0.0063 (7)
S5	0.0311 (10)	0.0206 (9)	0.0213 (10)	0.0160 (8)	0.0110 (8)	0.0041 (7)
S6	0.0270 (10)	0.0246 (10)	0.0191 (9)	0.0134 (8)	0.0119 (8)	0.0101 (7)
S7	0.0282 (10)	0.0221 (9)	0.0194 (9)	0.0145 (8)	0.0113 (8)	0.0048 (7)
S8	0.0267 (10)	0.0261 (10)	0.0185 (9)	0.0169 (8)	0.0109 (8)	0.0084 (7)
S9	0.0504 (13)	0.0232 (10)	0.0270 (11)	0.0150 (10)	0.0265 (10)	0.0058 (8)

Geometric parameters (Å, º)

C1—C2	1.337 (11)	C7—S7	1.755 (7)
C1—S4	1.746 (8)	C7—S8	1.762 (8)
C1—I1	2.083 (8)	C8—C9	1.349 (11)
C2—S5	1.741 (8)	C8—S6	1.755 (8)
C2—H2A	0.9500	C8—S8	1.763 (7)
C3—C4	1.365 (10)	C9—S9	1.736 (8)
C3—S5	1.737 (7)	C9—S7	1.765 (8)
C3—S4	1.751 (8)	C10—S6	1.792 (9)
C4—C5	1.444 (10)	C10—H10A	0.9800
C4—S3	1.764 (7)	C10—H10B	0.9800
C5—O1	1.230 (9)	C10—H10C	0.9800
C5—S2	1.777 (8)	C11—S9	1.813 (9)
C6—C7	1.350 (10)	C11—H11A	0.9800
C6—S2	1.747 (8)	C11—H11B	0.9800
C6—S3	1.747 (8)	C11—H11C	0.9800
C2—C1—S4	118.7 (6)	C8—C9—S9	124.2 (6)
C2—C1—I1	124.9 (6)	C8—C9—S7	116.2 (6)
S4—C1—I1	116.2 (4)	S9—C9—S7	119.4 (5)
C1—C2—S5	116.1 (6)	S6—C10—H10A	109.5
C1—C2—H2A	122.0	S6—C10—H10B	109.5

S5—C2—H2A	122.0	H10A—C10—H10B	109.5
C4—C3—S5	121.0 (6)	S6—C10—H10C	109.5
C4—C3—S4	124.0 (6)	H10A—C10—H10C	109.5
S5—C3—S4	115.1 (4)	H10B—C10—H10C	109.5
C3—C4—C5	119.7 (7)	S9—C11—H11A	109.5
C3—C4—S3	122.9 (6)	S9—C11—H11B	109.5
C5—C4—S3	117.3 (5)	H11A—C11—H11B	109.5
O1—C5—C4	124.7 (7)	S9—C11—H11C	109.5
O1—C5—S2	121.3 (6)	H11A—C11—H11C	109.5
C4—C5—S2	113.9 (5)	H11B—C11—H11C	109.5
C7—C6—S2	120.1 (6)	C6—S2—C5	96.5 (4)
C7—C6—S3	123.1 (6)	C6—S3—C4	95.3 (3)
S2—C6—S3	116.8 (4)	C1—S4—C3	94.2 (4)
C6—C7—S7	123.5 (6)	C3—S5—C2	95.8 (4)
C6—C7—S8	121.9 (6)	C8—S6—C10	102.2 (4)
S7—C7—S8	114.6 (4)	C7—S7—C9	96.0 (4)
C9—C8—S6	124.3 (6)	C7—S8—C8	95.1 (4)
C9—C8—S8	118.1 (6)	C9—S9—C11	101.7 (4)
S6—C8—S8	117.4 (4)		