Crystal and Molecular Structure of 2-Phenyl-1-phosphanaphthalene (2-Phenylphosphinoline)

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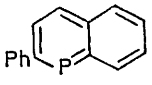
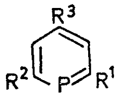
Crystals of the title compound are orthorhombic, space group *Pbca* with a = 8·027, b = 45·325, c = 6·277 Å. The structure was solved from diffractometer data for 615 planes by Patterson methods, and was refined by least-squares to a final R of 0·090. The phosphanaphthalene group is nearly planar and shows bond-length variations characteristic of a naphthalene system. Two different P–C bond lengths are found [1·707(14) and 1·802(14) Å] and C–P–C is 101·0(7)°. The plane of the phenyl group is inclined at 29° to that of the phosphanaphthalene.

THE first synthesis of a phosphorus analogue of pyridine, 2,4,6-triphenylphosphorin (IIa), was reported a few years ago.[1] Since then the parent compound, phosphorin (IIc), also called phosphobenzene, has been prepared by an elegant method.[2] More recently a phosphorus analogue of quinoline (I) has been made.[3] The structures of (IIb) [4] and (IIc) [5] show that the phosphorin ring is planar with effective C_{2v} ($mm2$) symmetry and has four equal C–C bond lengths. This confirms the spectroscopic evidence [1,6-8] that the rings have delocalised π-electron systems which have also been studied theoretically.[7,9] We now report the structure of the quinoline analogue, 2-phenyl-1-phosphanaphthalene (I) (2-phenylphosphinoline).



(I)



(II)

(II) a; $R^1 = R^2 = R^3 = Ph$
b; $R^1 = R^2 = Me, R^3 = Ph$
c; $R^1 = R^2 = R^3 = H$

EXPERIMENTAL

Crystal Data.—$C_{15}H_{11}P$, M = 222·2, Orthorhombic, a = 8·027(6), b = 45·325(25), c = 6·277(5) Å, U = 2283·7 Å^3, D_c = 1293 kg m^{-3}, Z = 8. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 163 m^{-1}. Space group, from systematic absences, *Pbca* (No 61, D_{2h}^{15}).

Unit-cell dimensions were obtained from zero-layer precession photographs by a least-squares procedure and the standard deviations quoted are estimates, to allow for systematic errors. Intensities were collected round a on a linear diffractometer equipped with a graphite monochromator; the 615 strongest measured reflections with $\theta \leqslant 20°$ were used in the analysis. No reflections with $\theta > 20°$ were observed.

Structure Determination and Refinement.—The positions of the phosphorus and carbon atoms were found from a sharpened three-dimensional Patterson function and the structure was refined by a block-diagonal (3 × 3 and 1 × 1 or 6 × 6) least-squares method, first with isotropic and then with anisotropic temperature factors until R was 0·099. A difference map was then calculated which showed the positions of the hydrogen atoms and the co-ordinates of the structure were further refined till R converged at 0·090. Hydrogen atoms were given fixed isotropic temperature factors 0·01 units of U higher than the carbon atoms to which they are bonded. Planes with $3|F_c| \leqslant |F_o|$ were omitted from the refinement, 4 of the 615 planes being subject to this restriction in the last cycle.

RESULTS AND DISCUSSION

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21112 (5 pp., 1 microfiche).† Final parameters are in Tables 1

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] G. Märkl, *Angew. Chem.*, 1966, **78**, 907.

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and 2, and bond lengths and angles in Table 3. The Figure shows the molecule projected onto the least-squares plane of the phosphanaphthalene group, together with the labelling of the atoms.

TABLE 1

Final co-ordinates (Å), with standard deviations in parentheses

	X	Y	Z
P	1·4589(44)	5·5172(36)	1·2195(40)
C(1)	0·651(14)	6·157(14)	−0·141(15)
C(2)	0·366(14)	5·442(12)	−1·316(14)
C(3)	0·715(15)	4·124(13)	−1·556(17)
C(4)	1·416(15)	3·353(12)	−0·578(14)
C(5)	1·803(15)	2·010(14)	−0·931(16)
C(6)	2·491(16)	1·254(13)	−0·039(17)
C(7)	2·910(14)	1·749(14)	1·214(19)
C(8)	2·571(16)	3·043(12)	1·558(14)
C(9)	1·825(12)	3·848(12)	0·648(14)
C(10)	0·204(17)	7·597(13)	−0·059(16)
C(11)	0·896(16)	8·538(15)	0·701(16)
C(12)	0·429(16)	9·878(14)	0·751(18)
C(13)	−0·720(16)	10·253(13)	0·109(16)
C(14)	−1·382(16)	9·358(15)	−0·669(17)
C(15)	−0·917(15)	7·985(13)	−0·753(16)
H(2)	−0·24(14)	5·90(12)	−1·88(15)
H(3)	0·56(14)	3·62(14)	−2·29(16)
H(5)	1·39(15)	1·82(13)	−1·98(16)
H(6)	2·96(16)	0·61(14)	−0·06(16)
H(7)	3·35(15)	1·36(13)	1·91(17)
H(8)	2·82(15)	3·41(13)	2·50(16)
H(11)	1·62(16)	8·38(14)	1·33(17)
H(12)	0·76(15)	10·41(12)	1·35(18)
H(13)	−1·19(15)	11·04(15)	0·07(16)
H(14)	−2·21(15)	9·70(13)	−1·12(16)
H(15)	−1·54(15)	7·42(12)	−1·60(15)

TABLE 2

Anisotropic * temperature factors ($\times 10^3$ Å^2) for the heavy atoms and isotropic † temperature factors ($\times 10^3$ Å^2) for the hydrogen atoms

Atom	U_{11}	U_{22}	U_{23}	$2U_{12}$	$2U_{23}$	$2U_{13}$
P	51(2)	34(2)	38(2)	9(5)	1(4)	−16(6)
C(1)	30(9)	28(7)	38(11)	2(14)	−7(15)	19(18)
C(2)	47(10)	26(7)	41(10)	17(16)	−7(16)	23(18)
C(3)	45(10)	48(8)	42(11)	14(16)	14(18)	19(17)
C(4)	41(10)	24(7)	43(9)	10(16)	−7(15)	0(21)
C(5)	45(11)	42(8)	63(12)	4(19)	−8(17)	−21(22)
C(6)	36(11)	38(9)	80(13)	3(15)	−21(20)	−6(20)
C(7)	23(10)	52(10)	88(14)	−27(17)	39(15)	0(19)
C(8)	44(10)	46(8)	39(10)	13(13)	26(13)	−22(16)
C(9)	20(9)	33(7)	38(9)	−19(17)	−16(16)	−8(19)
C(10)	64(12)	31(8)	44(10)	41(16)	29(15)	18(20)
C(11)	69(13)	40(8)	45(12)	−40(14)	−14(13)	−11(20)
C(12)	41(11)	41(8)	86(14)	2(16)	−34(16)	6(22)
C(13)	54(13)	45(9)	43(11)	0(20)	25(17)	−1(20)
C(14)	48(12)	67(10)	70(12)	17(20)	0(17)	−6(24)
C(15)	43(12)	39(9)	47(12)	28(15)	7(14)	29(19)

Atom	U_{iso}	Atom	U_{iso}
H(2)	48	H(11)	62
H(3)	56	H(12)	66
H(5)	61	H(13)	58
H(6)	62	H(14)	62
H(7)	65	H(15)	54
H(8)	53		

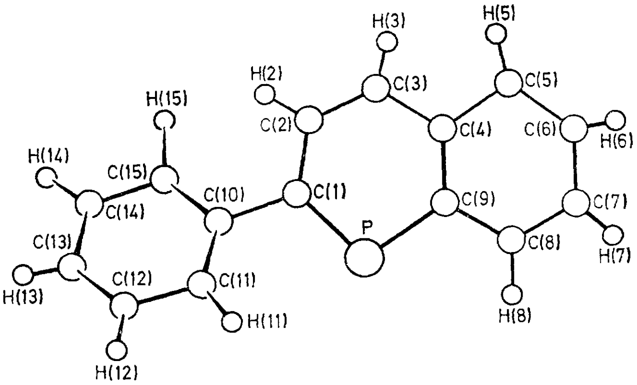
* In the form: exp $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$. † In the form: exp $-8\pi^2U_{iso}(\sin^2\theta)/\lambda^2$.

The phosphanaphthalene group is almost planar (Table 4) and the bond lengths in it show variations characteristic of those found in napthalene[10] and quinoline[11] groups. Thus the P$\overset{\cdots}{-}$C bond lengths are unequal [1·802(13) and 1·707(14) Å], and may be compared with the P–C length [1·743(5) Å] **in (IIb) and**

TABLE 3

Bond lengths (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances			
P–C(1)	1·707(14)	P–C(9)	1·802(13)
C(1)–C(2)	1·40(2)	C(4)–C(9)	1·38(2)
C(1)–C(10)	1·51(2)	C(5)–C(6)	1·36(2)
C(2)–C(3)	1·39(2)	C(6)–C(7)	1·41(2)
C(3)–C(4)	1·43(2)	C(7)–C(8)	1·38(2)
C(4)–C(5)	1·44(2)	C(8)–C(9)	1·43(2)
C(10)–C(11)	1·39(2)	C(13)–C(14)	1·36(2)
C(11)–C(12)	1·42(2)	C(14)–C(15)	1·45(2)
C(12)–C(13)	1·37(2)	C(15)–C(10)	1·38(2)
Mean C–H	0·98(15)		
(*b*) Angles			
C(1)–P–C(9)	101·0(7)		
P–C(1)–C(10)	117·0(10)	C(4)–C(5)–C(6)	119·6(14)
P–C(1)–C(2)	124·9(11)	C(5)–C(6)–C(7)	122·7(14)
C(2)–C(1)–C(10)	118·1(12)	C(6)–C(7)–C(8)	118·5(14)
C(1)–C(2)–C(3)	125·3(13)	C(7)–C(8)–C(9)	119·9(13)
C(2)–C(3)–C(4)	121·3(13)	C(8)–C(9)–C(4)	121·2(12)
C(3)–C(4)–C(5)	117·8(13)	C(8)–C(9)–P	115·3(10)
C(3)–C(4)–C(9)	124·0(13)	C(4)–C(9)–P	123·5(10)
C(5)–C(4)–C(9)	118·1(12)		
C(10)–C(11)–C(12)	119·5(14)	C(14)–C(15)–C(10)	120·0(14)
C(11)–C(12)–C(13)	121·2(15)	C(15)–C(10)–C(11)	119·3(14)
C(12)–C(13)–C(14)	119·9(15)	C(1)–C(10)–C(15)	118·9(13)
C(13)–C(14)–C(15)	120·0(14)	C(1)–C(10)–C(11)	121·8(14)
Mean C$\overset{\cdots}{-}$C–H	119(10)		



The molecule projected on the least-squares plane of the phosphanaphthalene ring, together with the labelling of the atoms

TABLE 4

Equations of some weighted (w = atomic number) least-squares planes in the molecule in the form: $lX + mY + nZ = p$, where X, Y, and Z are in Å. Deviations (Å) of constituent atoms from the planes are given square brackets

Plane (A): $0·86080X + 0·32170Y - 0·39438Z = 2·5644$

[P −0·015, C(1) 0·033, C(2) 0·021, C(3) −0·008, C(4) −0·038, C(5) 0·002, C(6) −0·001, C(7) 0·024, C(8) 0·133, C(9) −0·011]

Plane (B): $0·55856X + 0·24044Y - 0·79385Z = 1·9991$

[C(10) −0·011, C(11) −0·002, C(12) 0·019, C(13) −0·023, C(14) 0·010, C(15) 0·007]

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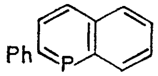
with the P–C (1·828 Å) and P=C (1·661 Å) lengths in PPh_3 (refs. 12 and 13) and $Ph_3P{:}CH_2$.[14]

The $\mathrm{C\overset{\cdots}{-}C}$ bond lengths also fall into two groups (Table 3): C(2)–C(3), C(5)–C(6), C(7)–C(8), and C(4)–C(9) are short (1·38 Å) while the rest are somewhat longer (1·42 Å), so that from a valence-bond point of view structure (III) should be more important than structure (I). However, since the standard deviations of Table **3** are rather large, it may be that this grouping of the bond lengths is fortuitous.



(III)

The bond angles (Table 3) in the phosphorin ring exhibit the pattern found in (IIb) [4] and the deviations from 120° are associated with the formation of a ring of approximate C_{2v} ($mm2$) symmetry in which the P–C bonds are considerably longer than the C–C bonds. In fact, such a ring with C—C 1·4, $\mathrm{P\overset{\cdots}{-}C}$ 1·743 Å and $\mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}C}$ angles of 120° would have $\mathrm{C\overset{\cdots}{-}P\overset{\cdots}{-}C}$ and $\mathrm{P\overset{\cdots}{-}C\overset{\cdots}{-}C}$ angles of 88·15 and 135·93°. On the other hand, sp^2 hybridised atoms form valence angles of 120° and the observed geometry is a compromise between the two. The resulting $\mathrm{C\overset{\cdots}{-}P\overset{\cdots}{-}C}$ angle of 101·0° is close to the value in (IIb) and suggests a reduced s contribution to the phosphorus hybrids. The geometry of the phosphanaphthalene group is consistent with the presence of a delocalised π-electron system.

The phenyl group is normal (mean $\mathrm{C\overset{\cdots}{-}C}$ 1·40 Å, mean $\mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}C}$ 120°) and its least-squares plane (Table 4) is inclined at 29·3° to that of the phosphanaphthalene group. This angle is somewhat smaller than that in (IIb) (39°) [4] and leads to some short contacts: H(2) · · · H(15) 2·0, C(2) · · · C(15) 2·90, H(11) · · · P 2·9, and C(11) · · · P 3·12 Å. The van der Waals contacts present no unusual features.

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