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THE P—P BOND LENGTH IN 1,2-DIPHENYL-1,2-DIPHOSPHOLANE-1,2-DISULPHIDE COMPARED WITH THAT IN OTHER COMPOUNDS

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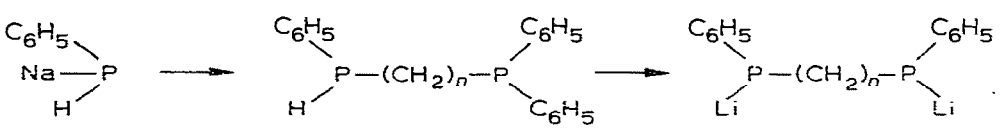
Summary

The X-ray structure of 1,2-diphenyl-1,2-diphospholane-1,2-disulphide has been determined (P—P 2.253 Å and P=S 1.944 and 1.943 Å). In this compound the two phosphorus atoms are linked by three methylene groups into a five-membered heterocyclic ring, which prevents free rotation about the P—P bond, and results in a non planar configuration for the S—P—P—S part of the molecule. The P—P bond length is very similar to that in the diphosphine disulphides which all have a *trans*-planar arrangement of phosphorus and sulphur atoms, and the phosphorus sulphides which are based on a tetrahedron of phosphorus atoms. This indicates that the bond length is unaffected by rotation, and hence does not involve any π interaction between phosphorus atoms. This is confirmed by the similarity of the P=S bond lengths with those in a number of compounds, showing that the π electron on phosphorus is localised in the P—S bond.

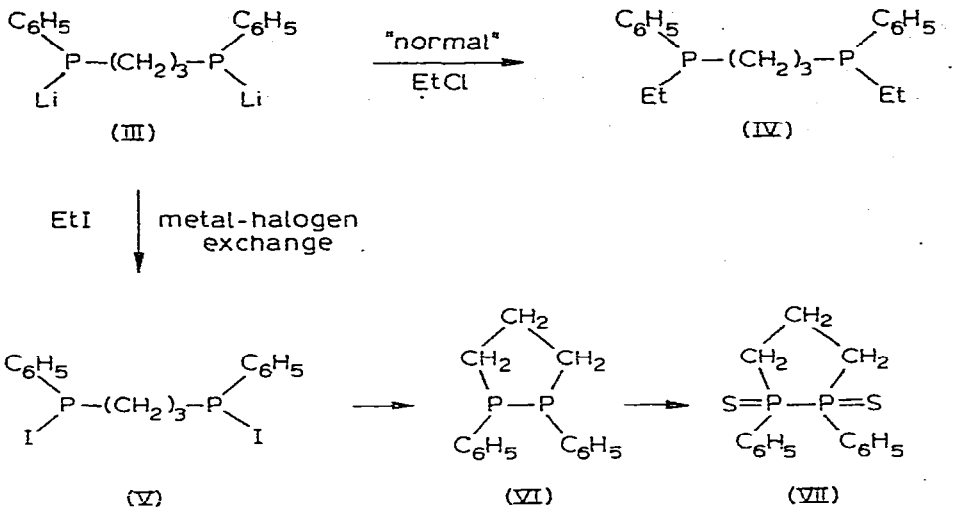
Introduction

It has been reported [1,2] that monophenylmonosodiophosphine compound (I) reacts with tri-, tetra-, penta- or hexa-methylene dibromide forming a series of disecondary phosphines (II) where n = 3—6 which with phenyllithium give the corresponding dilithio compounds III.



The dilithio compound III with n = 3 reacts normally with ethyl chloride to give the diethyl compound IV, but with ethyl bromide or iodide an unusual

metal—halogen exchange reaction occurs giving compound V which cyclises to form 1,2-diphenyl-1,2-diphospholane containing trivalent phosphorus VI, which can react with sulphur to form 1,2-diphenyl-1,2-diphospholane-1,2-disulphide (VII).



(III) (IV) (V) (VI) (VII)

The latter compound is crystalline, melting at 178—180°C, and its structure is of particular interest firstly because it may explain why compound V cyclises and why this is limited to a carbon chain length of $n = 3$, and secondly because it should throw some light on the nature of the P—P bond. The structures of a number of diphosphine disulphides are discussed [3], and in all of these the S—P—P—S part of the molecule is *trans* and planar. The inclusion of the two P atoms in a diphospholane ring in compound VII makes a *trans*-planar structure impossible, and if any π bonding occurs between the P atoms in the other diphosphine disulphides it cannot occur in compound VII.

Experimental

A three-dimensional X-ray determination of the crystal structure of compound VII has been performed, based on 1733 reflections. Compound VI was prepared by Professor K. Issleib, and this was converted into compound VII by Professor R. Schmutzler. Crystals are orthorhombic, and the space group is

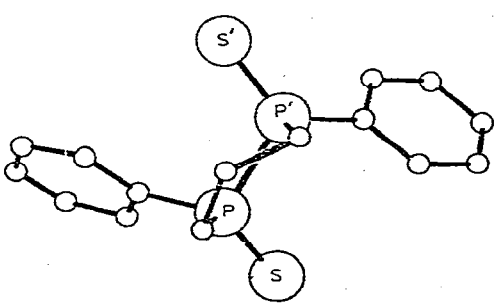


Fig. 1. A view of the 1,2-diphenyl-1,2-diphospholane-1,2-disulphide molecule.

$P2_12_12_1$. Molecules occupy general positions and there is no molecular symmetry. The shape of the molecule is shown in Fig. 1. The P—P bond is 2.25 Å and both P—S bonds are 1.94 Å. The dihedral angle between the planes through S—P—P′ and P—P′—S′ is 141°. The P atoms have an approximately tetrahedral configuration which is distorted by the large size of S and the shortness of the P=S bond, and also by the inclusion of the two P atoms in a 5-membered heterocyclic ring. The latter reduces the P′—P—C angle to 92° and the P—P′—C angle to 94°.

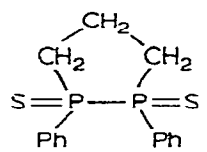
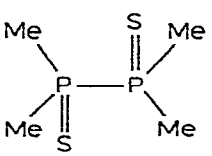
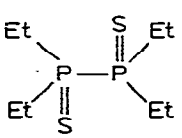
Conclusion

Relatively few compounds are known which contain P—P bonds. The P—P bond length of 2.25 Å in the present compound VII is compared with other

(continued on p. 198)

TABLE 1

SOME P—P BOND LENGTHS

Molecule	Bond length (Å)	Reference
P_4S_7	2.35 ± 0.01	4
	2.253 ± 0.002	present work
	2.245 ± 0.06 2.161 ± 0.04	5
P_4S_3	(average) 2.235 ± 0.005	6
$P_4S_3I_2$	2.23 & 2.25 ± 0.04 2.12 & 2.25	7
$(PCF_3)_5$	2.223	8
	2.22 ± 0.006	9
$(PCF_3)_4$	2.213 ± 0.005	10
P_2I_4	2.212 ± 0.06	11

(Table continued)

TABLE 1 (continued)

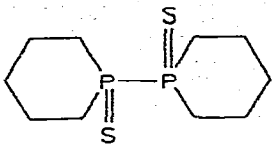
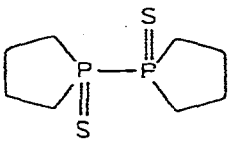
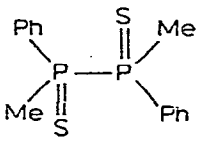
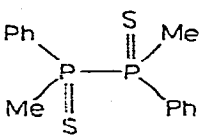
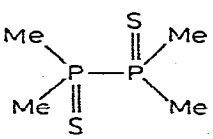
Molecule	Bond length (Å)	Reference
	2.21 ± 0.004	12
P_4	2.21 ± 0.2	13
	2.21 ± 0.004	14
	2.21	15
P_3S_5	2.10) 2.21) ± 0.025	16
$(PO_2)_6^{6-}$	(average) 2.20	17
black phosphorus	2.18	18
P_2	1.893	19

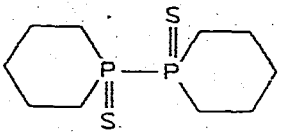
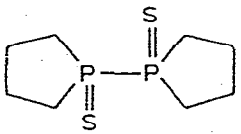
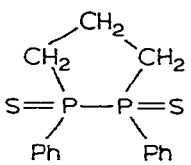
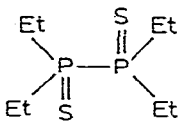
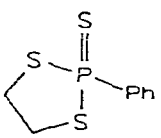
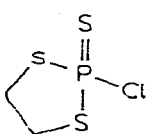
TABLE 2

SOME P—S BOND LENGTHS

Molecule	Bond length (Å)	Reference
	1.98	15
	1.95 ± 0.003 1.97 ± 0.004	4

(Table continued)

TABLE 2 (contined)

Molecule	Bond length (Å)	Reference
	1.95 ± 0.004	12
	1.95 ± 0.002	14
	1.944 ± 0.002 1.943 ± 0.002	present work
	1.94 ± 0.005	9
	(terminal S) 1.936 ± 0.002 (heterocyclic S) 2.087 ± 0.002	20
	(terminal S) 1.910 ± 0.005 (heterocyclic S) 2.051 ± 0.004 2.051 ± 0.005	21
P S Br_3	1.89 ± 0.06	
P S Br_2 F	1.89 ± 0.05	22
P S Br F_2	1.87 ± 0.05	
P S F_3	1.87 1.86 } ± 0.03	23, 24
Et_3P S	1.864 ± 0.03	25
P S Cl_3	1.85 ± 0.02	23
$P_4O_6S_4$	1.85 ± 0.02	26

distances in Table 1. Apart from P_4S_7 [4], which has an unusually long bond, and P_2 [19] which has a very short bond, the values all lie between 2.18—2.25 Å. The short lived P_2 species is only formed at high temperatures, and has a structure similar to N≡N. It is not obvious why P_4S_7 contains such a long bond, since the strain is no greater than in the other phosphorus sulphides [4,6,7,16], halides [11], P_4 [13] or black phosphorus [18].

Since there is little difference between the P—P bond lengths in the diphosphine disulphides [5,9,12,14,15] where the dihedral angle is 180°, the present compound where the dihedral angle is 141° and also in the tetrahedral P_4 molecule, it seems probable that no multiple bonding occurs in any of these compounds except P_2. This is confirmed by the similarity in P=S bond lengths with other compounds listed in Table 2. This lack of double bond character in P—P bonds is in contrast to that observed in S—S bonds [3].

The reason for the cyclization by compound V where $n = 3$ is undoubtedly due to the stability of a 5-membered heterocycle, but there is some strain in this ring, and it is surprising that similar behaviour is not observed with the compound where $n = 4$.

Bibliographie

1 K. Issleib and F. Krech, Chem. Ber., 94 (1961) 2656.
2 K. Issleib, Z. Chem., 2 (1962) 163.
3 J.D. Lee, J. Inorg. Nucl. Chem., 32 (1970) 3209.
4 A. Vos and E.H. Wiebenga, Acta Cryst., 8 (1955) 217; ibid., 9 (1956) 92.
5 J.D. Lee and G.W. Goodrace, Acta Cryst., B, 27 (1971) 302.
6 Y.C. Leung, J. Waser, S. van Houten, A. Vos, G.A. Weigers and E.H. Wiebenga, Acta Cryst., 10 (1957) 574.
7 D.A. Wright and B.R. Penfold, Acta Cryst., 12 (1959) 455.
8 C.J. Spencer and W.N. Lipscomb, Acta Cryst., 14 (1961) 250; ibid., 15 (1962) 509.
9 S.N. Dutta and M.M. Woolfson, Acta Cryst., 14 (1961) 178.
10 G.J. Palenik and J. Donohue, Acta Cryst., 15 (1962) 564.
11 Y.C. Leung and J. Waser, J. Phys. Chem., 60 (1956) 539.
12 J.D. Lee and G.W. Goodacre, Acta Cryst., B, 26 (1970) 507.
13 L.R. Maxwell, S.B. Hendricks and V.M. Mosley, J. Chem. Phys., 3 (1935) 699.
14 J.D. Lee and G.W. Goodacre, Acta Cryst., B, 25 (1969) 2127.
15 P.J. Wheatley, J. Chem. Soc., (1960) 523.
16 S. van Houten and E.H. Wiebenga, Acta Cryst., 10 (1957) 156.
17 J. Weiss, Z. Anorg. Allg. Chem. 306 (1960) 30.
18 R. Hultgren, N.S. Gingrich and B.E. Warren, J. Chem. Phys., 3 (1935) 351.
19 A.E. Douglas and K.S. Rao, Can. J. Phys., 36 (1958) 565.
20 J.D. Lee and G.W. Goodacre, Acta Cryst., B, 27 (1971) 1055.
21 J.D. Lee and G.W. Goodacre, Acta Cryst., B, 27 (1971) 1841.
22 J.H. Secrist and L.O. Brockway, J. Amer. Chem. Soc., 66 (1944) 1941.
23 Q. Williams, J. Sheridan and W. Gordy, J. Chem. Phys., 20 (1952) 164.
24 N.J. Hawkins, V.W. Cohen and W.S. Kosi, J. Chem. Phys., 20 (1952) 528.
25 M. van Meerssche and A. Léonard, Acta Cryst., 12 (1959) 1053.
26 A.J. Stosick, J. Amer. Chem. Soc., 61 (1939) 1130.