

## Structures of Linear Multisulphur Systems

### IV. The Crystal and Molecular Structure of 2,6-Bis(5-*t*-butyl-1,2-dithiole-3-ylidene)cyclohexanethione

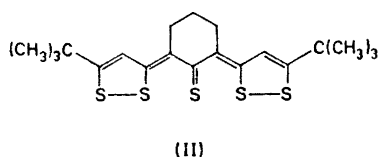
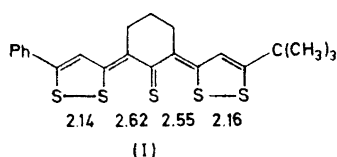
REIDAR KRISTENSEN and JORUNN SLETTEN

*Chemical Institute, University of Bergen, N-5000 Bergen, Norway*

Crystals of 2,6-bis(5-*t*-butyl-1,2-dithiole-3-ylidene)cyclohexanethione,  $C_{26}H_{28}S_5$ , are monoclinic, space group  $C2/c$  with  $Z=8$  in a unit cell of dimensions  $a=35.00(1)$  Å,  $b=6.34(1)$  Å,  $c=20.87(1)$  Å,  $\beta=110.65(1)^\circ$ . The structure was solved by three-dimensional Patterson synthesis and refined by full-matrix least-squares to  $R=0.106$ . The refinement comprises 1989 unique  $h0l-h3l$  and  $hk0$  reflections including 847 unobserved.

The five sulphur atoms are lying almost on a linear row with S-S bond distances in the region between a single bond and van der Waals distance, S(1)-S(2)=2.183 Å, S(2)-S(3)=2.580 Å, S(3)-S(4)=2.583 Å, S(4)-S(5)=2.172 Å. The molecule possesses a pseudo mirror plane perpendicular to the least-squares plane of the five membered rings and passing through S(3) and C(6).

The present investigation was undertaken as part of a program of X-ray crystallographic studies of linear multisulphur compounds. So far five four-sulphur compounds and two five-sulphur compounds have been investigated.<sup>1-6</sup> In these compounds sulphur-sulphur distances in the region between single bond and van der Waals distance have been found. The first structure determination of a linear five-sulphur compound (I) clearly indicates that partial covalent bonding exists between all five sulphur atoms.<sup>5</sup> In the present investigation the structure of a symmetrically substituted five-sulphur compound (II) is determined. A preliminary note on this work has been published.<sup>6</sup>



## CRYSTAL DATA

$C_{20}H_{26}S_6$ , M. W. = 414.75
Crystal system: monoclinic
Systematic absences: $hkl$ : $h + k = 2n + 1$
$h0l$ : $l = 2n + 1$
Space group: $C2/c$ (or $Cc$ )
$a$ = 35.00(1), $b$ = 6.34(1), $c$ = 20.87(1) Å
$\beta$ = 110.65(1)°
$V$ = 4330 Å <sup>3</sup>
$D_x$ = 1.309 g cm <sup>-3</sup> , $Z$ = 8
$F_{000}$ = 1760
$\mu_{(CuK\alpha)}$ = 47.2 cm <sup>-1</sup>

## EXPERIMENTAL

The compound was synthesized by Stavaux and Lozac'h.<sup>7</sup> Needle shaped tiny crystals grew from a solution of cyclohexane by slow evaporation at room temperature. The crystals were of poor quality and gave reflections which were partly split. A crystal with dimensions  $0.022 \times 0.670 \times 0.044$  mm<sup>3</sup> was used to collect integrated equi-inclination Weissenberg photographs of the  $h0l$ – $h3l$  levels employing the multiple film method. Correlation data were obtained from  $hk0$  Weissenberg photographs using a crystal of dimensions  $0.015 \times 0.340 \times 0.030$  mm<sup>3</sup>. A total of 1989 independent reflection were measured visually by comparison with a calibration strip. Space group and cell dimensions were deduced from oscillation and Weissenberg  $h0l$  and  $hk0$  photographs. Nickel filtered CuK radiation was used throughout the data collection.

The data were corrected for Lorentz, polarization and absorption effects. The absorption correction was made by the procedure described by Coppens *et al.*<sup>8</sup> the absorption integral being evaluated by the numerical method of Gauss.<sup>9</sup>

The density was not experimentally determined due to lack of material.

## STRUCTURE DETERMINATION AND REFINEMENT

The statistical distribution of the intensity data indicated a centrosymmetric space group. Therefore, as a working hypothesis it was assumed that the space group is  $C2/c$ . The orientation of the approximately linear row of sulphur atoms was easily found from a three-dimensional Patterson synthesis. However, in order to locate the actual position of the row in the unit cell it was necessary to consider several possibilities. This problem arose mainly because the relative heights of the peaks due to vectors between centrosymmetrically related sulphur rows, did not correspond to the theoretically expected peak heights. All together four possible solutions were tested, three of which are closely related; from one of the possibilities the two others may be derived by translating the sulphur row by half a S–S distance in one direction or the other. In each case phases determined by the sulphur atoms were used to calculate a three-dimensional Fourier map, and all four maps showed electron density peaks in positions for atoms C(2) through C(10) (Fig. 1). Each possibility was then tested by including these carbon atoms, refining atomic positions by least squares and calculating new electron density maps. Three of the possibilities were discarded as the Fourier maps did not reveal the remaining atoms. For

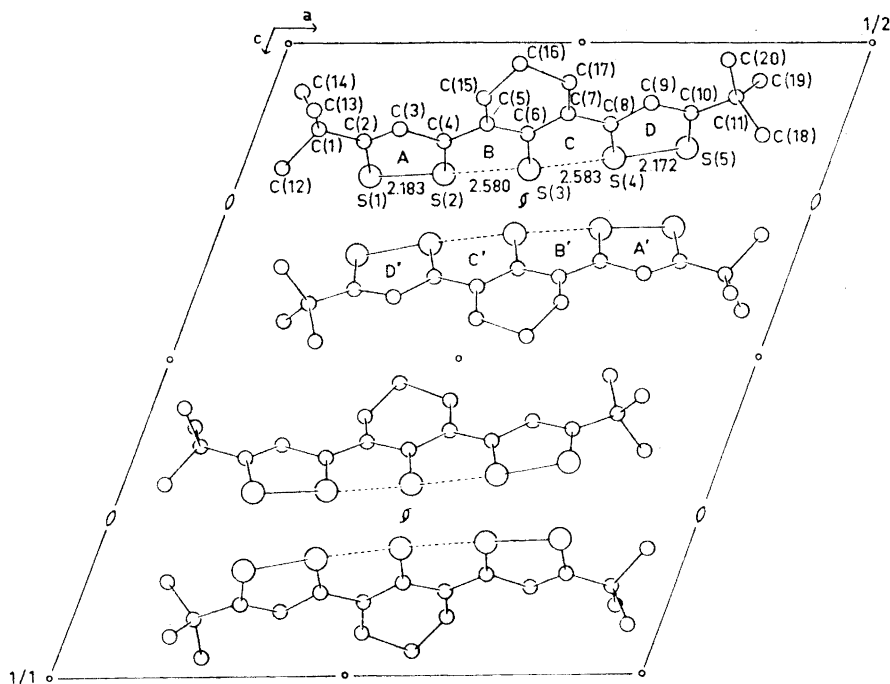


Fig. 1. Packing of molecules. The content in half a unit cell is shown.

the fourth possible solution all non-hydrogen atoms were found in successive Fourier maps, and this structure was successfully refined by a full-matrix least-squares procedure, minimizing the function  $\sum w(|F_o| - |1/k F_c|)^2$  and giving all observed reflections, and unobserved reflections with  $|F_c| > |F_o|$ , unit weight. Interlayer scale factors were introduced as variables in the refinement. In the final stages of refinement the sulphur atoms were given anisotropic thermal parameters. Hydrogen atoms were not located. The refinement converged at an  $R$  of 0.107 ( $R = \sum (||F_o| - |F_c||) / \sum |F_o|$ ). The atomic scattering factors used are for sulphur those of Dawson<sup>10</sup> and for carbon those of Berghuis *et al.*<sup>11</sup>

The calculations were carried out on an IBM 360/50 computer using programs made available by the Chemistry Department, Weizmann Institute of Science, Rehovoth, Israel and modified by D. Rabinovich and K. Åse. Programs for calculating interatomic distances and least-squares planes have been written by K. Maartmann-Moe.

## RESULTS AND DISCUSSION

Atomic coordinates and thermal parameters are listed in Tables 1a and b. Bond lengths and angles are given in Tables 2 and 3. The sulphur atoms are lying approximately on a linear row, the angles S(1)–S(2)–S(3),

Table 1a. Fractional atomic coordinates and isotropic thermal parameters with standard deviations in parentheses. Thermal parameters are multiplied by  $10^3$ . Isotropic temperature factor  $T = \exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>U</i>
S(1)	0.1130(1)	0.0559(10)	0.2090(3)	
S(2)	0.1753(1)	0.0739(9)	0.2092(2)	
S(3)	0.2474(1)	0.0941(9)	0.2023(3)	
S(4)	0.3163(1)	0.0578(9)	0.1838(3)	
S(5)	0.3737(1)	0.0424(11)	0.1658(3)	
C(1)	0.0500(5)	0.3348(33)	0.1378(8)	46(5)
C(2)	0.0959(4)	0.2740(32)	0.1595(8)	42(5)
C(3)	0.1232(4)	0.3848(32)	0.1393(8)	44(4)
C(4)	0.1653(4)	0.3029(30)	0.1566(8)	37(4)
C(5)	0.1945(4)	0.3860(32)	0.1328(8)	40(4)
C(6)	0.2335(4)	0.2988(30)	0.1471(8)	38(4)
C(7)	0.2610(4)	0.3689(32)	0.1165(8)	43(5)
C(8)	0.2996(4)	0.2850(31)	0.1302(8)	39(4)
C(9)	0.3294(5)	0.3683(32)	0.1009(8)	44(5)
C(10)	0.3685(4)	0.2555(33)	0.1146(8)	43(5)
C(11)	0.4003(5)	0.3271(35)	0.0885(9)	58(5)
C(12)	0.0346(5)	0.3055(35)	0.1988(9)	61(6)
C(13)	0.0432(6)	0.5650(41)	0.1077(10)	84(7)
C(14)	0.0257(6)	0.1801(37)	0.0779(10)	71(6)
C(15)	0.1840(5)	0.6001(35)	0.0915(9)	54(5)
C(16)	0.2043(6)	0.5974(38)	0.0378(10)	73(6)
C(17)	0.2506(5)	0.5588(36)	0.0679(9)	68(6)
C(18)	0.4337(7)	0.4369(43)	0.1493(11)	98(8)
C(19)	0.4164(5)	0.1373(37)	0.0626(9)	66(6)
C(20)	0.3841(6)	0.4956(39)	0.0285(10)	77(6)

Table 1b. Anisotropic thermal parameters for the sulphur atoms with standard deviations in parentheses. The numbers are multiplied by  $10^3$ .

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

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>
S(1)	53(3)	52(6)	99(4)	6(3)	34(4)	43(3)
S(2)	51(2)	40(5)	66(3)	5(3)	18(3)	33(2)
S(3)	44(2)	50(5)	71(3)	12(3)	34(4)	24(2)
S(4)	42(2)	38(5)	81(4)	17(3)	25(4)	25(2)
S(5)	45(2)	71(6)	107(4)	26(3)	37(4)	34(3)

S(2)–S(3)–S(4) and S(3)–S(4)–S(5) being 176.9°, 170.6° and 177.5°, respectively. Each of the five-membered rings A, B, C, and D (see Fig. 1) is almost planar. However, there is a significant bending of the molecule around S(3)–C(6), the angle between the least-squares planes through rings A+B and C+D being 7.8°. A similar geometry was found in molecule I.<sup>5</sup> Molecule II possesses a pseudo mirror plane perpendicular to the least-squares plane of rings A, B, C, D and passing through S(3)–C(6). The corresponding

Table 2. Bond distances (Å) with standard deviations referring to the last decimal places listed in parentheses.

S(1)–S(2)	2.183(7)	C(1)–C(12)	1.56(3)	C(7)–C(17)	1.53(3)
S(1)–C(2)	1.70(2)	C(1)–C(13)	1.57(3)	C(8)–C(9)	1.48(3)
S(2)–S(3)	2.580(7)	C(1)–C(14)	1.58(3)	C(9)–C(10)	1.40(2)
S(2)–C(4)	1.78(2)	C(2)–C(3)	1.37(3)	C(10)–C(11)	1.56(3)
S(3)–S(4)	2.583(7)	C(3)–C(4)	1.48(2)	C(11)–C(18)	1.55(3)
S(3)–C(6)	1.69(2)	C(4)–C(5)	1.39(3)	C(11)–C(19)	1.51(3)
S(4)–S(5)	2.172(7)	C(5)–C(6)	1.40(2)	C(11)–C(20)	1.59(3)
S(4)–C(8)	1.79(2)	C(5)–C(15)	1.58(3)	C(15)–C(16)	1.52(3)
S(5)–C(10)	1.70(2)	C(6)–C(7)	1.40(3)	C(16)–C(17)	1.54(3)
C(1)–C(2)	1.55(2)	C(7)–C(8)	1.38(2)		

Table 3. Bond angles (°) with the corresponding standard deviations in parentheses.

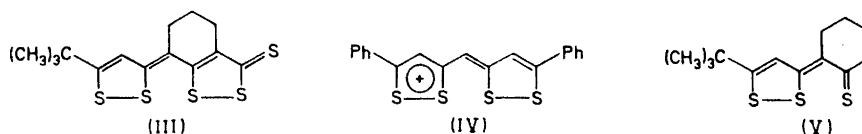
S(2)–S(1)–C(2)	95.6(6)	C(4)–C(5)–C(15)	118(1)
S(1)–S(2)–S(3)	176.9(2)	C(6)–C(5)–C(15)	118(1)
S(1)–S(2)–C(4)	93.5(6)	S(3)–C(6)–C(5)	118(1)
S(3)–S(2)–C(4)	84.8(6)	S(3)–C(6)–C(7)	118(1)
S(2)–S(3)–S(4)	170.6(2)	C(5)–C(6)–C(7)	124(1)
S(2)–S(3)–C(6)	91.3(6)	C(6)–C(7)–C(8)	124(1)
S(4)–S(3)–C(6)	91.5(6)	C(6)–C(7)–C(17)	121(1)
S(3)–S(4)–S(5)	177.5(3)	C(8)–C(7)–C(17)	115(2)
S(3)–S(4)–C(8)	84.6(6)	S(4)–C(8)–C(7)	121(1)
S(5)–S(4)–C(8)	93.0(6)	S(4)–C(8)–C(9)	115(1)
S(4)–S(5)–C(10)	96.5(6)	C(7)–C(8)–C(9)	124(1)
C(2)–C(1)–C(12)	111(1)	C(8)–C(9)–C(10)	117(1)
C(2)–C(1)–C(13)	110(1)	S(5)–C(10)–C(9)	118(1)
C(2)–C(1)–C(14)	107(1)	S(5)–C(10)–C(11)	119(1)
C(12)–C(1)–C(13)	113(2)	C(9)–C(10)–C(11)	123(2)
C(12)–C(1)–C(14)	109(1)	C(10)–C(11)–C(18)	107(2)
C(13)–C(1)–C(14)	107(1)	C(10)–C(11)–C(19)	109(2)
S(1)–C(2)–C(1)	119(1)	C(10)–C(11)–C(20)	112(1)
S(1)–C(2)–C(3)	118(1)	C(18)–C(11)–C(19)	112(2)
C(1)–C(2)–C(3)	123(1)	C(18)–C(11)–C(20)	107(2)
C(2)–C(3)–C(4)	119(1)	C(19)–C(11)–C(20)	109(2)
S(2)–C(4)–C(3)	114(1)	C(5)–C(15)–C(16)	108(2)
S(2)–C(4)–C(5)	121(1)	C(15)–C(16)–C(17)	113(2)
C(3)–C(4)–C(5)	125(1)	C(7)–C(17)–C(16)	111(2)
C(4)–C(5)–C(6)	124(1)		

bond lengths and angles in the two halves of the molecule are equal within the experimental error; however, the *t*-butyl groups are twisted in opposite directions relative to the molecular plane.

The S–S, S–C, and C–C bond lengths in the molecule resemble those found in some of the unsymmetrically substituted thiathiophthenes.<sup>12,13</sup> It is therefore natural to assume that the bonding schemes in thiathiophthenes and the five-sulphur compounds are quite similar. One of the concepts used to describe the S–S  $\sigma$ -bonding in the thiathiophthenes is “the 4-electron 3-center bond”.<sup>14</sup> Similarly one may combine one orbital from each of the five sulphur atoms in, *e.g.*, molecule II obtaining five molecular orbitals which are occupied by

six electrons. Thus the sulphur-sulphur  $\sigma$ -bonding in this type of molecules might be described in terms of "6-electron 5-center bonds." The sum of the four S-S bond lengths in molecule I is 9.47 Å and in molecule II 9.52 Å which is slightly longer than twice the S-S-S distances found in thiathiophthenes. This may indicate that on the average the S-S bonds in five-sulphur compounds are somewhat weaker than in thiathiophthenes.

While in thiathiophthenes and five-sulphur compounds both the results of structure determinations and theoretical models clearly suggest delocalized  $\sigma$ -bonding across the sulphur atoms, this is not the case for the four-sulphur compounds studied so far. X-Ray results for, *e.g.*, compounds III<sup>3</sup> and IV<sup>1</sup> indicate that the four-sulphur sequence may adequately be described in terms



of two separate disulphide systems. Simple Hückel MO theory also predicts two localized S-S  $\sigma$ -bonds to be energetically more favourable than a delocalized 4-center bond.

In addition to the  $\sigma$ -system, a delocalized system of 10  $\pi$ -electrons may be envisaged in thiathiophthenes. Results from MO calculations suggest that  $\pi$ -bonding exists between the three sulphur atoms.<sup>15</sup> With this model the visible band in the spectra of thiathiophthenes may be attributed to a  $\pi \rightarrow \pi^*$  transition. NMR data are also consistent with  $\pi$ -conjugation in the system. The ring protons are deshielded to the same extent as in benzene, indicating ring current and aromaticity.<sup>16</sup> The signal from the dithiol hydrogen in, *e.g.*, compound V has a chemical shift of  $\delta = 7.58$  ppm<sup>17</sup> compared to the  $\delta$  value of 7.27 ppm for hydrogen in benzene.

In the five-sulphur compounds a delocalized  $\pi$ -system with 18 electrons may exist. The features of the ultraviolet and visible spectra of five-sulphur compounds<sup>18,19</sup> are similar to those of thiathiophthenes, the absorption bands being shifted to longer wavelength. It is possible that the bands in the visible region also in this case may be due to  $\pi \rightarrow \pi^*$  transitions. The dithiol hydrogen in II has a chemical shift of  $\delta = 7.04$  ppm,<sup>18</sup> which is somewhat lower than the benzene value, but this may still be compatible with  $\pi$ -bonding throughout the rings.

In the crystal there are no intermolecular contacts shorter than van der Waals distance. The shortest intermolecular sulphur-sulphur distance occurs between molecules related by a screw axis, S(3)...S(3)' being 3.71 Å (the primed atom refers to the molecule in position  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ).

The least-squares plane through rings A', B', C', D' of the primed molecule makes an angle of approximately 70° with the corresponding plane of the reference molecule. S(1)' through S(5)' are situated above the plane through A, B, C, D at distances in the range 3.5–3.7 Å. Similar packing arrangements are often found in thiathiophthenes and related compounds. The reason for the difference in the twist of the *t*-butyl groups is probably packing forces.

If the butyl group at C(2) were twisted the same way as the C(10) group, C(14) would come too close to its inversion through (0,0,0). Similarly, if the group attached to C(10) were twisted as the C(2)-group, C(20) and C(16)'' (double prime refers to inversion through  $(\frac{1}{4}, \frac{3}{4}, 0)$ ) would come too close.

Lists of structure factors may be obtained from the authors.

*Acknowledgement.* The authors wish to thank Drs. M. Stavaux and N. Lozac'h for supplying a sample of the compound.

#### REFERENCES

1. Hordvik, A. *Acta Chem. Scand.* **19** (1965) 1253; Hordvik, A., Sletten, E. and Sletten, J. Paper given at *The 6th Nordic Structure Chemistry Meeting* in Århus, Denmark, Jan. 1967.
2. Sletten, J. *Chem. Commun.* **1969** 688; *Acta Chem. Scand.* **25** (1971) 3577.
3. Sletten, J. *Acta Chem. Scand.* **26** (1972) 873.
4. Sletten, J. *Acta Chem. Scand.* **27** (1973) 229, and unpublished results.
5. Sletten, J. *Acta Chem. Scand.* **24** (1970) 1464.
6. Kristensen, R. and Sletten, J. *Acta Chem. Scand.* **25** (1971) 2366.
7. Stavaux, M. and Lozac'h, N. *Bull. Soc. Chim. France* **1968** 4273.
8. Coppens, P., Leiserowitz, L. and Rabinovich, D. *Acta Cryst.* **18** (1965) 1035.
9. Busing, W. R. and Levy, H. A. *Acta Cryst.* **10** (1957) 180.
10. Dawson, B. *Acta Cryst.* **13** (1960) 403.
11. Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
12. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **23** (1969) 1852.
13. Johnson, S. M., Newton, M. G. and Paul, I. C. *J. Chem. Soc. B* **1969** 986.
14. Gleiter, R. and Hoffmann, R. *Tetrahedron* **24** (1968) 5899.
15. Johnstone, R. A. W. and Ward, S. D. *Theoret. Chim. Acta* **14** (1969) 420.
16. Dingwall, J. G., McKenzie, S. and Reid, D. H. *J. Chem. Soc. C* **1968** 2543.
17. Stavaux, M. and Lozac'h, N. *Bull. Soc. Chim. France* **1971** 4419.
18. Stavaux, M. *Bull. Soc. Chim. France* **1971** 4429.
19. Klingsberg, E. *Chem. Ind. (London)* **1968** 1813.

Received March 12, 1973.