A Symmetrically Substituted Thiathiophthen with Unequal Sulphur–Sulphur Bond Lengths: Crystal and Molecular Structure of 3,4-Diphenyl-6a-Thiathiophthen {3,4-Diphenyl[1,2]dithiolo[1,5-*b*][1,2]dithiole-*7*-S^{IV}}

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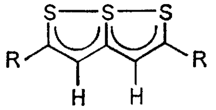
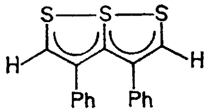
The molecular structure of the title compound (III) has been determined by single-crystal *X*-ray analysis. Crystals are monoclinic, with a = 13.924(13), b = 6.842(8), c = 15.350(13) Å, and β = 90° 45′(4′), Z = 4, space group $P2_1/c$. The structure was solved by the symbolic-addition method and refined to R 0.104 on 1 527 non-zero diffractometer reflections. This symmetrically substituted thiathiophthen occupies a crystallographically general position and has decidedly unequal S–S bond lengths [2.236(4) and 2.430(4) Å] and rather short ' external ' C–S bond lengths [1.649(12) and 1.653(12) Å]. Molecular dimensions give some indication of intramolecular strain. Correspondence of the *X*-ray results with those obtained by ESCA is discussed.

In the years since the demonstration[1] of the general structure of (I), there have been many *X*-ray structural studies of 6a-thiathiophthen {[1,2]dithiolo[1,5-*b*][1,2]dithiole-*7*-S^{IV}} derivatives. A point of particular interest has been the question of whether symmetrically substituted derivatives have equal S–S bond lengths.[2-4] In the structure of 2,5-diphenyl-6a-thiathiophthen (II),[4]



(I) R = Me
(II) R = Ph

where the results of the *X*-ray analysis could not be affected by a symmetry requirement of the crystal, lengths of 2.304(3) and 2.362(3) Å were obtained. This



(III)

near equality led Hordvik[4] to conclude that the S–S lengths are equal in an isolated symmetrically substituted thiathiophthen molecule and that differences of the order found in (II) were due to packing effects. A useful test of this could be made from the results of a structure analysis of a 3,4-symmetrically disubstituted thiathiophthen, and we have therefore determined that of 3,4-diphenyl-6a-thiathiophthen (III).[5] A preliminary report has appeared.[6]

EXPERIMENTAL

The crystals of (III) are thin, dark-red needles from cyclohexane. Unit-cell dimensions were determined by a least-squares fit to the settings for the 4 angles of 6 reflections centred on a Picker FACS 1 diffractometer.

Crystal Data.—$C_{17}H_{12}S_3$, M = 312.5. Monoclinic, a = 13.924(13), b = 6.842(8), c = 15.350(13) Å, β = 90° 45′(4′), U = 1 462.2 × 10^{-24} cm^3, Z = 4, D_c = 1.420 g cm^{-3}, $F(000)$ = 648. Space group $P2_1/c$ from systematic absences: $h0l$ when $l = 2n + 1$, and $0k0$, when $k = 2n + 1$. Cu-K_α radiation λ = 1.54178 Å; μ(Cu-K_α) = 43.2 cm^{-1}. While the crystals were too thin to provide an accurate measurement of D_m by flotation, our experiments were consistent with the D_c calculated for Z = 4.

A needle crystal of (III) *ca* 0.4 mm in the b direction and 0.15 × 0.05 mm in cross-section was chosen for data collection, which was carried out as described in the preceeding paper,[7] except that the base-width was 2.5°. No evidence for crystal decomposition was observed. Reflections in the octants $h\bar{k}l$ and $h\bar{k}\bar{l}$ were measured out to 2θ 130° and those in the octants $\bar{h}\bar{k}l$ and $\bar{h}\bar{k}\bar{l}$ to 90°. Symmetry-equivalent reflections were averaged. A total of 1 527 reflections was considered above zero using the

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[1] S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, 1958, **182**, 247.

[2] S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Comm.*, 1967, 1170.

[3] F. Leung and S. C. Nyburg, *Chem. Comm.*, 1969, 137.

[4] A. Hordvik, *Acta Chem. Scand.*, 1968, **22**, 2397; 1971, **25**, 1583.

[5] J. G. Dingwall and D. H. Reid, *Chem. Comm.*, 1968, 863.

[6] P. L. Johnson and I. C. Paul, *Chem. Comm.*, 1969, 1014.

[7] E. C. Llaguno and I. C. Paul, *J.C.S. Perkin II*, preceding paper.

criteria that the threshold count be 0.07 × total background count or >10 counts, whichever is greater. Data were corrected for Lorentz and polarization corrections, but not for absorption.

The structure was solved by the symbolic-addition method [8] as applied to centrosymmetric space groups by use of programs written by Dewar.[9] The positions of all twenty non-hydrogen atoms were recognized from an E map and full-matrix least-squares refinement on the positions and isotropic temperature factors for these atoms gave R 0.153 and R', defined as $[\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$, 0.156. All non-zero reflections were given unit weights and the quantity minimized was $\Sigma w||F_o| - |F_c||^2$. Introduction of anisotropic thermal parameters for the non-hydrogen atoms into the model, gave R 0.119 and R' 0.124. A difference map calculated at this stage allowed the positions of some of the hydrogen atoms to be located, but some others were positioned by standard criteria. The positions of the hydrogen atoms were included in the least-squares refinement and values for R and R' of 0.107 and 0.109 were obtained. At this stage thirteen low-order reflections that were judged to suffer from significant absorption or extinction effects were removed from the data set used in the refinement procedures, and two final cycles of full-matrix least-squares refinement were then carried out. Positional and anisotropic thermal parameters were varied for the non-hydrogen atoms; positional parameters were varied for the hydrogen atoms, for which a constant isotropic temperature factor of 3.0 Å^2 was assumed. The values of R and R' were 0.099 and 0.097. The co-ordinates and temperature factors obtained from this refinement are listed in Tables 1 and 2. When the thirteen low-order reflections which had previously been removed from the data were restored, the final R on all 1 527 non-zero reflections was 0.104. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21402 (3 pp., 1 microfiche).* Scattering factors for carbon and sulphur were those tabulated in ref. 10, and that for hydrogen was taken from ref. 11.

TABLE 1

Final atomic co-ordinates in fractions of unit cell edges, with standard deviations in parentheses

	x	y	z
S(1)	0.0827(2)	−0.1273(5)	0.0817(2)
S(6a)	0.0570(2)	−0.1230(4)	0.2252(2)
S(6)	0.0221(2)	−0.1231(5)	0.3799(2)
C(2)	0.1676(8)	0.0409(18)	0.0886(6)
C(3)	0.1977(6)	0.1226(16)	0.1681(6)
C(3a)	0.1456(6)	0.0525(14)	0.2428(6)
C(4)	0.1622(6)	0.1231(16)	0.3305(5)
C(5)	0.1055(7)	0.0449(18)	0.3957(6)
C(7)	0.2773(7)	0.2612(15)	0.1666(6)
C(8)	0.3701(8)	0.2141(20)	0.1929(7)
C(9)	0.4451(9)	0.3464(26)	0.1851(8)
C(10)	0.4274(10)	0.5263(28)	0.1505(8)
C(11)	0.3355(12)	0.5779(21)	0.1236(8)
C(12)	0.2608(9)	0.4453(19)	0.1323(7)
C(13)	0.2322(7)	0.2739(17)	0.3568(6)
C(14)	0.3111(7)	0.2221(20)	0.4090(6)
C(15)	0.3741(8)	0.3646(25)	0.4413(7)
C(16)	0.3601(9)	0.5575(24)	0.4216(8)
C(17)	0.2813(9)	0.6083(20)	0.3706(8)
C(18)	0.2178(8)	0.4701(18)	0.3392(7)
H(2) *	0.201(6)	0.101(13)	0.032(5)
H(5)	0.116(6)	0.115(13)	0.457(5)
H(8)	0.381(6)	0.072(14)	0.218(5)
H(9)	0.510(6)	0.293(13)	0.198(5)
H(10)	0.479(6)	0.598(14)	0.147(5)
H(11)	0.330(6)	0.689(14)	0.099(6)
H(12)	0.198(6)	0.454(14)	0.114(5)
H(14)	0.323(6)	0.083(14)	0.424(5)
H(15)	0.435(6)	0.349(13)	0.474(5)
H(16)	0.406(6)	0.684(13)	0.436(5)
H(17)	0.270(6)	0.740(14)	0.358(5)
H(18)	0.155(6)	0.505(13)	0.306(5)

* Hydrogen atoms are given the number of the atom to which they are attached.

TABLE 2

Final thermal parameters *,†

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	73(2)	275(8)	30(1)	−22(4)	−2(1)	−11(3)
S(6)	56(2)	293(9)	36(1)	−31(3)	11(1)	18(3)
S(6a)	46(1)	219(7)	34(1)	−14(3)	3(1)	2(2)
C(2)	64(7)	275(32)	24(4)	0(13)	5(4)	−8(10)
C(3)	40(5)	191(24)	29(4)	−2(11)	9(4)	4(9)
C(3a)	34(5)	173(24)	27(4)	−23(9)	1(3)	−15(8)
C(4)	39(5)	193(24)	28(4)	−13(11)	2(3)	−13(9)
C(5)	49(6)	264(32)	30(4)	11(12)	3(4)	15(10)
C(7)	46(6)	186(27)	25(4)	6(10)	8(4)	2(8)
C(8)	43(6)	298(34)	41(5)	10(13)	0(4)	4(11)
C(9)	45(7)	480(56)	54(7)	−4(17)	7(5)	5(16)
C(10)	64(9)	557(63)	42(6)	−108(20)	1(6)	1(15)
C(11)	106(11)	276(41)	47(6)	−49(18)	12(7)	23(13)
C(12)	53(6)	287(37)	44(6)	−8(14)	5(5)	15(11)
C(13)	42(5)	248(30)	23(4)	−1(11)	9(4)	6(9)
C(14)	42(6)	320(36)	33(5)	27(13)	5(4)	−3(11)
C(15)	36(6)	431(49)	45(6)	4(15)	−3(4)	−55(15)
C(16)	63(8)	346(45)	48(6)	−42(16)	7(6)	−47(14)
C(17)	77(8)	197(31)	64(7)	−5(15)	12(6)	−11(13)
C(18)	44(6)	244(32)	39(5)	−21(12)	−2(5)	0(10)

* Anisotropic temperature factors (× 10^4) expressed as exp $-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. † Constant isotropic temperature factors of B_θ 3.0 Å^2 were given to the hydrogen atoms.

RESULTS AND DISCUSSION

A stereoscopic view of a single molecule of (III) is shown in Figure 1. Bond lengths and angles in the molecule are shown in Figures 2 and 3.

The general features of the molecular structure are similar to those found in other thiathiophthen molecules. The central C–S bond [1.740(10) Å] is significantly longer than the two external bonds [1.649(12) and 1.653(12) Å]. These latter two bond lengths are considerably shorter than the values [1.715—1.727(8) Å] found, *e.g.* in the 3-amino-2-methylthio-5-phenyl-6a-thiathiophthen molecule (IV),[7] and in most of the symmetrically substituted thiathiophthens which have been studied by X-ray methods.[3,4,12-17] While a central C–S bond longer than

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

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

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

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, *A***24**, 321.

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

[12] O. Hjellum and A. Hordvik, *Acta Chem. Scand.*, 1973, **27**, 2666.

[13] A. Hordvik, O. Sjølset, and L. J. Saethre, *Acta Chem. Scand.*, 1973, **27**, 379.

[14] B. Birknes, A. Hordvik, and L. J. Saethre, *Acta Chem. Scand.*, 1973, **27**, 382.

[15] B. Birknes, A. Hordvik, and L. J. Saethre, *Acta Chem. Scand.*, 1972, **26**, 2140.

[16] E. C. Llaguno and I. C. Paul, unpublished data; E. C. Llaguno, Ph.D. Thesis, University of Illinois, 1973.

[17] A. Hordvik, personal communication, 1974.

the external ones is quite normal, only in thiathiophthen itself (V) [1.667(9) Å][18] and in one of the molecules of 3,4-trimethylenethiathiophthen (VI) [1.62—1.63(2) Å],[16] are the external ones comparably short with those found in the present study. The two 'internal' C–C bonds [1.446 and 1.448(12) Å] in the thiathiophthen nucleus are also considerably longer than the two 'external' C–C bonds [1.390 and 1.401(14) Å] although both sets of bonds are somewhat longer than are usually found in symmetrically substituted thiathiophthens; however, they agree quite well with those found in the tetraphenylthiathiophthen (VII).[12,17] There are also some interesting bond-angle patterns at C(3) and C(4). The steric repulsion between the phenyl substituents at C(3) and C(4) causes the external angles C(3a)–C(3)–C(7) and C(3a)–C(4)–C(13) to be much greater than 120°, and the angles C(2)–C(3)–C(7) and C(5)–C(4)–C(13) to be less than 120°. A somewhat similar effect was noted in the structure of 2,3,4-triphenylthiathiophthen (VIII), particularly at the 4-carbon atom.[19] There also appears to be an effect on the internal angles C(2)–C(3)–C(3a) [114.2(7)°] and C(3a)–C(4)–C(5) [117.1(9)°], which are much smaller than those normally found.

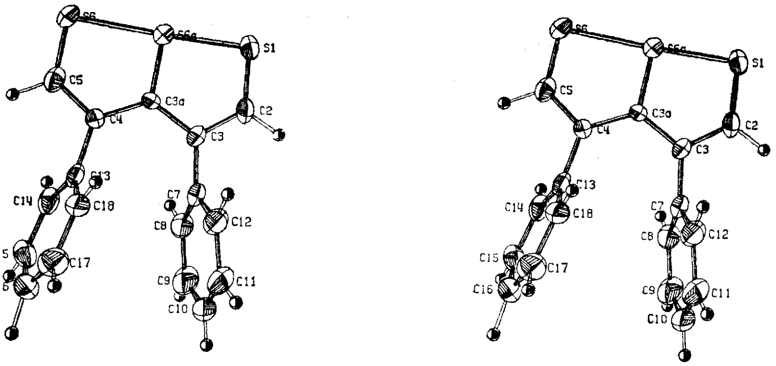

FIGURE 1 Stereoscopic view of a single molecule of (III)

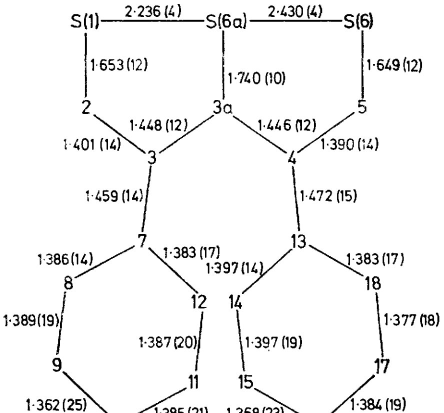

FIGURE 2 Bond lengths (Å) with estimated standard deviations for (III)

The S–S bonds in (III) are quite unequal, [2.236(4) and 2.430(4) Å]. (III) is one of four symmetrically-substituted thiathiophthens which are known not to use symmetry elements in the crystal, the others being (II)[4] and (VI),[16] and the 2,5-diphenyl-3,4-trimethylene derivative (IX).[15] Unlike the 2,5-disubstituted derivative (II),[4] and the tetrasubstituted derivative (VII),[12] the S–S bond lengths in (III) and (VI) are markedly unequal. In (VI), there are two independent molecules in the crystallographic asymmetric unit; in one molecule the S–S lengths are 2.300(7) and 2.385(7), while in the other, they are 2.276(7) and 2.412(7) Å.[16] Thus, on the basis of the rather limited data so far available, it appears that 3,4-symmetrically disubstituted derivatives may have a greater tendency for unequal S–S lengths than 2,5-symmetrically disubstituted ones. The sum of the two S–S lengths (4.666 Å) lies to the lower end of the range found in the thiathiophthens (4.62—4.74 Å),

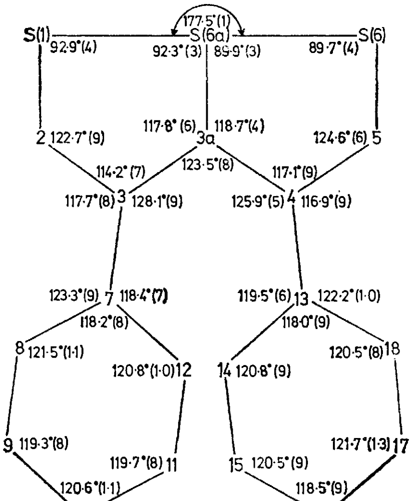

FIGURE 3 Bond angles (deg.), with estimated standard deviations for (III)

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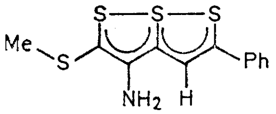
[18] L. K. Hansen and A. Hordvik, *Acta Chem. Scand.*, 1970, **24**, 2246; 1973, **27**, 411.

[19] A. Hordvik, *Acta Chem. Scand.*, 1971, **25**, 1822.

when certain 'anomalous thiathiophthens' reported recently are excluded.[20,21] An identical sum was reported for the 2,5-diphenyl derivative.[4]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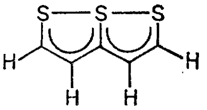
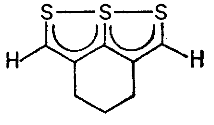

(V)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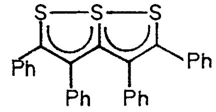
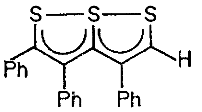
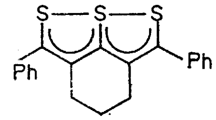

(VII)


(VIII)


(IX)

As in most thiathiophthen derivatives, the eight non-hydrogen atoms of the central nucleus approach planarity, deviations from the best plane ranging from —0.015 to 0.026 Å (Table 3). The two attached carbon atoms from the phenyl rings deviate by —0.073 [C(7)] and 0.037 Å [C(13)] from the best plane through the eight central atoms. Much greater deviations from planarity (—0.141 and 0.183 Å) were reported for the corresponding atoms in (VIII).[19] The two groups of five atoms which comprise the five-membered rings in (III) are each planar. The two five-membered rings are mutually inclined at 1.15°. A striking feature of the geometry of the molecule is the deviation from planarity at C(7) and C(13), as demonstrated by C(3) lying 0.097 and C(4) —0.113 Å from the best plane through the attached phenyl rings. The phenyl rings, C(7)—(12) and C(13)—(18), make angles of 74° 50′ and 70° 18′ with the central plane, thus π-electron conjugation between these rings and the thiathiophthen nucleus should be negligible. In the triphenyl derivative (VIII) the angles of twist of the 3- and 4-phenyl groups were reported to be 58.7 and 61.4°,[19] while in the tetraphenyl

TABLE 3

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

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

[S(1) 0.009, C(2) 0.026, C(3) —0.012, C(3a) —0.015, S(6a) —0.014, C(4) 0.003, C(5) 0.021, S(6) 0.007, C(7) —0.073, C(10) —0.144, C(13) 0.037, C(16) 0.105]

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

[S(1) —0.001, C(2) 0.017, C(3) —0.009, C(3a) 0, S(6a) 0, C(4) 0.033, C(5) 0.062, S(6) 0.046, C(7) —0.071, C(10) —0.147]

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

[S(1) 0.043, C(2) 0.058, C(3) 0.008, C(3a) —0.006, S(6a) 0.001, C(4) 0, C(5) 0.009, S(6) —0.001, C(13) 0.028, C(16) 0.084]

Plane (*D*): C(7)—(12)

[C(3) 0.097, C(7) 0.002, C(8) 0, C(9) —0.003, C(10) 0.002 C(11) 0.003, C(12) —0.005]

Plane (*E*): C(13)—(18)

[C(4) —0.113, C(13) 0.007, C(14) —0.002, C(15) —0.008, C(16) 0.008, C(17) 0.003, C(18) —0.009]

	(*A*)	(*B*)	(*C*)	(*D*)	(*E*)
χ^2	49.3	2.8	1.2	0.4	2.3
P †	<0.01	*ca.* 0.5	0.5	>0.99	~0.5

* Atoms were weighted as $1/\sigma^2$, where σ is standard deviation in position from the least-squares results. † Probability based on χ^2 test that deviations of atoms from plane form a normal distribution.

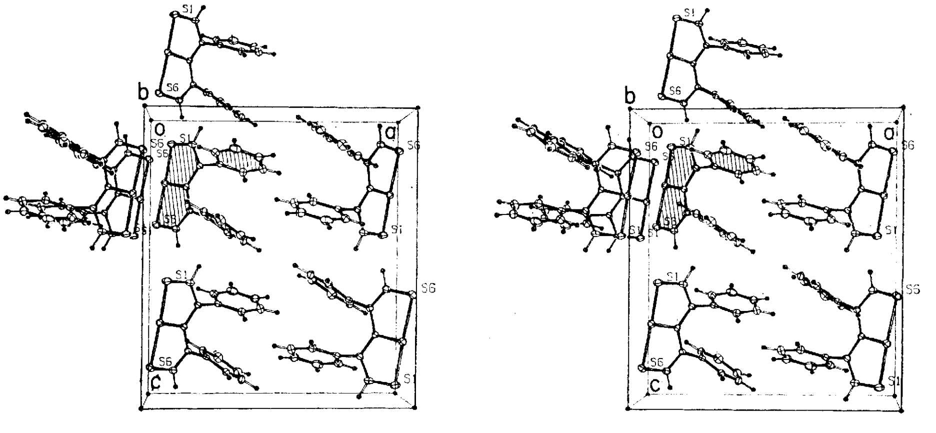


FIGURE 4 Stereoscopic view of the packing of the crystal of (III) looking along the *b* axis. The reference molecule at *x*, *y*, *z* is shaded

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[20] K.-T. Wei, I. C. Paul, R. J. S. Beer, and A. Naylor, *J.C.S. Chem. Comm.*, 1975, 264.

[21] L. K. Hansen and A. Hordvik, *J.C.S. Chem. Comm.*, 1974, 800.

derivative,[12] they are 70.7°. In the tetraphenyl derivative, the molecule has C_2 crystallographic symmetry.*

The packing in the crystal is shown in Figure 4. Intermolecular contacts are listed in Table 4. Most of the short contacts involve approaches between the linear S–S–S system and the near perpendicular thiathiophthen nucleus of the molecule at $-x$, $-\frac{1}{2}+y$, and $\frac{1}{2}-z$. Nyburg [22] sought an explanation of the difference in S–S lengths in (III) and in the 2,5-diphenyl derivative (II) in terms of intermolecular packing forces. He calculated the couples that should act on the external sulphur atoms along the S–S vectors. Whether because of inappropriate interatomic potentials, or the overriding importance of intramolecular effects, his calculations did not explain the observed pattern of bond lengths in (III). He calculated that the couple on S(6) was *ca.* 2.5 times greater than that on S(1).

TABLE 4

Important intermolecular contacts (Å) in the crystal

S(1) ··· S(6$^{\text{I}}$)	3.74	S(6) ··· C(2$^{\text{I}}$)	3.54
S(1) ··· C(5$^{\text{I}}$)	3.47	S(6) ··· C(3$^{\text{I}}$)	3.59
S(6a) ··· S(6a$^{\text{I}}$)	3.85	S(6) ··· C(3a$^{\text{I}}$)	3.72
S(6a) ··· S(6$^{\text{I}}$)	3.93	S(1) ··· S(6$^{\text{II}}$)	3.63
S(6a) ··· C(3a$^{\text{I}}$)	3.63	C(14) ··· C(2$^{\text{III}}$)	3.79
S(6a) ··· C(4$^{\text{I}}$)	3.61	C(14) ··· C(12$^{\text{III}}$)	3.69
S(6a) ··· C(5$^{\text{I}}$)	3.69	C(15) ··· C(2$^{\text{III}}$)	3.74
S(6) ··· S(1$^{\text{I}}$)	3.79	C(16) ··· C(2$^{\text{III}}$)	3.79

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

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

It is of interest that an ESCA study [23] on (III) shows three different binding energies for sulphur and is thus entirely consistent with the crystal structure. As has been shown by studies on other thiathiophthens, the core electrons of the central sulphur S(6a) are most tightly held, but in (III) there is a greater difference in binding energies between the two external sulphur atoms [S(1) and S(6)] than that between S(1) and S(6a). The lower binding energy for S(6) is interpreted in terms of a greater electron population for this atom.[23]

The present study clearly demonstrates, together with that on the 3,4-trimethylene derivative (VI),[16] that some symmetrically substituted thiathiophthens can have S–S lengths differing by as much as 0.2 Å. However, the question of whether symmetrically-substituted thiathiophthens which use crystallographic symmetry in the solid state have intrinsic molecular symmetry is still being widely pursued. ESCA results for 2,5-dimethylthiathiophthen (I) have been presented as supporting both a symmetrical [23] and an unsymmetrical [24] molecular structure. The electronic spectrum of (I) has also been interpreted [25] in terms of an unsymmetrical molecular structure, although the apparent discrepancy with the *X*-ray results could have several explanations.[26] Most recently a gas-phase electron-diffraction study of the unsubstituted thiathiophthen has been shown to indicate a symmetrical structure with C_{2v} symmetry.[27]

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* In ref. 12, the angles of twist of the 2- and 3-phenyl groups were erroneously transposed.[17]

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