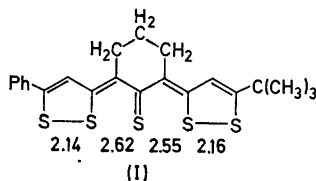


The Crystal Structure of a Symmetrically Substituted Linear 5-Sulphur Compound

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Structure investigations of linear four- and five-sulphur compounds have shown that intramolecular sulphur-sulphur distances in the range 2.0 Å–3.0 Å are present in this type of compounds.^{1,2} The first structure report on a compound containing five sulphur atoms in a row clearly indicates that partial covalent bonding exists between all five sulphur atoms (I).^{3b}



The present communication is a report on the structure of a linear five-sulphur compound which is symmetrically substituted (II).

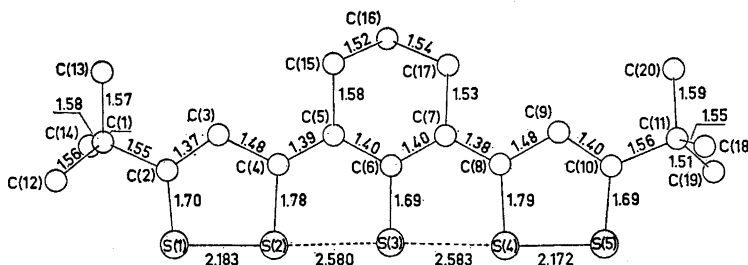
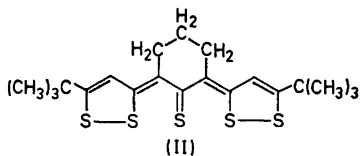


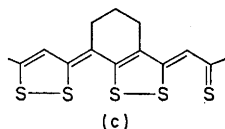
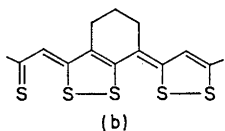
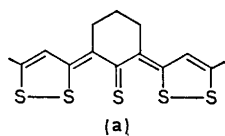
Fig. 1. Bond distances.

2,6-Bis-(5-*t*-butyl-1,2-dithiole-3-ylidene)-cyclohexanethione was synthesized by Stavaux and Lozac'h who kindly supplied a sample.⁸ The compound crystallized as thin needles from a cyclohexane solution by slow evaporation. The crystals are monoclinic, space group $C2/c$ with $Z=8$, and cell dimensions $a=35.00(1)$ Å, $b=6.34(1)$ Å, $c=20.87(1)$ Å, $\beta=110.65(1)^\circ$. The intensities of the $h0l-h3l$ and $hk0$ reflections were visually estimated from integrated Weissenberg photographs taken with $\text{CuK}\alpha$ radiation. A total of 1192 independent reflections were strong enough to be observed.

The structure was solved by three-dimensional Patterson synthesis and refined by full-matrix least-squares to an R of 0.106 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). Anisotropic thermal parameters were assigned to the sulphur atoms, while the carbon atoms were refined isotropically.

A drawing of the molecule with bond distances is shown in Fig. 1. The standard deviations in S-S, S-C and C-C bonds are 0.007 Å, 0.018 Å, and 0.02–0.03 Å, respectively. The molecule is almost symmetrical with a pseudo mirror plane perpendicular to the molecular plane and passing through the line S(3)C(6)C(16). Corresponding bond lengths in the two halves of the molecule are not significantly different.

The intramolecular sulphur-sulphur distances closely resemble those of molecule I. The half-lengths of the sulphur sequences in molecules I and II are 4.74 and 4.76 Å, respectively, and thus slightly longer than the average $\text{S}\cdots\text{S}\cdots\text{S}$ distance of 4.69 Å found in thiatthiophthenes. Using the simple valence bond picture to describe the bonding scheme, one finds that the distribution of bond lengths along the sulphur row in II is consistent with canonical forms of the following type.



Such a scheme is also in qualitative agreement with the lengths observed for the C-S and the C-C bonds except those of C(5)-C(6) and C(6)-C(7) (Fig. 1). According to the description above these bonds would be expected to be of the same lengths as C(3)-C(4) and C(8)-C(9).

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The Interpretation of the ^1H and ^{19}F NMR Spectrum of 1,2-Difluoroethane

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The high resolution ^1H and ^{19}F NMR spectrum of 1,2-difluoroethane, given in Fig. 1, are at first sight surprisingly complex. The four protons and the two fluorine atoms in the molecule are chemically equivalent, but due to the different spin-spin interactions, the nuclei are magnetically non-equivalent. The spectra can be classified as AA'A''A'''XX'. The ^1H spectrum is symmetrical about ν_{H} , the chemical shift of the protons, and the fine structure is determined by six different coupling constants (*vide infra*). Similarly the ^{19}F spectrum is symmetrical about ν_{F} , the chemical shift of the fluorine nuclei, and the fine structure is determined by the same six coupling constants.

Analogous six spin systems have earlier been studied in 1,1,2,2-tetrafluoroethane¹ and *p*-difluorobenzene.² However, the analysis of these spectra was difficult because of heavy overlap between the individual lines in the spectra. The final coupling constants arrived at are therefore uncertain.

We have analysed the spectra in Fig. 1 by using a version of the computer program LAOCOON, written by Castellano and Bothner-By³ as modified by Aksnes and Albrigtsen.⁴ The program calculates the position and intensity of all lines in the spectrum from a given set of chemical shifts and coupling constants. The program also fits by the method of least squares the calculated positions to observed positions by changing the coupling constants and chemical shifts. We must therefore start the analysis by estimating reasonable values of the coupling constants.

1,2-difluoroethane exists in two distinct conformers: *gauche* and *trans*:

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