

Structures of Linear Multisulphur Systems

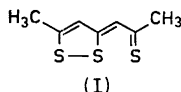
I. The Crystal and Molecular Structure of 2-*t*-Butyl-4,5-(1-(1,3-dithiolane-2-ylidene)-tetramethylene)-1,6,6a-thiathiophthene

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The crystal structure of $C_{16}H_{20}S_5$ has been determined by X-ray diffraction methods. 3942 independent reflections were measured on a computer-controlled diffractometer using $MoK\alpha$ radiation. The structure was solved by three-dimensional Patterson synthesis and refined to $R=0.036$ by full-matrix least squares. Standard deviations in bond lengths are 0.001 Å in S-S, 0.002 Å in S-C and C-C, and 0.02 Å in C-H bonds. Four of the sulphur atoms are arranged in an approximately linear row, with distances S(1)-S(2)=2.482 Å, S(2)-S(3)=2.209 Å, and S(3)-S(4)=2.965 Å. The S(1), S(2), S(3) part of the molecule formally constitutes a thiathiophthene resonance system, and the addition of a fourth sulphur atom in the row does not seem to perturb this system to any noticeable extent.

The thiathiophthene system was discovered when Bezzi *et al.*¹ in 1958 determined the structure of 2,5-dimethyl-6a-thiathiophthene (I).



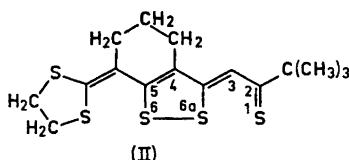
Since then there has been a number of structure reports on both symmetrically and unsymmetrically substituted thiathiophthenes.²⁻⁷ In all these structures, intramolecular sulphur-sulphur bonds in the region 2.10–2.60 Å have been observed, implying that partial bonding between sulphur atoms may exist. In valence bond language, the concept of “one-bond no-bond resonance” is used to describe the system.¹ In MO language, the sulphur-sulphur bonding may be described in terms of a delocalized σ -system, comprising the three

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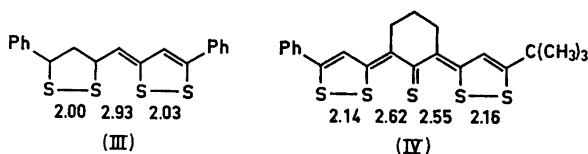
sulphur atoms. The first MO calculations on the thiathiophthene system were performed by Giacometti and Rigatti who considered only *p*-type orbitals for bonding on the sulphur atoms.⁸ Later, it has been suggested that the central sulphur atom may be tetravalent, forming localized σ -bonds to both of the terminal sulphur atoms through *pd*- or *p²d*-hybrid orbitals.⁹ Recently Gleiter and Hoffmann have used the concept of electron-rich three-center bonds to explain the bonding in thiathiophthenes.¹⁰ According to their calculations the potential energy curve shows a flat and almost symmetrical minimum when 3*d*-orbitals on sulphur are included, while an unsymmetrical location of the sulphur atoms is favoured when *d*-orbitals are not included.

Theoretically, the thiathiophthene system may be extended to include four, five, or even an infinite row of sulphur atoms. A number of four- and five-sulphur compounds where a bonding scheme equivalent to that in thiathiophthenes is possible, have been synthesized by Stavaux and Lozac'h¹¹ and by Klingsberg.¹²

To gain information on this new type of compounds a series of X-ray crystallographic structure determinations have been initiated at this laboratory. A preliminary note on the present crystal structure (II) has been published elsewhere.¹³



In addition, short communications on the crystal structures of another four-sulphur compound, (III), and a five-sulphur compound, (IV), have been published.^{14,15}



EXPERIMENTAL

The compound, (II), crystallizes as deep red needles from ethylacetate by slow evaporation. Determination of space group and preliminary cell dimensions were carried out using precession and Weissenberg methods. Final cell parameters were determined by measuring 2θ settings for 24 reflections on a manual diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a temperature of 20°C . The density as determined by flotation was 1.450 g cm^{-3} .

Crystal data

$\text{C}_{16}\text{H}_{20}\text{S}_6$

Space group $P\bar{1}$

$a = 10.0332 \pm 0.0007 \text{ \AA}$

M.W. 372.66

$\alpha = 93.228 \pm 0.005^\circ$

$$b = 13.3294 \pm 0.0009 \text{ \AA}$$

$$c = 7.0276 \pm 0.0005 \text{ \AA}$$

$$V = 859.124 \text{ \AA}^3$$

$$D_x = 1.441 \text{ g cm}^{-3}$$

$$\beta = 101.527 \pm 0.006^\circ$$

$$\gamma = 108.801 \pm 0.004^\circ$$

$$D_m = 1.450 \text{ g cm}^{-3}$$

Linear absorption coefficient: $\mu = 6.3 \text{ cm}^{-1}$ (MoK α -radiation)

The crystal selected for data collection had dimensions: 0.1 mm \times 0.1 mm \times 0.4 mm, and was mounted along the needle axis. Data were collected on a computer-controlled four-circle diffractometer with niobium-filtered MoK α -radiation ($\lambda = 0.71069 \text{ \AA}$). Integrated intensities were measured by the $\theta - 2\theta$ scan technique, the scan ranges being calculated as $\Delta 2\theta = A + B \tan \theta$.¹⁶ Backgrounds were measured at the beginning and end of the 2θ scan, each background being counted for 10 sec.

Of the 3942 unique reflections measured within a sphere limited at $\sin \theta/\lambda = 0.65$, ($2\theta = 55^\circ$), 1023 were coded unobserved, being less than the threshold limit of $2\sigma_c$, where $\sigma_c = (N_{Pk} + (N_{B1} + N_{B2}) \times T/20)^{1/2}$. N_{Pk} is the number of counts in the scan, N_{B1} and N_{B2} are the background counts, and T is the scan time in sec.

During the data collection, three standard reflections were measured for every 200 reflections. The net intensities of the reference reflections stayed constant to within 1 % throughout the data collection. Thus the total error assigned to the net intensity of each reflection is: $\sigma_I = (\sigma_c^2 + (0.01 \sigma_c^2)^2)^{1/2}$. The standard deviation in the structure factors was calculated as: $\sigma_F = (F^2 + \sigma_I(Lp)^{-1})^{1/2} - F$. Data were corrected for Lorentz and polarization effects and for coincidence loss.¹⁷ The apparent dead-time for the system was in this case found to be 3.47×10^{-8} sec/count. Absorption correction was not deemed necessary since the linear absorption coefficient is fairly low and the cross-section of the crystal is approximately equi-dimensional.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the heavy atom method. The four sulphur atoms lying in a row were located from a three-dimensional Patterson map. Structure factor calculation based on these atoms gave an R of 0.58 ($R = \sum(|F_o| - |F_c|) / \sum|F_o|$). In the corresponding Fourier map, the fifth sulphur atom and 12 of the 16 carbon atoms showed up clearly. A structure factor calculation based on the parameters of 17 atoms gave an R of 0.45, and the remaining 4 carbon atoms were located in the succeeding Fourier map.

After three cycles of full-matrix least-squares refinement, the agreement factor was 0.121. All atoms were then assigned anisotropic thermal parameters in the subsequent cycle, and R decreased to 0.068. At this stage, a difference map was calculated, and all of the 20 hydrogen atoms were nicely resolved. These atoms were included in the further refinement, with isotropic thermal parameters. Up to this point, only the 2270 reflections with $2\theta < 45^\circ$ had been included. The final refinement, which included all reflections, converged at an R of 0.036. Shifts in all parameters were less than 0.3σ . The function minimized in the refinement was $\sum w(|F_o| - |(1/k)F_c|)^2$, where $w = 1/\sigma_F^2$.

The atomic scattering factors used in the calculations were, for sulphur those given by Dawson,¹⁸ for carbon those of Berghuis *et al.*,¹⁹ and for hydrogen those of Stewart *et al.*²⁰ All calculations were carried out on an IBM 7094 computer with programs from the X-ray 67 system.²¹

The final coordinates and thermal parameters together with the corresponding standard deviations are given in Table 1 a and b. A list of the observed and calculated structure factors are given in Table 2.

RESULTS AND DISCUSSION

Bond lengths and angles derived from the final coordinates are listed in Tables 3 and 4 together with the corresponding standard deviations. The most important bond lengths and angles are also shown in Fig. 1. Four sulphur atoms, S(1), S(2), S(3) and S(4), are lying approximately on a linear row, with angles $\angle S(1) - S(2) - S(3) = 174.59(3)^\circ$ and $\angle S(2) - S(3) - S(4) = 177.57(3)^\circ$. The three S...S distances are all in the region between a single bond and van der Waals distance. The value usually referred to as van der Waals radius of sulphur is 1.85 Å.²² However, "short" van der Waals contacts between sulphur atoms have been found in several compounds, *e.g.*, S...S distances in the

Table 1a. Final coordinates with the corresponding standard deviations in parenthesis.

Atom	X/a	Y/b	Z/c
S(1)	0.54757(5)	0.82744(4)	0.84614(6)
S(2)	0.34644(5)	0.65323(4)	0.76533(6)
S(3)	0.15738(4)	0.50443(4)	0.71189(7)
S(4)	-0.10404(5)	0.31019(4)	0.64336(7)
S(5)	-0.14903(5)	0.21207(4)	0.99886(7)
C(1)	0.60910(18)	0.79796(13)	1.07218(24)
C(2)	0.53492(19)	0.70125(14)	1.12076(26)
C(3)	0.40776(17)	0.62630(13)	0.99964(22)
C(4)	0.32558(17)	0.53288(12)	1.06375(22)
C(5)	0.19419(18)	0.46789(13)	0.94158(22)
C(6)	0.09343(18)	0.37848(13)	1.00578(22)
C(7)	-0.03401(17)	0.31137(13)	0.89364(23)
C(8)	-0.26188(21)	0.13436(16)	0.77179(29)
C(9)	-0.27858(21)	0.20874(15)	0.62782(29)
C(10)	0.37782(18)	0.50694(13)	1.26557(23)
C(11)	0.29665(20)	0.39358(15)	1.29213(27)
C(12)	0.13543(21)	0.36588(16)	1.22033(26)
C(13)	0.74115(18)	0.87996(13)	1.21230(25)
C(14)	0.79506(21)	0.83317(16)	1.39404(27)
C(15)	0.69945(20)	0.97536(15)	1.27528(27)
C(16)	0.86430(22)	0.91819(16)	1.10742(26)
H(2)	0.5644(15)	0.6853(11)	1.2386(21)
H(81)	-0.3510(16)	0.0936(12)	0.7974(21)
H(82)	-0.2032(16)	0.0932(12)	0.7199(23)
H(91)	-0.3099(15)	0.1736(12)	0.4904(21)
H(92)	-0.3501(17)	0.2499(13)	0.6633(23)
H(101)	0.4831(15)	0.5205(11)	1.2874(22)
H(102)	0.3662(15)	0.5589(12)	1.3616(21)
H(111)	0.3190(16)	0.3828(12)	1.4299(23)
H(112)	0.3275(17)	0.3435(13)	1.2194(23)
H(121)	0.0905(17)	0.2890(12)	1.2404(23)
H(122)	0.0992(20)	0.4131(14)	1.2920(26)
H(141)	0.8836(19)	0.8878(14)	1.4789(25)
H(142)	0.8167(18)	0.7632(13)	1.3527(24)
H(143)	0.7178(18)	0.8125(12)	1.4725(24)
H(151)	0.6264(17)	0.9514(13)	1.3561(24)
H(152)	0.6589(17)	1.0031(14)	1.1583(24)
H(153)	0.7865(18)	1.0294(14)	1.3557(25)
H(161)	0.8301(17)	0.9485(13)	0.9863(24)
H(162)	0.8960(17)	0.8551(14)	1.0683(25)
H(163)	0.9520(17)	0.9706(13)	1.2042(24)

Table 1b. Final thermal parameters with the corresponding standard deviations in parentheses. The anisotropic thermal parameters are defined by the expression:

$$T_i = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)],$$

and the isotropic parameters by $T_i = \exp(-B \sin^2\theta/\lambda^2)$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	4.36(2)	3.64(2)	3.64(2)	0.87(2)	0.45(2)	1.38(2)
S(2)	3.73(2)	3.52(2)	2.39(2)	1.22(2)	0.50(2)	0.95(2)
S(3)	3.57(2)	4.13(2)	2.12(2)	0.50(2)	0.07(2)	0.80(2)
S(4)	3.50(2)	4.33(2)	2.79(2)	0.51(2)	0.33(2)	0.69(2)
S(5)	3.38(2)	4.21(2)	3.46(2)	0.30(2)	0.84(2)	0.81(2)
C(1)	3.26(8)	3.09(8)	3.32(8)	1.18(6)	0.78(6)	0.49(6)
C(2)	3.56(8)	3.22(8)	2.57(8)	0.98(7)	0.31(7)	0.73(7)
C(3)	3.16(8)	3.09(8)	2.30(7)	1.32(6)	0.46(6)	0.53(6)
C(4)	3.15(8)	2.75(7)	2.36(7)	1.13(6)	0.40(6)	0.49(6)
C(5)	3.38(8)	3.16(8)	2.01(7)	1.44(6)	0.35(6)	0.40(6)
C(6)	3.06(8)	3.39(8)	2.34(7)	1.04(6)	0.48(6)	0.57(6)
C(7)	3.07(8)	3.31(8)	2.62(7)	1.32(6)	0.54(6)	0.48(6)
C(8)	4.14(10)	4.94(11)	4.65(11)	-0.23(8)	0.53(8)	1.15(8)
C(9)	4.16(10)	4.13(10)	4.60(10)	0.01(8)	0.56(8)	0.55(8)
C(10)	3.87(9)	3.15(8)	2.62(8)	0.66(7)	0.05(6)	0.76(6)
C(11)	3.81(9)	3.46(9)	2.62(8)	0.85(7)	0.04(7)	0.90(7)
C(12)	3.87(9)	4.65(10)	2.63(8)	0.64(8)	0.36(7)	0.89(7)
C(13)	3.18(8)	3.14(8)	3.85(9)	0.49(7)	0.66(7)	0.46(7)
C(14)	4.90(9)	5.25(9)	5.05(9)	-0.46(8)	1.02(7)	1.36(8)
C(15)	4.79(9)	4.38(10)	6.36(9)	0.85(8)	0.82(7)	-0.97(7)
C(16)	3.73(10)	5.86(10)	6.17(10)	0.88(8)	1.57(8)	0.98(8)

	B (Å ²)		B (Å ²)		B (Å ²)
H(2)	2.42(30)	H(111)	3.41(32)	H(151)	6.70(49)
H(81)	6.22(34)	H(112)	3.49(37)	H(152)	7.96(45)
H(82)	9.51(35)	H(121)	5.78(41)	H(153)	6.75(50)
H(91)	5.94(33)	H(122)	5.39(43)	H(161)	6.71(50)
H(92)	9.58(35)	H(141)	6.45(53)	H(162)	7.81(55)
H(101)	3.67(30)	H(142)	7.88(53)	H(163)	6.91(54)
H(102)	3.87(31)	H(143)	7.31(54)		

region 3.37 Å – 3.60 Å in different allotropes of sulphur,²³ 3.65 Å in 6-mercaptapurine,²⁴ and 3.47 Å in rhodanine.²⁵ Values in the range 1.60 Å – 1.73 Å have been suggested for the van der Waals radius of sulphur,^{25–27} and according to the structural information available, a value within this region seems reasonable. For the further discussion, a van der Waals radius of 1.70 Å will be used.

The atoms S(1), S(2), S(3), and C(1) through C(5) formally constitute a thiathiophthene system, substituted at the 2, 4, and 5 positions. From one of the substituents a fourth sulphur atom is brought close to S(3), at a distance of 2.965 Å. This close contact, 0.44 Å shorter than van der Waals distance, might imply partial bonding between S(3) and S(4). If *p*-orbitals only are considered for σ -bonding, S(4) will have one *p*-orbital available for bonding in the C(9)···S(4)···S(3) directions. If a partial bond to S(3) exists, a lengthening of the S(4)–C(9) bond would be expected. This bond is found to be slightly longer than S(5)–C(8), but it is still shorter than the usually accepted S–C single bond value of 1.82 Å.²⁸ Thus the *p*-orbital apparently is effectively engaged in a “full” bond between S(4) and C(9), and accordingly

Table 2. Observed and calculated structure factors multiplied by 10. The reflections with observed intensity less than the threshold value of $2\sigma_c$ are marked with < signs.

0-16,L	421	43	-22	94	90	243	-244	2-6,L	221
0-15,L	420	73	86	102	60	137	141	2-6,L	220
0-14,L	419	114,L		107	29	47	137	2-6,L	219
0-13,L	418			112	30	103	137	2-6,L	218
0-12,L	417			117	31	174	137	2-6,L	217
0-11,L	416			122	32	166	137	2-6,L	216
0-10,L	415			127	33	162	137	2-6,L	215
0-9,L	414			132	34	158	137	2-6,L	214
0-8,L	413			137	35	154	137	2-6,L	213
0-7,L	412			142	36	150	137	2-6,L	212
0-6,L	411			147	37	146	137	2-6,L	211
0-5,L	410			152	38	142	137	2-6,L	210
0-4,L	409			157	39	138	137	2-6,L	209
0-3,L	408			162	40	134	137	2-6,L	208
0-2,L	407			167	41	130	137	2-6,L	207
0-1,L	406			172	42	126	137	2-6,L	206
0-0,L	405			177	43	122	137	2-6,L	205
1-16,L	404			182	44	118	137	2-6,L	204
1-15,L	403			187	45	114	137	2-6,L	203
1-14,L	402			192	46	110	137	2-6,L	202
1-13,L	401			197	47	106	137	2-6,L	201
1-12,L	400			202	48	102	137	2-6,L	200
1-11,L	399			207	49	98	137	2-6,L	199
1-10,L	398			212	50	94	137	2-6,L	198
1-9,L	397			217	51	90	137	2-6,L	197
1-8,L	396			222	52	86	137	2-6,L	196
1-7,L	395			227	53	82	137	2-6,L	195
1-6,L	394			232	54	78	137	2-6,L	194
1-5,L	393			237	55	74	137	2-6,L	193
1-4,L	392			242	56	70	137	2-6,L	192
1-3,L	391			247	57	66	137	2-6,L	191
1-2,L	390			252	58	62	137	2-6,L	190
1-1,L	389			257	59	58	137	2-6,L	189
1-0,L	388			262	60	54	137	2-6,L	188
2-16,L	387			267	61	50	137	2-6,L	187
2-15,L	386			272	62	46	137	2-6,L	186
2-14,L	385			277	63	42	137	2-6,L	185
2-13,L	384			282	64	38	137	2-6,L	184
2-12,L	383			287	65	34	137	2-6,L	183
2-11,L	382			292	66	30	137	2-6,L	182
2-10,L	381			297	67	26	137	2-6,L	181
2-9,L	380			302	68	22	137	2-6,L	180
2-8,L	379			307	69	18	137	2-6,L	179
2-7,L	378			312	70	14	137	2-6,L	178
2-6,L	377			317	71	10	137	2-6,L	177
2-5,L	376			322	72	6	137	2-6,L	176
2-4,L	375			327	73	2	137	2-6,L	175
2-3,L	374			332	74	<	137	2-6,L	174
2-2,L	373			337	75	<	137	2-6,L	173
2-1,L	372			342	76	<	137	2-6,L	172
2-0,L	371			347	77	<	137	2-6,L	171
3-16,L	370			352	78	<	137	2-6,L	170
3-15,L	369			357	79	<	137	2-6,L	169
3-14,L	368			362	80	<	137	2-6,L	168
3-13,L	367			367	81	<	137	2-6,L	167
3-12,L	366			372	82	<	137	2-6,L	166
3-11,L	365			377	83	<	137	2-6,L	165
3-10,L	364			382	84	<	137	2-6,L	164
3-9,L	363			387	85	<	137	2-6,L	163
3-8,L	362			392	86	<	137	2-6,L	162
3-7,L	361			397	87	<	137	2-6,L	161
3-6,L	360			402	88	<	137	2-6,L	160
3-5,L	359			407	89	<	137	2-6,L	159
3-4,L	358			412	90	<	137	2-6,L	158
3-3,L	357			417	91	<	137	2-6,L	157
3-2,L	356			422	92	<	137	2-6,L	156
3-1,L	355			427	93	<	137	2-6,L	155
3-0,L	354			432	94	<	137	2-6,L	154
4-16,L	353			437	95	<	137	2-6,L	153
4-15,L	352			442	96	<	137	2-6,L	152
4-14,L	351			447	97	<	137	2-6,L	151
4-13,L	350			452	98	<	137	2-6,L	150
4-12,L	349			457	99	<	137	2-6,L	149
4-11,L	348			462	100	<	137	2-6,L	148
4-10,L	347			467	101	<	137	2-6,L	147
4-9,L	346			472	102	<	137	2-6,L	146
4-8,L	345			477	103	<	137	2-6,L	145
4-7,L	344			482	104	<	137	2-6,L	144
4-6,L	343			487	105	<	137	2-6,L	143
4-5,L	342			492	106	<	137	2-6,L	142
4-4,L	341			497	107	<	137	2-6,L	141
4-3,L	340			502	108	<	137	2-6,L	140
4-2,L	339			507	109	<	137	2-6,L	139
4-1,L	338			512	110	<	137	2-6,L	138
4-0,L	337			517	111	<	137	2-6,L	137
5-16,L	336			522	112	<	137	2-6,L	136
5-15,L	335			527	113	<	137	2-6,L	135
5-14,L	334			532	114	<	137	2-6,L	134
5-13,L	333			537	115	<	137	2-6,L	133
5-12,L	332			542	116	<	137	2-6,L	132
5-11,L	331			547	117	<	137	2-6,L	131
5-10,L	330			552	118	<	137	2-6,L	130
5-9,L	329			557	119	<	137	2-6,L	129
5-8,L	328			562	120	<	137	2-6,L	128
5-7,L	327			567	121	<	137	2-6,L	127
5-6,L	326			572	122	<	137	2-6,L	126
5-5,L	325			577	123	<	137	2-6,L	125
5-4,L	324			582	124	<	137	2-6,L	124
5-3,L	323			587	125	<	137	2-6,L	123
5-2,L	322			592	126	<	137	2-6,L	122
5-1,L	321			597	127	<	137	2-6,L	121
5-0,L	320			602	128	<	137	2-6,L	120
6-16,L	319			607	129	<	137	2-6,L	119
6-15,L	318			612	130	<	137	2-6,L	118
6-14,L	317			617	131	<	137	2-6,L	117
6-13,L	316			622	132	<	137	2-6,L	116
6-12,L	315			627	133	<	137	2-6,L	115
6-11,L	314			632	134	<	137	2-6,L	114
6-10,L	313			637	135	<	137	2-6,L	113
6-9,L	312			642	136	<	137	2-6,L	112
6-8,L	311			647	137	<	137	2-6,L	111
6-7,L	310			652	138	<	137	2-6,L	110
6-6,L	309			657	139	<	137	2-6,L	109
6-5,L	308			662	140	<	137	2-6,L	108
6-4,L	307			667	141	<	137	2-6,L	107
6-3,L	306			672	142	<	137	2-6,L	106
6-2,L	305			677	143	<	137	2-6,L	105
6-1,L	304			682	144	<	137	2-6,L	104
6-0,L	303			687	145	<	137	2-6,L	103
7-16,L	302			692	146	<	137	2-6,L	102
7-15,L	301			697	147	<	137	2-6,L	101
7-14,L	300			702	148	<	137	2-6,L	100
7-13,L	299			707	149	<	137	2-6,L	99
7-12,L	298			712	150	<	137	2-6,L	98
7-11,L	297			717	151	<	137	2-6,L	97
7-10,L	296			722	152	<	137	2-6,L	96
7-9,L	295			727	153	<	137	2-6,L	95
7-8,L	294			732	154	<	137	2-6,L	94
7-7,L	293			737	155	<	137	2-6,L	93
7-6,L	292			742	156	<	137	2-6,L	92
7-5,L	291			747	157	<	137	2-6,L	91
7-4,L	290			752	158	<	137	2-6,L	90
7-3,L	289			757	159	<	137	2-6,L	89
7-2,L	288			762	160	<	137	2-6,L	88
7-1,L	287			767	161	<	137	2-6,L	87
7-0,L	286			772	162	<	137	2-6,L	86
8-16,L	285								

Table 3. Intramolecular bond distances. The corresponding standard deviations in parentheses refer to the last digit. Bond lengths corrected for rigid body motion are listed in brackets.

Bond		Bond	
S(1)–S(2)	2.482(1) [2.484] Å	C(13)–C(15)	1.530(4) [1.535] Å
S(1)–C(1)	1.701(2) [1.706]	C(13)–C(16)	1.526(3) [1.529]
S(2)–S(3)	2.209(1) [2.211]	C(2)–H(2)	0.88(2)
S(2)–C(3)	1.739(2) [1.745]	C(8)–H(81)	0.94(2)
S(3)–S(4)	2.965(1) [2.967]	C(8)–H(82)	1.03(3)
S(3)–C(5)	1.716(2) [1.721]	C(9)–H(91)	0.99(2)
S(4)–C(7)	1.756(2) [1.762]	C(9)–H(92)	1.09(3)
S(4)–C(9)	1.813(2) [1.814]	C(10)–H(101)	0.99(2)
S(5)–C(7)	1.760(2) [1.762]	C(10)–H(102)	0.99(2)
S(5)–C(8)	1.799(2) [1.803]	C(11)–H(111)	0.98(2)
C(1)–C(2)	1.366(2) [1.368]	C(11)–H(112)	0.98(2)
C(1)–C(13)	1.531(2) [1.533]	C(12)–H(121)	0.98(2)
C(2)–C(3)	1.414(2) [1.416]	C(12)–H(122)	1.01(2)
C(3)–C(4)	1.408(2) [1.410]	C(14)–H(141)	1.00(2)
C(4)–C(5)	1.398(2) [1.400]	C(14)–H(142)	1.06(3)
C(4)–C(10)	1.510(2) [1.515]	C(14)–H(143)	1.02(3)
C(5)–C(6)	1.453(2) [1.455]	C(15)–H(151)	1.00(2)
C(6)–C(7)	1.355(2) [1.357]	C(15)–H(152)	0.99(3)
C(6)–C(12)	1.516(2) [1.521]	C(15)–H(153)	0.98(2)
C(8)–C(9)	1.479(3) [1.483]	C(16)–H(161)	1.01(2)
C(10)–C(11)	1.510(2) [1.512]	C(16)–H(162)	1.03(3)
C(11)–C(12)	1.508(3) [1.511]	C(16)–H(163)	1.02(2)
C(13)–C(14)	1.531(3) [1.536]		

S(4) would not be expected to participate in σ -bonding to the neighbouring sulphur atom. If, on the other hand, it is assumed that S(4) is tetravalent and that pd -hybrid orbitals are utilized for σ -bonding, S(4) would be able to form bonds to both S(3) and C(9). In order to obtain sufficient overlap between 3 pd hybrids of sulphur and the 2 p orbitals of carbon, 3 d -orbital contraction is probably necessary. Such a contraction may be caused by the nuclear charges of the neighbouring atoms.²⁹

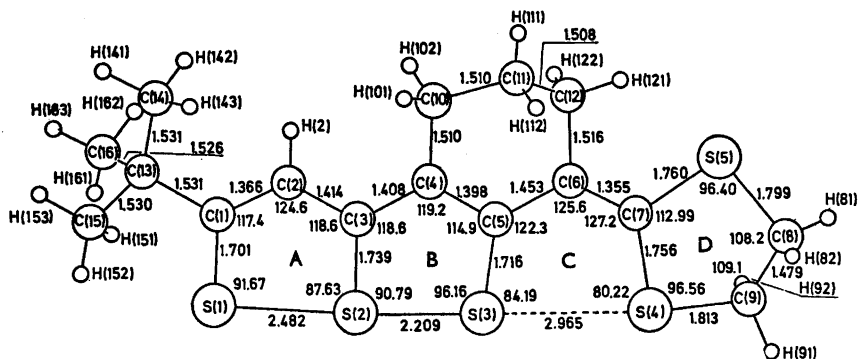


Fig. 1. Molecular dimensions.

Table 4. Intramolecular bond angles with the corresponding standard deviations in parentheses.

Angle		Angle	
S(2)–S(1)–C(1)	91.67(5) ^o	C(4)–C(10)–C(11)	112.2(1) ^o
S(1)–S(2)–S(3)	174.59(3)	C(4)–C(10)–H(101)	108(1)
S(1)–S(2)–C(3)	87.63(5)	C(4)–C(10)–H(102)	107(1)
S(3)–S(2)–C(3)	90.79(5)	C(11)–C(10)–H(101)	111(1)
S(2)–S(3)–S(4)	177.57(3)	C(11)–C(10)–H(102)	111(1)
S(2)–S(3)–C(5)	96.16(5)	H(101)–C(10)–H(102)	106(1)
S(4)–S(3)–C(5)	84.19(5)	C(10)–C(11)–C(12)	111.5(2)
S(3)–S(4)–C(7)	80.22(5)	C(10)–C(11)–H(111)	110.6(8)
S(3)–S(4)–C(9)	168.27(8)	C(10)–C(11)–H(112)	110.0(9)
C(7)–S(4)–C(9)	96.56(8)	C(12)–C(11)–H(111)	110(1)
C(7)–S(5)–C(8)	96.40(8)	C(12)–C(11)–H(112)	108.6(8)
S(1)–C(1)–C(2)	117.4(1)	H(111)–C(11)–H(112)	106(1)
S(1)–C(1)–C(13)	119.6(1)	C(6)–C(12)–C(11)	112.1(2)
C(2)–C(1)–C(13)	123.0(2)	C(6)–C(12)–H(121)	110(1)
C(1)–C(2)–C(3)	124.6(2)	C(6)–C(12)–H(122)	106(1)
C(1)–C(2)–H(2)	118.5(8)	C(11)–C(12)–H(121)	106(1)
C(3)–C(2)–H(2)	116.9(8)	C(11)–C(12)–H(122)	111(1)
S(2)–C(3)–C(2)	118.6(1)	H(121)–C(12)–H(122)	111(2)
S(2)–C(3)–C(4)	118.6(1)	C(1)–C(13)–C(14)	112.1(2)
C(2)–C(3)–C(4)	122.7(2)	C(1)–C(13)–C(15)	108.5(2)
C(3)–C(4)–C(5)	119.2(1)	C(1)–C(13)–C(16)	109.6(2)
C(3)–C(4)–C(10)	119.6(1)	C(14)–C(13)–C(15)	109.4(2)
C(5)–C(4)–C(10)	121.2(1)	C(14)–C(13)–C(16)	108.2(2)
S(3)–C(5)–C(4)	114.9(1)	C(15)–C(13)–C(16)	109.1(2)
S(3)–C(5)–C(6)	122.3(1)	C(13)–C(14)–H(141)	110(1)
C(4)–C(5)–C(6)	122.8(1)	C(13)–C(14)–H(142)	110(1)
C(5)–C(6)–C(7)	125.6(2)	C(13)–C(14)–H(143)	110(1)
C(5)–C(6)–C(12)	115.1(1)	H(141)–C(14)–H(142)	111(2)
C(7)–C(6)–C(12)	119.3(2)	H(141)–C(14)–H(143)	108(2)
S(4)–C(7)–S(5)	112.99(8)	H(142)–C(14)–H(143)	108(2)
S(4)–C(7)–C(6)	127.2(1)	C(13)–C(15)–H(151)	109(1)
S(5)–C(7)–C(6)	119.8(1)	C(13)–C(15)–H(152)	110(2)
S(5)–C(8)–C(9)	108.2(1)	C(13)–C(15)–H(153)	108(2)
S(5)–C(8)–H(81)	107(1)	H(151)–C(15)–H(152)	110(2)
S(5)–C(8)–H(82)	106(1)	H(151)–C(15)–H(153)	109(2)
C(9)–C(8)–H(81)	112(1)	H(152)–C(15)–H(153)	111(2)
C(9)–C(8)–H(82)	105(1)	C(13)–C(16)–H(161)	109(1)
H(81)–C(8)–H(82)	117(2)	C(13)–C(16)–H(162)	110(1)
S(4)–C(9)–C(8)	109.1(1)	C(13)–C(16)–H(163)	108(1)
S(4)–C(9)–H(91)	105(1)	H(161)–C(16)–H(162)	110(2)
S(4)–C(9)–H(92)	107(1)	H(161)–C(16)–H(163)	114(2)
C(8)–C(9)–H(91)	113(1)	H(162)–C(16)–H(163)	106(2)
C(8)–C(9)–H(92)	110(1)		
H(91)–C(9)–H(92)	112(2)		

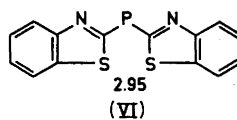
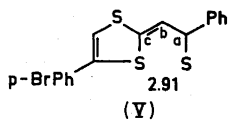
Regardless of the valence state of S(4), a partial bond between S(3) and S(4) would be expected to perturb the three-sulphur thiathiophthene system, S(1)···S(2)···S(3). In thiathiophthenes, sulphur-sulphur distances ranging from 2.16 to 2.56 Å have been found. S(1)···S(2) and S(2)···S(3) in the present molecule fall within this region. In Table 5, pertinent S–S and S–C distances in four unsymmetrically substituted thiathiophthenes are compiled. The bond lengths in the thiathiophthene part of the present molecule closely resemble

Table 5. S-S and S-C distances in unsymmetrically substituted thiathiophthenes.

Compound	Short S-S	Long S-S	Total			Ref.	
			dist. S-S...S	Terminal S-C	Central S-C		Terminal S-C
2,4-Diphenyl thiathiophthene	2.218(3)	2.499(3)	4.717	1.669(7)	1.741(5)	1.696(5)	2
2-Methyl-4-phenyl thiathiophthene	2.237(2)	2.475(2)	4.712	1.693(5)	1.747(4)	1.688(5)	6
3-Benzoyl-5- <i>p</i> -bromophenyl-	2.168(8)	2.454(8)	4.622	1.69(2)	1.70(2)	1.72(2)	4
2-methyl-thiathiophthene	2.163(8)	2.561(8)	4.724	1.72(2)	1.78(2)	1.68(2)	
2,3,4-Triphenyl-thiathiophthene	2.266(3)	2.371(3)	4.637	1.676(9)	1.755(9)	1.667(9)	7
Average	2.210	2.472	4.682	1.690	1.745	1.690	

the mean values of the corresponding dimensions in the tabulated structures, and the overall length $S(1)\cdots S(2)\cdots S(3)$ of 4.69 Å is nearly equal to the corresponding average distance of 4.68 Å. Thus the interaction between S(3) and S(4) apparently is too weak to affect the thiathiophthene system to any noticeable degree. Nor does it, as noted above, affect the length of the S(4)-C(9) bond.

The internal angles at the three sp^2 -hybridized carbon atoms in ring C (Fig. 1) are all larger than 120° . Also there is a small twist around the C(6)-C(7) bond, the dihedral angle C(5),C(6),C(7)/C(6),C(7),S(5) being 4.1° . This twist and the strain in ring C may indicate a repulsion between S(3) and S(4). Similar features are observed in other molecules with intramolecular S...S distances in the region 2.90-3.00 Å. For example, in the isothiathiophthene (V)³⁰ the S...S distance is 2.91 Å, and the internal angles a, b and c are 131° , 127° and 119° , respectively. An equally short intramolecular sulphur-sulphur distance (2.95 Å) has been found in bis-*N*-ethylbenzthiazol-(2) phosphamethincyanin perchlorate



(VI).³¹ The internal angles at the two carbon atoms in the central five-membered ring are 129° and 132° . The geometry of the present molecule thus indicates that the covalent bonding, if any, between S(3) and S(4) is very weak.

Comparing the results from the present investigation with those of the symmetrically substituted four-sulphur compound (III),¹⁴ it is seen that the sulphur atoms are arranged quite differently in the two structures. In compound (III) the central S...S distance is 2.93 Å while the two terminal bonds of 2.00 and 2.03 Å are of the same length as the S-S bonds normally found in isolated 1,2-dithiolium rings.³² Thus the short contact between the central sulphur atoms has not brought about a significant lengthening of the terminal S-S bonds.

Table 6. Least squares planes through each of the five-membered rings, and atomic deviation from these planes.

Equation of plane (X , Y , and Z triclinic coordinates in Å)	Atoms defining the plane and their deviation from the plane (Å)				
$0.8491X - 0.6310Y - 0.4798Z =$ -5.1422 (1)	S(1)	S(2)	C(1)	C(2)	C(3)
$0.8060X - 0.7103Y - 0.4419Z =$ -5.7436 (2)	-0.0093	0.0156	0.0007	0.0186	-0.0256
$0.7949X - 0.7673Y - 0.3580Z =$ -5.6585 (3)	S(2)	S(3)	C(3)	C(4)	C(5)
	-0.0181	0.0282	0.0052	0.0262	-0.0414
	S(3)	S(4)	C(5)	C(6)	C(7)
	-0.0387	0.0357	0.0506	0.0000	-0.0477

Angle between plane 1 and plane 2	6.24°
Angle between plane 1 and plane 3	11.17°
Angle between plane 2 and plane 3	5.71°

Table 6 lists deviations from the least squares planes through each of the 1,2-dithiole rings. Each ring shows a small but significant deviation from planarity. As mentioned above, there is a small twist of 4.1° around the C(6)–C(7) bond. The steric strain between S(5) and H(121) (Fig. 1) is somewhat relieved through this torsion, however, the S···H distance of 2.57 Å is significantly shorter than van der Waals distance. Short S···H distances are also found between S(1) and H(152) (2.71 Å) and between S(1) and H(152) (2.88 Å).

The 1,3-dithiolane ring is non-planar with atoms S(4), S(5), C(7) and C(9) approximately in a plane, and C(8) displaced 0.6 Å from this plane. The bond angles and S–C distances are normal and in fairly good agreement with angles and distances found, *e.g.*, in 2-desylidene-1,3-dithiolane.³³ However, the sp^3 – sp^3 carbon bond, C(8)–C(9), of 1.479 Å is extraordinary short. Thermal vibration alone cannot account for this shortening. A residual difference map calculated at the end of the refinement shows a peak of $0.26 \text{ e}\text{Å}^{-3}$ at a distance of 0.9 Å from C(9) and 1.3 Å from C(8) on the outside of the ring. This spurious peak may be due to errors in the data, and it could result in slightly erroneous positional parameters for the neighbouring atoms.

The S–C_{sp²} bonds in the molecule have partial double bond character, with π -bond orders in the range 0.37–0.64.³⁴ The two S–C_{sp³} bonds, S(4)–C(9) and S(5)–C(8), are slightly shorter than the usually accepted single bond value of 1.82 Å.^{28,34} A compilation of S(II)–C_{sp³} distances from recent literature is shown in Table 7. Only structures where the standard deviations in S–C bond lengths are less than 0.01 Å are included. The average of the 14 S–C_{sp³} distances is 1.823 Å, with an r.m.s. deviation of 0.016 Å. This is in excellent agreement with the single bond value mentioned above. The bond lengths tabulated vary within the limits 1.795 Å and 1.850 Å. This variation may be caused by the environment of the sulphur atom involved. The slight difference between the bond lengths S(4)–C(9) and S(5)–C(8) may indeed reflect that the environment of the two sulphur atoms S(4) and S(5) are quite different.

Table 7. S(II)–C_{sp}^{*} bond lengths in selected compounds.

Compound	S(II)–C _{sp} [*]	σ	Ref.
<i>trans</i> -2,3-Dichloro-1,4-thioxane	1.795	0.006	35
	1.820		
2- <i>p</i> -Methoxyphenyl-3,4-dibenzyl- 1,3,4-thiazolidine-5-thiole	1.842	0.007	36
D,L-Homocysteine thiolactone hydrochloride	1.814	0.003	37
	1.840	0.009	
2-(2-Pyridylmethylthio)- benzoic acid	1.834	0.003–0.01	38
	1.845	0.003	
2,5-Dimethyl-2,5-endothio- 1,4-dithiane	1.819	0.003	39
	1.850	0.003	
	1.822	0.003	
	1.810	0.003	
	1.821	0.003	
Present structure	1.799	0.002	
	1.813	0.002	
Average	1.823		

The arrangement of molecules in the unit cell as viewed along the *c*-axis is shown on Fig. 2. The reference molecule is marked with the atomic numbering used in the tables. The shortest intermolecular S···S contact of 3.54 Å (S(2)···S(4)) occurs between molecules related by a center of symmetry, *e.g.*, the reference molecule and the one inverted through $(0, \frac{1}{2}, \frac{1}{2})$. There are no intermolecular contacts shorter than van der Waals distances.

THERMAL ANALYSIS

The thermal motions of the sulphur atoms and atoms C(1) through C(9) have been analyzed in terms of possible rigid body motion using the method of Schomaker and Trueblood.⁴⁰ The observed mean-squares amplitudes of vibration, U_{ij} , and the corresponding values calculated based on the rigid-body approximation, agree reasonably well, the r.m.s. ΔU and $\sigma(U_{ij})$ being 0.0027 Å² and 0.0032 Å², respectively. Bond distances corrected for rigid body motion were calculated according to the method of Cruickshank⁴¹ (Table 3). In this calculation the atoms not included in the rigid body model were assumed to vibrate as the rigid body. This approximation is not satisfactory, especially

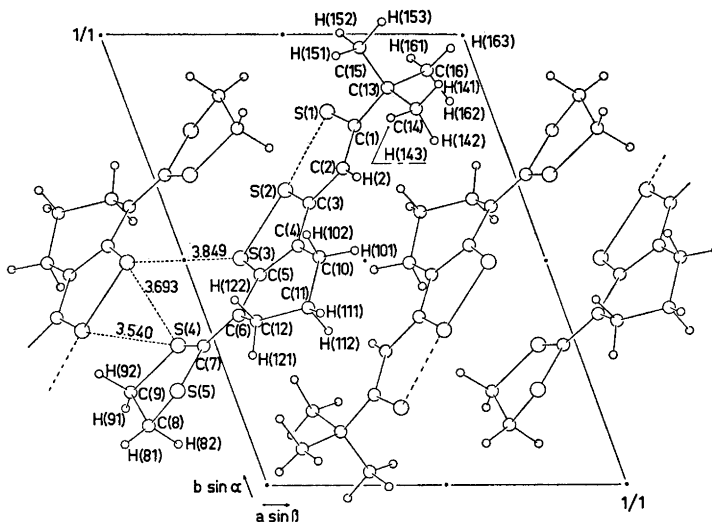


Fig. 2. Projection of the structure along [001].

not for the atoms in the *t*-butyl group which have additional torsional and riding motion. Therefore the bond length corrections are probably underestimated in these cases. The corrections range from 0.001 to 0.006 Å, and do not exceed 3σ in bond lengths. In the discussion throughout this paper, the distances without corrections are referred to, as the molecules with which comparison is being made, have not been corrected for RBM.

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