Preparation of 1,3,2-Benzodithiaphospholes and the *X*-Ray Crystal Structure of 2-Methyl-2,2′-spirobi-(1,3,2-benzodithiaphosphole)

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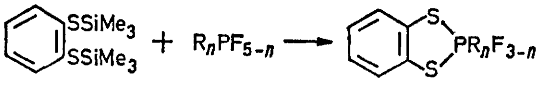
Summary A series of monocyclic and spiro 1,3,2-benzodithiaphospholes ($(C_6H_4S_2)PR_nF_{3-n}$ ($n = 2$, R = Ph, Me), ($n = 3$, R = Pr^i) and $(C_6H_4S_2)_2PR$ (R = Ph, Me) have been synthesised and the structure of one of these, $(C_6H_4S_2)_2PMe$, has been determined by *X*-ray diffraction.

We recently reported the preparation and stereochemical characteristics of fluorophosphosphoranes which contain a catechol ring system attached to five-co-ordinate phosphorus,[1] where the fluorine is apparently equatorial in the presumably trigonal-bipyramidal monofluorophosphorane $(C_6H_4O_2)_2PF$.[2] Catechol phosphoranes and the corresponding disulphur derivatives would be expected to have differing stereochemical arrangements owing to differences in size and electronegativity between sulphur and oxygen. Accordingly, a series of dithiocatechol derivatives (II) was synthesised as in reaction (1). With RPF_5 (R = Ph, Me) spiro-derivatives of the type $(C_6H_4S_2)_2PR$ were obtained. The reaction between (I) and PF_5 was different from that with o-$(Me_3SiO)_2C_6H_4$, in that an ionic compound (III), rather than the monofluorophosphorane, $(C_6H_4S_2)_2PF$, was obtained [reaction (2)]. In view of these structural aspects we have carried out a crystal structure determination of $(C_6H_4S_2)_2Me$.

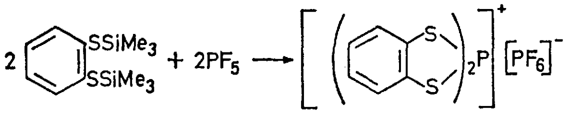


(1)

(I) (II)

(n=2, R=Ph,Me),(n=3,R=Pr^i) + $2Me_3SiF$

The crystals are orthorhombic $Pna2_1$ with $a = 17{\cdot}772(3)$, $b = 6{\cdot}150(1)$, $c = 13{\cdot}158(2)$ Å, $Z = 4$. Intensities were estimated visually from equi-inclination Weissenberg photographs (h0l—h6l inclusive). The structure was determined by three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares with anisotropic temperature factors for the phosphorus and sulphur atoms. The R value is 0·075 for 613 unique observed reflections. Attempts to refine the hydrogen positions have been unsatisfactory.



(2)

(I) (III)

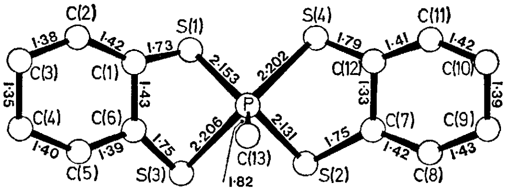


Figure. *The* $(C_6H_4S_2)_2PMe$ *molecule showing bond lengths in* Å. *The e.s.d.'s are* P–S 0·009, S–C 0·02, *and other bonds* 0·03 Å.

The principal features of the molecule are displayed in the Figure. In contrast to previous structural determinations of molecules containing pentaco-ordinate phosphorus,[3] the co-ordination at phosphorus in $(C_6H_4S_2)_2PMe$ shows a very considerable distortion from idealised trigonal-bipyramidal geometry and may be regarded as intermediate between this and square-pyramidal. For instance, the angle between the equatorial sulphur atoms is 132·0(8)° and that between the axial sulphur atoms 158·1(4)°. However, the existence of residual trigonal-bipyramidal character is shown by the fact that the mean P–S(equatorial) bond length of 2·14 Å is 0·06 Å shorter than the mean P–S(axial) bond length of 2·20 Å, in agreement with the effect normally associated with this type of co-ordination. The extent of the distortion from idealised square-pyramidal geometry may be gauged from a comparison of the mean C(13)–P–S(equatorial) angle of 108·3(8)° with the mean C(13)–P–S(axial) angle of 101·0(8)°. The five-membered PSCCS rings are puckered, with a mean angle of 100·4(8)° at sulphur, which is similar to previously observed values.[4,5]

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[1] G. O. Doak and R. Schmutzler, *Chem. Comm.*, 1970, 476.

[2] G. O. Doak and R. Schmutzler, *J. Chem. Soc.* (*A*), 1971, 1295.

[3] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

[4] J. D. Lee and G. W. Goodacre, *Acta Cryst.*, 1971, **B29**, 1055.

[5] J. D. Lee and G. W. Goodacre, *Acta Cryst.*, 1971, **B27**, 1841.