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The Crystal and Molecular Structure of 2,5-Diphenyl-3,4-trimethylene-6a-thiathiophthene

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2,5-Diphenyl-3,4-trimethylene-6a-thiathiophthene crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a=6.882(1)$ Å, $b=12.871(1)$ Å, $c=19.049(1)$ Å, and $\beta=94.98(2)°$.

The structure was solved by three-dimensional Patterson synthesis, and refined by full-matrix least squares to an R of 0.037.

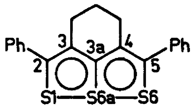
C(8) and C(10), bonded to C(3) and C(4), lie near the plane of the 6a-thiathiophthene system, and the 2- and 5-phenyl groups are twisted 47.3 and 54.3° about the respective connecting bonds.

S(1)—S(6a) and S(6a)—S(6) are 2.329(1) and 2.288(1) Å, respectively, with the angle S(1)—S(6a)—S(6)=179.28(4)°. Other bond lengths in the central ring system are, S(1)—C(2)= 1.710(2), S(6a)—C(3a)=1.755(2), S(6)—C(5)= 1.709(2), C(2)—C(3)=1.381(3), C(3)—C(3a)= 1.426(3), C(3a)—C(4)=1.425(3), and C(4)—C(5)=1.378(3) Å.

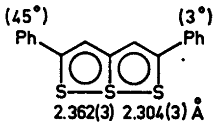
The present structure investigation of 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene (I) has been carried out in order to find the degree to which a 3,4-trimethylene bridge shortens the sulfur-sulfur bonds there relative to those in 2,5-diphenyl-6a-thiathiophthene II.[1] Structure studies on the 6a-selenaselenophthenes III [2] and IV [3] show that a 3,4-trimethylene bridge has a shortening effect on the Se—Se bonds. Furthermore, we wanted to test whether the phenyl substituents would affect the S—S bonds in accordance with theoretical predictions.[4]

STRUCTURE ANALYSIS

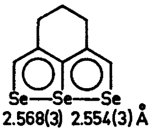
A brief account of the structure determination has been reported,[5] and a more detailed description is given here.



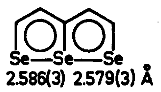
(I)



(II)



(III)



(IV)

A sample of I was generously supplied by M. Stavaux.[6] The crystals are dark red.

Crystal data

$C_{20}H_{16}S_3$ M.w.=352.54

Space group $P2_1/c$

$a=6.8824(8)$ Å, $b=12.8711(4)$ Å, $c=19.049(11)$ Å, $\beta=94.98(2)°$

$V=1680.9$ Å^3

$D_c=1.391$ g/cm^3, D_m(flotation)$=1.38$ g/cm^3

$Z=4$

$\mu=38.2$ cm^{-1} (Cu$K\alpha$)

All the X-ray measurements were carried out on a paper-tape controlled Siemens AED diffractometer using Cu$K\alpha$ radiation ($\lambda=1.5418$ Å).

The unit cell dimensions were determined from the 2θ values of 12 high order reflections measured at room temperature, $t=22$ °C, $\lambda\alpha_1=1.5404$ Å. A least squares procedure gave the values quoted above.

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The intensities of the reflections were measured by means of the five-value scan technique.[7] Reflections for which the net count was greater than two times the respective standard deviation in the net count, were accepted as observed. With this criterion 2546 independent reflections were observed within $\theta = 71°$; the unobserved reflections were neglected in order to save computer time.

Lp corrections and absorption corrections[8] were applied. The dimensions of the crystal were $0.2 \times 0.4 \times 0.07$ mm in the three axial directions; a grid of $16 \times 8 \times 4$ points was used.

The scattering factors for sulfur and carbon were taken from the *International Tables.*[9] For hydrogen, the scattering factor curve given by Stewart *et al.*[10] was used.

Approximate coordinates for the sulfur atoms were found from a three-dimensional Patterson synthesis, and the positions of the carbon atoms were found from a subsequent Fourier map; hydrogen positions were calculated. The atomic parameters were refined by full matrix least squares (see for example Ref. 11) to an R of 0.037.

Final atomic coordinates and temperature parameters are listed in Tables 1 and 2, respectively. The final structure factor list is available on request.

Rigid body analyses for the entire molecule as well as for certain parts of the molecule have been carried out according to the method of Schomaker and Trueblood.[12] The parts of the molecule treated in this way are, the three central rings plus C(7) and C(11), the 2-phenyl group plus C(2), and the 5-phenyl group plus C(5), cf. Fig. 1. The corresponding librational tensors, $\mathbf{L}_1$, $\mathbf{L}_2$, and $\mathbf{L}_3$, are given in Table 3. One notes from the values there that the libration is rather anisotropic in either case.

The calculations mentioned above were carried out on an IBM 360/50H computer. The programs, with some exeptions, originates from the Weizmann Institute of Science, Rehovoth, Israel, and have been modified for the 360 by D. Rabinovich, L. M. Milje, K. Maartmann-Moe and K. Åse.

DISCUSSION

Bond lengths and angles with standard deviations, calculated from the values in Table 1, are listed in Tables 4 and 5, respectively. A more realistic estimate of the standard deviations might probably be obtained by multiplying those given by a factor of two.[13]

The S–S, C–S, and C–C bond lengths have been corrected[14] for rigid-body libration according to the libration tensors given in Table 3. The corrections which give the l' values are based on the libration tensor $\mathbf{L}$, and the corrections leading to the l'' values are based on

Table 1. Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of the respective values.

Atom	*x*	*y*	*z*
S(1)	0.13658(11)	0.38796(5)	0.25399(4)
S(6a)	0.41424(10)	0.39356(4)	0.32917(4)
S(6)	0.69494(11)	0.39799(5)	0.40671(4)
C(2)	0.13425(36)	0.25623(17)	0.24082(12)
C(3)	0.28201(36)	0.20239(18)	0.28556(12)
C(3a)	0.42892(36)	0.25834(16)	0.32700(13)
C(4)	0.58586(36)	0.20837(18)	0.36724(12)
C(5)	0.71937(36)	0.26671(18)	0.40819(13)
C(7)	−0.02645(36)	0.21024(18)	0.20120(13)
C(8)	0.28780(50)	0.08470(20)	0.28620(18)
C(9)	0.40753(54)	0.04149(22)	0.34859(18)
C(10)	0.60259(50)	0.09178(21)	0.36009(18)
C(11)	0.88521(37)	0.22514(18)	0.45519(12)
C(12)	0.85509(43)	0.15319(20)	0.50828(15)
C(13)	1.00906(51)	0.11950(22)	0.55357(15)
C(14)	1.19584(47)	0.15674(24)	0.54689(16)
C(15)	1.22673(45)	0.22825(27)	0.49563(18)
C(16)	1.07174(42)	0.26247(23)	0.44973(15)
C(17)	−0.21615(42)	0.24588(23)	0.20446(15)
C(18)	−0.36673(44)	0.20771(28)	0.15833(18)
C(19)	−0.32898(50)	0.13536(25)	0.10800(16)
C(20)	−0.14040(50)	0.09955(21)	0.10372(15)
C(21)	0.00881(42)	0.13641(21)	0.15015(15)
H(12)	0.7193(37)	0.1317(19)	0.5105(13)
H(13)	0.9974(43)	0.0685(21)	0.5899(15)
H(14)	1.3291(39)	0.1362(18)	0.5762(14)
H(15)	1.3629(47)	0.2566(24)	0.4878(17)
H(16)	1.0914(40)	0.3164(20)	0.4147(14)
H(17)	−0.2441(40)	0.2994(20)	0.2392(14)
H(18)	−0.5069(43)	0.2371(22)	0.1622(15)
H(19)	−0.4413(45)	0.1075(22)	0.0758(16)
H(20)	−0.1155(52)	0.0515(26)	0.0626(18)
H(21)	0.1262(33)	0.1160(18)	0.1471(13)
H(81)	0.3465(52)	0.0594(25)	0.2426(18)
H(82)	0.1535(48)	0.0548(23)	0.2830(16)
H(91)	0.3490(63)	0.0500(31)	0.3931(20)
H(92)	0.4282(50)	−0.0410(29)	0.3430(17)
H(101)	0.6686(59)	0.0712(29)	0.3179(20)
H(102)	0.6858(46)	0.0665(22)	0.4012(16)

Table 2. Temperature parameters U_{ij} (Å^2) for sulfur and carbon, and U (Å^2) for hydrogen. The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11}+\cdots 2hka^*b^*U_{12}+\cdots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$. All values are multiplied by 10^4. Standard deviations in parentheses refer to the last digits of the respective values.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	575(5)	352(3)	626(4)	90(3)	29(3)	−91(4)
S(6a)	544(4)	277(3)	543(4)	7(3)	21(3)	7(3)
S(6)	604(5)	350(3)	650(5)	−69(3)	17(3)	−116(4)
C(2)	432(15)	388(13)	438(13)	13(11)	29(11)	68(12)
C(3)	425(15)	341(12)	490(14)	2(11)	16(10)	2(12)
C(3a)	438(14)	295(11)	451(13)	18(11)	13(10)	59(11)
C(4)	437(15)	355(13)	497(15)	34(11)	−22(10)	−6(12)
C(5)	422(15)	407(13)	462(14)	−7(11)	10(11)	55(12)
C(7)	426(15)	424(13)	449(14)	−12(11)	103(11)	29(12)
C(8)	672(22)	312(14)	841(23)	−8(14)	21(14)	−245(19)
C(9)	814(25)	335(14)	953(25)	−51(15)	54(15)	−357(21)
C(10)	673(21)	346(14)	910(24)	85(14)	−48(15)	−295(18)
C(11)	429(15)	429(13)	433(14)	7(12)	−48(11)	21(12)
C(12)	530(17)	445(14)	553(16)	−15(13)	3(12)	−9(14)
C(13)	750(22)	504(16)	542(17)	45(16)	28(13)	−113(16)
C(14)	587(20)	704(20)	611(19)	115(16)	−82(16)	−143(16)
C(15)	427(17)	885(23)	685(20)	4(17)	−97(18)	8(16)
C(16)	445(16)	723(20)	536(17)	−22(15)	0(14)	59(14)
C(17)	446(17)	681(19)	547(17)	32(15)	110(14)	50(14)
C(18)	436(18)	877(24)	671(20)	−31(16)	218(18)	23(18)
C(19)	681(23)	640(19)	625(19)	−200(17)	220(16)	−178(17)
C(20)	730(21)	474(16)	586(17)	−45(16)	62(14)	−117(16)
C(21)	511(17)	437(14)	544(16)	19(13)	29(12)	−21(14)

Atom	U	Atom	U	Atom	U
H(12)	610(134)	H(18)	903(167)	H(2)	993(193)
H(13)	849(167)	H(19)	947(158)	H(91)	1566(298)
H(14)	667(130)	H(20)	1390(229)	H(92)	1330(201)
H(15)	1130(198)	H(21)	434(122)	H(101)	1459(284)
H(16)	716(155)	H(81)	1172(239)	H(102)	958(205)
H(17)	691(151)				

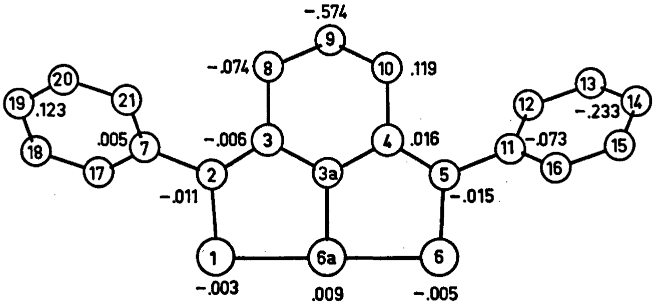

Fig. 1. The 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene molecule, with numbering of carbon and sulfur atoms. Deviations (Å) from a least squares plane through the atoms of the 6a-thiathiophthene system are given.

Table 3. Rigid body libration tensors for the entire molecule (**L**), the three central rings plus C(7) and C(11) ($\mathbf{L}_1$), the 2-phenyl group plus C(2) ($\mathbf{L}_2$), and the 5-phenyl group plus C(5) ($\mathbf{L}_3$).

	Eigenvalues	Eigenvectors		^{a}
L	37.30 (°)^2	−6631	−112	−7501
	2.25	−6720	−4355	5989
	0.86	−3333	9002	2804
$\mathbf{L}_1$	38.50	−7110	−309	−7025
	2.72	−6841	−2004	7013
	−0.38	−1625	9792	1212
$\mathbf{L}_2$	37.91	−5700	−1252	−8121
	12.87	−2231	−9276	2996
	2.82	−7902	3520	5008
$\mathbf{L}_3$	35.37	6565	−2415	7146
	15.86	1156	−9039	−4118
	5.66	7454	3529	−5656

^{a} Direction cosines × 10^4 relative to *a*, *b*, and c^*, respectively.

Table 4. Bond lengths (l) in 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene. Standard deviations in parentheses. Bond lengths (l') and (l'') with corrections for rigid-body libration are given for the S−S, S−C, and C−C bonds. The corrections in (l') are based on the libration tensor one arrives at by treating the whole molecule as a rigid body, and the corrections in (l'') are based on the libration tensors one gets when the three central rings and each of the phenyl groups are treated separately. For further explanation see the test.

Bond	l'' (Å)	l' (Å)	l (Å)
S(1)−S(6a)	2.288	2.289	2.287(1)
S(6a)−S(6)	2.329	2.330	2.328(1)
S(1)−C(2)	1.710	1.710	1.699(2)
S(6a)−C(3a)	1.755	1.754	1.744(2)
S(6)−C(5)	1.709	1.708	1.698(2)
C(2)−C(3)	1.381	1.381	1.378(3)
C(3)−C(3a)	1.426	1.426	1.423(3)
C(3a)−C(4)	1.425	1.425	1.423(3)
C(4)−C(5)	1.378	1.378	1.375(3)
C(3)−C(8)	1.525	1.525	1.515(4)
C(8)−C(9)	1.496	1.496	1.494(5)
C(9)−C(10)	1.494	1.494	1.489(5)
C(10)−C(4)	1.522	1.521	1.512(4)
C(2)−C(7)	1.487	1.485	1.482(3)
C(5)−C(11)	1.492	1.490	1.488(3)
C(7)−C(17)	1.399	1.396	1.390(4)
C(17)−C(18)	1.393	1.391	1.389(4)
C(18)−C(19)	1.386	1.385	1.377(5)
C(19)−C(20)	1.396	1.392	1.386(5)
C(20)−C(21)	1.384	1.382	1.380(4)
C(21)−C(7)	1.405	1.403	1.396(4)
C(11)−C(12)	1.408	1.407	1.400(4)
C(12)−C(13)	1.381	1.379	1.377(4)
C(13)−C(14)	1.397	1.394	1.388(5)
C(14)−C(15)	1.380	1.379	1.372(5)
C(15)−C(16)	1.395	1.392	1.391(4)
C(16)−C(11)	1.392	1.389	1.383(4)
C(12)−H(12)			0.98(3)
C(13)−H(13)			0.96(3)
C(14)−H(14)			1.07(3)
C(15)—H(15)			1.03(3)
C(16)−H(16)			0.98(3)
C(17)−H(17)			0.99(3)
C(18)−H(18)			1.04(3)
C(19)−H(19)			1.01(3)
C(20)−H(20)			1.02(3)
C(21)−H(21)			0.86(2)
C(8)−H(81)			1.01(4)
C(8)−H(82)			1.00(3)
C(9)−H(91)			0.98(4)
C(9)−H(92)			1.08(4)
C(10)−H(101)			0.99(4)
C(10)−H(102)			0.98(3)

$\mathbf{L}_1$, $\mathbf{L}_2$, and $\mathbf{L}_3$. There is close agreement between the l' and l'' values in this case, *cf.* Table 4, and one should note in this connection that the axes of maximum libration for $\mathbf{L}_1$, $\mathbf{L}_2$, and $\mathbf{L}_3$, *cf.* Table 3, are roughly parallel. In cases where this is not so, see for example Ref. 1, there will be a difference between the l' and l'' values.

The numbering of C and S atoms in the 2,5-diphenyl-3,4-trimethylene-6*a*-thiathiophthene molecule is shown in Fig. 1. Deviations from a least squares plane through the atoms of the thiathiophthene-system are given on the figure. The 2-phenyl group is twisted 47.3° about the C(2)−C(7) bond. This twist angle was taken as the angle between the normal to the plane through C(2), C(7), C(17), and C(21), and the normal to the plane through C(2), C(7), C(3), and S(1). Similarly, the twist angle of the 5-phenyl group about C(5)−C(11) is 54.3°.

From Table 4 the sum of the S−S bond lengths in the present compound is 4.617(1) Å as compared with the value 4.666(3) Å for the sum of the S−S bond lengths in II. Thus, the 3,4-trimethylene bridge in I causes a shortening of the three-sulfur sequence there relative that in II. This agrees with the results from the structure studies on the analogous selenium compounds mentioned in the introduction. In compounds III and IV the sums of the Se−S bond lengths are 5.122(3) and 5.165(3) Å,

Table 5. Bond angles ∠(ijk) in 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	k	∠(ijk)°
S(1)	S(6a)	S(6)	179.28(4)
C(2)	S(1)	S(6a)	94.35(8)
C(3)	C(2)	S(1)	117.7(2)
C(3a)	C(3)	C(2)	119.3(2)
S(6a)	C(3a)	C(3)	118.6(2)
S(1)	S(6a)	C(3a)	90.04(8)
C(3a)	S(6a)	S(6)	89.59(8)
C(4)	C(3a)	S(6a)	118.8(2)
C(5)	C(4)	C(3a)	119.8(2)
S(6)	C(5)	C(4)	118.3(2)
S(6a)	S(6)	C(5)	93.54(8)
C(3)	C(2)	C(7)	126.1(2)
S(1)	C(2)	C(7)	116.2(2)
C(11)	C(5)	C(4)	125.8(2)
C(11)	C(5)	S(6)	115.9(2)
C(4)	C(3a)	C(3)	122.7(2)
C(10)	C(4)	C(3a)	117.4(2)
C(5)	C(4)	C(10)	122.7(2)
C(4)	C(10)	C(9)	111.7(2)
C(10)	C(9)	C(8)	112.5(2)
C(9)	C(8)	C(3)	113.0(2)
C(3a)	C(3)	C(8)	119.0(2)
C(8)	C(3)	C(2)	121.6(2)
C(2)	C(7)	C(17)	119.7(2)
C(2)	C(7)	C(21)	121.7(2)
C(7)	C(17)	C(18)	120.5(2)
C(17)	C(18)	C(19)	120.3(3)
C(18)	C(19)	C(20)	120.0(3)
C(19)	C(20)	C(21)	119.8(3)
C(20)	C(21)	C(7)	121.1(2)
C(21)	C(7)	C(17)	118.5(2)
C(5)	C(11)	C(16)	119.9(2)
C(5)	C(11)	C(12)	121.2(2)
C(11)	C(12)	C(13)	120.5(2)
C(12)	C(13)	C(14)	120.1(2)
C(13)	C(14)	C(15)	119.9(3)
C(14)	C(15)	C(16)	120.1(3)
C(15)	C(16)	C(11)	120.6(2)
C(16)	C(11)	C(12)	118.7(2)
C(3)	C(8)	H(81)	109(2)
C(3)	C(8)	H(82)	111(2)
C(9)	C(8)	H(81)	108(2)
C(9)	C(8)	H(82)	110(2)
H(81)	C(8)	H(82)	105(3)
C(81)	C(9)	H(91)	114(2)
C(8)	C(9)	H(92)	111(2)
C(10)	C(9)	H(91)	105(2)
C(10)	C(9)	H(92)	109(2)
H(91)	C(9)	H(92)	105(3)
C(4)	C(10)	H(101)	112(2)
C(4)	C(10)	H(102)	107(2)
C(9)	C(10)	H(101)	104(2)
C(9)	C(10)	H(102)	115(2)
H(101)	C(10)	H(102)	106(3)
C(11)	C(16)	H(16)	119(2)
C(15)	C(16)	H(16)	121(2)
C(16)	C(15)	H(15)	117(2)
C(14)	C(15)	H(15)	123(2)
C(15)	C(14)	H(14)	111(1)
C(13)	C(14)	H(14)	129(1)
C(14)	C(13)	H(13)	116(2)
C(12)	C(13)	H(13)	124(2)
C(11)	C(12)	H(12)	115(1)
C(13)	C(12)	H(12)	125(1)
C(7)	C(17)	H(17)	120(2)
C(18)	C(17)	H(17)	120(2)
C(17)	C(18)	H(18)	118(2)
C(19)	C(18)	H(18)	122(2)
C(18)	C(19)	H(19)	119(2)
C(20)	C(19)	H(19)	121(2)
C(19)	C(20)	H(20)	118(2)
C(21)	C(20)	H(20)	122(2)
C(20)	C(21)	H(21)	120(2)
C(7)	C(21)	H(21)	119(2)

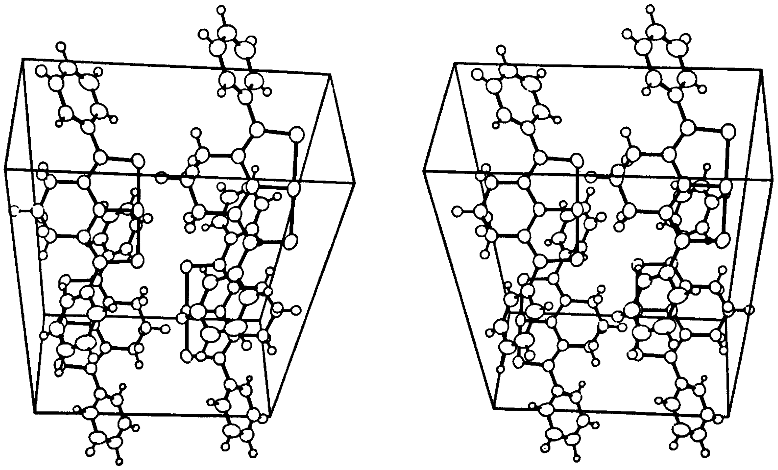

Fig. 2. Stereoview of the molecular packing.

respectively.[2,3] It should be mentioned in this connection that the Se—Se bond lengths in IV have not been corrected for libration, and the latter value is therefore probably somewhat too low.

The results from CNDO/2 calculations on mono-phenyl substituted 6a-thiathiophthenes show that a phenyl group in 2-position has a lengthening effect on the S(1)—S(6a) bond which varies with the twist angle of the phenyl group,[4] being negligible at twist angle 0° and most pronounced at 90°. As the twist angles of the 2- and 5-phenyl groups in the present structure deviate by 7° only, one might, in accordance with the CNDO/2 results, expect the S—S bond lengths to be almost equal. It is interesting, however, that the S(1)—S(6a) bond of 2.288(1) Å corresponds to twist angle 47.3°, while the S(6a)—S(6) bond of 2.329(1) Å corresponds to twist angle 54.3°.

CNDO/2 studies on 3,4-trimethylene-6a-thiathiophthene show that the trimethylene bridge does not affect the symmetry of the sulfur sequence.[15] This agrees with the results from the present study.

A stereoscopic view [16] of the molecular packing in the unit cell is given in Fig. 2. There are no intermolecular contacts shorter than corresponding van der Waals distance.

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