overlap is observed only in the C_{14} to C_{17} range. Since the distillation temperature determines the position of this range, the method is flexible and readily applied to a number of problems in flavour and natural product chemistry. It has been used with success in our laboratory for more than a year on various fractions from tobacco and tobacco additives of natural origin.

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The Crystal Structure of 2-(5′-Phenyl-1′,2′-dithiole-3′-ylidene)-6-(5″-*t*-butyl-1″,2″-dithiole-3″-ylidene)-cyclohexanethione. An Extended No-bond Resonance System Comprising Five Sulphur Atoms

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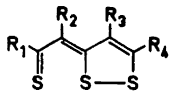
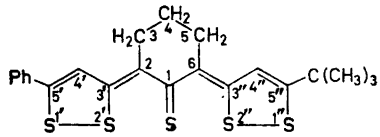
In thiathiophthenes (I) the sulphur-sulphur distance has been found in the



(I)

region single bond — van der Waals distance.[1–5] The nature of this type of bonding has been described in terms of one-bond, no-bond resonance. To see if this no-bond resonance can be extended to include more than three sulphur atoms, a series of X-ray crystallographic structure determinations of compounds containing linear four- and five-sulphur systems has been initiated. So far, structure reports on two linear four-sulphur compounds have been published.[6,7] In this communication, the first structure determination of a linear five-sulphur compound is reported.

The compound (II) was synthesized by Lozac'h and Stavaux.[8] It crystallizes from



(II)

dimethyl sulphoxide as extremely thin platelets. The crystals tend to be split, and have high mosaic spread. Several other crystallization procedures were tried, but did not give crystals of better quality.

The crystals belong to the monoclinic class, space group $P2_1/c$. Cell dimensions were derived from least-squares treatment of the 2θ settings for 12 reflections measured on a four-circle computer-controlled diffractometer: $a=20.009(9)$ Å, $b=8.066(6)$ Å, $c=13.457(7)$ Å, $\beta=103.07(2)°$. The crystal used for data collection had dimensions 0.15 mm × 0.15 mm × 0.01 mm. 1972 unique reflections within a sphere limited at $\sin\theta/\lambda=0.48$ were measured on the diffractometer using niobium-filtered Mo$K\alpha$ radiation ($\lambda=0.71069$ Å). Only 570 of these reflections had net counts significantly above the background. This extraordinary low number of observed reflections is a consequence of the small size of the crystal and the high mosaic spread.

The structure was solved by sharpened Patterson synthesis and refined by full-matrix least-squares to an R of 0.105. The sulphur atoms were refined anisotropically, while the carbon atoms were given isotropic thermal parameters. The hydrogen atoms have not been located. Standard deviations in S—S, S—C, and C—C bond lengths are 0.02 Å, 0.04—0.06 Å, and 0.06—0.10 Å, respectively.

71 of the reflections that had been coded unobserved, were calculated greater than the threshold value of $4\sigma_F$. These reflections were included with their threshold values in the final refinement together with the observed reflections.

The final coordinates from the least-squares refinement are listed in Table 1, and the molecular dimensions are shown in Fig. 1. Each of the four sulphur-sulphur

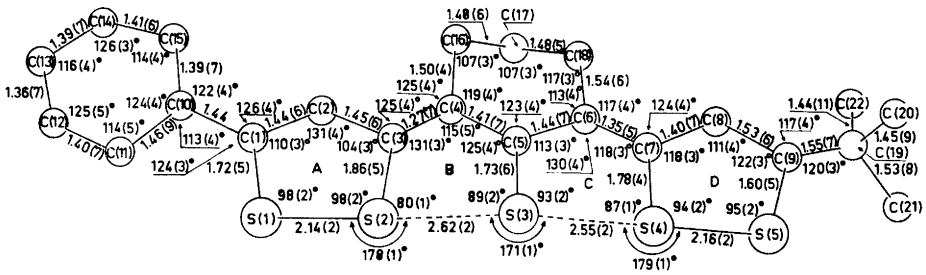


Fig. 1. Bond distances and angles.

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

Atom	x/a	y/b	z/c
S(1)	0.3465(6)	0.5023(22)	0.1497(10)
S(2)	0.4549(7)	0.5088(22)	0.2102(10)
S(3)	0.5885(7)	0.5131(22)	0.2773(10)
S(4)	0.7157(7)	0.4830(24)	0.3614(12)
S(5)	0.8229(7)	0.4582(23)	0.4351(11)
C(1)	0.3471(21)	0.3927(55)	0.0401(33)
C(2)	0.4164(20)	0.3459(54)	0.0386(33)
C(3)	0.4806(23)	0.3787(58)	0.1107(33)
C(4)	0.5388(27)	0.3217(75)	0.1042(41)
C(5)	0.5949(27)	0.3813(70)	0.1780(41)
C(6)	0.6638(22)	0.3212(63)	0.1863(35)
C(7)	0.7220(20)	0.3572(50)	0.2556(29)
C(8)	0.7864(25)	0.2893(64)	0.2545(40)
C(9)	0.8403(23)	0.3391(57)	0.3494(33)
C(10)	0.2863(28)	0.3538(64)	−0.0364(43)
C(11)	0.2228(30)	0.3981(71)	−0.0064(43)
C(12)	0.1627(28)	0.3560(67)	−0.0781(41)
C(13)	0.1607(22)	0.2698(59)	−0.1658(35)
C(14)	0.2237(25)	0.2319(59)	−0.1879(35)
C(15)	0.2886(21)	0.2710(53)	−0.1264(30)
C(16)	0.5517(23)	0.2228(54)	0.0155(31)
C(17)	0.6054(20)	0.1005(53)	0.0575(28)
C(18)	0.6686(19)	0.1947(49)	0.1027(28)
C(19)	0.9149(25)	0.2786(62)	0.3566(35)
C(20)	0.9579(38)	0.4118(94)	0.3353(53)
C(21)	0.9481(35)	0.2133(82)	0.4631(56)
C(22)	0.9192(52)	0.1257(99)	0.3032(71)

distances are longer than a normal S—S single bond,[9] but appreciably shorter than van der Waals distance. The deviation from symmetry in S—S bond lengths around the central sulphur atom, S(3), is small, but probably significant. The angles ∠S(1)S(2)S(3), ∠S(2)S(3)S(4), and ∠S(3)S(4)S(5) are 178(1)°, 171(1)° and 179(1)°, respectively; thus, the row of sulphur atoms is almost linear. The molecule is slightly bent around the central carbon-sulphur bond, C(5)—S(3), the angle between the least-squares planes through each "half" of the molecule, (A+B)/(C+D), being 6.7°. Each of the dithiole rings is planar within the experimental error. The phenyl group is twisted only 6.3° relative to the dithiole ring A.

The sulphur-sulphur distances in this molecule closely resembles those found in some of the unsymmetrical thiathiophthenes.[2,3] It is evident that there is a lengthening of the bonds S_1-S_2 and S_4-S_5 relative to the sulphur-sulphur bonds in isolated dithiolium rings,[10] and this lengthening is probably due to the formation of partial bonds between S(2)···S(3) and S(3)···S(4). One may therefore conclude that there probably exists partial bonding between all the sulphur atoms in the row.

The shortest intermolecular sulphur-sulphur distances are in the range 4.05—4.35 Å and occur between molecules related by screw axes.

The lack of precision in bond lengths and angles prevents a meaningful discussion of the structural details. A recollection of the data using film methods is planned, and the combined sets of data are hoped to improve the precision.

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Note on the Crystal Structures of Ru_5Si_3 and PdSi

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During the continued investigations of platinum metal silicides at this Institute the structure of a new ruthenium silicide, Ru_5Si_3, has been established from X-ray powder data, and the atomic parameters for PdSi have been refined from single crystal X-ray data.

Ru_5Si_3. Alloys were prepared by arc melting ruthenium powder (Heraeus, claimed purity 99.9 %) and silicon (Pechiney, claimed purity 99.9 %). By examining the powder photographs of the alloys the presence of a new intermediate phase was observed. The composition of the phase was found to be intermediate between Ru_2Si [1] and Ru_4Si_3.[2] A comparison of the powder diffraction pattern of the new phase and that of Rh_5Si_3 [3] showed fairly good agreement and it was possible to index the pattern on the basis of an orthorhombic unit cell. The striking similarity between the intensities of equivalent diffraction lines for Rh_5Si_3 and the new phase as well as the correspondence of the unit cells implies that the two phases are isostructural.

The unit cell dimensions of Ru_5Si_3 were evaluated from measurements of a powder pattern recorded in a Guinier-Hägg focusing camera using $CuK\alpha_1$ radiation. Silicon (a=5.43054 Å) was incorporated in the powder specimen as an internal calibration standard. A least-squares refinement of the unit cell dimensions was made (see the list of programmes in Ref. 2).

Crystallographic data for Ru_5Si_3: Structure type: Rh_5Ge_3. $Z=2$. $a=5.246(2)$ Å, $b=9.815(2)$ Å, $c=4.023(1)$ Å, $U=207.14$ Å^3.

PdSi. An alloy of the equi-atomic stoichiometry was prepared by arc melting palladium powder (Heraeus, claimed purity 99.9 %) and silicon (Pechiney, claimed purity 99.9 %). The X-ray powder analysis of the alloy showed the presence of one phase, PdSi. The unit cell dimensions of PdSi (Table 1) were determined in an analogous way to those of Ru_5Si_3 (see above). The lattice constants are uniformly about 0.3 % less than those found in an earlier investigation.[4]

The single crystal investigation was carried out in an equi-inclination Weissenberg camera using zirconium-filtered MoK radiation and the multiple film technique. The crystal was rotated about the b axis and the intensities of the $h0l$ reflexions were recorded. The intensities were estimated by visual comparison with a calibrated intensity scale. Nothing was found during the work that contradicted the correctness of the space group, *Pnma*, proposed earlier.[4]

Starting with the approximate atomic parameters given in Ref. 4 the structure of PdSi was refined by the method of least squares. The refinement was based on 128 $h0l$ reflexions. Four positional parameters, two individual temperature factors, and one scale factor were allowed to vary during the refinement. The weighting scheme according to Cruickshank *et al.*[5] $w=1/(a+|F_o|+c|F_o|^2)$, was used where the constants a and c were given the values 28.0 and 0.014, respectively. The atomic scattering factors for palladium and silicon were obtained from Ref. 6 together with the real and imaginary dispersion corrections. The computational work was carried out utilizing the various