

approximately coplanar to the molecular plane. The torsion angles S(5)—C(4)—S(9)—C(10) and S(5)—C(6)—S(11)—C(12) are 86.6 (2) and 32.7 (3)°, respectively.

The distances of the S(2)—C(1) and S(8)—C(1) bonds (1.764 and 1.766 Å, respectively) are slightly longer than those of the other endocyclic S—C bonds (1.738–1.744 Å). The C(3)—C(7) distance is longer than that of the terminal C=C bond of TTF and the central C=C distance [1.341 (7) Å] is slightly shorter than that of the neutral TTF molecule (1.349 Å) (Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens, 1971). This dimension of the TTF moiety of this compound is very close to that of dibenzotetrathiafulvalene (Emge, Wiygul, Chappell, Bloch, Ferraris, Cowan & Kistenmacher, 1982) which corresponds to a neutral TTF from the comparison of the structures of TTF in various electronic states (Kistenmacher, Phillips & Cowan, 1974; Yakushi, Nishimura, Sugano, Kuroda & Ikemoto, 1980). The exocyclic S—C bonds, S(9)—C(10) and S(11)—C(12), are longer than the other S—C bonds, S(9)—C(4) and S(11)—C(6). The difference of these lengths corresponds to that between S—C_{sp³} and S—C_{sp²}.

Fig. 2(a) shows the crystal structure viewed along the *c* axis. The molecules form a sheet-like network nearly parallel to the (1̄20) plane as shown in Fig. 2(b). The molecules in a sheet are connected with van der Waals S··S contacts such as S(11)··S(9ⁱⁱ) [(ii) = *x*, *y*, *z* + 1, 3.642 (2) Å] and S(5)··S(5ⁱⁱⁱ) [(iii) = 2 - *x*,

1 - *y*, -*z*, 3.753 (2) Å] and there are cavities between molecules along the *c* axis which are filled with methylthio groups of the adjacent sheet. The interplanar separation between the thiophene plane (III) of the molecule (*x*, *y*, *z*) and plane (I) of the molecule (*x* + 1, *y*, *z*) is 3.556 (8) Å.

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Structures of 2,6-Bis(methylthiomethyl)phenyl Phenyl Sulfoxide and 9,18-Epithio-2,11-dithia[3.3]metacyclophane-Trichloromethane (1/1)

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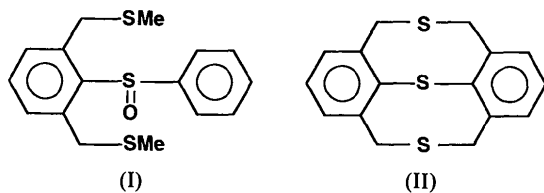
Abstract. (I) C₁₆H₁₈OS₃, *M_r* = 322.52, monoclinic, *P*_{2₁/n, *a* = 12.396 (3), *b* = 7.863 (2), *c* = 16.795 (4) Å, β = 105.37 (2)°, *V* = 1578.5 (6) Å³, *Z* = 4, *D_x* = 1.357 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ =}

0.443 mm⁻¹, *F*(000) = 680, *T* = 293 K, *R* = 0.044 for 2873 observed reflections. (II) 7,15,18-Trithiatetradecylo[7.7.3.0^{5,17}0^{13,19}]nonadeca-1(17),2,4,9,11,13(19)-hexaene-trichloromethane (1/1), C₁₆H₁₄S₃.CHCl₃, *M_r* = 421.86, monoclinic, *P*_{2₁/m, *a* = 8.749 (1), *b* = 12.007 (2), *c* = 8.686 (1) Å, β = 92.46 (1)°, *V* =}

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911.6 (2) Å³, $Z = 2$, $D_x = 1.537 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ Å}$, $\mu = 0.830 \text{ mm}^{-1}$, $F(000) = 432$, $T = 293 \text{ K}$, $R = 0.048$ for 1660 observed reflections. In (I) the conformations of the two methylthiomethyl groups are different from each other. There is a slightly shorter intramolecular S...S contact of 3.477 (1) Å between the thio and sulfinyl groups. Crystals of (II) contain CHCl_3 as a crystal solvent. (II) has a crystallographic mirror plane through the three S atoms and also has pseudo m symmetry through a C—S—C plane. Conformations of the two 1,5-dithiacyclooctane rings are of a chair-boat type.

Introduction. Some S atoms in compounds such as 1,5-dithiacyclooctanes and related derivatives often show transannular S...S contacts of 3.1–3.4 Å (Iwasaki & Furukawa, 1987). Recently, the structure of 1,5-dithionibicyclooctane has been determined where transannular S⁺—S⁺ bonding of 2.12 Å was formed (Iwasaki, Toyoda, Akaishi, Fujihara & Furukawa, 1988). However, no examples of transannular interactions between S atoms in trithia compounds have been reported. The crystal structures of a sulfoxide (I) and a cyclic trithioether (II) were determined to study the intramolecular S...S interactions.



Experimental. Details of data collection and structure refinement are listed in Table 1. Intensity data were collected using a Rigaku AFC-4 diffractometer with graphite monochromator. No absorption corrections were applied. The structure of (I) was solved by the program *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms were found from the difference maps. Block-diagonal least squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized. $w = 1/(0.6796 - 0.0086|F_o| + 0.0005|F_o|^2)$.

A crystal of (II) was sealed in a thin glass capillary with small amount of solvent because the crystals are very unstable in air. The space group $P2_1/m$ was assumed for (II). The preliminary structure of the trithioether was obtained by the program *MULTAN78* (Main *et al.*, 1978). During successive refinement it was revealed that the crystals had CHCl_3 as a crystal solvent. H atoms were found from the difference maps. Block-diagonal least squares with anisotropic temperature factors for

Table 1. Details of data collection and structure refinement

	(I)	(II)
Color	Colorless	Colorless
Crystal shape	Plates	Plates
Crystal size (mm)	0.40 × 0.20 × 0.30	0.65 × 0.35 × 0.52
2θ range (°) and number of reflections for cell parameters	30–35, 25	31–42, 25
Scan range 2θ (°)	2–55	2–55
Scan width Δω (°)	1.3 + 0.4tanθ	1.5 + 0.3tanθ
Scan speed 2θ (° min ⁻¹)	4	4
Scan mode	2θ-ω	2θ-ω
Monitored reflections (every 50 reflections)	131, 307, 322	080, 304, 304
Variation of intensities	1.002–0.982	1.001–0.951
Range of h, k, l	–16–16, 0–10, 0–21	–11–11, 0–15, 0–11
Time for background (s)	10	10
Number of reflections		
measured	3971	2164
unique, R_{int}	3625, 0.020	1943, 0.035
observed [$ F_o > 3\sigma(F)$]	2873	1660
R	0.044	0.048
wR	0.051	0.053
Δρ _{max} (e Å ⁻³)	0.378	0.259
(ΔI/σ) _{max}	0.250 [S(1), z]	0.265 [Cl(2), y]
S	1.026	0.9771

non-H atoms and isotropic ones for H. $w = 1/(0.5569 - 0.0458|F_o| + 0.0019|F_o|^2)$. The final R value was 0.048. A refinement with the space group $P2_1$ was also carried out to an R value of 0.048. Although the molecule has a pseudo mirror symmetry, the distances of chemically equivalent bonds are unreasonably different from each other. The space group was determined to be $P2_1/m$. The final atomic parameters are given in Table 2.* Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations were performed on a HITAC M260D computer at the Data Processing Center of the University of Electro-Communications with the programs *UNICSIII* (Sakurai & Kobayashi, 1979), *MULTAN78* (Main *et al.*, 1978) and *ORTEPII* (Johnson, 1976).

Discussion. The molecular structures with the atomic numbering are shown in Fig. 1. Bond distances, angles and some torsion angles are listed in Tables 3 and 4.

Structure of (I). Dimensions about the sulfinyl group are close to normal values. The conformations of the two exocyclic methylthiomethyl groups are different from each other. S(2) is nearly *gauche* to C(1) across the C(2)—C(7) bond and C(8) is *trans* to C(2) across S(2)—C(7), while S(3) is *trans* to C(1) across C(9)—C(6) and C(10) is *gauche* to C(6) across

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles for H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52994 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters [$\times 10^5$ for (I), $\times 10^4$ for (II)] and equivalent isotropic temperature factors (\AA^2) for non-H atoms

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

	x	y	z	B_{eq}
(I)				
S(1)	47881 (5)	-18943 (8)	15566 (4)	2.99 (2)
S(2)	21742 (6)	-11732 (11)	2020 (5)	4.18 (2)
S(3)	63774 (7)	25119 (10)	35098 (4)	4.18 (2)
O(1)	59712 (17)	-24763 (24)	18621 (13)	3.95 (6)
C(1)	47700 (19)	3558 (29)	13315 (14)	2.48 (5)
C(2)	40873 (19)	8348 (31)	5509 (15)	2.65 (6)
C(3)	40814 (22)	25457 (34)	3242 (15)	3.08 (6)
C(4)	47505 (25)	37132 (33)	8477 (17)	3.39 (7)
C(5)	54326 (23)	32107 (32)	15983 (16)	3.19 (7)
C(6)	54633 (20)	15256 (30)	18606 (14)	2.65 (6)
C(7)	34132 (21)	-4058 (35)	-675 (16)	3.20 (6)
C(8)	20763 (32)	-32629 (46)	-2382 (29)	6.27 (13)
C(9)	62739 (22)	10216 (34)	26720 (17)	3.39 (7)
C(10)	50306 (33)	22585 (53)	36876 (23)	5.68 (11)
C(11)	42100 (21)	-18619 (31)	24385 (16)	2.98 (6)
C(12)	46946 (24)	-29364 (36)	30903 (19)	3.76 (7)
C(13)	42485 (27)	-30196 (41)	37610 (19)	4.34 (9)
C(14)	33146 (27)	-20696 (43)	37805 (20)	4.47 (9)
C(15)	28254 (25)	-10318 (44)	31170 (21)	4.51 (9)
C(16)	32694 (24)	-9275 (38)	24447 (18)	3.79 (7)
(II)				
S(1)	-2279 (1)	2500	3489 (1)	4.01 (2)
S(2)	-79 (1)	2500	-156 (1)	2.80 (2)
S(3)	4222 (1)	2500	438 (1)	4.52 (3)
C(1)	-527 (3)	872 (2)	2039 (3)	3.12 (5)
C(2)	501 (3)	1342 (2)	1033 (3)	2.78 (5)
C(3)	1965 (3)	878 (2)	886 (3)	3.34 (6)
C(4)	2379 (4)	-45 (3)	1804 (4)	4.39 (7)
C(5)	1385 (4)	-487 (3)	2816 (4)	4.63 (8)
C(6)	-67 (4)	-50 (2)	2933 (3)	4.01 (7)
C(7)	-2123 (3)	1310 (2)	2203 (3)	3.67 (6)
C(8)	3074 (3)	1308 (3)	-234 (3)	4.02 (7)
C(11)	3755 (5)	2500	4785 (4)	3.67 (9)
Cl(1)	1769 (1)	2500	4768 (2)	5.18 (3)
Cl(2)	4482 (1)	1297 (1)	5671 (2)	7.54 (4)

S(3)—C(6). This asymmetry of the molecule is related to the conformation of the sulfinyl group. The torsion angle O(1)—S(1)—C(1)—C(6) is 43.8 (2)°. The intramolecular O(1)⋯C(9) and O(1)⋯H(91) contacts of 3.074 (4) and 2.47 (3) Å, respectively, are slightly shorter than the sum of the van der Waals radii, although the bond angle S(1)—C(1)—C(6) is larger than S(1)—C(1)—C(2) by 7.2° and the angle O(1)—S(1)—C(1) is larger than O(1)—S(1)—C(11). The intramolecular S(1)⋯S(2) contact is 3.477 (1) Å, which is slightly shorter than the van der Waals contact (3.7 Å). Since the angle O(1)—S(1)⋯S(2) is 159.38 (9)°, a linear arrangement of O—S⋯S, which is typical of hypervalent sulfur contacts, is not observed in this case. Bond angles smaller than 120°, which are observed at C(1)—C(2)—C(3) and C(1)—C(6)—C(5), are comparable to those of the endocyclic angles of a phenyl group attached through an alkyl group (Domenicano, Vaciago & Coulson, 1975). The dihedral angle between the two phenyl groups is 96.1 (1)°.

Fig. 2 shows the crystal structure of (I). The intermolecular contacts are van der Waals type.

Structure of (II). The molecule of (II) has exact mirror symmetry through the S(1)⋯S(2)⋯S(3) plane and also has approximate mirror symmetry through C(2)—S(2)—C(2') [(i) = x, $\frac{1}{2}$ -y, z]. The dithia-cyclooctanes both have chair-boat conformations. The distances S(1)⋯S(2) and S(2)⋯S(3) are 3.774 (1) and 3.777 (1) Å, respectively, so no hypervalent S⋯S contacts are observed in this molecule. The dihedral angle between the two benzene rings is 104.7 (1)°. The S(1)—C(7) and S(3)—C(8) bonds are longer than S(2)—C(2) by 0.03 Å; the difference corresponds to that between S—C_{sp³} and S—C_{sp²}. The C(7)—S(1)—C(7') and C(8)—S(3)—C(8') angles are larger than C(2)—S(2)—C(2').

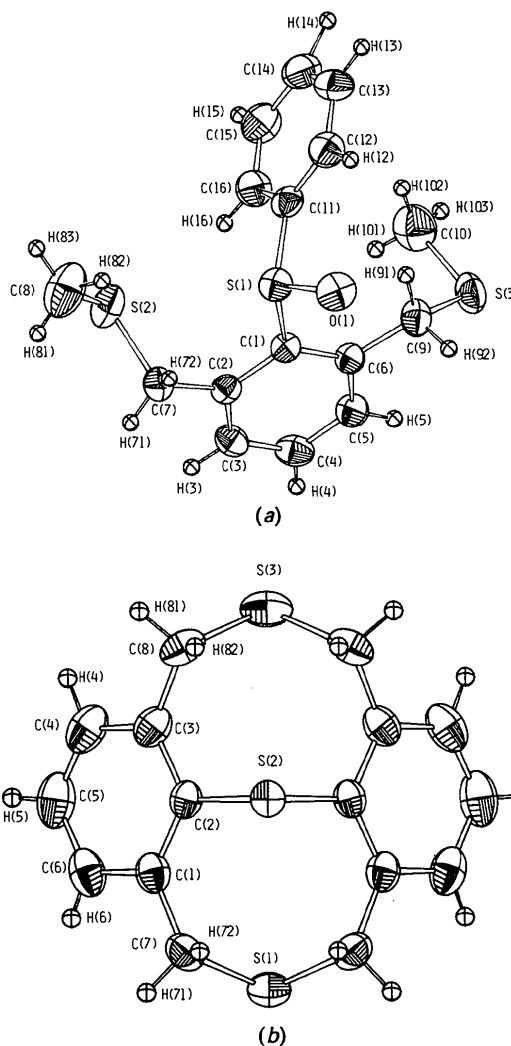


Fig. 1. The molecular structures of (a) (I) and (b) (II), with atomic numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 3. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

(I)			
S(1)—O(1)	1.492 (2)	C(3)—C(4)	1.385 (4)
S(1)—C(1)	1.808 (3)	C(4)—C(5)	1.377 (4)
S(1)—C(11)	1.808 (3)	C(5)—C(6)	1.394 (4)
S(2)—C(7)	1.816 (3)	C(6)—C(9)	1.516 (4)
S(2)—C(8)	1.793 (5)	C(11)—C(12)	1.387 (4)
S(3)—C(9)	1.809 (3)	C(11)—C(16)	1.380 (4)
S(3)—C(10)	1.783 (4)	C(12)—C(13)	1.382 (5)
C(1)—C(2)	1.410 (3)	C(13)—C(14)	1.385 (5)
C(1)—C(6)	1.403 (3)	C(14)—C(15)	1.385 (5)
C(2)—C(3)	1.398 (4)	C(15)—C(16)	1.383 (5)
C(2)—C(7)	1.506 (4)		
O(1)—S(1)—C(1)	109.2 (1)	C(1)—C(6)—C(5)	117.5 (2)
O(1)—S(1)—C(11)	106.8 (1)	C(1)—C(6)—C(9)	123.1 (2)
C(1)—S(1)—C(11)	99.9 (1)	C(5)—C(6)—C(9)	119.3 (2)
C(7)—S(2)—C(8)	99.9 (2)	S(2)—C(7)—C(2)	113.3 (2)
C(9)—S(3)—C(10)	100.4 (2)	S(3)—C(9)—C(6)	115.0 (2)
S(1)—C(1)—C(2)	115.3 (2)	S(1)—C(11)—C(12)	117.1 (2)
S(1)—C(1)—C(6)	122.5 (2)	S(1)—C(11)—C(16)	122.2 (2)
C(2)—C(1)—C(6)	122.0 (2)	C(12)—C(11)—C(16)	120.5 (3)
C(1)—C(2)—C(3)	118.0 (2)	C(11)—C(12)—C(13)	119.3 (3)
C(1)—C(2)—C(7)	123.7 (2)	C(12)—C(13)—C(14)	120.8 (3)
C(3)—C(2)—C(7)	118.3 (2)	C(13)—C(14)—C(15)	119.3 (3)
C(2)—C(3)—C(4)	120.4 (2)	C(14)—C(15)—C(16)	120.5 (3)
C(3)—C(4)—C(5)	120.7 (3)	C(11)—C(16)—C(15)	119.6 (3)
C(4)—C(5)—C(6)	121.4 (3)		
(II)			
S(1)—C(7)	1.822 (3)	C(3)—C(4)	1.404 (4)
S(2)—C(2)	1.793 (3)	C(3)—C(8)	1.494 (4)
S(3)—C(8)	1.829 (4)	C(4)—C(5)	1.369 (5)
C(1)—C(2)	1.399 (4)	C(5)—C(6)	1.383 (5)
C(1)—C(6)	1.402 (4)	C(11)—Cl(1)	1.737 (5)
C(1)—C(7)	1.504 (4)	C(11)—Cl(2)	1.744 (5)
C(2)—C(3)	1.408 (4)		
C(7)—S(1)—C(7')	103.3 (1)	C(2)—C(3)—C(8)	122.7 (2)
C(2)—S(2)—C(2')	101.7 (1)	C(4)—C(3)—C(8)	118.9 (3)
C(8)—S(3)—C(8')	102.9 (2)	C(3)—C(4)—C(5)	121.0 (3)
C(2)—C(1)—C(6)	119.2 (2)	C(4)—C(5)—C(6)	120.7 (3)
C(2)—C(1)—C(7)	122.8 (2)	C(1)—C(6)—C(5)	120.1 (3)
C(6)—C(1)—C(7)	118.0 (2)	S(1)—C(7)—C(1)	115.2 (2)
S(2)—C(2)—C(1)	119.9 (2)	S(3)—C(8)—C(3)	115.2 (2)
S(2)—C(2)—C(3)	119.4 (2)	Cl(1)—C(1)—Cl(2)	110.5 (2)
C(1)—C(2)—C(3)	120.6 (2)	Cl(2)—C(11)—Cl(2')	117.8 (2)
C(2)—C(3)—C(4)	118.3 (3)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 4. Selected torsion angles (°)

(I)			
O(1)—S(1)—C(1)—C(2)	130.5 (2)	C(1)—S(1)—C(11)—C(12)	-139.0 (2)
O(1)—S(1)—C(1)—C(6)	-43.8 (2)	C(1)—S(1)—C(11)—C(16)	46.5 (2)
C(11)—S(1)—C(1)—C(2)	-117.7 (2)	C(1)—C(2)—C(7)—S(2)	74.8 (2)
C(11)—S(1)—C(1)—C(6)	68.0 (2)	C(2)—C(7)—S(2)—C(8)	-148.9 (2)
O(1)—S(1)—C(11)—C(12)	-25.3 (2)	C(1)—C(6)—C(9)—S(3)	-141.2 (2)
O(1)—S(1)—C(11)—C(16)	160.1 (2)	C(6)—C(9)—S(3)—C(10)	68.7 (2)
(II)			
C(2)—C(1)—C(7)—S(1)	-82.6 (2)	C(2)—C(3)—C(8)—S(3)	84.1 (2)
C(1)—C(7)—S(1)—C(7')	91.6 (2)	C(3)—C(8)—S(3)—C(8')	-91.3 (2)
C(1)—C(2)—S(2)—C(2)	91.7 (2)	C(3)—C(2)—S(2)—C(2)	-91.5 (2)
S(2)—C(2)—C(1)—C(7)	-1.2 (3)	S(2)—C(2)—C(3)—C(8)	-0.2 (3)

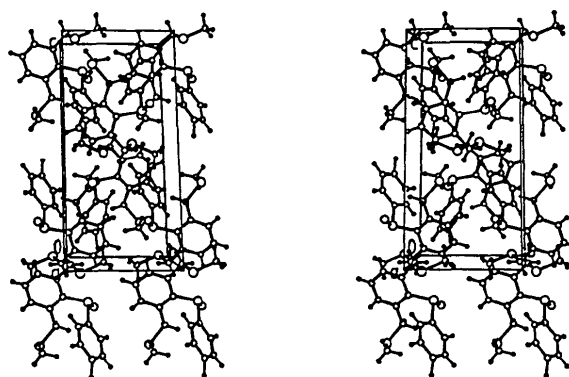
Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Fig. 2. Stereoscopic view of the crystal structure of (I).

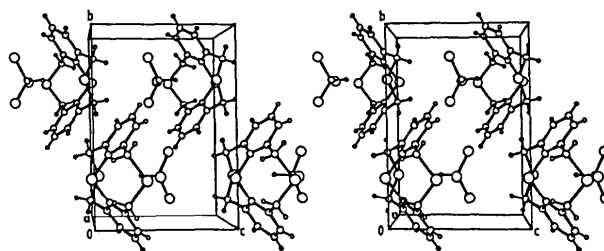


Fig. 3. Stereoscopic view of the crystal structure of (II).

The crystal structure viewed along the a axis is shown in Fig. 3. The crystals include CHCl_3 stoichiometrically, which also has crystallographic mirror symmetry. C(11), H(11) and Cl(1) of CHCl_3 are on the mirror plane at $y = \frac{1}{4}$. The trithioether molecule and CHCl_3 are stacked alternately along the c axis. The intermolecular distance $\text{S}(3)\cdots\text{H}(11)$ is 2.72 (8) Å, which is slightly shorter than the sum of van der Waals radii. This intermolecular interaction may, however, be very weak, since the crystals are not very stable.

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