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The Crystal and Molecular Structure of 1,6-Dimethyl-3,4-trimethylene-6a-thia-azophthene

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Crystals of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene belong to the orthorhombic space group *Pbca*, with unit cell dimensions, $a = 16.115(5)$ Å, $b = 21.676(8)$ Å, and $c = 5.825(14)$ Å. There are eight molecules per unit cell.

The structure was solved by three-dimensional Patterson synthesis, and refined by full-matrix least squares methods. The refinement comprises 1671 $hk0 - hk4$ reflections including 582 unobserved.

The atoms of the two fused five-membered rings lie in the same plane, and the methyl carbons C(7) and C(8) lie −0.069 and −0.077 Å, respectively, out of this plane. Furthermore, the distances from the plane for the methylene carbons C(9), C(10), and C(11) are 0.075, −0.566, and −0.024 Å, respectively.

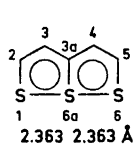
Bond lengths: N(1) – S(6a) = 1.901(5) Å, N(6) – S(6a) = 1.948(5) Å, N(1) – C(2) = 1.338(7) Å, N(1) – C(7) = 1.441(9) Å, N(6) – C(5) = 1.317(8) Å, N(6) – C(8) = 1.454(9) Å, C(2) – C(3) = 1.367(8) Å, C(3) – C(3a) = 1.421(7) Å, C(3) – C(9) = 1.517(8) Å, C(4) – C(3a) = 1.374(8) Å, C(4) – C(5) = 1.358(9) Å, C(4) – C(11) = 1.523(9) Å, C(9) – C(10) = 1.527(13) Å, C(10) – C(11) = 1.512(13) Å, and S(6a) – C(3a) = 1.742(5) Å. The N(1) – S(6a) – N(6) angle is 168.5(2)°.

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

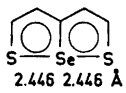
Structure studies of the analogous compounds 6a-thiathiophthene (I),[1] 6a-selenathiophthene (II),[2] and 6a-selenaselenophthene (III),[3] have been carried out.

Crystals of I are isomorphous with crystals of II, and the molecules lie in both cases across a crystallographic mirror plane passing through the 3a and 6a positions perpendicular to the molecular plane. Hence the sulphur-sulphur bonds in I, and also the selenium-sulphur bonds in II, are of equal length; they are 2.363(1) and 2.446(5) Å, respectively. The selenium-selenium bonds in III are 2.586(3) and 2.579(3) Å, and thus equal within three standard deviations.

Accepted values for the lengths of the S – S, the Se – S, and the Se – Se single bonds are 2.10, 2.22, and 2.34 Å, respectively.[4,5] Thus the S – S, the



(I)



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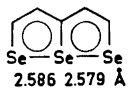

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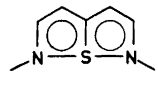
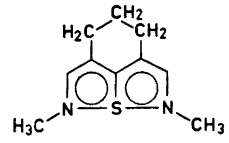


(IV)



(V)

Se – S, and the Se – Se bonds in compounds I – III are 0.26, 0.23, and 0.24 Å, or 12.4, 10.4, and 10.3 % longer than the corresponding single bonds.

The preparation of compounds containing ring system IV, analogous to the 6a-thiathiophthene system,* has recently been described by Reid and Symon.[6] We thought it might be of interest to obtain molecular dimensions for IV and compare them with those of compounds I – III. The present structure study of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene has therefore been carried out.

STRUCTURE DETERMINATION

Crystals of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene (V) were generously supplied by Reid.[7] The crystals are yellow and belong to the orthorhombic space group *Pbca*.

The structure study is based on photographic data, taken with Weissenberg camera and Cu$K\alpha$ radiation. The data comprise 1671 independent $hk0 - hk4$ reflections including 582 unobserved.

The sulphur position was found from a three-dimensional Patterson map, and the nitrogen and carbon atoms revealed themselves during a subsequent Fourier synthesis. The hydrogen positions were found from difference Fouriers.

The structure was refined by a full-matrix least squares procedure (see for example Ref. 8). The constants a_1 and a_2 in the weighting scheme were in the present case set equal to 1.0.

Anisotropic temperature factors were applied to sulphur, nitrogen, and carbon, and isotropic to hydrogen.

Six low-order reflections, supposed to be affected by secondary extinction, were excluded from the least squares refinement. The final R factor is 7.3 % when unobserved reflections are included, and 7.2 % when they are omitted.

A rigid-body analysis of the thermal parameters has been carried out according to the method of Schomaker and Trueblood,[9] and the S – N, S – C, N – C, and C – C bond lengths have been corrected for rigid-body libration according to Cruickshank's formula.[10] For further details with respect to the structure determination, see Experimental.

DISCUSSION

Molecular shape and dimensions. Bond lengths and angles in the 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene molecule, together with their standard deviations, are listed in Tables 1 and 2, and shown in Fig. 1, a and b.

* We name the ring system IV "6a-thia-azophthene" in order to bring out the structure analogy with 6a-thiathiopthene.

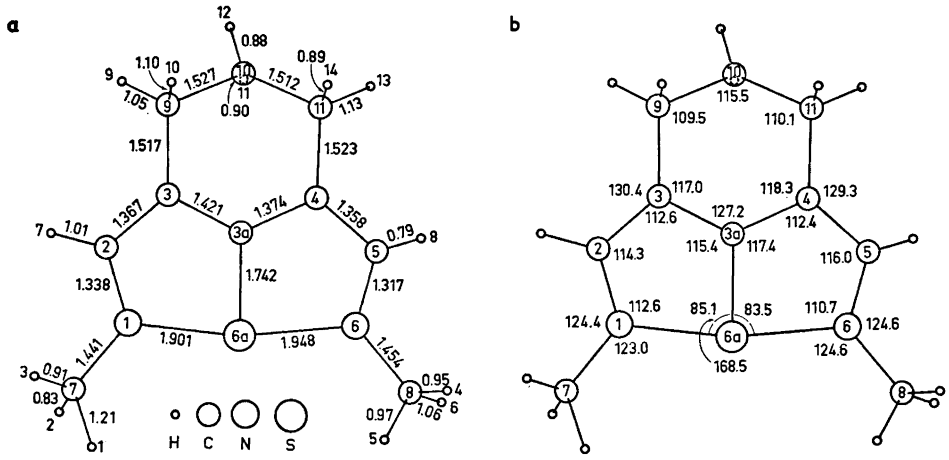


Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°) in the 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene molecule.

Table 1. Bond lengths (l) and standard deviations in bond lengths $\sigma(l)$. Bond lengths (l') include correction for rigid-body libration.

Bond	l'(Å)	l(Å)	$\sigma(l)$(Å)
N(1) – S(6a)	1.901	1.892	0.005
N(1) – C(2)	1.338	1.330	0.007
N(1) – C(7)	1.441	1.434	0.009
N(6) – S(6a)	1.948	1.939	0.005
N(6) – C(5)	1.317	1.310	0.008
N(6) – C(8)	1.454	1.446	0.009
C(2) – C(3)	1.367	1.361	0.008
C(3) – C(3a)	1.421	1.413	0.007
C(3) – C(9)	1.517	1.508	0.008
C(4) – C(3a)	1.374	1.368	0.008
C(4) – C(5)	1.358	1.351	0.009
C(4) – C(11)	1.523	1.514	0.009
C(9) – C(10)	1.527	1.520	0.013
C(10) – C(11)	1.512	1.504	0.013
S(6a) – C(3a)	1.742	1.732	0.005
H(1) – C(7)		1.21	0.07
H(2) – C(7)		0.83	0.06
H(3) – C(7)		0.91	0.08
H(4) – C(8)		0.95	0.05
H(5) – C(8)		0.97	0.08
H(6) – C(8)		1.06	0.07
H(7) – C(2)		1.01	0.04
H(8) – C(5)		0.79	0.06
H(9) – C(9)		1.05	0.06
H(10) – C(9)		1.10	0.07
H(11) – C(10)		0.90	0.08
H(12) – C(10)		0.88	0.06
H(13) – C(11)		1.13	0.06
H(14) – C(11)		0.89	0.07

Table 2. Bond angles ∠(ijk). The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	k	∠(ijk)°	i	j	k	∠(ijk)°
C(7)	N(1)	S(6a)	123.0(4)	H(1)	C(7)	H(3)	95(5)
C(7)	N(1)	C(2)	124.4(5)	H(2)	C(7)	H(3)	116(6)
C(2)	N(1)	S(6a)	112.6(4)	N(6)	C(8)	H(4)	111(3)
N(1)	C(2)	C(3)	114.3(5)	N(6)	C(8)	H(5)	109(5)
C(2)	C(3)	C(3a)	112.6(5)	N(6)	C(8)	H(6)	119(4)
C(2)	C(3)	C(9)	130.4(6)	H(4)	C(8)	H(5)	92(5)
C(3a)	C(3)	C(9)	117.0(5)	H(4)	C(8)	H(6)	110(5)
C(3)	C(3a)	C(4)	127.2(5)	H(5)	C(8)	H(6)	112(6)
C(3)	C(3a)	S(6a)	115.4(4)	N(1)	C(2)	H(7)	121(2)
C(4)	C(3a)	S(6a)	117.4(4)	C(3)	C(2)	H(7)	124(2)
C(3a)	C(4)	C(5)	112.4(5)	C(3)	C(9)	H(9)	111(3)
C(3a)	C(4)	C(11)	118.3(5)	C(3)	C(9)	H(10)	112(4)
C(5)	C(4)	C(11)	129.3(6)	C(10)	C(9)	H(9)	105(3)
C(4)	C(5)	N(6)	116.0(6)	C(10)	C(9)	H(10)	103(4)
C(5)	N(6)	C(8)	124.6(6)	H(9)	C(9)	H(10)	115(5)
C(5)	N(6)	S(6a)	110.7(4)	C(9)	C(10)	H(11)	112(5)
C(8)	N(6)	S(6a)	124.6(5)	C(9)	C(10)	H(12)	86(4)
N(1)	S(6a)	N(6)	168.5(2)	C(11)	C(10)	H(11)	108(5)
N(1)	S(6a)	C(3a)	85.1(2)	C(11)	C(10)	H(12)	114(4)
C(3a)	S(6a)	N(6)	83.5(2)	H(11)	C(10)	H(12)	119(6)
C(3)	C(9)	C(10)	109.5(6)	C(10)	C(11)	H(13)	107(2)
C(9)	C(10)	C(11)	115.5(8)	C(10)	C(11)	H(14)	107(4)
C(10)	C(11)	C(4)	110.1(6)	C(4)	C(11)	H(13)	110(2)
N(1)	C(7)	H(1)	116(3)	C(4)	C(11)	H(14)	115(4)
N(1)	C(7)	H(2)	125(4)	H(13)	C(11)	H(14)	108(5)
N(1)	C(7)	H(3)	105(4)	C(4)	C(5)	H(8)	122(4)
H(1)	C(7)	H(2)	98(5)	N(6)	C(5)	H(8)	121(4)

The molecule is presented in Fig. 1, a and b in a projection on to the least squares plane of the atoms of the 6a-thia-azophthene system. The equation for this plane, with weights inversely proportional to standard deviations in atomic coordinates, is

$$0.21716\,X + 0.77553\,Y - 0.59278\,Z = 4.97249$$

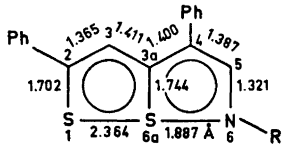
with X, Y, and Z in Å units. The 6a-thia-azophthene system is planar within the limits of error. The methyl carbons, C(7) and C(8), lie −0.069 and −0.077 Å off the plane, and the methylene carbons, C(9), C(10), and C(11), lie 0.075, −0.566, and −0.024 Å off.

One notes from Fig. 1, a and b that the molecule is almost symmetric about a plane through S (6a) and C(10) perpendicular to the molecular plane. The greatest differences in length between corresponding bonds in the two halves occur between C(3)−C(3a) = 1.421(7) Å and C(3a)−C(4) = 1.374(8) Å, and between N(1)−S(6a) = 1.901(5) Å and N(6)−S(6a) = 1.948(5) Å. These differences are greater than three times the respective standard deviations, and they are therefore significant.

Comparison with related molecules. The nitrogen-sulphur bonds in the present structure (Fig. 1) are longer than a nitrogen-sulphur single bond, 1.75 Å;[5] the average length of the N(1)−S(6a) and the N(6)−S(6a) bonds, 1.925 Å, is 10 % longer than the N−S single bond. This agrees with the lengthening

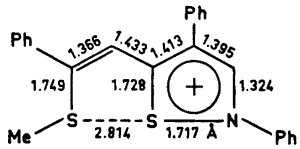
of the S – S bonds in I, 12.4 %, the Se – S bonds in II, 10.4 %, and the Se – Se bonds in III, 10.3 %, relative to the respective single bonds.

The structures of the 6a-thiathiophthene isosters VI and VII have been determined by Leung and Nyburg;[11] it is the iodide of VII which has been studied.



R = 3-quinolyl

(VI)



(VII)

The S(6a) – N(6) bond in VI, 1.887(2) Å, is slightly shorter than the S – N bonds in V (Fig. 1a); it is, however, 0.13 Å or 7 % longer than an S – N single bond. The S(6a) – N(6) bond in VII, 1.717(7) Å, is found to be somewhat shorter than a single bond. According to Leung and Nyburg,[11] the "S-methylation weakens the S···S interaction and forms a normal S – N single bond".

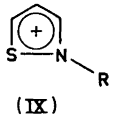
The present authors look at the S – N bond in VII in a slightly different way. We believe that this S – N bond is not a normal single bond, as discussed below.

The S(6a) – C(3a) – C(4) – C(5) – N(6) ring system in VII possesses a sextet of $p-\pi$ electrons available for bonding and is isoelectronic with the π-system of the 1,2-dithiolium ion (VIII). Structure investigations of 1,2-dithiolium salts[12] have shown that the S – S bond in the 1,2-dithiolium ion is shortened through π-bonding. The S – S bond in VIII, from these studies,

(VIII)

1,2-Dithiolium ion.

is 2.00 Å, as compared with the S – S single bond length of 2.10 Å in a *cis* planar disulphide group. In analogy with the bonding in the 1,2-dithiolium ion, one may expect that the S – N bond in an isothiazolium ion (IX) is shortened through π-bonding by about 0.10 Å. Hence a reasonable guess at the S – N bond length in IX is 1.65 Å.



(IX)

Isothiazolium ion.

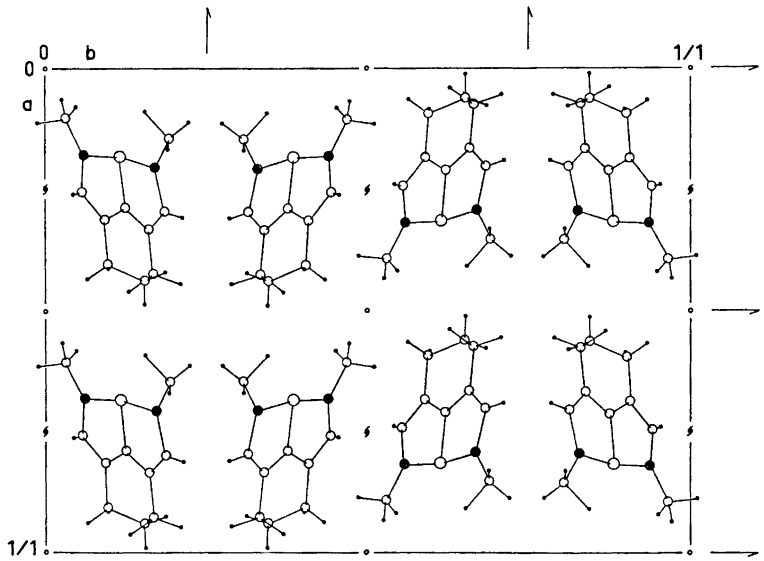


Fig. 2. The crystal structure of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene as seen along the *c*-axis.

Table 3. 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(6a)	0.18308(7)	0.38565(6)	0.6214(3)
N(1)	0.20719(26)	0.32999(19)	0.3803(8)
N(6)	0.18127(28)	0.43999(18)	0.8857(9)
C(2)	0.28638(37)	0.31264(24)	0.3784(12)
C(3)	0.33375(30)	0.33956(24)	0.5437(10)
C(3a)	0.28707(30)	0.37812(20)	0.6907(9)
C(4)	0.31524(34)	0.40983(23)	0.8782(10)
C(5)	0.25484(44)	0.44318(27)	0.9804(12)
C(7)	0.14536(54)	0.30752(33)	0.2244(15)
C(8)	0.10755(47)	0.46927(34)	0.9760(17)
C(9)	0.42522(40)	0.33363(36)	0.5936(14)
C(10)	0.44062(49)	0.34451(47)	0.8478(19)
C(11)	0.40582(42)	0.40358(35)	0.9430(14)
H(1)	0.0933(45)	0.3443(32)	0.165(12)
H(2)	0.1143(35)	0.2780(24)	0.249(10)
H(3)	0.1701(39)	0.3084(30)	0.083(14)
H(4)	0.1150(28)	0.5129(24)	0.986(9)
H(5)	0.0665(41)	0.4735(33)	0.854(14)
H(6)	0.0812(40)	0.4527(30)	1.130(13)
H(7)	0.3088(22)	0.2856(17)	0.252(8)
H(8)	0.2609(35)	0.4579(25)	1.104(10)
H(9)	0.4459(28)	0.2884(26)	0.562(10)
H(10)	0.4614(39)	0.3702(32)	0.511(13)
H(11)	0.4221(43)	0.3128(35)	0.935(14)
H(12)	0.4935(37)	0.3464(24)	0.811(10)
H(13)	0.4128(26)	0.4012(19)	1.137(9)
H(14)	0.4381(37)	0.4339(30)	0.892(12)

The S–N bond in VII, therefore, is affected by the S···S interaction, and the lengthening of the bond relative to the S–N bond in the isothiazolium ion is about 0.07 Å.

From Fig. 1a the bonds between nitrogen and methyl carbon, N(1)–C(7) = 1.441(9) Å and N(6)–C(8) = 1.454(9) Å, are slightly shorter than the accepted length, 1.47 Å,[5] for a C–N single bond. The lengths of the cyclic C–N bonds, N(1)–C(2) = 1.338(7) Å and N(6)–C(5) = 1.317(8) Å, agree with the length of the aromatic C–N bond, 1.340 Å, found in pyridine.[13] The cyclic C–N bonds in compounds VI and VII are reported to be 1.321* and 1.324* Å, respectively.[11]

The average length of the C(2)–C(3) and C(4)–C(5) bonds (Fig. 1a), and that of the C(3)–C(3a) and C(3a)–C(4) bonds, are 1.363 and 1.398 Å,

Table 4. Temperature parameters U_{ij} (Å²) for sulphur, nitrogen, and carbon, and U (Å²) for hydrogen. The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11}\times\cdots+2hka^*b^*U_{12}+\cdots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$, respectively. All values are multiplied by 10^4. Standard deviations in parentheses refer to the last digits of the respective values.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(6a)	537(6)	547(6)	540(10)	−67(6)	28(7)	29(7)
N(1)	742(27)	555(23)	461(31)	−67(20)	−92(23)	42(25)
N(6)	684(26)	612(24)	601(34)	−81(22)	−47(24)	53(29)
C(2)	858(38)	542(29)	652(47)	47(26)	−26(31)	271(38)
C(3)	594(30)	579(28)	523(40)	−58(23)	72(27)	61(26)
C(3a)	627(28)	457(24)	313(35)	−80(21)	31(20)	113(24)
C(4)	709(30)	561(25)	598(40)	−114(25)	−17(31)	32(33)
C(5)	856(46)	605(32)	499(47)	−179(32)	−11(32)	−1(38)
C(7)	1018(53)	761(43)	538(54)	−229(42)	−70(39)	−56(45)
C(8)	825(48)	670(40)	989(63)	51(36)	−245(42)	213(50)
C(9)	709(39)	799(44)	901(64)	38(34)	90(44)	79(40)
C(10)	670(46)	1137(70)	1367(95)	51(46)	240(66)	−37(54)
C(11)	808(44)	942(51)	693(57)	−230(38)	183(38)	−65(35)

	U		U
H(1)	890	H(8)	379
H(2)	478	H(9)	436
H(3)	632	H(10)	847
H(4)	373	H(11)	761
H(5)	943	H(12)	386
H(6)	730	H(13)	164
H(7)	112	H(14)	615

Table 5. Libration tensor **L** from the rigid-body analysis.

Eigenvalues	Eigenvectors (Direction cosines × 10^4 relative to a, b, and c, respectively).		
L 22.0 (°)²	−4421	−7838	−4362
L 19.4	−5041	−1851	8436
L 8.9	−7419	5928	−3132

* The standard deviations for these bond lengths are not given in Ref. 11.

Table 6. Observed and calculated structure factors for 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene. The values 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)
4	0	C	440	-447	6	26	0	74	76	16	4	0	88	-101	3	10	1	237	234	7	9	1	-35	20
6	0	0	293	293	8	1	0	338	-313	14	7	0	98	-84	3	11	1	196	-189	7	10	1	284	-304
8	0	C	1280	-1306	8	2	0	164	148	16	8	0	104	90	3	12	1	402	433	7	11	1	59	-48
10	0	C	497	492	8	3	0	260	-264	16	9	0	-44	32	3	13	1	231	237	7	12	1	225	-235
12	0	0	188	189	8	4	0	1084	1038	16	10	0	-43	5	3	14	1	53	53	7	13	1	66	-64
14	0	0	242	-239	8	5	0	44	-38	16	11	0	124	118	3	15	1	130	148	7	14	1	84	71
16	0	C	203	152	8	6	0	59	55	16	12	0	69	-67	3	16	1	67	-53	7	15	1	90	86
18	0	C	-41	-7	8	7	0	314	328	16	13	0	-38	-5	3	17	1	119	-132	7	16	1	246	238
20	0	C	63	-51	8	8	0	263	-275	16	14	0	-35	-20	3	18	1	-42	15	7	17	1	-43	-9
0	6	0	520	522	8	9	0	300	315	16	15	0	69	-75	3	19	1	71	-49	7	18	1	-42	-3
0	8	C	631	-566	8	10	0	161	-160	16	16	0	-29	37	3	20	1	63	-55	7	19	1	59	-54
0	10	0	163	166	8	11	0	311	-302	16	17	0	-24	-13	3	21	1	88	85	7	20	1	138	-138
0	12	C	89	-100	8	12	0	-45	-3	18	1	0	88	-68	3	22	1	69	-55	7	21	1	-38	39
0	14	0	692	-656	8	13	0	91	79	18	2	0	-41	-17	3	23	1	-37	-10	7	22	1	-36	33
0	16	C	175	163	8	14	0	199	206	18	3	0	149	-133	3	24	1	59	-65	7	23	1	-33	1
0	18	C	433	425	8	15	0	217	225	18	4	0	-40	26	3	25	1	-31	-37	7	24	1	86	99
0	20	0	70	-65	8	16	0	78	-50	18	5	0	44	22	4	1	1	519	501	8	1	1	169	-177
0	22	C	230	-214	8	17	0	106	-111	18	6	0	58	59	4	3	1	282	-271	8	2	1	729	743
0	24	C	-42	12	8	18	0	267	-278	18	7	0	169	153	4	4	1	100	87	8	3	1	63	51
0	26	C	75	76	8	19	0	-48	-15	18	8	0	-36	-12	4	5	1	276	-283	8	4	1	183	166
2	1	C	205	197	8	20	0	69	51	18	9	0	-35	-18	4	6	1	32	22	8	5	1	308	322
2	2	0	210	-209	8	21	0	65	-51	18	10	0	-33	-32	4	7	1	-27	17	8	6	1	283	-304
2	3	C	168	-160	8	22	0	166	152	18	11	0	128	-125	4	8	1	111	99	8	7	1	120	-125
2	4	C	838	905	8	23	0	-37	-45	18	12	0	-27	28	4	9	1	95	82	8	8	1	136	-139
2	5	C	766	-767	8	24	0	-32	-41	20	1	0	95	81	4	10	1	143	-136	8	9	1	63	-71
2	6	C	458	431	8	25	0	50	45	20	2	0	-28	-5	4	11	1	146	-148	8	10	1	117	130
2	7	C	141	-128	10	1	0	69	47	20	3	0	57	62	4	12	1	65	48	8	11	1	61	72
2	8	C	273	258	10	2	0	153	136	20	4	0	77	55	4	13	1	184	-194	8	12	1	111	123
2	9	0	261	-255	10	3	0	367	382	20	5	0	79	-76	4	15	1	-40	1	8	13	1	-41	11
2	10	C	251	-261	10	4	0	307	-314	0	8	1	189	172	4	14	1	132	136	8	14	1	112	-121
2	11	C	688	-618	10	5	0	159	150	0	10	1	536	-497	4	16	1	84	-71	8	15	1	76	71
2	12	0	301	310	10	6	0	152	-162	0	12	1	66	54	4	17	1	212	221	8	16	1	141	-138
2	13	C	237	239	10	7	0	395	-416	0	14	1	76	63	4	18	1	-42	-30	8	17	1	137	-128
2	14	C	293	312	10	8	0	202	214	0	16	1	232	224	4	19	1	138	137	8	18	1	-42	47
2	15	C	455	476	10	9	0	-45	35	0	18	1	-42	-29	4	20	1	-42	20	8	19	1	61	-52
2	16	C	375	-415	10	10	0	244	227	0	20	1	265	-260	4	21	1	71	-64	8	20	1	108	101
2	17	C	58	-51	10	11	0	379	373	0	22	1	-40	40	4	22	1	-39	5	8	21	1	89	91
2	18	C	268	-280	10	12	0	83	-61	0	24	1	96	102	4	23	1	105	-121	8	22	1	-34	7
2	19	C	200	-184	10	13	0	238	-240	0	26	1	-28	-34	4	24	1	-33	17	8	23	1	-30	-26
2	20	C	78	78	10	14	0	189	-191	1	2	1	527	-545	4	25	1	-30	-6	8	24	1	55	-67
2	21	0	103	-65	10	15	0	336	-342	1	3	1	297	-283	5	1	1	441	417	9	1	1	111	-119
2	22	C	91	101	10	16	0	-49	36	1	4	1	524	1674	5	2	1	374	360	9	2	1	287	291
2	23	C	71	72	10	17	0	99	82	1	5	1	903	-930	5	3	1	62	-55	9	3	1	75	-59
2	24	0	-42	-8	10	18	0	-46	35	1	7	1	109	-105	5	4	1	229	220	9	4	1	237	-227
2	25	C	108	123	10	19	0	174	161	1	8	1	149	-142	5	5	1	89	-82	9	5	1	160	167
2	26	0	57	-47	10	20	0	135	-125	1	9	1	471	493	5	6	1	288	-275	9	6	1	146	-147
4	1	C	1281	1182	10	21	0	95	95	1	10	1	204	-201	5	7	1	356	337	9	7	1	103	-109
4	2	C	95	-92	10	22	0	-35	-23	1	11	1	186	182	5	8	1	83	79	9	8	1	116	117
4	3	C	790	788	10	23	0	-30	-34	1	12	1	411	-418	5	9	1	201	211	9	9	1	382	-375
4	4	C	135	-127	10	24	0	35	41	1	13	1	60	-49	5	10	1	130	136	9	10	1	103	99
4	5	0	633	-613	12	1	0	317	-318	1	14	1	36	22	5	11	1	-34	-3	9	11	1	-40	36
4	6	C	40	-51	12	2	0	153	135	1	15	1	-38	-17	5	12	1	81	-66	9	12	1	87	87
4	7	C	210	-219	12	3	0	342	-339	1	16	1	293	282	5	13	1	198	-202	9	13	1	271	280
4	8	C	114	-91	12	4	0	114	-120	1	17	1	-41	40	5	14	1	48	-46	9	14	1	167	-158
4	9	C	-33	-32	12	5	0	156	149	1	18	1	151	-158	5	15	1	224	-224	9	15	1	-43	17
4	10	C	267	-253	12	6	0	158	-155	1	19	1	70	53	5	16	1	132	-135	9	16	1	180	-177
4	11	C	104	54	12	7	0	95	77	1	20	1	175	-184	5	17	1	110	95	9	17	1	-42	-14
4	12	0	102	-65	12	8	0	-48	-4	1	21	1	-42	23	5	18	1	-43	-41	9	18	1	87	105
4	13	0	-41	25	12	9	0	208	-212	1	22	1	109	112	5	19	1	-42	15	9	19	1	48	47
4	14	C	112	109	12	10	0	-49	-25	1	23	1	-38	-11	5	20	1	124	141	9	20	1	121	115
4	15	C	403	-402	12	11	0	154	-138	1	24	1	121	136	5	21	1	155	-157	9	21	1	-35	7
4	16	C	241	238	12	12	0	-49	10	1	25	1	-32	1	5	22	1	-38	40	9	22	1	-32	-30
4	17	C	209	-208	12	13	0	69	64	1	26	1	-27	-18	5	23	1	-36	2	9	23	1	-28	38
4	18	C	98	85	12	14	0	-48	-34	2	1	1	163	134	5	24	1	46	-54	9	24	1	48	-49
4	19	C	317	314	12	15	0	234	231	2	2	1	291	263	5	25	1	35	53	10	1	1	209	215
4	20	C	-49	-40	12	16	0	80	-77	2	3	1	805	-862	6	1	1	-26	-4	10	2	1	162	-163
4	21	C	235	213	12	17	0	70	63	2	4	1	1149	1170	6	2	1	342	-336	10	3	1	44	-33
4	22	C	-46	36	12	18	0	115	117	2	6	1	678	-708	6	3	1	93	-81	10	4	1	202	-211
4	23	C	92	-65	12	19	0	217	-200	2	7	1	69	65	6	4	1	506	-486	10	5	1	279	-281
4	24	0	-40	17	12	20	0	114	112	2	8	1	612	-537	6	5	1	88	-62	10	6	1	147	148
4	25	C	69	-67	12	21	0	100	-90	2	9	1	406	-393	6	6	1	297	309	10	7	1	-38	19
4	26	C	-21	-21	12	22	0	44	-50	2	10	1	510	506	6	7	1	289	298	10	8	1	194	210
6	1	0	387	349	14	1	0	141	123	2	11	1	239	234	6	8	1	221	226	10	9	1	220	232
6	2	C	180	-165	14	2	0	282	-269	2	12	1	41	28	6	9	1	183	-188	10	10	1	189	-180
6	3	C	257	-269	14	3	0	120	129	2	13	1	256	254	6	10	1	152	-148	10	11	1	100	-100
6	4	0	573	-568	14	4	0	144	130	2	14	1	245	-257	6	11	1	36	-27	10	12	1	134	-121
6	5	C	-31	-3	14	5	0	89	-80	2	15	1	82	-68	6	12	1	70	-67	10	13	1	219	-214
6	6	C	325	-300	14	6	0	288	300	2	16	1	107	-104	6	13	1	238	251	10	14	1	155	148
6	7	C	375	380	14	7	0	55	-49	2	17	1	164	-180	6	14	1	99	100	10	15	1	-42	30
6	8	0	287	295	14	8	0	153	-148	2	18	1	67	81	6	15	1	104	-100	10	16	1	-42	-4
6	9	C	-37	-35	14	9	0	-49	15	2	19	1	60	-55	6	16	1	154	145	10	17	1	187	188
6	10	0	306	321	14	10	0	-48	-64	2	20	1	117	122	6	17	1	85	-81	10	18	1	-39	-58
6	11	C	57	46	14	11	0	-48	21	2	21	1	83	70	6	18	1	-43	-32	10	19	1	-38	43
6	12	0	148	-157	14	12	0	129	123	2	22	1	-40	-22	6	19	1	-42	-9	10	20	1	-35	-9
6	13	0	-44	-45	14	13	0	-46	41	2	23	1	66	85	6	20	1	87	-87	10	21	1	89	-90
6	14	C	100	-89	14	14	0	76	57	2	24	1	61	-61	6	21	1	-39	-43	10	22	1	-29	10
6	15	0	152	144	14	15	0	103	-80	2	25	1	-31	16	6	22	1	-37	-17	11	1	1	173	160
6	16	C	138	129	14	16	0	-40	15	2	26	1	-27	24	6	23	1	95	85	11	2	1	80	-76
6	17	0	171	157	14	17	0	45	-42	3	1	1	125	-115	6	24	1	38	32	11	3	1	181	-189
6	18	0	164	155	14	18	0	91	-87	3	2	1	670	656	7	1	1	215	-216	11	4	1	-39	28
6	19	C	193	-197	14	19	0	81	84	3	3	1	272	256	7	2	1	669	-679	11	5	1	345	-359
6	20	C	-48	6	14	20	0	46	-39	3	4	1	220	-230	7	3	1	137	130	11	6	1	-40	-11
6	21	C	107	-95	16	1	0	-48	33	3	5	1	858	890	7	4	1	94	-102	11	7	1	-40	39
6	22	0	142	-139	16	2	0	90	81	3	6	1	306	-312	7	5	1	148	150	11	8	1	-41	23
6	23	C	-41	53	16	3	0	104	92	3	7	1	41	-54	7	6	1	255	267	11	9	1	440	445
6	24	C	-37	-1	16	4	0	154	-141	3	8	1	39	-32	7	7	1	72	-62	11	10	1	-42	-3
6	25	0	-32	-13	16	5	0	-47	23	3	9	1	709	-721	7	8	1	63	-55	11	11	1	122	114

Table 6. 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)
11	12	1	-43	7	17	9	1	82	86	2	18	2	75	-73	6	24	2	-30	23	11	13	2	100	-93
11	13	1	241	-229	17	10	1	73	-75	2	19	2	-48	-36	6	25	2	-24	-19	11	14	2	70	-57
11	14	1	186	161	17	11	1	-30	6	2	20	2	66	-55	7	1	2	-34	-28	11	15	2	158	144
11	15	1	72	-62	17	12	1	49	-51	2	21	2	55	55	7	2	2	67	50	11	16	2	76	-65
11	16	1	-41	39	17	13	1	51	-60	2	22	2	-43	3	7	3	2	56	69	11	17	2	72	79
11	17	1	56	58	17	14	1	-23	15	2	23	2	-40	38	7	4	2	362	371	11	18	2	-39	-2
11	18	1	75	-69	18	1	1	94	-84	2	24	2	-36	32	7	5	2	74	68	11	19	2	77	-81
11	19	1	-35	14	18	2	1	-34	5	2	25	2	-31	11	7	6	2	65	54	11	20	2	-33	-3
11	20	1	-32	-6	18	3	1	51	52	2	26	2	-25	23	7	7	2	153	-148	11	21	2	-28	-21
12	1	1	228	+244	18	4	1	-34	22	3	1	2	313	307	7	8	2	517	-512	11	22	2	-22	5
12	2	1	155	-161	18	5	1	90	85	3	2	2	358	352	7	9	2	51	-54	12	1	2	-46	-31
12	3	1	179	157	18	6	1	-32	-12	3	3	2	345	353	7	10	2	301	-308	12	2	2	-46	-3
12	4	1	64	60	18	7	1	-31	-18	3	4	2	234	-232	9	11	2	273	256	12	3	2	-47	5
12	5	1	110	113	18	8	1	-30	-27	3	5	2	171	-155	7	12	2	272	290	12	4	2	143	-131
12	6	1	50	-43	18	9	1	79	-73	3	8	2	592	666	7	13	2	46	-48	12	5	2	58	-56
12	7	1	72	-86	18	10	1	-27	13	3	9	2	232	-236	7	14	2	236	247	12	6	2	-47	9
12	8	1	-42	-30	18	11	1	-24	19	3	10	2	130	123	7	15	2	-48	0	12	7	2	92	-86
12	9	1	100	-100	19	1	1	63	-71	3	12	2	297	-306	7	16	2	89	-83	12	8	2	-48	-3
12	10	1	93	108	19	2	1	44	-42	3	13	2	196	176	7	17	2	-47	43	12	9	2	-48	-13
12	11	1	67	61	19	3	1	43	35	3	14	2	-44	-7	7	18	2	151	-143	12	10	2	-48	-49
12	12	1	75	-65	19	4	1	-28	-8	3	15	2	256	-239	7	19	2	78	-68	12	11	2	-47	-26
12	13	1	153	154	19	5	1	82	72	3	16	2	-47	-3	7	20	2	-43	38	12	12	2	-47	5
12	14	1	62	-48	19	6	1	-26	15	3	17	2	-47	-9	7	21	2	-40	29	12	13	2	-46	34
12	15	1	-40	-13	19	7	1	-25	-21	3	18	2	-48	10	7	22	2	141	145	12	14	2	-45	-25
12	16	1	83	92	19	8	1	-23	14	3	19	2	-47	9	7	23	2	40	35	12	15	2	-43	21
12	17	1	127	-138	19	9	1	77	-88	3	20	2	-46	-12	7	24	2	-28	10	12	16	2	-41	13
12	18	1	-35	19	20	1	1	39	59	3	21	2	-45	26	8	1	2	142	143	12	17	2	-39	-21
12	19	1	56	-56	20	2	1	47	46	3	22	2	73	-83	8	2	2	225	241	12	18	2	51	68
12	20	1	-29	-30	20	3	1	37	-53	3	23	2	-39	-30	8	3	2	-38	-34	12	19	2	-32	-6
12	21	1	68	84	20	4	1	-20	6	3	24	2	-35	6	8	4	2	104	103	12	20	2	-28	4
13	1	1	65	-91	20	5	1	33	-47	3	25	2	75	-90	8	5	2	95	-97	13	1	2	152	146
13	2	1	-42	7	0	2	2	605	647	3	26	2	34	49	8	6	2	112	-104	13	2	2	126	120
13	3	1	223	233	0	4	2	52	41	4	1	2	50	53	8	7	2	128	133	13	3	2	163	173
13	4	1	84	85	0	6	2	99	-92	4	2	2	172	-157	8	8	2	-42	20	13	4	2	164	169
13	5	1	97	111	0	8	2	235	-234	4	3	2	181	170	8	9	2	108	92	13	5	2	145	-130
13	6	1	217	221	0	10	2	289	-283	4	4	2	165	165	8	10	2	98	-81	13	6	2	121	-112
13	7	1	91	-95	0	12	2	162	150	4	5	2	-30	12	8	11	2	78	79	13	7	2	202	-191
13	8	1	-43	16	0	14	2	48	-64	4	6	2	114	-103	8	12	2	87	-80	13	8	2	82	-71
13	9	1	90	-89	0	16	2	144	-138	4	7	2	310	-318	8	13	2	-47	-15	13	9	2	-47	36
13	10	1	104	-113	0	18	2	83	76	4	8	2	291	-290	8	14	2	-48	22	13	10	2	70	-64
13	11	1	52	-56	0	20	2	-47	24	4	9	2	-36	-19	8	15	2	-48	-41	13	11	2	150	127
13	12	1	-42	-21	0	22	2	-43	-15	4	10	2	-38	-22	8	16	2	-47	-8	13	12	2	-45	-1
13	13	1	-41	49	0	24	2	-37	-12	4	11	2	134	134	8	17	2	-47	11	13	13	2	66	49
13	14	1	-40	-12	0	26	2	-26	-38	4	12	2	51	-62	8	18	2	-45	3	13	14	2	104	107
13	15	1	54	55	1	0	2	117	107	4	13	2	61	-50	8	19	2	-44	4	13	15	2	69	-71
13	16	1	-36	26	2	0	2	79	-59	4	14	2	81	87	8	20	2	-41	-2	13	16	2	-38	-13
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Table 6. Continued.

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2	19	4	190	189
2	20	4	61	-57
2	21	4	93	84
2	22	4	35	-25
2	23	4	33	-56
3	1	4	-27	-10
3	2	4	72	53
3	3	4	98	87
3	4	4	90	79
3	5	4	-31	-19
3	6	4	73	-57
3	7	4	174	-179
3	8	4	-35	11
3	9	4	45	44
3	10	4	92	97
3	11	4	98	106
3	12	4	-39	38
3	13	4	-39	-45
3	14	4	-40	-16
3	15	4	56	-52
3	16	4	64	-78
3	17	4	-37	24
3	18	4	89	-71
3	19	4	-34	23
3	20	4	-31	29
3	21	4	-28	-29
3	22	4	-24	15
3	23	4	-17	-16
4	1	4	342	-306
4	2	4	163	148
4	3	4	357	-368
4	4	4	55	-53
4	5	4	220	218
4	6	4	203	-199
4	7	4	131	129
4	8	4	95	78
4	9	4	168	-175
4	10	4	77	-62
4	11	4	78	-71
4	12	4	48	-40
4	13	4	-40	14
4	14	4	56	53
4	15	4	203	215
4	16	4	-38	20
4	17	4	159	144
4	18	4	87	83
4	19	4	234	-230
4	20	4	43	42
4	21	4	102	-103
4	22	4	-22	-19
5	1	4	-32	-44
5	2	4	51	61
5	3	4	-33	-10
5	4	4	94	-94
5	5	4	59	68
5	6	4	47	-44
5	7	4	-36	10
5	8	4	83	79
5	9	4	106	-102
5	10	4	61	-51
5	11	4	109	-100
5	12	4	48	-35
5	13	4	49	40
5	14	4	-39	-9
5	15	4	75	65
5	16	4	-38	1
5	17	4	70	-54
5	18	4	51	58
5	19	4	48	-54
5	20	4	-29	-2
5	21	4	-25	29
5	22	4	-20	-27
6	1	4	184	188
6	2	4	236	-259
6	3	4	157	164
6	4	4	203	203
6	5	4	51	-62
6	6	4	294	312
6	7	4	65	-50
6	8	4	113	-114
6	9	4	68	79
6	10	4	65	-75
6	11	4	114	106
6	12	4	148	137
6	13	4	-39	-14
6	14	4	96	100
6	15	4	146	-139
6	16	4	78	-75
6	17	4	61	-55
6	18	4	121	-117
6	19	4	111	125
6	20	4	-27	-6
6	21	4	40	40
6	22	4	29	40
7	1	4	95	92
7	2	4	44	-42
7	3	4	82	78
7	4	4	74	71
7	5	4	59	-63
7	6	4	-38	-15
7	7	4	89	-86
7	8	4	55	-41
7	9	4	-39	10
7	10	4	-40	24
7	11	4	74	75
7	12	4	-39	-21
7	13	4	-39	-32
7	14	4	-38	19
7	15	4	52	-41
7	16	4	69	54
7	17	4	-34	28
7	18	4	38	-27
7	19	4	-28	14
7	20	4	-25	-5
7	21	4	-20	9
8	1	4	-37	34
8	2	4	122	123
8	3	4	60	63
8	4	4	303	-290
8	5	4	-38	8
8	6	4	116	-114
8	7	4	-39	-22
8	8	4	-39	32
8	9	4	-40	28
8	10	4	79	72
8	11	4	-39	56

Table 6. 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)
8	12	4	80	-75	9	17	4	-30	20	11	4	4	84	-85	12	12	4	45	55	14	7	4	48	46
8	13	4	-38	4	9	18	4	-27	13	11	5	4	-39	11	12	13	4	43	-29	14	8	4	124	115
8	14	4	154	-141	9	19	4	-23	-13	11	6	4	48	65	12	14	4	-28	25	14	9	4	-30	-23
8	15	4	54	-51	10	1	4	136	-144	11	7	4	-39	25	12	15	4	97	-117	14	10	4	87	100
8	16	4	72	75	10	2	4	-39	22	11	8	4	-38	33	12	16	4	-22	9	14	11	4	51	-58
8	17	4	-32	-21	10	3	4	158	-151	11	9	4	57	56	13	1	4	56	47	14	12	4	67	-74
8	18	4	106	119	10	4	4	140	136	11	10	4	-37	-6	13	2	4	53	48	14	13	4	26	20
8	19	4	-26	-3	10	5	4	-40	29	11	11	4	-36	-30	13	3	4	-37	-28	14	14	4	23	-39
8	20	4	-22	-12	10	6	4	-40	9	11	12	4	-35	23	13	4	4	64	64	15	1	4	-32	-9
9	1	4	92	-108	10	7	4	108	96	11	13	4	-33	-31	13	5	4	48	-52	15	2	4	-31	-13
9	2	4	48	-31	10	8	4	56	43	11	14	4	-31	-24	13	6	4	54	-45	15	3	4	-31	17
9	3	4	48	-56	10	9	4	48	-36	11	15	4	-29	11	13	7	4	-35	50	15	4	4	46	-46
9	4	4	44	40	10	10	4	58	-54	11	16	4	-26	-6	13	8	4	51	-44	15	5	4	-30	19
9	5	4	71	76	10	11	4	168	-168	11	17	4	-23	-4	13	9	4	-33	-10	15	6	4	-29	-6
9	6	4	52	45	10	12	4	-37	9	12	1	4	202	179	13	10	4	-32	-1	15	7	4	-28	-32
9	7	4	-40	12	10	13	4	-35	29	12	2	4	67	-65	13	11	4	-30	-22	15	8	4	46	46
9	8	4	-40	-41	10	14	4	58	64	12	3	4	124	122	13	12	4	-28	27	15	9	4	-25	-30
9	9	4	-40	-1	10	15	4	150	149	12	4	4	54	38	13	13	4	-26	15	15	10	4	-23	28
9	10	4	-39	-39	10	16	4	82	-78	12	5	4	118	-117	13	14	4	-24	10	16	1	4	47	-38
9	11	4	-38	41	10	17	4	-27	11	12	6	4	89	92	14	1	4	49	-41	16	2	4	-27	-29
9	12	4	-38	15	10	18	4	49	-62	12	7	4	79	-91	14	2	4	60	54	16	3	4	40	-39
9	13	4	-37	16	10	19	4	38	-63	12	8	4	100	-101	14	3	4	-35	-28	16	4	4	91	108
9	14	4	-36	18	11	1	4	-40	-15	12	9	4	-36	26	14	4	4	116	-118	16	5	4	-25	7
9	15	4	-34	-5	11	2	4	-40	-26	12	10	4	60	-57	14	5	4	47	41	16	6	4	46	59
9	16	4	-32	7	11	3	4	-40	13	12	11	4	107	106	14	6	4	126	-134	16	7	4	32	23
																				16	8	4	65	-72

respectively. These bond lengths agree with the lengths of the terminal and central C–C bonds, 1.354(3) and 1.409(3) Å, in 6a-thiathiophthene (I).[1] The average lengths for the equivalent bonds in VI are 1.376 and 1.406 Å, respectively.

The S(6a)–C(3a) bond length in the present structure, 1.742(5) Å, agrees closely with that of 1.748(3) Å in I and also with that of 1.744* Å in VI.

The lengths of the exocyclic C–C bonds (Fig. 1a), ranging from 1.512 to 1.527 Å, are quite normal for such single bonds.

The crystal structure of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene as seen along the *c*-axis is shown in Fig. 2. There are no intermolecular atomic distances shorter than corresponding van der Waals distance.

EXPERIMENTAL

The unit cell dimensions for crystals of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene were determined from high-order reflections on *hk*0 and 0*kl* Weissenberg photographs where sodium chloride powder lines had been superimposed for reference ($a_{NaCl} = 5.6396$ Å). A least squares procedure on 56 measured 2θ-values gave $a = 16.115(5)$ Å, $b = 21.676(8)$ Å, and $c = 5.825(14)$ Å.

Eight molecules per unit cell give a calculated density of 1.269 g/cm³ as compared with the density 1.28 – 1.30 g/cm³ found by flotation.

The intensities of the *hk*0 – *hk*4 and 0*kl* reflections were estimated visually from Weissenberg photographs taken with Ni-filtered Cu$K\alpha$ radiation ($\mu = 23.7$ cm^{-1}). 0*kl* reflections from the zero layer about *a* were used for scaling only.

A crystal with dimensions about $0.08 \times 0.04 \times 0.4$ mm in the three axial directions was used for the intensity data collection. Lp corrections, and corrections for extended spots on upper layer Weissenberg films, were applied, but absorption corrections were not applied.

The scattering factors used for sulphur, nitrogen, carbon, and hydrogen in the structure factor calculations were those given in the *International Tables*.[14]

Final atomic coordinates from the least squares refinement are listed in Table 3, and the temperature parameters in Table 4.

An analysis of the thermal parameters of the S, N, and C atoms, assuming the whole molecule except the methyl groups a rigid body, was carried out according to the method of Schomaker and Trueblood.[9] The libration tensor, **L**, arrived at is given in Table 5. Bond lenghts, which have been corrected according to the libration tensor **L**, are listed in the first column of Table 1.

The final list of structure factors is given in Table 6.

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