

N(3)—C(13)	1.464 (3)	1.461 (3)	N(3)—N(4)—C(15)—C(14)	1.9 (3)	-16.0 (4)
N(3)—N(4)	1.415 (3)	1.404 (3)	N(4)—C(15)—C(14)—C(13)	18.5 (3)	-0.1 (3)
C(13)—C(14)	1.513 (4)	1.486 (5)	C(15)—C(14)—C(13)—N(3)	-31.9 (3)	15.2 (5)
C(14)—C(15)	1.513 (4)	1.487 (5)	C(14)—C(13)—N(3)—N(4)	33.0 (3)	-25.2 (4)
C(15)—N(4)	1.471 (3)	1.467 (3)	C(13)—N(3)—N(4)—C(15)	-22.3 (3)	26.4 (3)
N(4)—C(16)	1.344 (4)	1.351 (3)	N(3)—N(4)—C(16)—O(5)	15.5 (3)	-16.1 (3)
C(16)—O(4)	1.206 (3)	1.211 (3)	N(4)—C(16)—O(5)—C(17)	168.6 (3)	-176.2 (3)
C(16)—O(5)	1.344 (2)	1.339 (3)	C(16)—O(5)—C(17)—C(18)	-179.1 (3)	162.5 (3)
O(5)—C(17)	1.431 (4)	1.447 (3)			
C(17)—C(18)	1.487 (4)	1.502 (4)			
C(18)—C(19)	1.369 (5)	1.386 (5)			
C(18)—C(23)	1.366 (5)	1.388 (4)			
C(19)—C(20)	1.374 (4)	1.384 (4)			
C(20)—C(21)	1.357 (6)	1.379 (6)			
C(21)—C(22)	1.353 (6)	1.373 (5)			
C(22)—C(23)	1.380 (4)	1.380 (4)			
C(2)—C(1)—C(6)	118.9 (2)	120.0 (4)			
C(1)—C(2)—C(3)	121.0 (3)	120.4 (4)			
C(2)—C(3)—C(4)	120.2 (3)	119.8 (4)			
C(3)—C(4)—C(5)	117.9 (2)	118.9 (3)			
C(3)—C(4)—C(7)	121.1 (2)	120.7 (3)			
C(5)—C(4)—C(7)	120.9 (2)	120.9 (3)			
C(4)—C(5)—C(6)	121.7 (3)	120.5 (3)			
C(1)—C(6)—C(5)	120.2 (3)	120.4 (5)			
C(4)—C(7)—O(1)	106.8 (2)	107.9 (3)			
C(7)—O(1)—C(8)	114.7 (2)	114.9 (2)			
O(1)—C(8)—O(2)	125.1 (3)	125.7 (3)			
O(1)—C(8)—N(1)	111.1 (2)	111.8 (2)			
O(2)—C(8)—N(1)	123.8 (2)	122.4 (2)			
C(8)—N(1)—C(9)	122.9 (2)	124.0 (3)			
C(8)—N(1)—N(2)	120.2 (2)	120.5 (2)			
C(9)—N(1)—N(2)	116.6 (2)	110.7 (3)			
N(1)—C(9)—C(10)	102.9 (2)	104.6 (3)			
O(3)—C(12)—N(3)	124.0 (2)	125.0 (2)			
C(12)—N(3)—C(13)	122.7 (2)	124.5 (2)			
C(12)—N(3)—N(4)	115.1 (2)	115.5 (2)			
C(13)—N(3)—N(4)	105.4 (2)	107.1 (2)			
N(3)—C(13)—C(14)	103.6 (2)	104.4 (3)			
C(13)—C(14)—C(15)	104.9 (2)	108.3 (3)			
C(14)—C(15)—N(4)	103.4 (2)	103.9 (3)			
N(3)—N(4)—C(15)	111.2 (2)	109.5 (2)			
N(3)—N(4)—C(16)	120.6 (2)	118.7 (2)			
C(15)—N(4)—C(16)	121.8 (2)	123.4 (2)			
N(4)—C(16)—O(4)	123.7 (2)	123.6 (2)			
N(4)—C(16)—O(5)	111.2 (2)	111.2 (2)			
O(4)—C(16)—O(5)	125.0 (2)	125.2 (2)			
C(16)—O(5)—C(17)	116.3 (2)	116.7 (2)			
O(5)—C(17)—C(18)	107.0 (3)	106.6 (2)			
C(17)—C(18)—C(19)	122.0 (3)	120.7 (3)			
C(17)—C(18)—C(23)	119.9 (3)	120.1 (3)			
C(9)—C(10)—C(11)	105.0 (2)	106.7 (3)			
C(10)—C(11)—N(2)	103.8 (2)	105.0 (3)			
N(1)—N(2)—C(11)	105.1 (2)	105.1 (2)			
N(1)—N(2)—C(12)	113.4 (2)	112.3 (2)			
C(11)—N(2)—C(12)	121.3 (2)	119.4 (2)			
N(2)—C(12)—O(3)	124.8 (2)	124.6 (3)			
N(2)—C(12)—N(3)	111.1 (2)	110.4 (2)			
C(19)—C(18)—C(23)	118.0 (2)	119.2 (2)			
C(18)—C(19)—C(20)	121.0 (4)	120.0 (3)			
C(19)—C(20)—C(21)	119.9 (3)	120.2 (3)			
C(20)—C(21)—C(22)	120.2 (3)	119.9 (3)			
C(21)—C(22)—C(23)	119.7 (4)	120.2 (3)			
C(18)—C(23)—C(22)	121.1 (3)	120.4 (3)			
C(4)—C(7)—O(1)—C(8)	-179.8 (2)	-170.7 (2)			
C(7)—O(1)—C(8)—N(1)	172.5 (2)	-178.8 (3)			
O(1)—C(8)—N(1)—N(2)	11.4 (3)	-10.5 (4)			
O(1)—C(8)—N(1)—C(9)	163.5 (2)	-163.5 (3)			
C(8)—N(1)—N(2)—C(12)	-93.2 (3)	101.1 (3)			
N(1)—N(2)—C(11)—C(10)	33.4 (3)	-26.8 (3)			
N(2)—C(11)—C(10)—C(9)	-32.0 (3)	16.1 (4)			
C(11)—C(10)—C(9)—N(1)	18.1 (3)	0.1 (4)			
C(10)—C(9)—N(1)—N(2)	2.5 (3)	-18.0 (3)			
C(9)—N(1)—N(2)—C(11)	-22.9 (3)	28.5 (3)			
N(1)—N(2)—C(12)—N(3)	178.2 (2)	177.2 (2)			
N(2)—C(12)—N(3)—N(4)	-173.0 (2)	179.7 (2)			
N(2)—C(12)—N(3)—C(13)	-42.4 (3)	43.4 (3)			
C(12)—N(3)—N(4)—C(16)	-91.2 (3)	93.6 (4)			

Program used to solve the structure: *SHELXS86* (Sheldrick, 1990). Refinement was by full-matrix least-squares methods using *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Five 3,3'-Bridged 2,2'-Dithiophenes

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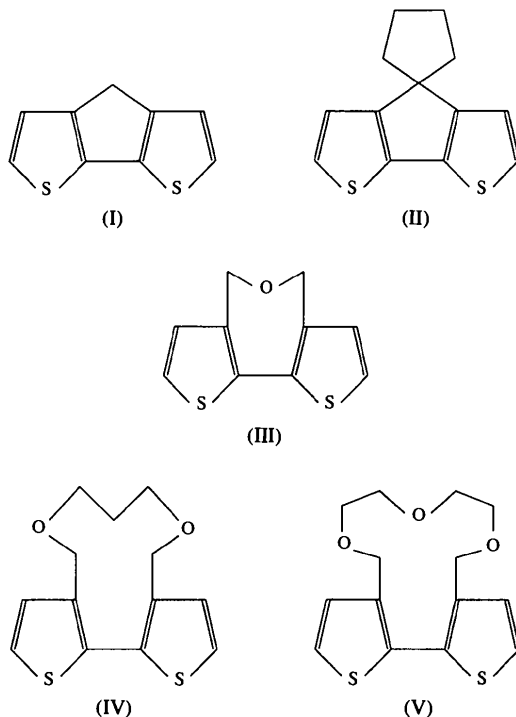
Abstract

The crystal structures of the compounds 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, C₉H₆S₂ (I), spiro[4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-4,1'-cyclopentane], C₁₃H₁₂S₂ (II), 4*H*,6*H*-dithieno[3,2-*c*:2',3'-*e*]oxepine, C₁₀-

H₈OS₂ (III), 6*H*-4,7,8,10-tetrahydrodithieno[3,2-*g*:2',3'-*i*][1,5]dioxacycloundecene, C₁₃H₁₄O₂S₂ (IV) and 4,6,7,9,10,12-hexahydrodithieno[3,2-*i*:2',3'-*k*][1,4,7]trioxacyclotridecene, C₁₄H₁₆O₃S₂ (V), have been determined at room temperature. For low values of the S—C—C—S torsion angle [(I), (II) and (III)], the C—C bond length between the rings is *ca* 0.02 Å shorter than the values found for (IV) and (V), where torsion angles are *ca* 90°; this is in agreement with the change of the conjugation between the thiophene rings.

Comment

Polyheterocycles are a growing class of advanced materials for electronics and non-linear optics; among them, poly-2,5-thiophene derivatives are particularly interesting due to their chemical stability. There are many papers (Roncali, 1992, and references therein) studying the relationships between the structure of the monomeric thiophene unit and the electrical and spectroscopic properties of the resulting polymer. Recently, Benincori *et al.* (1994) synthesized and studied the properties of polymers of bithiophene and terthiophene monomers showing a well defined torsion angle (θ_{SCCS}) between the thiophene rings. As part of this project it was planned to determine the variation of the electrical properties of the polymers with the introduction of various 3,3'-bridges on the 2,2'-bithiophene monomer, with particular attention to the variation of θ_{SCCS} and, consequently, to the conjugation between the thiophene rings. On this basis, we decided to undertake the crystallographic study of the five compounds (I)–(V).



(I) is the fundamental 3,3'-bridged 2,2'-bithiophene structure and its crystal structure has been previously determined at 113 K (Koster, van Bolhuis & Visser, 1970, hereinafter KBV); we decided to redetermine this structure at room temperature to make the comparison between the bond lengths of the different structures more reliable. The structure of (I) is confirmed: no phase transition has been found between 113 K and room temperature. Figs. 1–5 show *ORTEP* plots (Johnson, 1976) of (I) (molecule *a*), (II) (molecule *a*), (III) (molecule *b*), (IV) and (V), respectively. It can be seen that the numbering scheme of the dithiophene group is the same for all compounds in order to to make the comparison of chemically equivalent parameters easier. When the asymmetric unit holds more than one molecule [(I), (II) and (III)], the chemically equivalent atoms are marked with a suffix *a*, *b* or *c*. As expected, for (I), due to the large increase of thermal libration with temperature, an apparent shortening of bond distances with respect to the KBV data has been found; the mean bond-length variation involving heavy atoms is 0.012 Å. Using the rigid-body assumption, fitting the thermal parameters using the LST model (Schomaker & Trueblood, 1968), the following eigenvalues of libration tensor have been obtained: 0.0076 (5), 0.0033 (1), 0.0022 (1) and 0.0083 (5), 0.0024 (1), 0.0015 (2) rad² for molecules (Ia) and (Ib), respectively; this corresponds to a mean bond-length correction of 0.006 Å, which is clearly too small. For non-rigid molecules such as (IV), (V) and possibly (III), the corrections are even less reliable. For these reasons, only homogeneous data can be compared, obtained at the same temperature and uncorrected for thermal libration. Table 11 reports the mean values of some chemically equivalent parameters of the five compounds listed above and of additional two-bridged dithiophenes, namely 7,9,10,12-tetrahydrodithieno[3,2-*f*:2',3'-*h*][1,4]dioxecene (VI) and 7,9,10,12,19,21,22,24-octahydrodithieno[3,2-*f*:2',3'-*h*:3''':2''-*p*:2''':3''']-[1,4,11,14]tetraoxacycloicosene (VII), recently studied by Zimmer *et al.* (1993). The seven structures can be divided into two groups: (I), (II) and (III) with syn-periplanar arrangement of thiophenes and the remaining with synclinal or anticlinal conformation. In the first group, where the torsion angles θ_{SCCS} are less than 11.8°, the mean inter-ring bond length $d_{\text{C5-C6}}$ ranges between 1.441 and 1.450 Å, while in the second, with θ_{SCCS} between 45.1 and 117.4°, $d_{\text{C5-C6}}$ is 1.461–1.469 Å. The increase of θ_{SCCS} , the lengthening of $d_{\text{C5-C6}}$ and the reduction of the conjugation between the thiophene ring are connected phenomena; together with the difference in electric properties of the 3,3'-bridge, they can explain the variation of some chemical and physical properties such as infrared and Raman spectra, redox potential and conductivity of doped polymers of these compounds (see Benincori *et al.*, 1994). The strain induced by the presence of the short bridge

(—C11—) in (I) and (II) is also evident in Table 11; in fact, these two compounds show a very large (*ca* 20°) variation of the angles C4—C5—C6 and S1—C5—C6 in opposite directions and a significant shortening of the

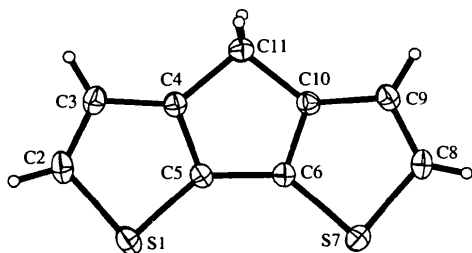


Fig. 1. ORTEP (Johnson, 1976) plot of (I) (molecule *a*). Displacement ellipsoids are at the 20% probability level and H atoms are not drawn to scale.

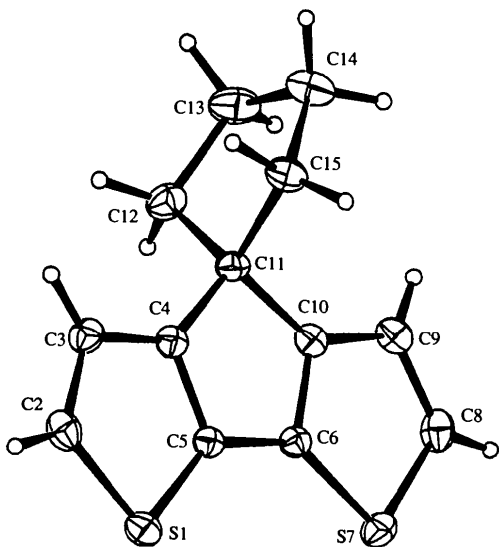


Fig. 2. ORTEP (Johnson, 1976) plot of (II) (molecule *b*). Displacement ellipsoids are at the 20% probability level and H atoms are not drawn to scale.

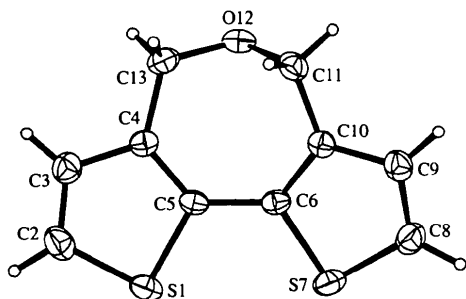


Fig. 3. ORTEP (Johnson, 1976) plot of (III) (molecule *a*). Displacement ellipsoids are at the 20% probability level and H atoms are not drawn to scale.

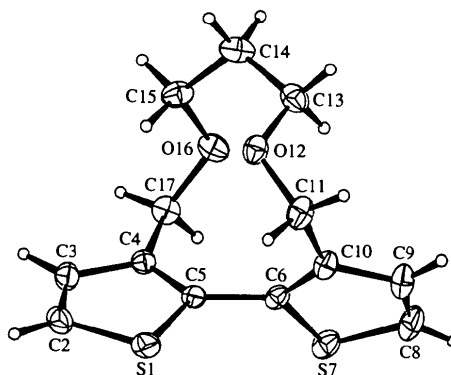


Fig. 4. ORTEP (Johnson, 1976) plot of (IV). Displacement ellipsoids are at the 20% probability level and H atoms are not drawn to scale.

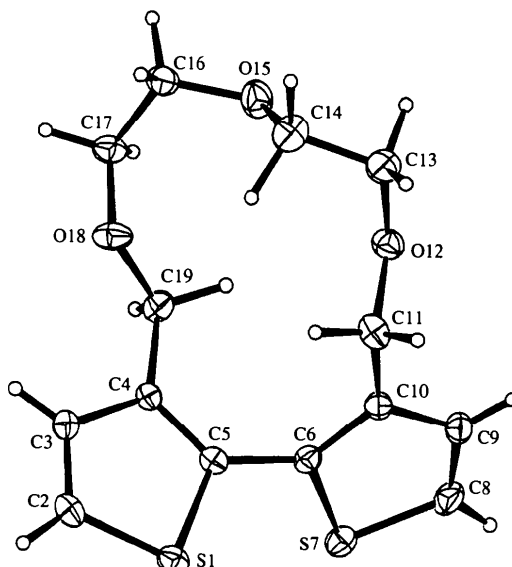


Fig. 5. ORTEP (Johnson, 1976) plot of (V). Displacement ellipsoids are at the 20% probability level and H atoms are not drawn to scale.

S1—C5 bond length with respect to all the other structures.

The packing of (I) and (II) is ruled only by residual forces; particularly impressive is the packing of (II), shown in Fig. 6, which has three independent molecules in the asymmetric unit; the projection along the *c* axis has the appearance of two gears; the first gear consists of six molecules *c*, around the site symmetry 3, the second of three molecules *a* and three molecules *b* located around the threefold axis. In spite of the complex crystal packing, the differences between the three independent molecules are not particularly relevant. For (I) the two independent molecules are also very similar, whereas for (III) there are further differences, such as the modulus of θ_{SCS} which is 7.7(2) and 11.8(2)° in molecules *a* and *b*, respectively.

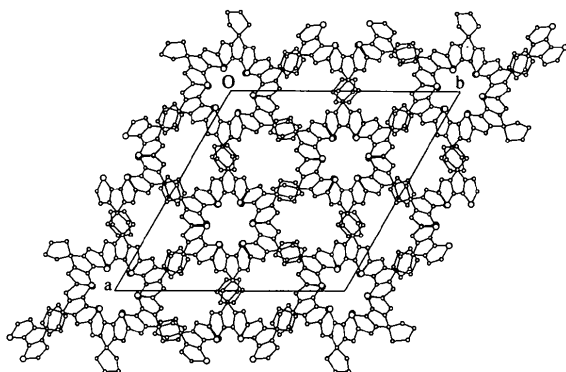


Fig. 6. Packing of (II) projected down the *c* axis. H atoms are omitted for clarity.

Experimental

The synthesis of compounds (I)–(V) is described in Benincori *et al.* (1995).

Compound (I)

Crystal data

$C_9H_6S_2$
 $M_r = 178.266$
 Monoclinic
 $P2_1/c$
 $a = 12.653$ (1) Å
 $b = 11.233$ (1) Å
 $c = 11.388$ (1) Å
 $\beta = 98.40$ (1)°
 $V = 1601.2$ (3) Å³
 $Z = 8$
 $D_x = 1.479$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 8.1$ – 14.6 °
 $\mu = 0.562$ mm⁻¹
 Room temperature
 Crystal sealed in Lindemann glass capillary to prevent sublimation
 $0.30 \times 0.30 \times 0.28$ mm
 Colourless; became yellowish

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 3126 measured reflections
 3126 independent reflections
 2274 observed reflections
 $[I_o > 2\sigma(I_o)]$

$\theta_{max} = 26$ °
 $h = -15 \rightarrow 15$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 10$
 1 standard reflection
 frequency: 360 min
 intensity decay: negligible

Refinement

Refinement on F
 $R = 0.031$
 $wR = 0.035$
 $S = 1.951$
 2274 reflections
 248 parameters
 All H-atom parameters refined
 $w = 2F_o/Lp/[\sigma^2(I_o) + (0.02I_o)^2]^{1/2}$
 $(\Delta/\sigma)_{max} = 0.04$

$|\Delta\rho| = 0.22$ e Å⁻³
 Extinction correction: Stout & Jensen (1968)
 Extinction coefficient: 3.9 (2) $\times 10^{-6}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.3.1 and 2.2C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (I)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S1a	0.31929 (5)	0.02325 (5)	0.45912 (5)	0.0561 (2)
S7a	0.53241 (4)	0.29049 (5)	0.46326 (5)	0.0520 (2)
C2a	0.2170 (2)	-0.0230 (2)	0.3515 (2)	0.0587 (7)
C3a	0.2103 (2)	0.0417 (2)	0.2512 (2)	0.0527 (7)
C4a	0.2892 (2)	0.1315 (2)	0.2590 (2)	0.0425 (6)
C5a	0.3540 (2)	0.1320 (2)	0.3668 (2)	0.0403 (6)
C6a	0.4322 (2)	0.2257 (2)	0.3669 (2)	0.0392 (6)
C8a	0.5531 (2)	0.3937 (2)	0.3575 (2)	0.0519 (7)
C9a	0.4867 (2)	0.3789 (2)	0.2542 (2)	0.0502 (7)
C10a	0.4160 (2)	0.2828 (2)	0.2595 (2)	0.0417 (7)
C11a	0.3221 (2)	0.2285 (2)	0.1806 (2)	0.0492 (6)
S1b	0.06874 (4)	0.41533 (5)	0.28951 (5)	0.0519 (2)
S7b	-0.00778 (5)	0.65612 (5)	0.02972 (5)	0.0533 (2)
C2b	0.1848 (2)	0.3933 (2)	0.3878 (2)	0.0499 (7)
C3b	0.2621 (2)	0.4730 (2)	0.3734 (2)	0.0457 (7)
C4b	0.2282 (2)	0.5550 (2)	0.2825 (2)	0.0412 (6)
C5b	0.1257 (2)	0.5349 (2)	0.2285 (2)	0.0400 (6)
C6b	0.0974 (2)	0.6221 (2)	0.1369 (2)	0.0419 (6)
C8b	0.0634 (2)	0.7729 (2)	-0.0190 (2)	0.0556 (7)
C9b	0.1624 (2)	0.7837 (2)	0.0435 (2)	0.0547 (7)
C10b	0.1826 (2)	0.6968 (2)	0.1331 (2)	0.0455 (6)
C11b	0.2741 (2)	0.6614 (2)	0.2270 (2)	0.0504 (7)

Table 2. Selected geometric parameters (Å, °) for (I)

S1a–C2a	1.727 (2)	S1b–C2b	1.729 (2)
S1a–C5a	1.710 (2)	S1b–C5b	1.718 (2)
S7a–C6a	1.713 (2)	S7b–C6b	1.712 (2)
S7a–C8a	1.719 (2)	S7b–C8b	1.728 (2)
C2a–C3a	1.346 (3)	C2b–C3b	1.354 (3)
C3a–C4a	1.413 (3)	C3b–C4b	1.405 (3)
C4a–C5a	1.373 (3)	C4b–C5b	1.370 (3)
C4a–C11a	1.505 (3)	C4b–C11b	1.508 (3)
C5a–C6a	1.444 (3)	C5b–C6b	1.438 (3)
C6a–C10a	1.370 (3)	C6b–C10b	1.372 (3)
C8a–C9a	1.352 (3)	C8b–C9b	1.353 (3)
C9a–C10a	1.409 (3)	C9b–C10b	1.408 (3)
C10a–C11a	1.510 (3)	C10b–C11b	1.510 (3)
C2a–S1a–C5a	90.7 (1)	C2b–S1b–C5b	90.4 (1)
C6a–S7a–C8a	90.7 (1)	C6b–S7b–C8b	90.6 (1)
S1a–C2a–C3a	112.8 (2)	S1b–C2b–C3b	112.8 (2)
C2a–C3a–C4a	112.1 (2)	C2b–C3b–C4b	112.0 (2)
C3a–C4a–C11a	137.2 (2)	C3b–C4b–C11b	137.2 (2)
C3a–C4a–C5a	112.5 (2)	C3b–C4b–C5b	112.9 (2)
C5a–C4a–C11a	110.3 (2)	C5b–C4b–C11b	109.9 (2)
S1a–C5a–C4a	111.9 (2)	S1b–C5b–C4b	111.9 (2)
C4a–C5a–C6a	108.9 (2)	C4b–C5b–C6b	109.4 (2)
S1a–C5a–C6a	139.2 (2)	S1b–C5b–C6b	138.7 (2)
S7a–C6a–C5a	138.8 (2)	S7b–C6b–C5b	139.0 (2)
C5a–C6a–C10a	109.1 (2)	C5b–C6b–C10b	109.0 (2)
S7a–C6a–C10a	111.9 (2)	S7b–C6b–C10b	111.9 (2)
S7a–C8a–C9a	112.8 (2)	S7b–C8b–C9b	112.7 (2)
C8a–C9a–C10a	112.0 (2)	C8b–C9b–C10b	112.0 (2)
C6a–C10a–C9a	112.6 (2)	C6b–C10b–C9b	112.7 (2)
C9a–C10a–C11a	137.2 (2)	C9b–C10b–C11b	137.3 (2)
C6a–C10a–C11a	110.1 (2)	C6b–C10b–C11b	110.0 (2)
C4a–C11a–C10a	101.6 (2)	C4b–C11b–C10b	101.7 (2)

Compound (II)

Crystal data

$C_{13}H_{12}S_2$
 $M_r = 232.36$
 Trigonal
 $P\bar{3}$
 $a = 21.792$ (4) Å
 $b = 21.792$ (4) Å
 $c = 12.566$ (2) Å
 $\alpha = 90.00$ °

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 9.7$ – 17.9 °
 $\mu = 0.4079$ mm⁻¹
 Room temperature
 Irregular prism

$V = 5168 (2) \text{ \AA}^3$
 $Z = 18$
 $D_x = 1.3439 \text{ Mg m}^{-3}$

$0.034 \times 0.030 \times 0.022 \text{ mm}$
 Golden yellow

C4c	0.1715 (1)	-0.0487 (1)	0.6676 (2)	0.0379 (9)
C5c	0.1212 (1)	-0.0333 (1)	0.7017 (2)	0.0395 (10)
C6c	0.0868 (1)	-0.0753 (1)	0.7954 (2)	0.0383 (9)
C8c	0.0335 (1)	-0.1484 (1)	0.9515 (2)	0.0510 (11)
C9c	0.0843 (1)	-0.1595 (1)	0.9082 (2)	0.0470 (10)
C10c	0.1157 (1)	-0.1171 (1)	0.8176 (2)	0.0372 (9)
C11c	0.1729 (1)	-0.1049 (1)	0.7368 (2)	0.0377 (9)
C12c	0.2441 (1)	-0.0861 (1)	0.7875 (2)	0.0538 (11)
C13c	0.2377 (1)	-0.1560 (1)	0.8197 (3)	0.0642 (11)
C14c	0.1783 (1)	-0.2132 (1)	0.7505 (2)	0.0597 (11)
C15c	0.1559 (1)	-0.1731 (1)	0.6761 (2)	0.0473 (10)

Data collection

Enraf-Nonius CAD-4
 diffractometer

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 25^\circ$

$\theta/2\theta$ scans

$h = 0 \rightarrow 22$

Absorption correction:
 none

$k = 0 \rightarrow 13$

$l = -14 \rightarrow 12$

6637 measured reflections

1 standard reflection

6045 independent reflections

frequency: 360 min

3498 observed reflections

intensity decay: negligible

$[I_o > 2\sigma(I_o)]$

Refinement

Refinement on F^2

$|\Delta\rho| = 0.21 \text{ e \AA}^{-3}$

$R = 0.034$

Extinction correction: Stout
 & Jensen (1968)

$wR = 0.035$

Extinction coefficient:

$S = 1.654$

$7.7 (6) \times 10^{-8}$

3498 reflections

Atomic scattering factors

551 parameters

All H-atom parameters

from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV, Tables
 2.2A, 2.3.1 and 2.2C)

refined

$w = 2F_o Lp / [\sigma^2(I_o) + (0.02I_o)^2]^{1/2}$

$(\Delta/\sigma)_{\text{max}} = 0.15$

Table 4. Selected geometric parameters (\AA , $^\circ$) for (II)

S1a—C2a	1.716 (2)	C4b—C11b	1.517 (3)
S1a—C5a	1.707 (2)	C5b—C6b	1.447 (3)
S7a—C6a	1.708 (2)	C6b—C10b	1.369 (3)
S7a—C8a	1.722 (2)	C8b—C9b	1.355 (2)
C2a—C3a	1.352 (3)	C9b—C10b	1.418 (3)
C3a—C4a	1.421 (3)	C10b—C11b	1.516 (2)
C4a—C5a	1.365 (2)	S1c—C2c	1.719 (2)
C4a—C11a	1.503 (3)	S1c—C5c	1.711 (2)
C5a—C6a	1.448 (3)	S7c—C6c	1.708 (2)
C6a—C10a	1.374 (3)	S7c—C8c	1.711 (2)
C8a—C9a	1.355 (2)	C2c—C3c	1.354 (3)
C9a—C10a	1.421 (3)	C3c—C4c	1.411 (3)
C10a—C11a	1.518 (2)	C4c—C5c	1.366 (3)
S1b—C2b	1.712 (2)	C4c—C11c	1.515 (3)
S1b—C5b	1.711 (2)	C5c—C6c	1.449 (3)
S7b—C6b	1.707 (2)	C6c—C10c	1.370 (3)
S7b—C8b	1.717 (2)	C8c—C9c	1.359 (3)
C2b—C3b	1.355 (3)	C9c—C10c	1.409 (3)
C3b—C4b	1.408 (3)	C10c—C11c	1.525 (3)
C4b—C5b	1.369 (2)	C14c—C15c	1.517 (3)

C2a—S1a—C5a	90.6 (1)	S7b—C6b—C5b	138.3 (2)
C6a—S7a—C8a	90.5 (1)	C5b—C6b—C10b	108.7 (2)
S1a—C2a—C3a	112.9 (2)	S7b—C6b—C10b	113.0 (2)
C2a—C3a—C4a	111.9 (2)	S7b—C8b—C9b	113.0 (2)
C3a—C4a—C11a	136.5 (2)	C8b—C9b—C10b	112.0 (2)
C3a—C4a—C5a	111.8 (2)	C6b—C10b—C9b	111.6 (2)
C5a—C4a—C11a	111.7 (2)	C9b—C10b—C11b	137.6 (2)
S1a—C5a—C4a	112.7 (2)	C6b—C10b—C11b	110.9 (2)
C4a—C5a—C6a	108.6 (2)	C4b—C11b—C10b	100.7 (2)
S1a—C5a—C6a	138.7 (2)	C2c—S1c—C5c	90.4 (1)
S7a—C6a—C5a	138.2 (2)	C6c—S7c—C8c	90.4 (1)
C5a—C6a—C10a	108.6 (2)	S1c—C2c—C3c	112.8 (2)
S7a—C6a—C10a	113.1 (2)	C2c—C3c—C4c	112.1 (2)
S7a—C8a—C9a	112.7 (2)	C3c—C4c—C11c	136.7 (2)
C8a—C9a—C10a	112.6 (2)	C3c—C4c—C5c	112.1 (2)
C6a—C10a—C9a	111.1 (2)	C5c—C4c—C11c	111.2 (2)
C9a—C10a—C11a	138.1 (2)	S1c—C5c—C4c	112.6 (2)
C6a—C10a—C11a	110.8 (2)	C4c—C5c—C6c	109.0 (2)
C4a—C11a—C10a	100.4 (2)	S1c—C5c—C6c	138.4 (2)
C2b—S1b—C5b	90.6 (1)	S7c—C6c—C5c	138.3 (2)
C6b—S7b—C8b	90.4 (1)	C5c—C6c—C10c	108.7 (2)
S1b—C2b—C3b	113.0 (2)	S7c—C6c—C10c	112.9 (2)
C2b—C3b—C4b	111.9 (2)	S7c—C8c—C9c	112.9 (2)
C3b—C4b—C11b	137.1 (2)	C8c—C9c—C10c	112.2 (2)
C3b—C4b—C5b	112.3 (2)	C6c—C10c—C9c	111.5 (2)
C5b—C4b—C11b	110.6 (2)	C9c—C10c—C11c	137.6 (2)
S1b—C5b—C4b	112.2 (2)	C6c—C10c—C11c	110.8 (2)
C4b—C5b—C6b	109.1 (2)	C4c—C11c—C10c	100.3 (2)
S1b—C5b—C6b	138.7 (2)		

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S1a	-0.56533	-0.23274	0.40489	0.0487 (3)
S7a	-0.56931 (3)	-0.34072 (3)	0.14458 (6)	0.0491 (3)
C2a	-0.4967 (1)	-0.1702 (1)	0.4799 (2)	0.0530 (10)
C3a	-0.4324 (1)	-0.1550 (1)	0.4427 (2)	0.0477 (10)
C4a	-0.4379 (1)	-0.1957 (1)	0.3511 (2)	0.0387 (8)
C5a	-0.5068 (1)	-0.2395 (1)	0.3223 (2)	0.0367 (9)
C6a	-0.5081 (1)	-0.2794 (1)	0.2293 (2)	0.0375 (8)
C8a	-0.5029 (1)	-0.3419 (1)	0.0719 (2)	0.0539 (10)
C9a	-0.4375 (1)	-0.2970 (1)	0.1110 (2)	0.0488 (11)
C10a	-0.4396 (1)	-0.2602 (1)	0.2030 (2)	0.0397 (9)
C11a	-0.3876 (1)	-0.2044 (1)	0.2793 (2)	0.0410 (9)
C12a	-0.3317 (1)	-0.1363 (1)	0.2223 (2)	0.0557 (12)
C13a	-0.2742 (1)	-0.1516 (2)	0.1876 (3)	0.0734 (14)
C14a	-0.2788 (1)	-0.2089 (2)	0.2606 (3)	0.0708 (13)
C15a	-0.3392 (1)	-0.2269 (1)	0.3368 (2)	0.0531 (11)
S1b	0.56049 (3)	0.23704 (3)	0.09478 (6)	0.0486 (3)
S7b	0.66407 (3)	0.23250 (3)	0.35527 (6)	0.0470 (3)
C2b	0.4943 (1)	0.1710 (1)	0.0212 (2)	0.0538 (11)
C3b	0.4737 (1)	0.1054 (1)	0.0595 (2)	0.0473 (10)
C4b	0.5122 (1)	0.1078 (1)	0.1509 (2)	0.0380 (9)
C5b	0.5611 (1)	0.1757 (1)	0.1791 (2)	0.0379 (8)
C6b	0.5990 (1)	0.1739 (1)	0.2725 (2)	0.0364 (9)
C8b	0.6590 (1)	0.1636 (1)	0.4286 (2)	0.0509 (12)
C9b	0.6098 (1)	0.0992 (1)	0.3912 (2)	0.0463 (10)
C10b	0.5742 (1)	0.1047 (1)	0.3004 (2)	0.0370 (8)
C11b	0.5160 (1)	0.0550 (1)	0.2253 (2)	0.0386 (10)
C12b	0.5327 (1)	0.0021 (1)	0.1695 (2)	0.0495 (10)
C13b	0.5128 (2)	-0.0572 (1)	0.2499 (3)	0.0634 (12)
C14b	0.4559 (2)	-0.0572 (1)	0.3205 (3)	0.0685 (14)
C15b	0.4462 (1)	0.0040 (1)	0.2823 (2)	0.0515 (11)
S1c	0.11542 (4)	0.02733 (3)	0.62210 (6)	0.0549 (3)
S7c	0.02192 (3)	-0.08705 (3)	0.88315 (6)	0.0485 (3)
C2c	0.1817 (1)	0.0323 (1)	0.5420 (2)	0.0566 (13)
C3c	0.2061 (1)	-0.0108 (1)	0.5747 (2)	0.0479 (10)

Compound (III)*Crystal data*

C₁₀H₈OS₂

$M_r = 208.29$

Monoclinic

$P2_1/c$

$a = 14.030 (2) \text{ \AA}$

$b = 9.009 (2) \text{ \AA}$

$c = 16.306 (5) \text{ \AA}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 10.7\text{--}17.0^\circ$

$\mu = 0.4940 \text{ mm}^{-1}$

Room temperature

$\beta = 113.49 (2)^\circ$
 $V = 1890.2 (8) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.4639 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4
 diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

3848 measured reflections

3701 independent reflections

2466 observed reflections

$[I_o > 2\sigma(I_o)]$

Refinement

Refinement on F

$R = 0.032$

$wR = 0.036$

$S = 1.841$

2466 reflections

300 parameters

All H-atom parameters

refined

$w = 2F_o Lp / [\sigma^2(I_o)$

$+ (0.02I_o)^2]^{1/2}$

$(\Delta/\sigma)_{\max} = 0.003$

Irregular and partially
 rounded prism
 $0.38 \times 0.32 \times 0.25 \text{ mm}$
 Yellow

$R_{\text{int}} = 0.018$

$\theta_{\max} = 26^\circ$

$h = 0 \rightarrow 17$

$k = 0 \rightarrow 11$

$l = -20 \rightarrow 18$

1 standard reflection

frequency: 360 min

intensity decay: negligible

$|\Delta\rho| = 0.21 \text{ e \AA}^{-3}$

Extinction correction: Stout

& Jensen (1968)

Extinction coefficient:

$5.2 (4) \times 10^{-7}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Tables

2.2A, 2.3.1 and 2.2C)

S7a—C8a	1.704 (2)	S7b—C8b	1.701 (2)
O12a—C11a	1.421 (2)	O12b—C11b	1.427 (2)
O12a—C13a	1.411 (3)	O12b—C13b	1.411 (3)
C2a—C3a	1.340 (4)	C2b—C3b	1.334 (3)
C3a—C4a	1.419 (2)	C3b—C4b	1.420 (3)
C4a—C5a	1.364 (2)	C4b—C5b	1.366 (1)
C4a—C13a	1.504 (3)	C4b—C13b	1.498 (3)
C5a—C6a	1.450 (2)	C5b—C6b	1.450 (2)
C6a—C10a	1.368 (3)	C6b—C10b	1.366 (2)
C8a—C9a	1.340 (4)	C8b—C9b	1.344 (3)
C9a—C10a	1.409 (3)	C9b—C10b	1.410 (3)
C10a—C11a	1.497 (4)	C10b—C11b	1.492 (2)
C2a—S1a—C5a	92.0 (1)	C2b—S1b—C5b	91.8 (1)
C6a—S7a—C8a	91.7 (1)	C6b—S7b—C8b	92.0 (1)
C11a—O12a—C13a	113.7 (1)	C11b—O12b—C13b	113.1 (2)
S1a—C2a—C3a	111.5 (2)	S1b—C2b—C3b	111.7 (2)
C2a—C3a—C4a	113.7 (2)	C2b—C3b—C4b	113.8 (3)
C3a—C4a—C13a	121.1 (2)	C3b—C4b—C13b	121.3 (2)
C3a—C4a—C5a	112.0 (2)	C3b—C4b—C5b	112.1 (2)
C5a—C4a—C13a	126.9 (2)	C5b—C4b—C13b	126.6 (2)
S1a—C5a—C4a	110.8 (1)	S1b—C5b—C4b	112.5 (1)
C4a—C5a—C6a	129.3 (2)	C4b—C5b—C6b	129.6 (2)
S1a—C5a—C6a	119.9 (1)	S1b—C5b—C6b	119.8 (1)
S7a—C6a—C5a	120.9 (1)	S7b—C6b—C5b	121.5 (1)
C5a—C6a—C10a	128.3 (2)	C5b—C6b—C10b	127.9 (2)
S7a—C6a—C10a	110.8 (1)	S7b—C6b—C10b	110.5 (1)
S7a—C8a—C9a	111.8 (2)	S7b—C8b—C9b	111.7 (2)
C8a—C9a—C10a	113.7 (3)	C8b—C9b—C10b	113.3 (2)
C6a—C10a—C9a	112.1 (3)	C6b—C10b—C9b	112.5 (2)
C9a—C10a—C11a	124.2 (2)	C9b—C10b—C11b	124.2 (2)
C6a—C10a—C11a	123.8 (2)	C6b—C10b—C11b	123.3 (2)
O12a—C11a—C10a	113.0 (2)	O12b—C11b—C10b	112.7 (2)
O12a—C13a—C4a	115.1 (2)	O12b—C13b—C4b	115.8 (2)

Compound (IV)*Crystal data*

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}_2$

$M_r = 266.37$

Monoclinic

$P2_1/n$

$a = 7.643 (2) \text{ \AA}$

$b = 24.604 (3) \text{ \AA}$

$c = 7.767 (1) \text{ \AA}$

$\beta = 115.29 (2)^\circ$

$V = 1320.6 (5) \text{ \AA}^3$

$Z = 4$

$D_x = 1.3398 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4

diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

3017 measured reflections

3017 independent reflections

2344 observed reflections

$[I_o > 2\sigma(I_o)]$

Refinement

Refinement on F

$R = 0.032$

$wR = 0.038$

$S = 2.097$

2344 reflections

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 10.2\text{--}16.9^\circ$

$\mu = 0.3736 \text{ mm}^{-1}$

Room temperature

Prism

$0.38 \times 0.38 \times 0.30 \text{ mm}$

Yellow–brown

$\theta_{\max} = 27.5^\circ$

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 31$

$l = -10 \rightarrow 9$

1 standard reflection

frequency: 360 min

intensity decay: negligible

$|\Delta\rho| = 0.15 \text{ e \AA}^{-3}$

Extinction correction: Stout

& Jensen (1968)

Extinction coefficient:

$1.47 (7) \times 10^{-6}$

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (III)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
S1a	−0.24609 (4)	0.35192 (7)	0.13717 (4)	0.0611 (2)
S7a	−0.29924 (5)	0.69592 (7)	0.09094 (4)	0.0701 (2)
O12a	−0.5328 (1)	0.4976 (2)	0.19257 (8)	0.0591 (5)
C2a	−0.2682 (2)	0.1859 (3)	0.1767 (2)	0.0659 (7)
C3a	−0.3563 (2)	0.1883 (2)	0.1903 (1)	0.0605 (8)
C4a	−0.4092 (1)	0.3264 (2)	0.1693 (1)	0.0467 (6)
C5a	−0.3582 (1)	0.4277 (2)	0.1394 (1)	0.0438 (6)
C6a	−0.3850 (1)	0.5808 (2)	0.1126 (1)	0.0484 (7)
C8a	−0.3855 (2)	0.8394 (3)	0.0635 (2)	0.0838 (12)
C9a	−0.4735 (2)	0.8023 (3)	0.0722 (2)	0.0765 (11)
C10a	−0.4753 (2)	0.6542 (2)	0.0994 (1)	0.0551 (7)
C11a	−0.5646 (2)	0.5855 (3)	0.1138 (1)	0.0652 (9)
C13a	−0.5100 (2)	0.3490 (3)	0.1797 (1)	0.0661 (8)
S1b	0.08620 (5)	0.36056 (7)	−0.00522 (4)	0.0737 (2)
S7b	0.00317 (5)	0.11700 (8)	−0.16322 (4)	0.0805 (3)
O12b	0.2730 (1)	−0.0809 (2)	0.07309 (9)	0.0689 (6)
C2b	0.1692 (2)	0.4134 (3)	0.0997 (2)	0.0815 (10)
C3b	0.2308 (2)	0.3020 (3)	0.1442 (2)	0.0717 (9)
C4b	0.2135 (1)	0.1678 (2)	0.0947 (1)	0.0547 (7)
C5b	0.1364 (1)	0.1817 (2)	0.0112 (1)	0.0505 (7)
C6b	0.0907 (1)	0.0702 (2)	−0.0575 (1)	0.0514 (6)
C8b	−0.0186 (2)	−0.0642 (3)	−0.1944 (2)	0.0825 (11)
C9b	0.0394 (2)	−0.1557 (3)	−0.1282 (2)	0.0682 (8)
C10b	0.1024 (1)	−0.0803 (2)	−0.0494 (1)	0.0523 (7)
C11b	0.1753 (2)	−0.1551 (2)	0.0335 (2)	0.0674 (8)
C13b	0.2743 (2)	0.0302 (3)	0.1345 (2)	0.0731 (10)

Table 6. Selected geometric parameters (\AA , $^\circ$) for (III)

S1a—C2a	1.705 (3)	S1b—C2b	1.709 (2)
S1a—C5a	1.728 (1)	S1b—C5b	1.736 (1)
S7a—C6a	1.728 (1)	S7b—C6b	1.723 (1)

211 parameters
All H-atom parameters
refined
 $w = 2F_oLp/[\sigma^2(I_o) + (0.02I_o)^2]^{1/2}$
 $(\Delta/\sigma)_{\max} < 0.001$

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Tables
2.2A, 2.3.1 and 2.2C)

$\theta/2\theta$ scans
Absorption correction:
none
2842 measured reflections
2842 independent reflections
2087 observed reflections
 $[I_o > 2\sigma(I_o)]$

$k = 0 \rightarrow 14$
 $l = -18 \rightarrow 17$
1 standard reflection
frequency: 360 min
intensity decay: negligible

Table 7. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (IV)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
S1	0.10207 (5)	0.35739 (2)	-0.13381 (5)	0.0568 (1)
S7	-0.22889 (5)	0.35134 (2)	0.15004 (6)	0.0619 (2)
O12	0.3455 (1)	0.44319 (4)	0.3387 (1)	0.0529 (3)
O16	0.3201 (2)	0.32357 (4)	0.5110 (1)	0.0582 (3)
C2	0.2629 (2)	0.30620 (7)	-0.1020 (2)	0.0608 (5)
C3	0.3114 (2)	0.28112 (6)	0.0658 (2)	0.0547 (5)
C4	0.2177 (2)	0.30267 (5)	0.1744 (2)	0.0422 (4)
C5	0.0981 (2)	0.34495 (5)	0.0837 (2)	0.0410 (4)
C6	-0.0244 (2)	0.37871 (6)	0.1425 (2)	0.0443 (4)
C8	-0.2887 (2)	0.41224 (8)	0.2148 (2)	0.0752 (7)
C9	-0.1592 (2)	0.45076 (7)	0.2317 (2)	0.0697 (6)
C10	-0.0049 (2)	0.43231 (6)	0.1908 (2)	0.0516 (5)
C11	0.1666 (2)	0.46608 (6)	0.2111 (2)	0.0604 (5)
C13	0.3663 (2)	0.43828 (7)	0.5298 (2)	0.0611 (5)
C14	0.5291 (3)	0.39985 (8)	0.6358 (2)	0.0729 (7)
C15	0.5037 (2)	0.34511 (7)	0.5421 (2)	0.0615 (6)
C17	0.2531 (2)	0.28245 (6)	0.3689 (2)	0.0530 (5)

Refinement

Refinement on F
 $R = 0.035$
 $wR = 0.046$
 $S = 2.024$
2087 reflections
237 parameters
All H-atom parameters
refined
 $w = 2F_oLp/[\sigma^2(I_o) + (0.02I_o)^2]^{1/2}$
 $(\Delta/\sigma)_{\max} = 0.24$

$|\Delta\rho| = 0.40 \text{ e \AA}^{-3}$
Extinction correction: Stout
& Jensen (1968)
Extinction coefficient:
 $1.4 (2) \times 10^{-7}$
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Tables
2.2A, 2.3.1 and 2.2C)

Table 9. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (V)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Table 8. Selected geometric parameters (\AA , $^\circ$) for (IV)

S1—C2	1.703 (1)	C4—C5	1.365 (1)
S1—C5	1.730 (1)	C4—C17	1.501 (2)
S7—C6	1.726 (1)	C5—C6	1.463 (2)
S7—C8	1.704 (2)	C6—C10	1.362 (2)
O12—C11	1.418 (1)	C8—C9	1.336 (2)
O12—C13	1.429 (1)	C9—C10	1.421 (2)
O16—C15	1.421 (2)	C10—C11	1.502 (2)
O16—C17	1.422 (1)	C13—C14	1.498 (2)
C2—C3	1.343 (2)	C14—C15	1.503 (2)
C3—C4	1.422 (2)		
C2—S1—C5	92.3 (1)	S1—C5—C6	119.0 (1)
C6—S7—C8	91.6 (1)	S7—C6—C5	119.9 (1)
S1—C2—C3	111.3 (1)	C5—C6—C10	128.8 (2)
C2—C3—C4	113.8 (1)	S7—C6—C10	111.3 (1)
C3—C4—C17	123.6 (1)	S7—C8—C9	111.8 (1)
C3—C4—C5	112.0 (1)	C8—C9—C10	113.7 (2)
C5—C4—C17	124.4 (1)	C6—C10—C9	111.6 (2)
S1—C5—C4	110.6 (1)	C9—C10—C11	124.8 (1)
C4—C5—C6	130.4 (1)	C6—C10—C11	123.5 (2)

Compound (V)

Crystal data

C₁₄H₁₆O₃S₂
 $M_r = 296.40$
Monoclinic
 $P2_1/n$
 $a = 7.999 (1) \text{ \AA}$
 $b = 12.060 (2) \text{ \AA}$
 $c = 14.930 (2) \text{ \AA}$
 $\beta = 102.46 (1)^\circ$
 $V = 1406.3 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.3999 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4
diffractometer

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25
reflections

$\theta = 9.8\text{--}17.9^\circ$

$\mu = 0.3629 \text{ mm}^{-1}$

Room temperature

Prism

$0.35 \times 0.33 \times 0.20 \text{ mm}$

Colourless

$\theta_{\max} = 26^\circ$

$h = 0 \rightarrow 9$

	x	y	z	U_{eq}
S1	-0.22770 (7)	0.12441 (5)	0.20634 (4)	0.0477 (2)
S7	-0.30744 (8)	0.12454 (5)	-0.03069 (4)	0.0534 (2)
O12	0.2434 (2)	0.2946 (1)	0.01204 (9)	0.0523 (5)
O15	0.3168 (2)	0.5138 (1)	0.0878 (1)	0.0648 (5)
O18	0.0479 (2)	0.4812 (1)	0.1920 (1)	0.0579 (5)
C2	-0.2132 (3)	0.2227 (2)	0.2900 (1)	0.0503 (7)
C3	-0.1534 (3)	0.3194 (2)	0.2653 (1)	0.0437 (6)
C4	-0.1168 (2)	0.3169 (2)	0.1752 (1)	0.0372 (6)
C5	-0.1485 (2)	0.2147 (2)	0.1357 (1)	0.0378 (6)
C6	-0.1302 (3)	0.1759 (2)	0.0451 (1)	0.0397 (7)
C8	-0.1906 (3)	0.0975 (2)	-0.1113 (2)	0.0587 (8)
C9	-0.0258 (3)	0.1249 (2)	-0.0814 (2)	0.0548 (8)
C10	0.0125 (3)	0.1700 (2)	0.0089 (1)	0.0435 (6)
C11	0.1884 (3)	0.2032 (2)	0.0578 (1)	0.0535 (8)
C13	0.4098 (3)	0.3358 (2)	0.0540 (2)	0.0650 (9)
C14	0.4060 (3)	0.4169 (3)	0.1267 (2)	0.0673 (9)
C16	0.2793 (3)	0.5872 (2)	0.1543 (2)	0.0544 (8)
C17	0.0943 (3)	0.5850 (2)	0.1578 (2)	0.0521 (7)
C19	-0.0651 (3)	0.4171 (2)	0.1288 (1)	0.0470 (7)

Table 10. Selected geometric parameters (\AA , $^\circ$) for (V)

S1—C2	1.708 (2)	C3—C4	1.437 (2)
S1—C5	1.729 (2)	C4—C5	1.366 (3)
S7—C6	1.727 (2)	C4—C19	1.495 (3)
S7—C8	1.707 (3)	C5—C6	1.468 (2)
O12—C11	1.416 (2)	C6—C10	1.366 (3)
O12—C13	1.432 (2)	C8—C9	1.339 (3)
O15—C14	1.426 (3)	C9—C10	1.424 (3)
O15—C16	1.410 (3)	C10—C11	1.493 (3)
O18—C17	1.431 (2)	C13—C14	1.466 (4)
O18—C19	1.392 (2)	C16—C17	1.492 (3)
C2—C3	1.342 (3)		
C2—S1—C5	91.9 (1)	S1—C5—C6	118.9 (2)
C6—S7—C8	91.9 (1)	S7—C6—C5	119.2 (2)
S1—C2—C3	112.0 (1)	C5—C6—C10	129.7 (2)
C2—C3—C4	113.3 (2)	S7—C6—C10	111.1 (1)
C3—C4—C19	123.3 (2)	S7—C8—C9	111.6 (2)
C3—C4—C5	111.5 (2)	C8—C9—C10	113.9 (2)
C5—C4—C19	125.0 (2)	C6—C10—C9	111.5 (2)
S1—C5—C4	111.3 (1)	C9—C10—C11	123.6 (2)
C4—C5—C6	129.7 (2)	C6—C10—C11	124.9 (2)

Table 11. Selected values of chemically equivalent bond distances (Å), angles and absolute value of torsion angles (°) in compounds (I)–(VII)

E.s.d.'s of single values are in parentheses; if the reported value is a mean, the number in parentheses is the larger of the r.m.s. and the mean e.s.d.'s.

	(I) ^a	(II) ^a	(III) ^a	(IV) ^a
S1—C5	1.715 (2)	1.708 (2)	1.728 (3)	1.728 (2)
C4—C5	1.371 (3)	1.369 (3)	1.366 (3)	1.364 (2)
C5—C6	1.441 (3)	1.448 (3)	1.450 (2)	1.463 (2)
S1—C5—C4	111.9 (2)	112.6 (2)	110.6 (1)	110.9 (3)
S1—C5—C6	138.9 (2)	138.4 (2)	120.6 (4)	119.5 (5)
C4—C5—C6	109.1 (2)	108.8 (2)	128.7 (4)	129.8 (8)
S1—C5—C6—S7	4.3 (10)	2.6 (5)	9.7 (20)	109.6 (1)
	(V) ^a	(VI) ^b	(VII) ^b	
S1—C5	1.728 (2)	1.734 (4)	1.733 (4)	
C4—C5	1.366 (3)	1.363 (4)	1.365 (6)	
C5—C6	1.468 (2)	1.467 (3)	1.461 (5)	
S1—C5—C4	111.2 (1)	111.0 (2)	110.7 (3)	
S1—C5—C6	119.0 (2)	119.1 (2)	120.3 (3)	
C4—C5—C6	129.7 (2)	129.9 (2)	129.0 (3)	
S1—C5—C6—S7	56.8 (2)	45.1 (3)	61.1 (6)	

Notes: (a) This work. (b) Zimmer *et al.* (1993).

Data collection: *SDP* (Frenz, 1983). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Preparation and Structural Characterization of the Charge-Transfer Complex (12[ane]S₄.I₂)_∞ (12[ane]S₄ = 1,4,7,10-Tetrathiacyclododecane)

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Abstract

The X-ray crystal structure of the new addition compound (12[ane]S₄.I₂)_∞, C₈H₁₆S₄.I₂, is reported. The I₂ moieties bridge symmetrically between thioether groups; the I—I and S··I bond lengths of 2.736(1) and 3.220(3) Å, respectively, indicate relatively weak charge transfer. The nature of the interaction has been probed by semi-empirical molecular-orbital calculations using the PM3 method.

Comment

The interaction of thioethers with diiodine constitutes a textbook example of charge-transfer (CT) complexation (Downs & Adams, 1973); the nature of the S··I₂ interaction was first characterized in the 1960s by X-ray structural analyses of (PhCH₂)₂S.I₂ (Rømme, 1960) and 6[ane]S₂.(I₂)₂ (Chao & McCullough, 1960) (6[ane]S₂ = 1,4-dithiane), and other examples of such complexes have appeared from time to time (Herbstein *et al.*, 1986; Tipton, Lonergan, Stern & Shriver, 1992). Very recently, interest in this area has been rekindled by the structural characterization of complexes of diiodine with the macrocyclic thioether 1,4,7-trithiacyclononane, *viz.* (9[ane]S₃)₂.(I₂)₄ (Blake, Gould, Radek & Schröder, 1993) and 9[ane]S₃.(I₂)₃ (Cristiani *et al.*, 1993).

In this paper we describe the preparation and X-ray crystal structure of a complex of a larger macrocycle, (12[ane]S₄.I₂)_∞ (12[ane]S₄ = 1,4,7,10-tetrathiacyclododecane). This complex differs from previous examples in that the diiodine bridges symmetrically between two macrocycles in an unusually weak CT interaction. In order to probe the differences in electronic structures in going from terminal R₂S··I—I to bridging R₂S··I—I··SR₂, we have carried out semi-empirical molecular-orbital calculations on Me₂S.I₂ and