X-Ray and Molecular Structure of 2,2'-(Ethylenedithio)bis-1,3,2-dithiaphospholan

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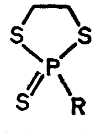
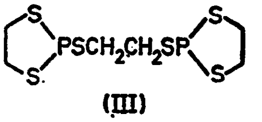
Summary *X*-Ray structural studies of a five-membered ring phosphine trisulphide, 2,2'-(ethylenedithio)bis-1,3,2-dithiaphospholan, show a five-membered ring approximately in an envelope conformation with one of the sulphur atoms in a flap position.

Detailed n.m.r. studies of several 1,3,2-dithiaphospholan ring systems which contain three- and four-co-ordinate phosphorus have been recently reported[1,2] and *X*-ray diffraction studies of 2-chloro-1,3,2-dithiaphospholan-2-thione (I)[3] and 2-phenyl-1,3,2-dithiaphospholan-2-thione (II)[4] have appeared. Electron diffraction studies on 2-chloro-1,3,2-dithiaphospholan have also been completed.[5] However, no *X*-ray structural information on a 1,3,2-dithiaphospholan in which phosphorus is three-co-ordinate is available. We now report the results of an *X*-ray structural analysis of 2,2'-(ethylenedithio)bis-1,3,2-dithiaphospholan (III) and a comparison with (I) and (II).



(I) R=Cl
(II) R=Ph



(III)

Two independent *X*-ray studies were initiated, one at Grenoble (J.B.R., J.M., and D.T.) and one at the University of Georgia (M.G.N., H.C.B., and C.J.F.) The study described here is that done at the University of Georgia and is in agreement with that obtained by the Grenoble group. Full details of both structure determinations will be reported elsewhere.

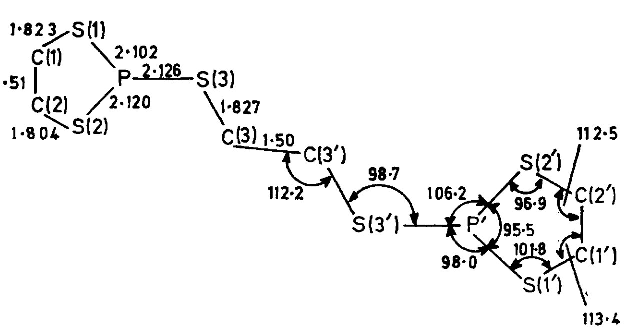


Figure 1. Bond lengths and angles calculated for (III). Average standard deviations are: P–S 0·003, S–C 0·009, and C–C 0·013 Å; ∠ S–P–S 0·1, P–S–C 0·3, and S–C–C 0·7°

Crystals of (III) were prepared by the method of Arbuzov and Zaroastrova.[6] Initial precession photographs revealed a monoclinic system with the unique b axis along the direction of elongation of the needle-like crystals. Systematic absences uniquely indicated the space group as $P2_1/c$. *Crystal data:* $a = 7{\cdot}282(3)$, $b = 6{\cdot}001(2)$, $c = 16{\cdot}431(6)$ Å, $\beta = 106{\cdot}50°$, $Z = 2$, λ (Cu-K_α) $= 1{\cdot}5418$ Å. 1440 reflections were measured with Cu-K_α radiation on an Enraf-Nonius CAD-3 diffractometer, of which 1141 were considered to be unique and observed [$I > 1{\cdot}5\,\sigma$ (I)]. No decomposition of the sample was evident from control reflections. The data were corrected for Lorentz-polarization effects, and placed on an absolute scale by Wilson's method.[7] The structure was solved by MULTAN[8] and Fourier analysis, and refined by full-matrix least-squares to a final unweighted R-value of 0·075. Hydrogen atoms were not located.

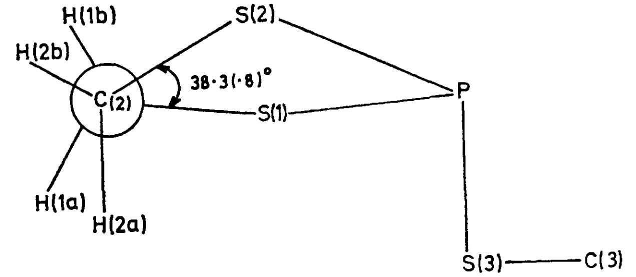
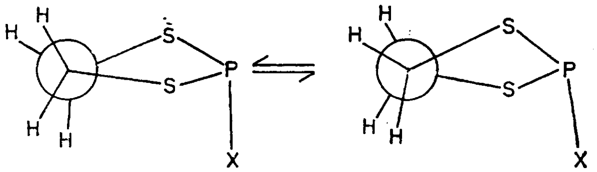


Figure 2. A Newman projection of the unique portion of (III) viewed down the C(1)–C(2) ring bond. H positions are calculated

The molecules of (III) occupy the inversion centre of $P2_1/c$; thus only one-half of the molecule is unique. Bond lengths and angles are in Figure 1. The P–S bonds are on average *ca.* 0·06 Å longer than P–S single bonds in (I) and (II). A similar lengthening in a three-co-ordinate phosphorus derivative was noted in comparisons of the structures of methyl meso-hydrobenzoin phosphite and phosphate esters.[9] The average of the three S–P–S angles in (III) is 99·9°, a value in reasonable agreement with that observed in (I) (100·4°)[3] and (II) (98·5°),[4] although there is a difference of >10° between the smallest and largest value. Other bond lengths and angles in the ring are in agreement with corresponding values in (I).

The ring of (III) approximates to an envelope conformation with S(2) in the flap position (Figure 2). The PS(1)-C(1)C(2) dihedral angle is 8·8° compared with the ideal envelope angle of 0°. The amount of twist in the ring is indicated by the S(1)C(1)C(2)S(2) dihedral angle of 38·3°.

The ring conformation of (I) is similar to (III) but substantially more twisted (less envelope-like) with a corresponding PS(1)C(1)C(2) angle of 15·7° and S(1)C(1)C(2)S(2) angle of 45·0°. The ring of (II) is in an ideal envelope conformation with P in the flap position and this differs considerably from the conformations of (I) and (III).



(1)

Idealized H positions were calculated for (III) assuming a C–H bond length of 1·08 Å, H–C–H angles of 109°, and an equidistant placement of a H above and below the appropriate SCC plane. The PSCH dihedral angles of the ring calculated using these idealized H positions are: PS(1)C(1)-H(1a) = 129·1°, PS(2)C(2)H(2a) = 75·1°, PS(1)C(1)H(1b) = 112·8°, and PS(2)C(2)H(2b) = 166·4°. Assuming that the predominant conformations in solution approximate to that in the solid state and that a rapid equilibrium exists between the forms in equation (1), the average PSCH dihedral angle is *ca.* 140° for hydrogen atoms *trans* to phosphorus, and *ca.* 102° for those *cis*. PSCH coupling constants observed in 1,3,2-dithiaphospholans are small magnitudes and of opposite signs.[1,2] However, the absolute sign of ^3J(PSCH) is not known and the nature of the dihedral angle dependency in these systems is not well understood. The average dihedral angles calculated above may be of use in future studies on these n.m.r. parameters.

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