The Crystal and Molecular Structure of 2-Methyl-6a-thiathiophthene

LEIF J. SÆTHRE AND ASBJØRN HORDVIK*

Department of Chemistry, University of Bergen, N-5000 Bergen, Norway

2-Methyl-6a-thiathiophthene crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions: $a=5.9558(9)$, $b=7.8563(8)$, $c=16.014(4)$ Å, and $\beta=91.31(2)°$.

The structure was solved by direct methods and refined by full matrix least squares.

Unequal $S-S$ distances occur in the linear three sulphur sequence of the molecule, i.e $S(1)-S(6a)=2.4311(16)$ and $S(6a)-S(6)=2.3076(17)$ Å, as predicted by the results from CNDO/2 calculations.

The 6a-thiathiophthene system is almost planar, and other bond lengths in the molecule are, $S(1)-C(2) = 1.698(4)$, $S(6a)-C(3a) = 1.763(5)$, $S(6)-C(5)=1.681(5)$, $C(2)-C(3)= 1.362(7)$, $C(3)-C(3a)=1.408(6)$, $C(3a)-C(4)= 1.428(7)$, $C(4)-C(5)=1.367(7)$, and $C(2)-C(6)= 1.526(8)$ Å. The $S-S$, $S-C$, and $C-C$ bond lengths have been corrected for libration.

CNDO/2 calculations on 6a-thiathiophthene (I) and on its mono-methyl derivatives have been carried out,[1] cf. Fig. 1. The change in CNDO/2 total energy as a function of the $S(1)-S(6a)$ bond length shows that a 2-methyl group causes a lengthening of the $S(1)-S(6a)$ bond, and that a 3-methyl group causes a shortening of this bond relative to the symmetric structure of the unsubstituted compound.

(I)
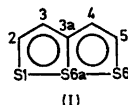
The present structure study of 2-methyl-6a-thiathiophthene has been carried out in order to test the CNDO/2 predictions.

* Present address: University of Tromsø, Box 790, N-9001 Tromsø, Norway.
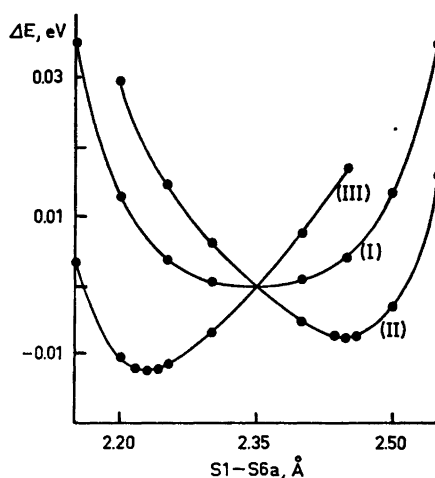
Fig. 1. The change ΔE in CNDO/2 total energy for 6a-thiathiophthene (I), 2-methyl-6a-thiathiophthene (II), and 3-methyl-6a-thiathiophthene (III) as a function of the $S(1)-S(6a)$ bond length.

STRUCTURE ANALYSIS AND REFINEMENT

A brief account of the structure analysis has been reported,[2] and a more detailed description is given here.

Crystals of 2-methyl-6a-thiathiophthene from cyclohexane are orange red plates with {001} predominant.

CRYSTAL DATA

$C_6H_6S_3$ M.w.$=174.31$

Monoclinic, systematic extinctions: $h0l$ when $l=2n+1$;

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)	0.22743(18)	0.05761(19)	0.38631(7)
S(6a)	0.04167(18)	0.05576(16)	0.25001(8)
S(6)	−0.12664(19)	0.06320(19)	0.11928(7)
C(2)	0.4320(7)	0.1880(6)	0.3533(3)
C(3)	0.4300(8)	0.2372(6)	0.2721(3)
C(3a)	0.2585(7)	0.1871(5)	0.2158(3)
C(4)	0.2494(9)	0.2368(7)	0.1304(3)
C(5)	0.0750(8)	0.1851(6)	0.0801(3)
C(6)	0.6129(11)	0.2495(11)	0.4146(4)
H(3)	0.536(6)	0.319(4)	0.2531(27)
H(4)	0.363(7)	0.305(6)	0.1166(29)
H(5)	0.064(6)	0.224(5)	0.0240(24)
H(61)	0.667(11)	0.169(9)	0.444(4)
H(62)	0.751(9)	0.278(7)	0.388(4)
H(63)	0.558(9)	0.340(8)	0.442(4)

$0k0$ when $k=2n+1$
Space group $P2_1/c$ with $Z=4$
$a=5.9558(9)$ Å, $b=7.8563(8)$ Å, $c=16.014(4)$ Å,
$\beta=91.31(2)°$
$V=749.1$ Å³
$D_{\text{calc}}=1.545$ g/cm³, $D_{\text{exp}}=1.54$ g/cm³
$\mu_{\text{MoK}\alpha}=8.56$ cm⁻¹

The crystal used for all X-ray measurements had the shape of a rectangular prism, and the dimensions were $0.15 \times 0.17 \times 0.05$ mm along [110], [Ī10], and [001], respectively.

Unit cell dimensions and intensity data were measured on a paper-tape controlled Siemens AED diffractometer using MoKα radiation.

A least squares procedure on the 2θ values of 16 high order reflections, measured at 20 °C, gave the cell dimensions quoted above.

The intensities were collected by means of the five-value scan technique.[3] 790 independent reflections, measured within $\theta=27°$, and for which the net count was greater than 2.5 times the respective standard deviation in the net count, were accepted as observed. Unobserved reflections were neglected in order to save computing time.

Lp corrections and absorption corrections were applied, the latter according to a procedure of Coppens, Leiserowitz and Rabinovich.[4] A grid of $12 \times 14 \times 4$ points along a, b, and c, respectively, was used.

Observed structure factors were put on an absolute scale[5] and converted to normalized structure factors by means of a program written by Shiono.[6] The scattering factors used for sulfur and carbon were those given in the

Table 2. Temperature parameters U_{ij} (Å²) for sulfur and carbon, and U (Å²) 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)	467(7)	431(7)	384(7)	−43(7)	37(8)	43(5)
S(6a)	356(5)	338(6)	459(6)	−38(8)	8(9)	65(5)
S(6)	444(7)	510(8)	479(7)	−37(8)	−33(9)	−68(5)
C(2)	343(28)	348(26)	422(29)	63(20)	27(23)	14(24)
C(3)	402(31)	333(29)	402(30)	−80(25)	24(23)	25(25)
C(3a)	303(27)	280(26)	432(30)	−28(20)	−89(23)	112(24)
C(4)	433(29)	426(30)	377(30)	−58(25)	−9(23)	108(24)
C(5)	570(36)	467(30)	401(31)	69(24)	100(27)	−54(28)
C(6)	446(38)	689(45)	578(39)	−62(36)	−65(37)	−76(33)

Atom	U	Atom	U	Atom	U
H(3)	300(110)	H(5)	420(130)	H(62)	740(210)
H(4)	490(150)	H(61)	1240(300)	H(63)	920(240)

Table 3. Librational tensor L from the rigid-body analysis of 2-methyl-6a-thiathiophthene.

Eigenvalues	Eigenvectors		
L ⎧ 37.5 (°) [2]	4131	864	9066
⎨ 9.3	8160	−4770	−3264
⎩ 8.6	4043	8746	−2676

[a] Direction cosines × 10⁴ relative to a, b, and $c*$, respectively.

Table 4. Bond lengths (l) in 2-methyl-6a-thiathiophthene. The values (l') have been corrected for rigid-body libration. Standard deviations in parentheses refer to the last digits of the respective values.

Bond	l' (Å)	l (Å)
S(1)—S(6a)	2.4311	2.4244(16)
S(6a)—S(6)	2.3076	2.3012(17)
S(1)—C(2)	1.698	1.686(4)
S(6a)—C(3a)	1.763	1.750(5)
S(6)—C(5)	1.681	1.670(5)
C(2)—C(3)	1.362	1.356(7)
C(3)—C(3a)	1.408	1.403(6)
C(3a)—C(4)	1.428	1.422(7)
C(4)—C(5)	1.367	1.362(7)
C(2)—C(6)	1.526	1.520(8)
C(3)—H(3)		0.96(4)
C(4)—H(4)		0.89(5)
C(5)—H(5)		0.95(4)
C(6)—H(61)		0.85(7)
C(6)—H(62)		0.96(6)
C(6)—H(63)		0.90(6)

International Tables.[7] For hydrogen, the scattering factor given by Stewart *et al.*[8] was used.

The structure was solved by direct methods [9] and refined by full matrix least squares procedure (see for example Ref. 10). With anisotropic temperature factor coefficients for all atoms except hydrogen, the final R factor is 0.035.

Final atomic coordinates from the least squares refinement are listed in Table 1, and the temperature parameters are listed in Table 2. The final list of structure factors is available on request.

An analysis of the thermal parameters of the S and C atoms, assuming the molecule to be a rigid body, was carried out according to the method by Schomaker and Trueblood.[11] The librational tensor arrived at is given in Table 3. The r.m.s. difference between observed and calculated U_{ij}'s was found to be 0.0032 Å² as compared with the value 0.0041 Å² for the e.s.d. of U_{ij}. The S—S, S—C, and C—C bond lengths have been corrected for rigid body libration.[12]

All the calculations mentioned above were carried out on an IBM 360/50H computer. The programs, with a few exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel, and have been modified for the 360 by D. Rabinovich, L. M. Milje and K. Åse. The diffractometer programs have been written by K. Maartmann-Moe.
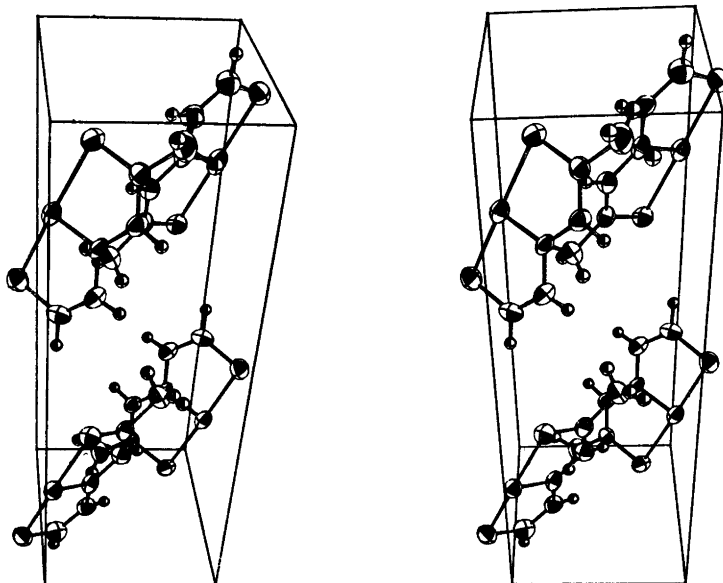
Table 5. Bond angles ∠(ijk) in 2-methyl-6a-thiathiophthene. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	k	∠(ijk)°	i	j	k	∠(ijk)°
S(1)	S(6a)	S(6)	177.77(6)	C(3a)	C(4)	C(5)	119.9(4)
S(1)	S(6a)	C(3a)	87.32(16)	C(2)	C(3)	H(3)	120(3)
S(6a)	S(6)	C(5)	93.12(18)	H(3)	C(3)	C(3a)	118(3)
C(2)	S(1)	S(6a)	92.25(16)	C(3a)	C(4)	H(4)	113(3)
C(3a)	S(6a)	S(6)	90.55(16)	H(4)	C(4)	C(5)	127(3)
S(1)	C(2)	C(6)	119.8(4)	C(4)	C(5)	H(5)	120(3)
S(1)	C(2)	C(3)	118.9(3)	H(5)	C(5)	S(6)	120(3)
S(6a)	C(3a)	C(3)	119.8(3)	C(2)	C(6)	H(61)	112(5)
S(6a)	C(3a)	C(4)	116.8(3)	C(2)	C(6)	H(62)	113(3)
S(6)	C(5)	C(4)	119.6(4)	C(2)	C(6)	H(63)	108(4)
C(6)	C(2)	C(3)	121.3(4)	H(61)	C(6)	H(62)	96(6)
C(2)	C(3)	C(3a)	121.7(4)	H(62)	C(6)	H(63)	111(5)
C(3)	C(3a)	C(4)	123.5(4)	H(61)	C(6)	H(63)	117(6)

Fig. 2. A stereoscopic view of the arrangement of 2-methyl-6a-thiathiophthene molecules in the unit cell.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and angles in the 2-methyl-6a-thiathiophthene molecule, as calculated from the positional parameters in Table 1, are listed in Table 4 and 5, respectively. Bond lengths which have been corrected for rigid-body libration are listed in the first column of Table 4.

The standard deviations given for bond lengths and angles are based on the standard deviations in positional parameters from the least squares refinement. According to Hamilton and Abrahams [13] a more realistic estimate of the standard deviations would probably be obtained by multiplying those given by a factor of two.

Deviations from a least squares plane for the atoms of the 6a-thiathiophthene system, with triple weight on sulfur, are, S(1) -0.007; S(6a) -0.010; S(6) 0.015; C(2) 0.035; C(3) 0.010; C(3a) -0.005; C(4) -0.022; C(5) -0.013; and C(6) 0.116 Å. One notes that the methyl carbon, C(6), lies slightly out of the plane.

The S(1)$-$S(6a) bond in the present compound is 2.4311(16) Å and thus longer than the S(6a)$-$S(6) bond of 2.3076(17) Å. This agrees with the CNDO/2 prediction. The C$-$S and

C$-$C bond lengths, *cf.* Table 4, are compatible with those usually found in 6a-thiathiophthenes.[14]

A stereoscopic view of the arrangement of 2-methyl-6a-thiathiophthene molecules in the unit cell is given in Fig. 2.[15]

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