Structure of an Unsymmetrically-substituted Thiathiophthen: Crystal and Molecular Structure of 5-Methyl-3-[4-methyl-5-(methylthio)thiocarbonyl-2-thienyl]-2-methylthio-6a-thiathiophthen {5-Methyl-3-[4-methyl-5-(methylthio)thiocarbonyl-2-thienyl]-2-methylthio[1,2]dithiolo-[1,5-*b*][1,2]dithiole-*7-S*^{IV}}

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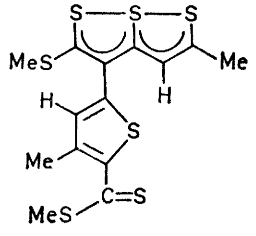
The structure of the title compound (I) has been determined by single-crystal *X*-ray analysis. Crystals are monoclinic, with $a = 26.787(12)$, $b = 7.485(4)$, $c = 19.420(7)$ Å, and $\beta = 110° 41'(2')$, $Z = 8$, space group $C2/c$. The structure was solved by the symbolic-addition method and refined by full-matrix least-squares to R 0.102 for 1 738 non-zero reflections. The S–S distances in (I) are very different [2.197(6) and 2.546(6) Å] and are indicative of the electron-withdrawing effect of the 2-methylthio-group which causes a long S(1)–S(6a) bond.

THE Halphen test is a useful analytical method for determining the cyclopropene fatty acid content of oils.[1] Cyclopropene fatty acids give a red colour upon heating with amyl alcohol and carbon disulphide, and three products have been isolated from this coloured material.[2] One of these products was shown to have a thiathiophthen structure, and although it was unsuitable for *X*-ray work a model compound was prepared in suitable crystalline form.[3] Its crystal structure was determined to provide information on the structure of the red-pigment component. The dimensions of this derivative (I) (which contains a thiathiophthen nucleus) are compared with those for related compounds.



(I)

EXPERIMENTAL

Crystals were reddish-pink prisms. The structure was initially solved on a limited set of data collected by use of Mo-K_α radiation. However, as the number of reflections was inadequate for reasonable definition of the structure, refinement was carried out on a second set of data collected with Cu-K_α radiation, and only experimental conditions for the second data set are described here.

Crystal Data.—$C_{14}H_{14}S_7$, $M = 406.7$. Monoclinic, $a = 26.787(12)$, $b = 7.485(4)$, $c = 19.420(7)$ Å, and $\beta = 110° 41'(2')$, $U = 3\,643 \times 10^{-24}$ cm^3, $D_c = 1.48$ g cm^{-3}, $Z = 8$, $F(000) = 1\,680$. Space group $C2/c$ or Cc from systematic absences: hkl, when $h + k = 2n + 1$, $h0l$, when $l = 2n + 1$; the former was assumed initially and confirmed by the results of the analysis. Cu-K_α radiation $\lambda = 1.541\,78$ Å; μ(Cu-K_α) = 75.6 cm^{-1}.

Cell data were determined by a least-squares fit to the settings for 10 reflections hand-centred on the diffractometer. The procedures for data collection were as described earlier.[4] A crystal $0.20 \times 0.40 \times 0.15$ mm was mounted along the b axis (0.40 mm). Of 3 457 possible intensities in the 2θ sphere out to 130°, 1 738 were considered non-zero at the 2σ level.

TABLE 1

Final atomic co-ordinates for (I) in fractions of cell edges with estimated standard deviations in parentheses

	x	*y*	*z*
S(1)	0.2624(2)	0.6847(6)	0.3500(2)
S(6)	0.1743(2)	0.6672(7)	0.0911(2)
S(6a)	0.2144(2)	0.6839(6)	0.2110(2)
S(8)	0.2252(2)	0.4407(6)	0.4456(2)
S(14)	0.0917(1)	0.3667(5)	0.3319(2)
S(16)	−0.0041(2)	0.2742(8)	0.3779(3)
S(18)	0.0138(2)	−0.1138(7)	0.3641(3)
C(2)	0.2212(5)	0.5246(19)	0.3585(8)
C(3)	0.1807(5)	0.4519(20)	0.2975(6)
C(3a)	0.1750(5)	0.5112(18)	0.2254(8)
C(4)	0.1370(5)	0.4367(20)	0.1612(7)
C(5)	0.1336(6)	0.5002(21)	0.0930(7)
C(7)	0.0959(7)	0.4207(27)	0.0217(9)
C(9)	0.2865(6)	0.5295(23)	0.5088(8)
C(10)	0.1453(4)	0.3083(18)	0.3070(6)
C(11)	0.1481(5)	0.1314(21)	0.3005(7)
C(12)	0.1093(5)	0.0331(18)	0.3164(7)
C(13)	0.0753(5)	0.1442(18)	0.3364(7)
C(15)	0.0290(5)	0.1103(23)	0.3587(7)
C(17)	0.1095(5)	−0.1665(20)	0.3139(9)
C(19)	−0.0436(7)	−0.1117(34)	0.3892(10)
H(4) [a,b]	0.112	0.336	0.165
H(7A)	0.049	0.423	0.010
H(7B)	0.106	0.290	0.019
H(7C)	0.101	0.484	−0.021
H(9A)	0.318	0.462	0.500
H(9B)	0.289	0.512	0.561
H(9C)	0.290	0.661	0.501
H(11)	0.176	0.071	0.285
H(17A)	0.111	−0.222	0.363
H(17B)	0.140	−0.218	0.300
H(17C)	0.073	−0.192	0.274
H(19A)	−0.036	−0.061	0.440
H(19B)	−0.060	−0.233	0.387
H(19C)	−0.073	−0.033	0.355

[a] Hydrogen atoms are numbered according to the carbon atom to which they are attached. [b] The co-ordinates of the hydrogen atoms were not varied in the least-squares refinement.

The structure was solved by symbolic-addition methods [5] using the programs FAME–MAGIC–SYMPL[6] on 647 reflections collected by use of Mo-K_α radiation. Full-matrix

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[1] F. L. Carter and V. L. Frampton, *Chem. Rev.*, 1964, **64**, 697.

[2] K. L. Rinehart, U. I. Zahorszky, and R. Srinivasan, to be published.

[3] C. T. Mabuni, Ph.D. Thesis, University of Illinois, Urbana, Illinois, 1972.

[4] E. C. Llaguno and I. C. Paul, *J.C.S. Perkin II*, 1976, 228.

[5] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[6] R. B. K. Dewar, Ph.D. Thesis, University of Chicago, 1968.

least-squares refinement on the positional and anisotropic thermal parameters for all non-hydrogen atoms gave *R* 0.106. All non-zero reflections were given unit weight. A difference map revealed the positions of most of the hydrogen atoms. Others were positioned according to standard criteria. As trial refinements indicated that some of the hydrogen parameters became chemically unreasonable, all hydrogen positional and thermal parameters were held constant. A difference map at this stage contained no unusual features. A final cycle of refinement gave *R* 0.102 for all 1 738 non-zero reflections. Atomic scattering factors for carbon, oxygen, and sulphur were taken from ref. 7, and that for hydrogen from ref. 8. Final atomic co-ordinates and temperature factors are listed in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21403 (4 pp., 1 microfiche).*

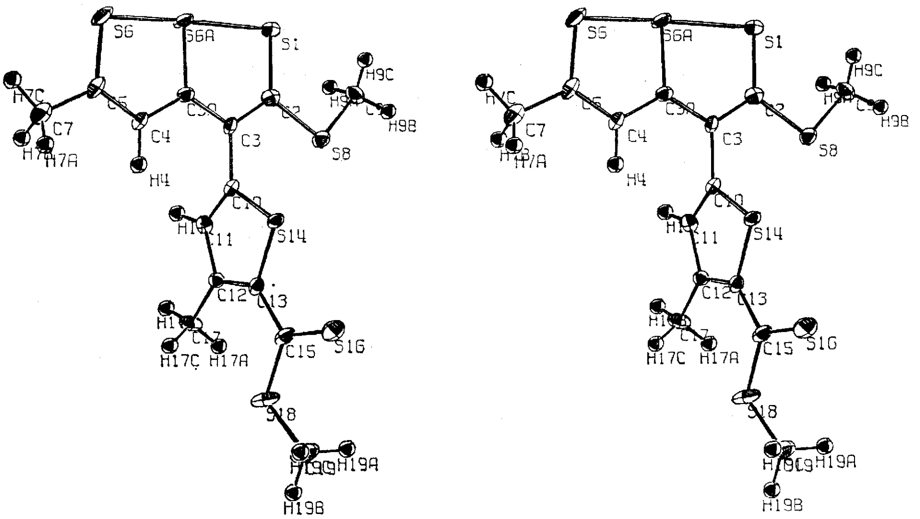

FIGURE 1 Stereoview of a single molecule of (I)

TABLE 2

Final thermal parameters for (I) with estimated standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	17(1)	209(10)	36(2)	−23(2)	11(1)	−11(3)
S(6)	26(1)	279(12)	30(2)	−7(3)	18(1)	26(4)
S(6a)	18(1)	191(9)	37(2)	−9(2)	18(1)	11(3)
S(8)	17(1)	214(10)	22(1)	−10(2)	5(1)	8(3)
S(14)	12(1)	138(7)	30(1)	−1(2)	12(1)	−1(2)
S(16)	17(1)	336(14)	63(2)	−13(3)	24(1)	−32(5)
S(18)	20(1)	281(13)	59(2)	−24(3)	17(1)	36(5)
C(2)	14(2)	122(31)	34(6)	10(7)	10(3)	7(10)
C(3)	10(2)	199(33)	16(4)	−3(7)	5(2)	−8(10)
C(3a)	12(2)	127(29)	29(5)	−1(6)	9(3)	1(10)
C(4)	14(2)	186(32)	19(4)	3(8)	8(3)	9(10)
C(5)	18(3)	216(37)	22(5)	20(8)	11(3)	25(11)
C(7)	29(4)	297(50)	29(6)	−16(12)	12(4)	15(14)
C(9)	20(3)	214(41)	32(6)	−22(9)	3(4)	−23(12)
C(10)	9(2)	134(29)	17(4)	13(6)	5(2)	13(9)
C(11)	7(2)	192(34)	28(5)	2(7)	4(2)	−17(11)
C(12)	11(2)	135(31)	24(5)	−4(6)	6(3)	−6(10)
C(13)	10(2)	186(32)	17(4)	2(7)	3(2)	−1(10)
C(15)	11(2)	282(42)	24(5)	−12(8)	6(3)	12(12)
C(17)	13(2)	113(32)	52(7)	−2(7)	9(4)	−0(12)
C(19)	24(4)	550(80)	42(8)	−55(15)	11(4)	16(21)

The anisotropic thermal parameters are expressed as: $\exp - [\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. The isotropic thermal parameter is in the form: $\exp - [B_\theta \sin^2\theta/\lambda^2]$. $B_\theta = 3.0$ for all hydrogen atoms, not varied during least-squares refinement.

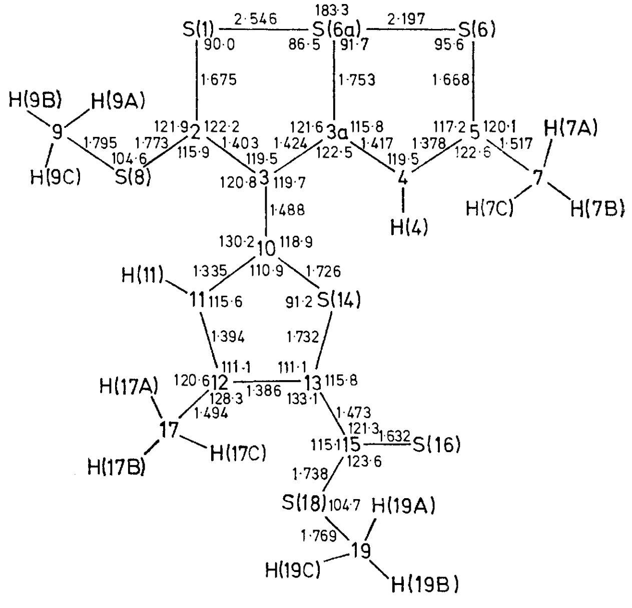

FIGURE 2 Bond lengths (Å) and angles (deg.) in the molecule of (I). σ for S–S, C–S, and C–C bonds range from 0.006, 0.012—0.020, and 0.019—0.024 Å; for S–S–S, C–S–S, C–S–C, and C–C–C angles in the range 0.5, 0.5—0.6, 0.6—0.8, and 0.8—1.4°

RESULTS AND DISCUSSION

A stereoscopic view of the molecule of (I) is shown in Figure 1. The structure is seen to be 5-methyl-3-[4-methyl-5-(methylthio)thiocarbonyl-2-thienyl]-2-methyl-

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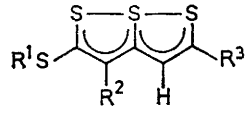
* For details see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

thio-6a-thiathiophthen. Bond lengths and angles are shown in Figure 2; σ for S–S, C–S, and C–C bond lengths are 0.006, 0.012—0.020, and 0.019—0.024 Å, those for bond angles involving sulphur are in the range 0.5—0.6°, those for angles about carbon 0.6—1.4°.

This thiathiophthen has the usual general characteristics of a near-planar central group (deviations from best plane range from −0.050 to 0.065 Å, Table 3) and S–S–S 176.7(5)°. The central C–S bond [1.753(14) Å] is significantly longer than the two outer ones [1.675(15) and 1.668(16) Å]. The two C–S bonds of the methylthio-group attached to the thiathiophthen nucleus are similar, in contrast to the situation in 3-amino-2-methylthio-5-phenyl-6a-thiathiophthen (II),[4] where the C–S bond attached to the ring is 0.07 Å shorter than the S–CH$_3$ bond. In (II), the methylthio-group was essentially coplanar with the thiathiophthen nucleus, whereas in the present structure the methylthio-group is twisted out of the plane of the nucleus [S(8) −0.052, C(9) 0.294 Å].



(II)

	R¹	R²	R³
(II)	Me	NH$_2$	Ph
(III)	Me	PhC(:O)	p-Br-C$_6$H$_4$

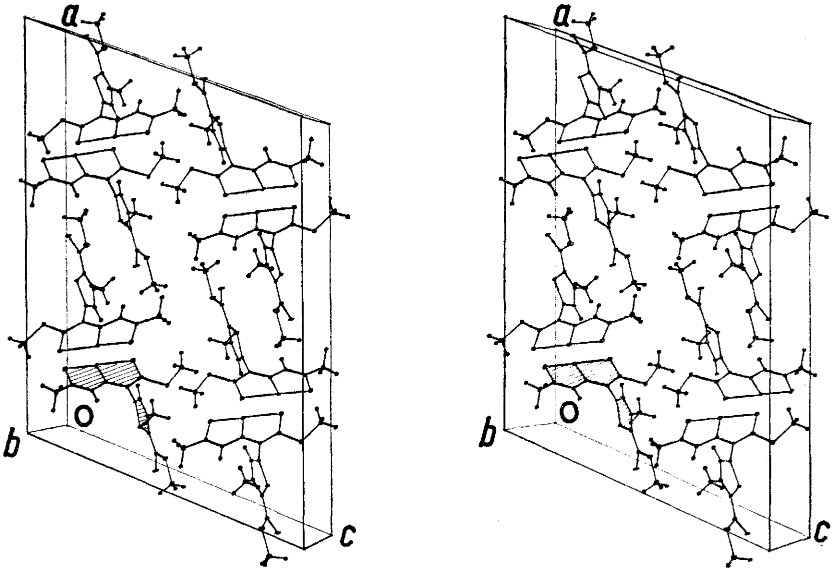


FIGURE 3 Stereoview of the packing of the molecules of (I) in the crystal. The molecule at x, y, z is shaded

The two S–S lengths in (I) are unequal [2.197(6) and 2.546(6) Å]. These lengths, together with those found[9] in the two molecules of 3-benzoyl-5-p-bromophenyl-2-methylthio-6a-thiathiophthen (III) differ by the greatest amount yet found for such bonds in a thiathiophthen structure. The substituent pattern in (I) and (III) is similar, the 3-substituents in each case being twisted out of the ring by nearly 90°, and the two sets of S–S lengths are similar. There are indications that a methylthio-group in the 2-position causes a long S(1)–S(6a) bond. There is also evidence from other studies[4,10] that a MeS·C(:S)-group forms a relatively weak S···S interaction.

TABLE 3

Details of best planes, with (in square brackets) deviations (Å) of relevant atoms from the planes

Plane (A): S(1), S(6a), C(2), C(3), C(3a)

[S(1) 0.002, S(6) 0.100, S(6a) −0.003, C(2) −0.016, C(3) −0.017, C(3a) 0.040, C(4) 0.117, C(5) 0.171, C(7) 0.326]

Plane (B): S(6), S(6a), C(3a), C(4), C(5)

[S(1) 0.126, S(6) −0.001, S(6a) 0.001, S(8) 0.040, C(2) 0.058, C(3) −0.022, C(3a) −0.004, C(4) −0.006, C(5) 0.014, C(7) 0.086]

Plane (C): S(1), S(6), S(6a), C(2)—(5), C(3a)

[S(1) 0.024, S(6) 0.016, S(6a) −0.038, S(8) −0.052, C(2) −0.014, C(3) −0.050, C(3a) −0.013, C(4) 0.029, C(5) 0.065, C(7) 0.182, C(9) 0.294, C(10) −0.064]

Plane (D): S(14), C(10)—(13)

[S(14) 0.001, S(16) −0.055, C(3) −0.077, C(10) −0.015, C(11) 0.010, C(12) 0.010, C(13) −0.021, C(15) −0.046, C(17) −0.016]

χ^2 *	11.2	1.0	120.5	6.1
P †	<0.01	~0.5	<0.01	~0.05

* Atoms are weighted as $1/\sigma^2$ where σ is from the least-squares results. † The probability that the deviations from the best planes describe a normal distribution.

The dimensions of the 3-thiophen group agree with those reported for the thiophen molecule by both

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[9] S. M. Johnson, M. G. Newton, and I. C. Paul, *J. Chem. Soc.* (*B*), 1969, 986.

[10] P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc.* (*B*), 1971, 946.

TABLE 4

Some important intermolecular contacts (Å) in the crystal of (I)

S(14) $\cdots$ C(17$^{\mathrm{I}}$)	3.56	S(6) $\cdots$ S(8$^{\mathrm{V}}$)	3.65
C(2) $\cdots$ C(17$^{\mathrm{I}}$)	3.64	S(6a) $\cdots$ C(2$^{\mathrm{V}}$)	3.60
C(3) $\cdots$ C(17$^{\mathrm{I}}$)	3.51	S(6a) $\cdots$ C(3$^{\mathrm{V}}$)	3.50
S(16) $\cdots$ C(4$^{\mathrm{II}}$)	3.58	S(1) $\cdots$ C(3a$^{\mathrm{V}}$)	3.56
S(6) $\cdots$ S(8$^{\mathrm{III}}$)	3.63	S(6a) $\cdots$ C(3a$^{\mathrm{V}}$)	3.71
S(8) $\cdots$ S(8$^{\mathrm{IV}}$)	3.52	S(1) $\cdots$ C(4$^{\mathrm{V}}$)	3.36
S(8) $\cdots$ C(9$^{\mathrm{IV}}$)	3.67	S(1) $\cdots$ C(5$^{\mathrm{V}}$)	3.52
C(9) $\cdots$ C(12$^{\mathrm{IV}}$)	3.59	S(6) $\cdots$ C(9$^{\mathrm{V}}$)	3.69

Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z:

I $x, 1 + y, z$
II $-x, y, \frac{1}{2} - z$
III $x, 1 - y, -\frac{1}{2} + z$
IV $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
V $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

electron diffraction [11] and microwave measurements.[12] The thiocarbonyl C–S distance [1.632(16) Å] is almost a pure double bond.[13] The plane of the thiophen ring is at 80.9° to that of the thiathiophthen nucleus.

A number of best planes in the molecule are listed in Table **3**. The two five-membered rings of the central nucleus make an angle of 3.2° with each other.

The molecular packing of (I) is shown in Figure **3**. Some important intermolecular contacts are listed in Table **4**. The molecules pack such that the S–S–S linear arrays are all almost mutually parallel; one thiathiophthen nucleus approaches another at almost 90°. The shortest S $\cdots$ S contact is 3.52 Å involving centrosymmetrically related S(8) atoms.

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[11] V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769.

[12] B. Bak, D. Christensen, J. Rastrup-Andersen, and E. Tannenbaum, *J. Chem. Phys.*, 1956, **25**, 892.

[13] P. L. Johnson and I. C. Paul, *J. Chem. Soc.* (*B*), 1970, 1296.