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The Crystal and Molecular Structure of 6a-Thiathiophthene

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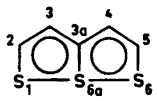
6a-Thiathiophthene crystallizes in the orthorhombic space group *Pnma* with four molecules in a unit cell of dimensions: $a = 7.768(6)$, $b = 15.784(6)$, and $c = 5.385(2)$ Å.

The structure was solved from Patterson and Fourier syntheses, and the atomic parameters were refined by the full-matrix least squares method. The refinement comprises the 1145 independent reflections (Mo$K\alpha$) in the range $10° < \theta < 32°$.

The 6a-thiathiophthene molecule is almost planar, and lies across a crystallographic mirror plane passing through the central carbon and sulphur atoms. The S–S distances are thus exactly equal, 2.363(1) Å, and the S(1)–S(6a)–S(6) angle is 177.93(8)°. Other bond lengths in the molecule are S(1)–C(2) = 1.684(3) Å, S(6a)–C(3a) = 1.748(3) Å, C(2)–C(3) = 1.354(3) Å, and C(3)–C(3a) = 1.409(2) Å.

The S–S, S–C and C–C bond lengths have been corrected for libration.

A number of 6a-thiathiophthene structures has been studied.[1] We carried out the present structure study of 6a-thiathiophthene (I) because we thought that the molecular dimensions of this compound would be of interest



(I)

as a reference when judging the degree to which different substituents perturb the bonding in the 6a-thiathiophthene system.

STRUCTURE DETERMINATION

A brief account of a structure determination of I based on photographic data has been reported,[2] and a more detailed description of a diffractometer study of the compound is given here.

Crystals of 6a-thiathiophthene were generously supplied by Reid.[3] The crystals are orange red and belong to the orthorhombic space group *Pnma*.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using Mo$K\alpha$ radiation.

The structure was solved by the heavy atom (S) method, and the atomic parameters were refined by full-matrix least squares to a final R factor of 4.0 %.

A rigid body analysis of the 6a-thiathiophthene molecule has been carried out according to the method of Schomaker and Trueblood,[4] and the S–S, S–C, and C–C bond lengths have been corrected for rigid body libration according to Cruickshank's formula.[5] For further details with respect to the structure determination, see Experimental.

STRUCTURE DESCRIPTION

Bond lengths and angles in the 6a-thiathiophthene molecule, together with their standard deviations, are listed in Tables 1 and 2, and shown in Fig. 1.

The 6a-thiathiophthene molecule lies across the crystallographic mirror plane m, which passes through the crystal normal to the b-axis. The dimensions of the two fused rings are therefore exactly equal.

Table 1. Bond lengths (l) and standard deviations in bond lengths $\sigma(l)$ in 6a-thiathiophthene. Bond lengths (l') with corrections for rigid-body libration are given for the S–S, S–C, and C–C bonds.

Bond	l' (Å)	l (Å)	$\sigma(l)$ (Å)
S(1)–S(6a)	2.363	2.350	0.001
S(1)–C(2)	1.684	1.673	0.003
S(6a)–C(3a)	1.748	1.737	0.003
C(2)–C(3)	1.354	1.347	0.003
C(3)–C(3a)	1.409	1.401	0.002
C(2)–H(2)		0.88	0.04
C(3)–H(3)		0.85	0.03

Table 2. Bond angles ∠(ijk) in 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)	177.9(1)
C(2)	S(1)	S(6a)	92.0(1)
S(1)	C(2)	C(3)	120.1(2)
C(2)	C(3)	C(3a)	120.3(2)
C(3)	C(3a)	C(4)	123.0(2)
C(3)	C(3a)	S(6a)	118.5(1)
S(1)	S(6a)	C(3a)	89.1(1)
S(1)	C(2)	H(2)	119(2)
H(2)	C(2)	C(3)	121(2)
C(2)	C(3)	H(3)	124(2)
H(3)	C(3)	C(3a)	116(2)

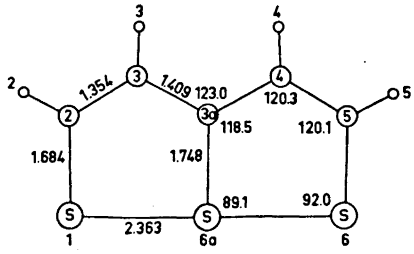


Fig. 1. Bond lengths (Å) and bond angles (°) in 6a-thiathiophthene.

The equation for the least squares plane of the atoms of the rings, with weights inversely proportional to the respective standard deviations in coordinates, is

$$0.82581\ X + 0.56396\ Z = 1.01260$$

with X and Z in Å units. Deviations from the plane for the atoms S(1), S(6a), C(2), C(3), and C(3a) are −0.008, 0.017, −0.009, 0.004, and 0.009 Å, respectively. Thus the 6a-thiathiophthene system is very nearly planar.

Comparison with other 6a-thiathiophthene structures. A comparison of the S−S bond lengths, the sums of the S−S bond lengths, and the C−S bond lengths in the 6a-thiathiophthenes so far studied (compounds I−XII [6–16]), is given in Table 3. One notes from Table 3 that the S−S bond lengths in compounds I−XII lie in the range 2.163(8)−2.561(8) Å, and that equal S−S bond lengths occur in symmetric as well as unsymmetric derivatives, *cf.* compounds I, II, and VI.

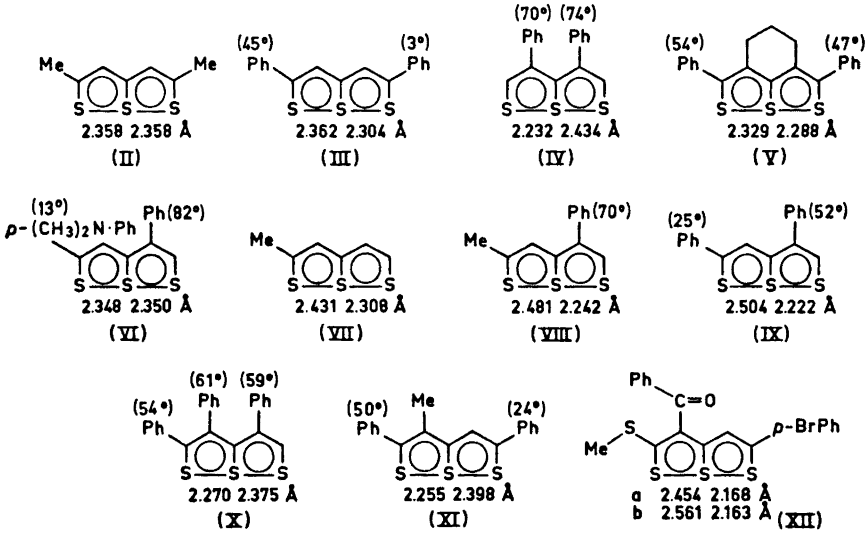
Table 3. A comparison of the S−S bond lengths, the sum of the S−S bond lengths, and the C−S bond lengths in different 6a-thiathiophthenes. Values in Å units.

Compound	S(1)–S(6a)	S(6a)–S(6)	∑(S–S)	S(1)–C(2)	S(6a)–C(3a)	S(6)–C(5)	Ref. No.
I	2.363(1)	2.363(1)	4.726(1)	1.684(3)	1.748(3)	1.684(3)	This paper
II [a]	2.358(1)	2.358(1)	4.716(1)	1.701(4)	1.745(4)	1.701(4)	6
III	2.362(3)	2.304(3)	4.666(3)	1.712(6)	1.753(6)	1.703(6)	7
IV [a]	2.232(4)	2.434(4)	4.666(4)	1.664(13)	1.749(13)	1.664(13)	8
V	2.329(1)	2.288(1)	4.617(1)	1.709(3)	1.755(3)	1.710(3)	9
VI	2.348(2)	2.350(2)	4.698(2)	1.705(4)	1.748(3)	1.689(3)	10
VII	2.431(2)	2.308(2)	4.739(2)	1.698(4)	1.763(5)	1.681(5)	11
VIII	2.481(2)	2.242(2)	4.723(2)	1.691(5)	1.751(4)	1.696(5)	12
IX	2.504(3)	2.222(3)	4.726(3)	1.701(5)	1.745(5)	1.673(7)	13
X	2.270(4)	2.375(4)	4.645(4)	1.680(8)	1.759(8)	1.669(10)	14
XI	2.255(1)	2.398(1)	4.653(1)	1.714(2)	1.749(2)	1.698(2)	15
XIIa [a]	2.454(8)	2.168(8)	4.622(8)	1.72(3)	1.70(2)	1.69(2)	16
XIIb [a]	2.561(8)	2.163(8)	4.724(8)	1.68(2)	1.78(2)	1.72(2)	16

[a] The bond lengths have not been corrected for rigid-body libration.

The sum of the S – S bonds varies from one derivative to the next, being as small as 4.617(1) Å in 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene (V), and as great as 4.739(2) Å in 2-methyl-6a-thiathiophthene (VII).

There is no clear indication that the sum of the S – S bond lengths increases with the asymmetry of the S – S bond lengths. Thus, in the asymmetric structure XIIa the sum of the S – S distances is 4.622(8) Å, while in the symmetric structure I it is 4.726 Å. Furthermore, if one also takes into account that $\sum$(S – S) for XIIb is 4.724(8) Å, it seems likely that changes in $\sum$(S – S) may be caused by intermolecular packing as well as by substituents.



The S(6a) – C(3a) bond length is remarkably constant in different 6a-thiathiophthene derivatives. The first eleven entries in Table 3 vary from 1.745(4) Å for II to 1.763(5) Å for VII, and none of the listed S(6a) – C(3a) bond lengths deviate significantly from the value 1.748(3) Å for the mother compound (I).

The S(1) – C(2) and the S(6) – C(5) bond lengths vary more, the former from 1.664(13) Å in IV to 1.714(2) Å in XI, and the latter from 1.664(13) Å in IV to 1.710 Å in V. Thus, the terminal C – S bonds seem to be more affected by the substituents than is the central C – S bond.

A comparison of the C – C bond lengths in compounds I – XII is given in Table 4. One finds from the values there that for each of the various structures the sum of the C(3) – C(3a) and C(3a) – C(4) bond lengths is greater than the sum of the C(2) – C(3) and C(3) – C(4) bond lengths. In this respect the structure of the 6a-thiathiophthene system resembles that of naphthalene.[17] One should remember that 6a-thiathiophthene and naphthalene are analogous compounds as far as their π-bonding systems are concerned; there is a 10 π-electron system in both. The lengths of the terminal and central C – C bonds

Table 4. A comparison of the C–C bond lengths in the 6a-thiathiophthene system of different 6a-thiathiophthene derivatives.

Compound	C(2)–C(3)	C(3)–C(3a)	C(3a)–C(4)	C(4)–C(5)
I	1.354(3)	1.409(2)	1.409(2)	1.354(3)
II [a]	1.363(4)	1.402(4)	1.402(4)	1.363(4)
III	1.374(9)	1.413(9)	1.391(9)	1.393(8)
IV [a]	1.404(20)	1.450(20)	1.437(20)	1.398(20)
V	1.378(4)	1.425(4)	1.426(4)	1.381(4)
VI	1.388(4)	1.394(4)	1.428(4)	1.360(4)
VII	1.362(7)	1.408(6)	1.428(7)	1.367(7)
VIII	1.387(6)	1.397(6)	1.442(5)	1.366(6)
IX	1.377(11)	1.403(9)	1.451(11)	1.363(9)
X	1.379(12)	1.433(11)	1.414(12)	1.371(12)
XI	1.377(2)	1.429(3)	1.406(2)	1.374(3)
XIIa [a]	1.38(4)	1.45(2)	1.46(4)	1.40(3)
XIIb [a]	1.39(4)	1.42(3)	1.41(4)	1.37(2)

[a] The bond lengths have not been corrected for rigid-body libration.

in the present structure are 1.354(3) and 1.409(2) Å, respectively, and the average lengths of the corresponding bonds in naphthalene are 1.357(5) and 1.420(5) Å.

The arrangement of 6a-thiathiophthene molecules in the unit cell as seen along the *c*-axis is shown in Fig. 2. There are no intermolecular atomic distances shorter than corresponding van der Waals distances.

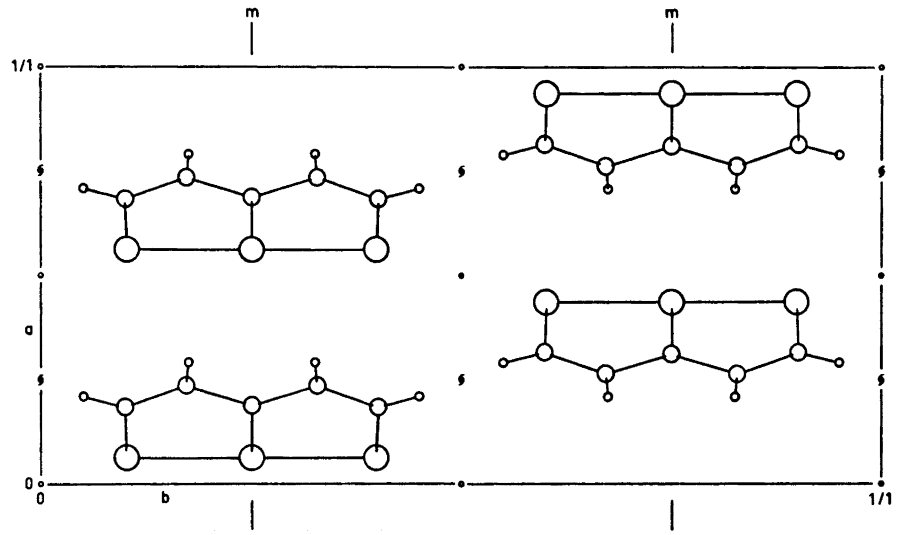


Fig. 2. The arrangement of 6a-thiathiophthene molecules in the unit cell as seen along the *c*-axis.

EXPERIMENTAL

The unit cell dimensions for crystals of 6a-thiathiophthene were determined from the 2θ values for 12 high order reflections. The 2θ values were measured at room temperature, $t = 22°C$, on the diffractometer using Mo$K\alpha$ radiation. A least squares procedure gave $a = 7.768(6)$ Å, $b = 15.784(6)$ Å, and $c = 5.385(2)$ Å.

The molecular weight of the compound ($C_5H_4S_3$) is 160.29, and four molecules per unit cell give a calculated density of 1.612 g/cm³, as compared with the density 1.61 g/cm³ found by flotation.

The intensities of the reflections were measured on the diffractometer by means of the five-value scan technique.[18] 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 817 out of 1145 independent reflections in the range $10° < \theta < 32°$ were accepted as observed. Reflections below $\theta = 10°$ were neglected.[19]

A small crystal, with dimensions of about $0.15 \times 0.15 \times 0.15$ mm in the three axial directions, was used for the data collection. Lp corrections were applied, but absorption corrections were considered unnecessary, $\mu_{MoK\alpha} = 9.6$ cm^{-1}.

The scattering factors used for sulphur and carbon were those given in *International Tables*.[20] For hydrogen the scattering factor curve given by Stewart *et al.*[21] was used.

The full-matrix least squares program which was applied minimizes the function

$$D = \sum w(|F_o| - (1/K)|F_c|)^2$$

The weight was taken to be

$$w = 1/\sigma^2(F_o)$$

where

$$\sigma^2(F_o) = F_o^2(I_{total} + I_{background} + (k\, I_{net})^2)/4I^2_{net}$$

In the latter expression k is the relative standard deviation in the scaling curve from the reference reflections. It was estimated to be 0.014 in the present case.

Final atomic coordinates from the least squares refinement are listed in Table 5, and the temperature parameters are listed in Table 6. A pictorial representation of the thermal motion of the sulphur and carbon atoms is given in Fig. 3.[22] The final list of structure factors is given in Table 8.

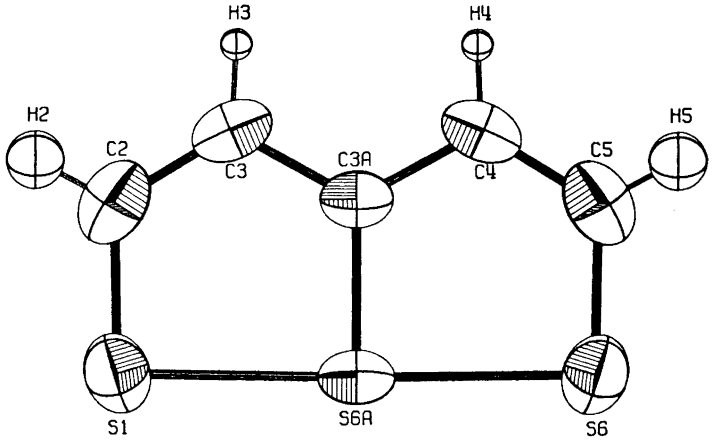


Fig. 3. The thermal ellipsoid plot showing the anisotropic vibration of the sulphur and carbon atoms and the isotropic vibration of the hydrogen atoms. The latter has been scaled down by a factor of 2.

Table 5. 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)	0.06293(7)	0.10115(3)	0.19801(12)
S(6a)	0.06296(8)	0.25000(0)	0.20590(11)
C(2)	0.18421(29)	0.09902(16)	−0.05864(48)
C(3)	0.23620(27)	0.17199(14)	−0.16434(39)
C(3a)	0.18825(29)	0.25000(0)	−0.06116(44)
H(2)	0.2096(40)	0.0499(25)	−0.1267(70)
H(3)	0.2920(34)	0.1746(16)	−0.2996(54)

Table 6. Temperature parameters U_{ij} (Å²) for sulphur 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)	563(3)	448(3)	688(4)	−10(2)	84(2)	5(3)
S(6a)	332(3)	609(4)	334(3)	0	0	40(3)
C(2)	555(12)	535(11)	713(15)	99(10)	−143(11)	−47(11)
C(3)	434(9)	663(13)	435(10)	73(10)	−119(10)	37(8)
C(3a)	298(10)	555(14)	335(11)	0	0	−9(9)

Atom	U
H(2)	615(90)
H(3)	335(66)

Table 7. Results from the rigid-body analysis of the 6a-thiathiophthene molecule.

	Eigenvalues	Eigenvectors. Direction cosines $\times 10^4$ relative to a, b, and c, respectively		
Librational tensor, **L**	22.2 (°)²	9750	0	2221
	21.5	0	−10000	0
	13.8	2221	0	−9750
Translational tensor, **T**	0.0472 Å²	0	10000	0
	0.0316	2610	0	−9654
	0.0286	−9654	0	−2610

Symmetrized screw tensor, **S**

$$\begin{bmatrix} 0 & -112 & 0 \\ -112 & 0 & 116 \\ 0 & 116 & 0 \end{bmatrix} \times 10^5 \text{ rad. Å}$$

Center of gravity of the molecule is at $x=0.12120$, $y=0.25000$, $z=0.07705$.
The origin which symmetrizes **S** is at $x=0.11723$, $y=0.25000$, $z=0.06736$.

Table 8. Observed and calculated structure factors for 6a-thiathiophthene. The values given are ten times the absolute values. Unobserved reflections are marked with a minus sign in front of F_o.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
0	8	C	448	499	10	10	0	-17	-6	5	11	1	-11	4	11	3	1	-14	3	5	1	2	202	193
0	10	0	287	303	10	11	0	18	-5	5	12	1	22	24	11	4	1	-14	6	5	2	2	13	14
0	12	0	372	395	0	9	1	14	-12	5	13	1	70	-66	11	5	1	-15	4	5	3	2	48	49
0	14	0	473	-500	0	11	1	121	-128	5	14	1	20	-23	11	6	1	-15	-17	5	4	2	15	17
0	16	0	103	-100	0	13	1	310	-313	5	15	1	20	22	0	6	2	305	332	5	5	2	44	41
0	18	0	-22	28	0	15	1	90	86	5	16	1	-13	2	0	8	2	222	-231	5	6	2	312	309
0	20	0	169	169	0	17	1	92	92	5	17	1	18	20	0	10	2	106	-112	5	7	2	132	-126
0	22	0	-18	-7	0	19	1	105	105	5	18	1	-13	1	0	12	2	131	-133	5	8	2	168	-165
2	7	0	783	789	0	21	1	91	-88	5	19	1	-14	6	0	14	2	233	239	5	9	2	-12	-3
2	8	0	359	362	0	23	1	36	-35	5	20	1	-15	6	0	16	2	17	18	5	10	2	73	-73
2	9	0	36	40	1	7	1	240	239	5	21	1	-15	-10	0	18	2	35	-31	5	11	2	-12	-10
2	10	0	158	159	1	8	1	151	146	6	0	1	269	-271	0	20	2	69	-73	5	12	2	68	-63
2	11	0	44	-45	1	9	1	35	38	6	1	1	239	234	0	22	2	-14	14	5	13	2	98	94
2	12	C	56	50	1	10	1	102	99	6	2	1	53	53	1	5	2	142	-143	5	14	2	85	87
2	13	0	371	-371	1	11	1	15	21	6	3	1	66	68	1	6	2	159	155	5	15	2	20	-23
2	14	0	146	-146	1	12	1	109	108	6	4	1	15	16	1	7	2	349	350	5	16	2	27	28
2	15	C	93	93	1	13	1	165	-163	6	5	1	176	171	1	8	2	84	-79	5	17	2	22	-22
2	16	0	46	-45	1	14	1	120	-118	6	6	1	247	246	1	9	2	38	39	5	18	2	-14	17
2	17	C	95	93	1	15	1	30	32	6	7	1	336	-339	1	10	2	54	-52	5	19	2	24	-20
2	18	0	-13	-4	1	16	1	43	-42	6	8	1	148	-149	1	11	2	37	-33	5	20	2	55	-54
2	19	C	98	93	1	17	1	34	35	6	9	1	25	27	1	12	2	21	26	6	0	2	351	360
2	20	C	87	90	1	18	1	-13	-6	6	10	1	57	-57	1	13	2	176	-175	6	1	2	172	166
2	21	0	73	-72	1	19	1	34	31	6	11	1	23	22	1	14	2	-13	-11	6	2	2	101	-101
2	22	0	-14	-7	1	20	1	54	52	6	12	1	58	-58	1	15	2	31	30	6	3	2	25	24
2	23	0	33	-30	1	21	1	20	-19	6	13	1	136	132	1	16	2	15	15	6	4	2	20	-20
4	0	0	174	172	1	22	1	-14	4	6	14	1	93	97	1	17	2	49	47	6	5	2	52	51
4	1	0	416	-429	1	23	1	-14	-9	6	15	1	32	-39	1	18	2	18	16	6	6	2	219	-216
4	2	0	101	-101	2	6	1	462	495	6	16	1	17	12	1	19	2	53	53	6	7	2	148	-140
4	3	C	145	-137	2	7	1	440	462	6	17	1	26	-27	1	20	2	23	-20	6	8	2	126	124
4	4	0	45	-47	2	8	1	277	-274	6	18	1	-14	4	1	21	2	29	-31	6	9	2	15	12
4	5	0	190	-190	2	9	1	40	42	6	19	1	53	-49	1	22	2	-14	-4	6	10	2	37	39
4	6	0	151	140	2	10	1	142	-141	7	0	1	156	-159	2	3	2	75	69	6	11	2	-13	2
4	7	0	489	499	2	11	1	12	-12	7	1	1	76	-75	2	4	2	66	65	6	12	2	100	96
4	8	0	72	-65	2	12	1	132	-125	7	2	1	44	42	2	5	2	99	100	6	13	2	81	83
4	9	0	-10	6	2	13	1	327	-332	7	3	1	22	-20	2	6	2	504	535	6	14	2	118	-117
4	10	C	25	-21	2	14	1	203	200	7	4	1	16	17	2	7	2	297	-299	6	15	2	31	-34
4	11	0	64	-66	2	15	1	105	110	7	5	1	73	-72	2	8	2	310	-313	6	16	2	-14	-8
4	12	C	22	31	2	16	1	44	40	7	6	1	87	84	2	9	2	25	24	6	17	2	20	-19
4	13	0	237	-233	2	17	1	82	83	7	7	1	121	121	2	10	2	105	-105	6	18	2	-14	-5
4	14	0	27	-34	2	18	1	-13	-6	7	8	1	55	-54	2	11	2	32	32	6	19	2	-15	-13
4	15	0	78	77	2	19	1	52	53	7	9	1	-13	-8	2	12	2	104	-106	7	0	2	71	-70
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4	21	C	56	-56	3	5	1	106	-105	7	15	1	-14	9	2	18	2	-13	1	7	6	2	14	-17
4	22	C	-14	-3	3	6	1	82	74	7	16	1	15	8	2	19	2	26	-28	7	7	2	139	-141
6	0	0	363	-369	3	7	1	207	195	7	17	1	-14	4	2	20	2	85	-84	7	8	2	-13	11
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6	2	0	114	113	3	9	1	25	22	8	0	1	27	-20	2	22	2	-15	13	7	10	2	-12	0
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6	4	0	54	54	3	11	1	35	-37	8	2	1	-13	12	3	1	2	319	-300	7	12	2	32	-23
6	5	0	130	-124	3	12	1	38	-36	8	3	1	-12	10	3	2	2	144	135	7	13	2	62	58
6	6	C	148	141	3	13	1	62	-55	8	4	1	14	12	3	3	2	90	-86	7	14	2	24	21
6	7	0	325	324	3	14	1	20	22	8	5	1	78	75	3	4	2	139	133	7	15	2	-14	-9
6	8	0	94	-93	3	15	1	-12	-2	8	6	1	31	-30	3	5	2	79	-79	7	16	2	-14	1
6	9	0	18	-21	3	16	1	-12	5	8	7	1	167	-170	3	6	2	265	255	7	17	2	-14	-9
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6	14	0	126	123	3	21	1	-15	-13	8	12	1	-14	-6	3	11	2	-11	4	8	4	2	-12	9
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6	17	C	42	43	4	1	1	142	137	8	15	1	38	-43	3	14	2	174	171	8	7	2	-14	-2
6	18	0	17	-14	4	2	1	178	170	8	16	1	-14	-1	3	15	2	23	32	8	8	2	93	94
6	19	0	43	41	4	3	1	11	-13	9	0	1	69	-69	3	16	2	45	41	8	9	2	14	7
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8	1	C	30	31	4	6	1	560	572	9	3	1	-13	3	3	19	2	34	30	8	12	2	31	33
8	2	0	86	85	4	7	1	80	81	9	4	1	-13	-6	3	20	2	56	-55	8	13	2	-15	-13
8	3	0	13	-8	4	8	1	337	-336	9	5	1	37	38	3	21	2	21	-23	8	14	2	51	-53
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8	5	0	27	-22	4	10	1	143	-139	9	7	1	62	-63	4	0	2	62	-62	8	16	2	-14	-1
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8	7	0	21	20	4	12	1	196	-192	9	9	1	-14	11	4	2	2	26	26	9	1	2	84	86
8	8	0	193	-197	4	13	1	45	40	9	10	1	15	-13	4	3	2	124	119	9	2	2	-13	-8
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8	12	0	95	-89	4	17	1	-13	-6	9	14	1	17	22	4	7	2	509	-521	9	6	2	-14	12
8	13	C	26	12	4	18	1	-13	-11	10	0	1	103	113	4	8	2	41	39	9	7	2	53	-51
8	14	0	114	119	4	19	1	-14	10	10	1	1	73	75	4	9	2	21	21	9	8	2	17	-15
8	15	0	-15	-6	4	20	1	108	-105	10	2	1	44	-45	4	10	2	13	-6	9	9	2	-14	8
8	16	C	-15	11	4	21	1	-15	-5	10	3	1	-13	-6	4	11	2	21	24	9	10	2	-14	6
8	17	0	-15	-5	5	0	1	120	109	10	4	1	-14	4	4	12	2	17	-17	9	11	2	15	-14
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10	1	0	90	96	5	2	1	38	-34	10	6	1	50	-55	4	14	2	-14	11	9	13	2	43	42
10	2	0	36	36	5	3	1	25	-22	10	7	1	92	-94	4	15	2	84	-86	10	0	2	96	95
10	3	C	-14	-4	5	4	1	-10	-6	10	8	1	33	38	4	16	2	-13	-2	10	1	2	40	-43
10	4	0	-14	1	5	5	1	12	4	10	9	1	23	25	4	17	2	49	-50	10	2	2	38	-43
10	5	0	81	81	5	6	1	29	-28	10	10	1	-14	-3	4	18	2	-14	-3	10	3	2	-14	11
10	6	0	53	45	5	7	1	51	53	10	11	1	-14	-5	4	19	2	72	-68	10	4	2	18	15
10	7	0	118	-125	5	8	1	20	20	11	0	1	-15	4	4	20	2	-16	7	10	5	2	34	-35
10	8	0	27	-25	5	9	1	-11	7	11	1	1	23	19	4	21	2	60	59	10	6	2	60	-61
10	9	0	18	18	5	10	1	-11	-10	11	2	1	-14	0	5	0	2	256	-258	10	7	2	53	55

Table 8. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
10	8	2	43	44	5	0	3	127	130	1	2	4	31	-27	6	9	4	18	-15	3	10	5	-13	4
10	9	2	19	-18	5	1	3	320	323	1	3	4	78	76	6	10	4	-13	6	3	11	5	16	10
10	10	2	-14	-2	5	2	3	17	-14	1	4	4	-11	4	6	11	4	-13	-4	3	12	5	24	26
11	0	2	39	43	5	3	3	52	52	1	5	4	171	179	6	12	4	-14	1	3	13	5	98	-103
11	1	2	22	21	5	4	3	-11	0	1	6	4	268	-276	6	13	4	-15	-17	3	14	5	44	-45
11	2	2	15	-16	5	5	3	78	79	1	7	4	364	-379	6	14	4	25	24	3	15	5	40	37
11	3	2	-14	-8	5	6	3	158	-157	1	8	4	161	164	6	15	4	20	17	3	16	5	-14	2
11	4	2	-15	12	5	7	3	213	-209	1	9	4	-12	11	6	16	4	-14	-13	3	17	5	-15	16
0	1	3	472	519	5	8	3	79	78	1	10	4	40	41	7	0	4	165	147	4	0	5	65	-59
0	3	3	95	98	5	9	3	18	-17	1	11	4	13	6	7	1	4	134	-134	4	1	5	27	-28
0	5	3	196	203	5	10	3	34	37	1	12	4	60	54	7	2	4	57	-60	4	2	5	43	44
0	7	3	438	-476	5	11	3	18	-22	1	13	4	194	198	7	3	4	-13	5	4	3	5	-13	-9
0	9	3	71	64	5	12	3	42	37	1	14	4	76	-75	7	4	4	-13	8	4	4	5	35	-37
0	11	3	16	13	5	13	3	170	169	1	15	4	59	-57	7	5	4	97	-97	4	5	5	38	37
0	13	3	213	223	5	14	3	48	-45	1	16	4	17	-18	7	6	4	74	-72	4	6	5	64	63
0	15	3	94	-95	5	15	3	45	-44	1	17	4	42	-38	7	7	4	160	163	4	7	5	42	-38
0	17	3	44	-50	5	16	3	-14	-12	1	18	4	-15	-15	7	8	4	41	43	4	8	5	57	-58
0	19	3	49	-48	5	17	3	33	-31	1	19	4	59	-58	7	9	4	28	-28	4	9	5	-14	15
0	21	3	60	62	5	18	3	-15	-13	1	20	4	54	49	7	10	4	-14	2	4	10	5	17	14
1	0	3	527	-550	5	19	3	35	-34	2	0	4	176	162	7	11	4	-14	5	4	11	5	-14	12
1	1	3	247	238	6	0	3	203	199	2	1	4	105	-100	7	12	4	47	47	4	12	5	-14	-9
1	2	3	99	91	6	1	3	94	-91	2	2	4	81	-74	7	13	4	71	-70	4	13	5	-15	-14
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1	4	3	94	88	6	3	3	-12	11	2	4	4	14	-11	8	0	4	71	-72	4	15	5	-15	0
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1	7	3	20	-24	6	6	3	144	-139	2	7	4	107	105	8	3	4	17	-11	5	1	5	177	-176
1	8	3	194	-194	6	7	3	81	81	2	8	4	56	59	8	4	4	19	-12	5	2	5	34	30
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1	14	3	165	166	6	13	3	37	-39	2	14	4	55	-57	8	10	4	-14	12	5	8	5	60	-59
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1	19	3	-14	0	6	18	3	-15	2	2	19	4	-15	8	9	2	4	34	36	5	13	5	90	-88
1	20	3	72	-69	7	0	3	217	225	2	20	4	-15	9	9	3	4	-14	15	5	14	5	30	32
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4	2	3	74	-73	10	3	3	-14	2	5	8	4	141	139	2	10	5	23	25	1	0	6	49	-50
4	3	3	15	5	10	4	3	19	-20	5	9	4	-13	9	2	11	5	15	-14	1	1	6	146	-142
4	4	3	-10	1	10	5	3	-15	-7	5	10	4	24	22	2	12	5	15	19	1	2	6	24	22
4	5	3	19	-16	10	6	3	51	54	5	11	4	-13	6	2	13	5	14	2	1	3	6	25	25
4	6	3	142	-139	10	7	3	-16	16	5	12	4	43	48	2	14	5	-14	-3	1	4	6	-13	0
4	7	3	-12	11	10	8	3	33	-37	5	13	4	29	-28	2	15	5	17	18	1	5	6	74	-78
4	8	3	113	112	0	0	4	132	130	5	14	4	69	-70	2	16	5	-14	-15	1	6	6	23	24
4	9	3	17	10	0	2	4	52	-58	5	15	4	-14	4	2	17	5	-14	-10	1	7	6	131	135
4	10	3	15	18	0	4	4	39	44	5	16	4	-14	-10	2	18	5	19	-11	1	8	6	34	-30
4	11	3	-12	-2	0	6	4	164	-171	5	17	4	15	10	3	0	5	132	119	1	9	6	41	-40
4	12	3	30	34	0	8	4	125	126	6	0	4	50	-44	3	1	5	202	-201	1	10	6	16	10
4	13	3	-13	-7	0	10	4	-12	12	6	1	4	38	-37	3	2	5	59	-41	1	11	6	-14	14
4	14	3	80	-80	0	12	4	16	14	6	2	4	30	31	3	3	5	-12	-5	1	12	6	-14	-11
4	15	3	-14	2	0	14	4	58	-60	6	3	4	-12	14	3	4	5	-13	12	1	13	6	61	-66
4	16	3	-14	7	0	16	4	24	19	6	4	4	29	-33	3	5	5	122	-122	1	14	6	-15	15
4	17	3	-14	-5	0	18	4	-14	-6	6	5	4	32	-32	3	6	5	103	-101	1	15	6	42	35
4	18	3	16	10	0	20	4	28	24	6	6	4	66	67	3	7	5	230	230	2	0	6	-14	16
4	19	3	-15	6	1	0	4	238	229	6	7	4	49	50	3	8	5	77	75	2	1	6	-14	-5
4	20	3	23	24	1	1	4	371	368	6	8	4	59	-60	3	9	5	47	-46	2	2	6	14	11

Table 8. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
2	3	6	21	-24	3	13	6	43	-42	5	10	6	16	16	1	0	7	110	-108	3	3	7	30	-28
2	4	6	-14	11	3	14	6	67	64	5	11	6	-15	-13	1	1	7	47	43	3	4	7	-14	-2
2	5	6	-14	6	4	0	6	40	39	5	12	6	39	-44	1	2	7	60	62	3	5	7	30	31
2	6	6	74	-77	4	1	6	34	-34	6	0	6	43	-42	1	3	7	23	-23	3	6	7	-15	6
2	7	6	-14	-2	4	2	6	22	-25	6	1	6	-15	-16	1	4	7	32	-37	3	7	7	55	-50
2	8	6	42	41	4	3	6	16	-11	6	2	6	15	12	1	5	7	46	49	3	8	7	-15	-7
2	9	6	18	21	4	4	6	-14	-3	6	3	6	-14	-5	1	6	7	80	81	3	9	7	30	28
2	10	6	-14	12	4	5	6	33	-33	6	4	6	-14	12	1	7	7	61	-63	4	0	7	62	-62
2	11	6	-14	1	4	6	6	24	19	6	5	6	-15	4	1	8	7	63	-65	4	1	7	-15	8
2	12	6	-14	4	4	7	6	53	53	6	6	6	-16	1	1	9	7	21	21	4	2	7	22	23
2	13	6	-15	-9	4	8	6	-15	-12	6	7	6	-15	-3	1	10	7	-15	16	4	3	7	-15	1
2	14	6	-15	-6	4	9	6	-14	4	6	8	6	-15	6	1	11	7	-15	-2	4	4	7	-15	-6
2	15	6	-15	-12	4	10	6	-14	-6	6	9	6	-15	7	2	0	7	22	-22	4	5	7	-15	-15
3	0	6	174	-170	4	11	6	-15	-1	7	0	6	-15	-11	2	1	7	62	-59	4	6	7	37	39
3	1	6	84	-81	4	12	6	-15	16	7	1	6	60	63	2	2	7	-14	3	4	7	7	24	18
3	2	6	81	79	4	13	6	25	-25	7	2	6	-15	8	2	3	7	-14	7	4	8	7	23	-18
3	3	6	-14	15	5	0	6	135	-137	7	3	6	16	-20	2	4	7	-14	1	5	0	7	-15	16
3	4	6	38	-41	5	1	6	68	66	7	4	6	-14	-7	2	5	7	16	-14	5	1	7	42	42
3	5	6	48	-47	5	2	6	61	63	7	5	6	39	41	2	6	7	20	24	5	2	7	-15	-10
3	6	6	134	135	5	3	6	-15	-19	7	6	6	-15	12	2	7	7	-16	21	5	3	7	24	-25
3	7	6	71	72	5	4	6	23	-27	0	1	7	-14	-14	2	8	7	16	-12	5	4	7	-15	4
3	8	6	94	-92	5	5	6	41	40	0	3	7	-14	-9	2	9	7	-15	4	5	5	7	40	41
3	9	6	15	-15	5	6	6	97	96	0	5	7	31	-32	2	10	7	-15	-6	0	0	8	72	-72
3	10	6	-14	2	5	7	6	57	-56	0	7	7	45	52	3	0	7	19	-13	0	2	8	35	39
3	11	6	16	13	5	8	6	73	-72	0	9	7	-15	-8	3	1	7	77	80	1	0	8	34	36
3	12	6	45	-46	5	9	6	22	14	0	11	7	-15	-4	3	2	7	-15	7	1	1	8	46	43

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.[4] The rigid-body tensors arrived at are given in Table 7. The r.m.s. difference between observed and calculated U_{ij}'s is 0.0021 Å^2. Bond lengths which have been corrected according to the libration tensor **L** in Table 7 are given in the first column of Table 1.

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REFERENCES

1. Hordvik, A. and Sæthre, L. J. *Israel J. Chem.* **10** (1972) 239.
2. Hansen, L. K. and Hordvik, A. *Acta Chem. Scand.* **24** (1970) 2246.
3. Dingwall, J. G., McKenzie, S. and Reid, D. H. *J. Chem. Soc.* **C 1968** 2543.
4. Schomaker, V. and Trueblood, K. N. *Acta Cryst.* **B 24** (1968) 63.
5. Cruickshank, D. W. J. *Acta Cryst.* **9** (1956) 757; **14** (1961) 896.
6. Leung, F. and Nyburg, S. C. *Chem. Commun.* **1969** 137.
7. Hordvik, A. *Acta Chem. Scand.* **25** (1971) 1583.
8. Johnson, P. L. and Paul, I. C. *Chem. Commun.* **1969** 1014.
9. Birknes, B., Hordvik, A. and Sæthre, L. J. *Acta Chem. Scand.* **26** (1972) 2140; and *to be published.*
10. Hordvik, A. and Sæthre, L. J. *Acta Chem. Scand.* **24** (1970) 2261; **26** (1972) 1729.
11. Hordvik, A. and Sæthre, L. J. *Acta Chem. Scand.* **26** (1972) 3114; and *to be published.*
12. Hordvik, A. and Julshamn, K. *Acta Chem. Scand.* **25** (1971) 1835.
13. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **23** (1969) 1852.
14. Hordvik, A. *Acta Chem. Scand.* **25** (1971) 1822.
15. Hordvik, A., Sjølset, O. and Sæthre, L. J. *Acta Chem. Scand.* **26** (1972) 1297; and *to be published.*
16. Johnson, S. M., Newton, M. G. and Paul, I. C. *J. Chem. Soc.* **B 1969** 986.
17. Cruickshank, D. W. J. *Acta Cryst.* **10** (1957) 504.
18. Troughton, P. G. H. *Siemens Review* XXXVII (1970), Fourth Special Issue: X-Ray and Electron Microscopy News.
19. Furberg, S. and Jensen, L. H. *Acta Cryst.* **B 26** (1970) 1260.
20. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1968, Vol. III, p. 202.
21. Stewart, R. F., Davidson, E. R. and Simpson, W. R. *J. Chem. Phys.* **42** (1965) 3175.
22. Johnson, C. K. *A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-3794, Oak Ridge National Laboratory, Tennessee 1965.

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