The Crystal Structure of a Compound Containing a Linear 4-Sulphur System

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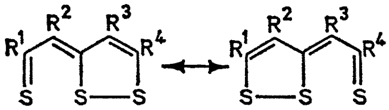
FOR some years there has been considerable interest in the so-called one-bond no-bond resonance system assumed to be present in 5-membered cyclic disulphides with partial bonding to external atoms (I) The sulphur–sulphur distances in such structures have been found to vary with the nature of the substituents R^1—R^4.[1–3]

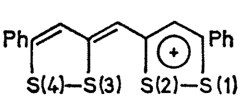
Klingsberg[4] synthesized a compound containing an array of four sulphur atoms in an attempt to produce an extended thiathiophthen system (II). An *X*-ray crystallographic investigation by Hordvik, Sletten and Sletten[6] gave normal disulphide bond lengths (2·00 Å and 2·03 Å) for S(1)–S(2) and S(3)–S(4), while the central S(2)–S(3) distance was found to be 2·93 Å, which is considerably shorter than the van der Waal's distance.

A series of compounds containing linear 4- and 5-sulphur systems have been synthesized by Stavaux and Lozac'h[5] and structure determinations have now been initiated on some of these compounds to study the effects of different substituents on bonding between sulphur atoms. A preliminary report on the first of these investigations is given here.

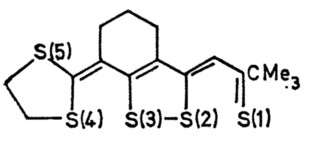
Crystals of (III) $C_{16}H_{20}S_5$, red needles from ethyl acetate, are triclinic, space group $P\bar{1}$, with $a = 10{\cdot}036$, $b = 13{\cdot}323$ $c = 7{\cdot}028$ Å, $\alpha = 93{\cdot}24°$, $\beta = 101{\cdot}53°$ $\gamma = 108{\cdot}79°$. 3970 unique reflections within a sphere limited at $2\theta = 55°$ were collected on a computer-controlled diffractometer using niobium filtered Mo-K_α radiation. In the initial analysis only the 2270 reflections with $2\theta < 45°$ were included. The structure was solved by sharpened Patterson synthesis and refined by full-matrix least-squares to an R of 0·039. All the hydrogen atoms have been located and refined isotropically; the sulphur and carbon atoms were given anisotropic temperature factors. The refinement will be continued when the complete set of data has been processed. Standard deviations in S–S, C–S, and C–C bond lengths are 0·001, 0·006, and 0·01 Å, respectively.



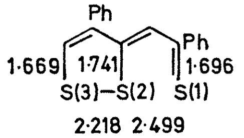
(I)



(II)



(III)



(IV)

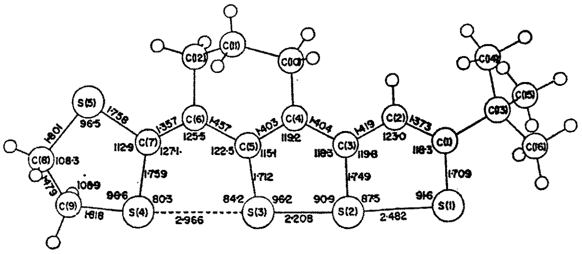


FIGURE. *Molecular dimensions*

The figure shows the molecular dimensions based on the low order data. There is a noticeable similarity between the bond lengths involving the S(1)–S(2)–S(3) part of the molecule and the corresponding portion of 2,4-diphenylthiathiophthen[2] (IV). The fourth sulphur in the row seems to have only negligible influence on the bonding in the 3-sulphur system. The internal angles at the carbons in the five-membered ring S(3)S(4)C(5)C(6)C(7) are all larger than 120°, indicating a repulsion between S(4) and S(3) rather than the attraction expected from partial covalent bonding. Valence angles larger than normal are also found in the central five-membered ring of (II),[6] indicating the same kind of repulsion. The non-bonding S(3) · · · · S(4) distance in (III) is only 2·966 Å and thus substantially shorter than the normal van der Waals distance of 3·40 Å. The S(5) · · · C(12) contact of 2·98 Å is also less than van der Waals distance. The slight torsion of about 4·5° around the C(6)–C(7) bond does little to relieve this non-bonding strain.

Molecular orbital calculations on the positively charged linear 4-sulphur system (II)[7] is consistent with absence of bonding between the central S(2) · · · S(3) atoms; however, the calculations also indicate that a similar negatively charged molecule would probably constitute an extended no-bond resonance system. The same effect might be obtained in the present structure by introducing strongly electron releasing substituents. Similar MO calculations

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on the 3-sulphur system indicate that the one-bond no-bond resonance system is easily perturbed by minor changes in the substituents and that a continuous range of S–S distances from 2·0—2·6 Å might be obtained. In the symmetrically substituted diphenylthiathiophthen the S–S distances are 2·30 and 2·36 Å, respectively.[8] The slight asymmetry in the bonds is believed to be induced through intermolecular close contacts. Presently there is no firm evidence to support the idea that there exists one typical "short" S–S distance (2·12—2·22 Å) and one typical "long" S–S distance (2·47—2·57 Å) in thiathiophthen systems.[3]

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