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## Structure of 4,4',6,6'-Tetrakis(methylthio)-2,2'-bithieno[3,4-d][1,3]dithiolylidene

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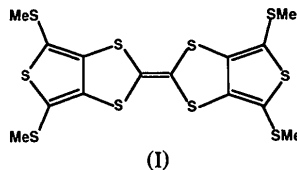
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**Abstract.** C<sub>14</sub>H<sub>12</sub>S<sub>10</sub>, *M<sub>r</sub>* = 500.91, triclinic, *P* $\bar{1}$ , *a* = 7.050 (2), *b* = 8.229 (2), *c* = 9.540 (2) Å,  $\alpha$  = 112.08 (2),  $\beta$  = 78.87 (2),  $\gamma$  = 100.97 (2)°, *V* = 499.0 (2) Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 1.667 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 1.059 mm<sup>-1</sup>, *F*(000) = 256, *T* = 293 K, *R* = 0.038 for 1984 observed reflections. The conformation of the molecular frame is that of a very shallow chair with the 1,3-dithiole rings of envelope type. One of the exocyclic methylthio groups is perpendicular to the frame while the other is approximately coplanar to the molecular plane. The molecules form a sheet-like network nearly parallel to the ( $\bar{1}20$ ) plane where the molecules are connected with van der Waals S...S contacts of 3.642 (2) and 3.753 (2) Å. The intersheet interaction is also van der Waals type and unfavorable to the intermolecular charge-transfer interaction.

**Introduction.** Recently many efforts have been made to obtain new types of organic donors and acceptors. The title compound, (I), a thiophene-fused tetrathiafulvalene (TTF) modified by methylthio groups, has been prepared to introduce interstack interactions (Kobayashi, 1985). Unfortunately, the molecule does not show a strong electron-donating character. The crystal structure analysis was carried out to investi-

gate relations between structure and donating character.



**Experimental.** Yellow needles, 0.70 × 0.35 × 0.35 mm, unit-cell parameters by least squares from 25 reflections (30 < 2θ < 47°), Rigaku AFC-4 diffractometer with graphite monochromator, 2 ≤ 2θ ≤ 55°, *h* = -9 → 9, *k* = 0 → 10, *l* = -12 → 12, ω-2θ scan, scan range (1.4 + 0.4 tan θ)°, scan speed 4° min<sup>-1</sup> in 2θ, three reflections (132, 211, 240) monitored every 50 reflections, variations within 3%. 2591 reflections measured, 2422 unique, *R<sub>int</sub>* = 0.02, 1984 observed, |*F<sub>o</sub>*| ≥ 3σ(*F*). No absorption corrections were applied. Structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms were found from the difference map. Block-diagonal least-squares refinement with anisotropic temperature factors for non-H atoms and isotropic ones for H.  $\sum w(|F_o| - k^{-1}|F_c|)^2$  was minimized. *w* = 1 for all reflections.  $\Delta\rho_{\text{max}}$  = 0.3 e Å<sup>-3</sup>,  $\Delta/\sigma_{\text{max}}$  = 0.08 for

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Table 1. Positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) for non-H atoms
$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
S(2)	2024 (1)	1206 (1)	-1503 (1)	3.15 (2)
S(5)	7535 (1)	3652 (1)	24 (1)	3.40 (3)
S(8)	1969 (1)	1468 (1)	1719 (1)	3.68 (3)
S(9)	6452 (1)	3022 (1)	-3108 (1)	3.58 (3)
S(11)	6319 (2)	3342 (1)	3208 (1)	4.26 (3)
C(1)	832 (4)	559 (4)	44 (4)	2.68 (9)
C(3)	4176 (4)	2134 (4)	-699 (3)	2.48 (9)
C(4)	5899 (5)	2826 (4)	-1314 (4)	2.86 (10)
C(6)	5854 (5)	3069 (4)	1403 (4)	2.99 (10)
C(7)	4144 (4)	2263 (4)	826 (3)	2.62 (9)
C(10)	7656 (8)	1098 (7)	-4207 (5)	5.28 (16)
C(12)	8028 (7)	5290 (7)	3666 (5)	5.59 (17)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

S(2)—C(1)	1.764 (4)	S(9)—C(10)	1.801 (6)
S(2)—C(3)	1.744 (3)	S(11)—C(6)	1.738 (4)
S(5)—C(4)	1.743 (4)	S(11)—C(12)	1.775 (6)
S(5)—C(6)	1.738 (4)	C(1)—C(1 <sup>i</sup> )	1.341 (7)
S(8)—C(1)	1.766 (4)	C(3)—C(4)	1.362 (5)
S(8)—C(7)	1.743 (4)	C(3)—C(7)	1.414 (5)
S(9)—C(4)	1.741 (4)	C(6)—C(7)	1.369 (5)
C(1)—S(2)—C(3)	94.4 (2)	C(4)—C(3)—C(7)	114.1 (3)
C(4)—S(5)—C(6)	92.6 (2)	S(5)—C(4)—S(9)	122.6 (2)
C(1)—S(8)—C(7)	94.2 (2)	S(5)—C(4)—C(3)	109.8 (3)
C(4)—S(9)—C(10)	101.9 (2)	S(9)—C(4)—C(3)	127.6 (3)
C(6)—S(11)—C(12)	103.3 (2)	S(5)—C(6)—S(11)	125.1 (2)
S(2)—C(1)—S(8)	115.9 (2)	S(5)—C(6)—C(7)	109.9 (3)
S(2)—C(1)—C(1 <sup>i</sup> )	122.1 (3)	S(11)—C(6)—C(7)	124.8 (3)
S(8)—C(1)—C(1 <sup>i</sup> )	122.0 (3)	S(8)—C(7)—C(3)	117.1 (3)
S(2)—C(3)—C(4)	129.1 (3)	S(8)—C(7)—C(6)	129.3 (3)
S(2)—C(3)—C(7)	116.8 (2)	C(3)—C(7)—C(6)	113.6 (3)

Symmetry code: (i)  $-x, -y, -z$ .

non-H, 0.17 for H atoms.  $R = 0.038$ ,  $wR = 0.038$ ,  $S = 0.646$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations were performed on a HITAC M260D computer of 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). The final atomic parameters are given in Table 1.\*

**Discussion.** The molecular structure with the atomic numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. The molecule has a crystallographic center of inversion and the molecular frame has a very shallow chair form. The plane (I) defined by the central six atoms, C(1), C(1<sup>i</sup>), S(2), S(2<sup>i</sup>), S(8), and S(8<sup>i</sup>) [(i) =  $-x, -y, -z$ ], is planar

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52991 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

within 0.001 (3)  $\text{\AA}$ . The 1,3-dithiole ring is in an envelope conformation. The dihedral angle between plane (I) and plane (II) defined by the four atoms S(2), C(3), C(7) and S(8) is 14.2 (1) $^\circ$ . The dihedral angle between plane (II) and the terminal thiophene ring (III) is 1.9 (1) $^\circ$ . The conformations of the two independent exocyclic methylthio groups are quite different; the S(9)—C(10) bond is almost perpendicular to the molecular frame while S(11)—C(12) is

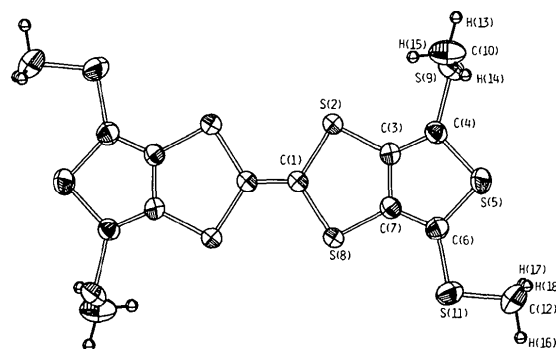


Fig. 1. The molecular structure with atomic numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

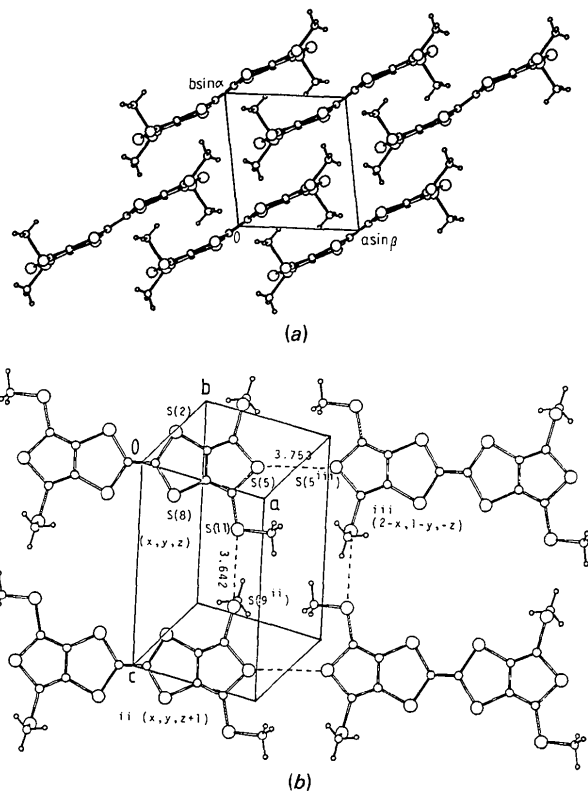


Fig. 2. (a) The projection of the crystal structure viewed along the *c* axis. (b) Sheet-like network of the molecules parallel to the (120) plane. Distances are given in  $\text{\AA}$ .

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<sub>sp<sup>3</sup></sub> and S—C<sub>sp<sup>2</sup></sub>.

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(9<sup>ii</sup>) [(ii) = *x*, *y*, *z* + 1, 3.642 (2) Å] and S(5)··S(5<sup>iii</sup>) [(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) C<sub>16</sub>H<sub>18</sub>OS<sub>3</sub>, *M<sub>r</sub>* = 322.52, monoclinic, *P*<sub>2<sub>1</sub>/n, *a* = 12.396 (3), *b* = 7.863 (2), *c* = 16.795 (4) Å, β = 105.37 (2)°, *V* = 1578.5 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.357 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ =</sub>

0.443 mm<sup>-1</sup>, *F*(000) = 680, *T* = 293 K, *R* = 0.044 for 2873 observed reflections. (II) 7,15,18-Trithiatetradecylo[7.7.3.0<sup>5,17</sup>0<sup>13,19</sup>]nonadeca-1(17),2,4,9,11,13(19)-hexaene-trichloromethane (1/1), C<sub>16</sub>H<sub>14</sub>S<sub>3</sub>.CHCl<sub>3</sub>, *M<sub>r</sub>* = 421.86, monoclinic, *P*<sub>2<sub>1</sub>/m, *a* = 8.749 (1), *b* = 12.007 (2), *c* = 8.686 (1) Å, β = 92.46 (1)°, *V* =</sub>

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