

Structure of 3,4'-Dimethyl-3',4-bis(methylthio)-2,2',5,5'-tetrathiafulvalene,* C₁₀H₁₂S₆

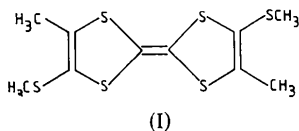
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Abstract. $M_r = 324.59$, triclinic, $P\bar{1}$, $a = 7.883$ (9), $b = 9.101$ (9), $c = 5.193$ (7) Å, $\alpha = 96.32$ (9), $\beta = 106.63$ (8), $\gamma = 99.73$ (8)°, $V = 346.9$ (9) Å³, $Z = 1$, $D_x = 1.55$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 9.2$ cm⁻¹, $F(000) = 168$, room temperature, $R = 0.062$ based on 1171 unique observed reflections. The configuration of the compound is *trans* and the low symmetry is reflected in the tetrathiafulvalene valence-bond framework. The sulfur-linked methyl substituents are not coplanar with the tetrathiafulvalene core (1.29 Å out of plane).

Introduction. The coupling of 2-alkoxy-4-alkylthio-1,3-dithiols in an acidic medium was recently shown (Souizi & Robert, 1984) to generate in high yields dissymmetrically substituted tetrathiafulvalene (TTF). It is remarkable that only one of the *cis* or *trans* isomers is obtained and we deemed it necessary to determine the configuration. In this paper we investigate the structure of the dimethylbis(methylthio) derivative (I) (DMDTTTF) and find that its configuration is *trans*.



Experimental. Suitable crystals of title compound grown by slow evaporation of an ethyl acetate solution. Crystal 0.36 × 0.14 × 0.07 mm. Enraf–Nonius CAD-4 diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation. Cell dimensions: least-squares refinement from setting angles of 25 accurately centered reflections ($\theta < 15^\circ$). Intensities collected by θ -2 θ scans. Three standard reflections measured every hour: no fluctuations in intensity. One set of reflections collected up to $2\theta = 60^\circ$. 2027 independent reflections measured ($-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $0 \leq l \leq 7$), 1171 with $I \geq 3\sigma(I)$. Lorentz and polarization corrections, no absorption correction. Direct methods

* Fulvalene is 2,2'-bi-1,3-dithiolyliidene.

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Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal-motion parameters with their e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
S(1)	259 (2)	2369 (1)	1734 (2)	3.37 (2)
S(2)	2037 (2)	32 (1)	3875 (2)	3.45 (2)
S(5)	2293 (2)	4653 (1)	6820 (2)	3.61 (2)
C(1)	466 (6)	486 (4)	1154 (7)	2.76 (7)
C(2)	1924 (6)	2841 (4)	4959 (7)	2.84 (7)
C(3)	2744 (6)	1751 (4)	5935 (7)	2.89 (8)
C(7)	2764 (8)	5834 (5)	4430 (10)	4.3 (1)
C(30)	4162 (7)	1891 (6)	8626 (9)	3.75 (9)

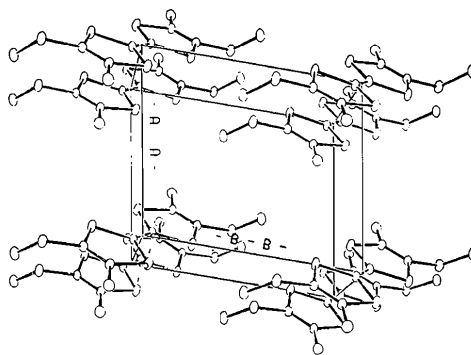


Fig. 1. Perspective view of the crystal structure.

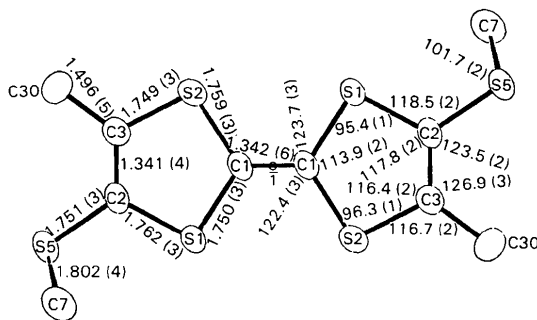


Fig. 2. View of (I) illustrating atomic labeling, bond lengths (Å) and bond angles (°).

(*MULTAN82*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All H atoms from difference Fourier map. Full-matrix least-squares anisotropic (β_y) refinement (H atoms isotropic, not refined), $R = 0.062$, $wR = 0.082$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/[\sigma(|F_o|^2) + (0.07 F_o)^2]$, $S = 1.94$, $(\Delta/\sigma)_{\max} = 0.01$, $\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows a perspective view of the crystal structure. Final atomic parameters are in Table 1,* bond distances and angles on Fig. 2.

We are concerned here with the relative positions of the methylthio substituents. They are *trans* to each other on a planar TTF unit located at a center of symmetry in the crystal. The sulfur atom S(5) of the methylthio substituent is in the TTF plane while the methyl carbon C(7) is 1.29 Å out of this plane.

All the bond lengths are longer than in TTF itself (Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens,

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39985 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1971). The dissymmetry imposed by the non-coplanar methylthio substituents is reflected strongly in the disparity of the C—S bond lengths. Of particular interest is the pronounced departure from the usual *m* molecular symmetry due to alternating long–short bonds in the –C–S– sequence. This indicates that the difference in coordination (and possibly in charge) of carbon atoms C(2) and C(3) bearing different substituents is reflected over to the inner S(1) and S(2) atoms. Then the *trans* configuration of the two TTF halves across the center of symmetry ($\bar{1}$) may indeed minimize repulsions between equivalently charged sulfur atoms.

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2-Methyl-1-benzothiophene, C₉H₈S

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Abstract. $M_r = 148.2$, orthorhombic, $Pna2_1$, $a = 11.71$ (2), $b = 11.03$ (2), $c = 5.96$ (1) Å, $V = 769.8$ Å³, $Z = 4$, $D_m = 1.27$, $D_x = 1.28$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 2.876$ mm⁻¹, $F(000) = 312$, $T = 283$ K, $R = 0.079$ for 553 observed densitometer and visually measured equi-inclination Weissenberg data. The five- and six-membered rings are planar and inclined to one another at 0.6 (4)°. The average C—C bond length in the phenyl ring is 1.398 (20) Å. In the five-membered ring the average C—S bond length is 1.756 (16) Å, the C—S—C angle is 92.4 (6)°; the C—C bond lengths are 1.485 (17) and 1.382 (16) Å. The C—Me bond makes an angle of 1.5 (4)° with the five-membered ring.

Introduction. This paper forms part of an investigation into 1-benzothiophene derivatives. These frequently discolour on exposure to the atmosphere and sublime quite rapidly under X-ray irradiation.

Experimental. D_m measured by flotation using aqueous cadmium *n*-dodecatungstoborate. White transparent crystals used in data collection about c and b had dimensions 0.08 × 0.1 × 0.3 mm and 0.09 × 0.15 × 0.12 mm respectively. Since 2-methyl-1-benzothiophene sublimes rapidly, these crystals together with some additional material were sealed in Lindemann-glass capillaries. Data for 400 reflexions measured with Joyce–Loebl flying-spot densitometer and 500 by