Crystal Structure of 10-Phenylphenoxaphosphine.

By **Frederick G. Mann,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Ian T. Millar, Department of Chemistry, The University, Keele, Staffordshire ST5 SBG
H. Marcus Powell and **David J. Watkin,*** Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD

The molecular structure of 10-phenylphenoxaphosphine has been determined by *X*-ray diffraction (heavy-atom) methods. The unit cell is monoclinic, $a = 8.47(1)$, $b = 9.48(1)$, $c = 19.83(1)$ Å, $\gamma = 118.85(2)°$, space group $P2_1/a, Z = 4$. Diffractometer data were refined to R 0.054 for 2 159 observed reflections. The phenoxaphosphine residue is folded about a line almost passing through the oxygen and phosphorus atoms, and the geometry at the phosphorus atom is nonplanar.

10-PHENYLPHENOXAPHOSPHINE (I) gives only four-co-ordinate complexes with certain Group VIII and other transition-metal halides and pseudohalides, in contrast to the related alkylphenoxaphosphine ligands which give both four- and five-co-ordinate complexes.[1] The crystal structure of the phenylphenoxaphosphine was determined in preference to that of the alkyl derivatives for these are liquids at room temperature and solidify to glasses on cooling.

If the title compound exists predominantly in the form

---

[1] D. W. Allen, I. T. Millar, and F. G. Mann, *J. Chem. Soc. (A)*, 1969, 1101.

(Ia) so that the bond angles at P and O have expected values (98 and 112°) then the molecule should take up a folded configuration giving two geometric isomers (Figure 1a and 1b). No such isomerism has been observed, possibly because one form is substantially more stable, or because the two forms interconvert very rapidly.[2] If the polar forms (Ib) and (Ic) make substantial contributions to the structure, then the molecule can be expected to be more nearly planar. The u.v. absorption spectrum, which for a molecule with three independent absorbing rings should have a main absorption at 255 nm, suggests that these forms are important, because not only are the general benzenoid bands absent, but the main absorption is moved up to 294 nm.

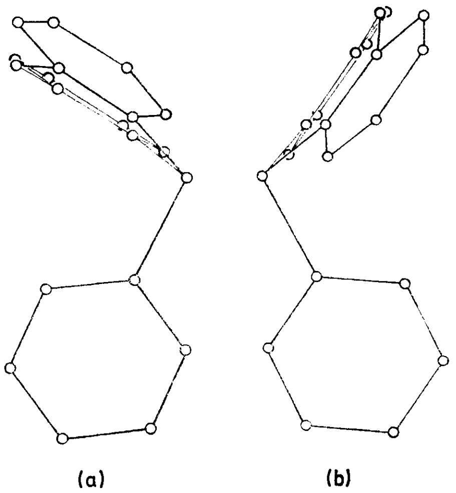


FIGURE 1 (a) Observed molecule projected onto the plane containing P(1), O(7), and C(14); (b) Postulated molecule obtained from that shown in (a) by reversing the fold of the phenoxaphosphine group

EXPERIMENTAL

The material crystallised from ethanol[3] as pale yellow plates (m.p. 94.5—95°). Space group and approximate cell dimensions were determined from Weissenberg photographs.

Crystal Data.—$C_{18}H_{13}O_1P_1$, $M = 276$. Monoclinic, $a = 8.47(1)$, $b = 9.48(1)$, $c = 19.83(1)$ Å, $\gamma = 118.85(2)°$, $U = 1\,395$ Å^3, $D_c = 1.31$ g cm^{-3}. Space group $P2_1/a$ (C^5_{2h}, No. 14) non-standard setting, equivalent positions $\pm(x, y, z; \frac{1}{2} + x, y, \frac{1}{2} - z)$; four-circle diffractometer data. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 17.1 cm^{-1}.

Balanced filters $\theta < 35°$, β filter $35° < \theta < 75°$.

Intensity data were measured on a Hilger and Watts Y 290 four-circle diffractometer from an approximately hexagonal plate-like crystal (0.3 mm side, 0.2 mm thick) by ω–2θ scan and a modified ordinate-analysis method.[4] The setting angles of 15 reflections were measured on both positive and negative sides of the incident beam and used in a least-squares calculation to determine accurate cell parameters. 5 893 Reflections were observed yielding 2 605 independent intensities of which 2 160 had $\hat{I} \geqslant 3\sigma(\hat{I})$. The merging R $(=\sum|\hat{I} - I_i|/\sum I_i)$ was 0.016. Lorentz, polarisation, and empirical absorption corrections[5] were applied. The position of the phosphorus atom was found from a sharpened Patterson function, the carbon and oxygen atoms from a heavy-atom phased F_o Fourier synthesis, and the hydrogen atoms from a difference synthesis. The structure was refined by full-matrix least-squares, the hydrogen atoms having individual isotropic temperature factors. The reflection weights were calculated from a Chebychev polymomial[6] $\{w = [591 \times T[0'](x) + 761 \times T[1'](x) + 195 \times T[2'](x)]^{-1};\ x = F_o/F_o(\text{max.})\}$. The final R factor was 0.054 with the reflection 0.004 excluded (F_o 632, F_c 789). Scattering factors were taken from ref. 7. Observed structure amplitudes and structure factors calculated from the atomic parameters in Tables 1 and 2 are listed in Supplementary Publication No. SUP 21695 (5pp.).* The atom numbering system is shown in Figure 2. Molecular parameters are listed in Tables 3 and 4.

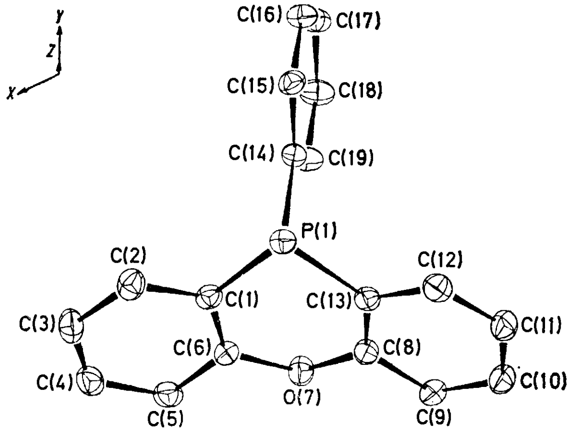
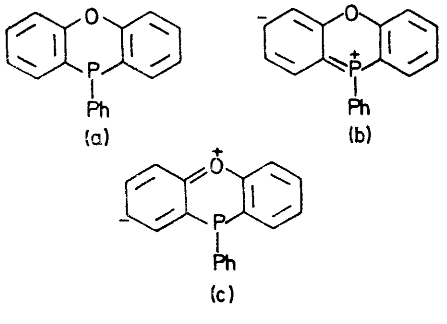


FIGURE 2 10-Phenylphenoxaphosphine projected on the plane containing C(1), C(13), C(14)



(I)

---

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[2] F. G. Mann, ' Heterocyclic Derivatives of P, As, Sb and Bi,' Wiley–Interscience, New York, 1970, p. 289.

[3] F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 1953, 3746.

[4] H. C. Watson, D. M. Shotten, J. M. Cox, and H. Muirhead, *Nature*, 1970, **225**, 806.

[5] A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Cryst.*, 1968, **A24**, 351.

[6] ' Crystals ' User Manual, J. R. Carruthers, Oxford University Computing Laboratory, 1975.

[7] ' International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

DISCUSSION

The phenoxaphosphine system is not planar, the central ring being in a boat-like conformation. The four central carbon atoms are coplanar (ΔZ 0.01 Å), with phosphorus and oxygen deviations of 0.22 and 0.18 Å on the same side of the plane. Each outer ring is planar, these two planes making a dihedral angle of 15°. The phosphorus atom deviates by 0.07 and 0.02 Å from these planes, and the oxygen atom by 0.01 and 0.03 Å. The inter-bond angle at oxygen is 122°, compared with the expected value of 112° if (Ia) were the sole canonical.

TABLE 1

Atomic co-ordinates (Å) and isotropic thermal parameters (Å^2)

Atom	x/a	y/b	z/c	U_{iso}
P(1)	0.159 3(1)	0.285 3(1)	0.054 35(4)	
C(1)	−0.039 0(5)	0.098 3(4)	0.077 4(2)	
C(2)	−0.201 3(6)	0.053 7(5)	0.044 5(2)	
C(3)	−0.358 7(6)	−0.082 9(5)	0.062 1(3)	
C(4)	−0.356 2(6)	−0.182 0(5)	0.112 3(3)	
C(5)	−0.196 9(5)	−0.143 0(4)	0.146 1(2)	
C(6)	−0.040 1(5)	−0.002 9(4)	0.128 0(2)	
O(7)	0.108 3(3)	0.022 7(3)	0.165 9(1)	
C(8)	0.282 5(4)	0.128 5(4)	0.146 1(2)	
C(9)	0.414 0(5)	0.105 4(5)	0.177 9(2)	
C(10)	0.592 1(6)	0.206 3(5)	0.162 4(2)	
C(11)	0.640 8(5)	0.328 9(6)	0.116 4(2)	
C(12)	0.507 0(5)	0.349 3(5)	0.084 6(2)	
C(13)	0.326 9(5)	0.251 8(4)	0.098 9(2)	
C(14)	0.136 3(4)	0.427 7(4)	0.111 5(2)	
C(15)	0.145 6(5)	0.565 8(4)	0.083 6(2)	
C(16)	0.123 6(6)	0.674 1(4)	0.123 8(2)	
C(17)	0.091 4(6)	0.647 1(5)	0.191 6(2)	
C(18)	0.084 3(7)	0.510 4(5)	0.220 2(2)	
C(19)	0.106 7(6)	0.402 3(5)	0.179 9(2)	
H(1)	0.182(5)	0.586(4)	0.029(2)	0.018(8)
H(2)	0.124(5)	0.775(4)	0.097(2)	0.022(9)
H(3)	0.084(7)	0.720(6)	0.218(2)	0.05(1)
H(4)	0.067(7)	0.487(6)	0.269(3)	0.05(1)
H(5)	0.103(5)	0.307(5)	0.197(2)	0.03(1)
H(6)	−0.192(7)	0.137(5)	0.002(3)	0.06(1)
H(7)	−0.469(8)	−0.112(7)	0.031(3)	0.08(2)
H(8)	−0.483(6)	−0.280(5)	0.124(2)	0.04(1)
H(9)	−0.191(6)	−0.205(5)	0.182(2)	0.04(1)
H(10)	0.381(5)	0.015(5)	0.210(2)	0.025(9)
H(11)	0.681(9)	0.190(7)	0.191(3)	0.07(2)
H(12)	0.783(5)	0.404(5)	0.100(2)	0.03(1)
H(13)	0.540(5)	0.439(5)	0.049(2)	0.03(1)

TABLE 2

Anisotropic temperature factors * (× 10^3; for P × 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	516(5)	442(5)	410(5)	33(3)	52(4)	234(4)
C(1)	48(2)	44(2)	47(2)	−9(1)	− 3(1)	23(1)
C(2)	63(2)	61(2)	56(2)	−13(2)	−12(2)	33(2)
C(3)	51(2)	63(2)	88(3)	−24(2)	−14(2)	22(2)
C(4)	50(2)	52(2)	95(3)	−16(2)	0(2)	14(2)
C(5)	53(2)	44(2)	82(3)	5(2)	6(2)	18(2)
C(6)	42(2)	44(2)	53(2)	−4(1)	2(1)	18(1)
O(7)	46(1)	58(1)	68(2)	20(1)	−2(1)	20(1)
C(8)	43(2)	38(2)	54(2)	−3(1)	−1(1)	17(1)
C(9)	62(2)	52(2)	62(2)	−8(2)	−10(2)	31(2)
C(10)	54(2)	71(3)	78(3)	−22(2)	−17(2)	34(2)
C(11)	43(2)	79(3)	76(3)	−16(2)	2(2)	24(2)
C(12)	53(2)	63(2)	57(2)	−2(2)	13(2)	20(2)
C(13)	50(2)	40(2)	47(2)	−3(1)	6(1)	19(1)
C(14)	44(2)	41(2)	49(2)	4(1)	−1(1)	22(1)
C(15)	52(2)	38(2)	58(2)	7(1)	−0(2)	17(1)
C(16)	70(3)	45(2)	78(3)	3(2)	−2(2)	31(2)
C(17)	72(3)	52(2)	67(2)	−14(2)	−15(2)	37(2)
C(18)	93(3)	61(2)	48(2)	−6(2)	−4(2)	46(2)
C(19)	85(3)	54(2)	50(2)	2(2)	−2(2)	43(2)

* In the form: $T = \exp[-2\pi^2 (U_{11}h^2a^{*2} \ldots 2 + U_{23}klb^*c^* \ldots)]$.

The geometry at phosphorus is pyramidal, as in Figure 1a, with the angle C(1)–P(1)–C(13) 98°, and the other two C–P–C angles 101° (*cf.* 103° in triphenyl phosphine [8]). The phosphorus atom is 0.85 Å from the plane through the three adjacent carbon atoms, so that the two geometries (Figure 1a and 1b) are quite distinct. Conversion of the form in Figure 1a into that in Figure 1b can be achieved either by moving the phenyl group to the opposite side of the C(1)–C(13)–P(1) plane, or by reversing the fold in the phenoxaphosphine group. The anisotropic temperature factors indicate that although the libration of the isolated phenyl group is independent of the rest of the molecule, the amplitudes of vibration are consistent with an ordered structure. The phenoxaphosphine group behaves as a rigid body, that is, there is little flexing about the line passing through the oxygen and phosphorus atoms.

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

P(1)–C(1)	1.817(3)	C(8)–C(13)	1.399(5)
P(1)–C(13)	1.826(3)	C(9)–C(10)	1.376(6)
P(1)–C(14)	1.844(3)	C(10)–C(11)	1.375(7)
C(1)–C(2)	1.390(5)	C(11)–C(12)	1.389(6)
C(1)–C(6)	1.384(5)	C(12)–C(13)	1.379(5)
C(2)–C(3)	1.382(6)	C(14)–C(15)	1.388(4)
C(3)–C(4)	1.377(7)	C(15)–C(16)	1.381(5)
C(4)–C(5)	1.387(6)	C(16)–C(17)	1.372(6)
C(5)–C(6)	1.398(5)	C(17)–C(18)	1.389(5)
C(6)–O(7)	1.382(4)	C(18)–C(19)	1.384(5)
O(7)–C(8)	1.382(4)	C(19)–C(14)	1.379(5)
C(8)–C(9)	1.386(5)		

The atom labelling system is shown in Figure 2.

TABLE 4

Inter-bond angles (°) with estimated standard deviations in parentheses

C(1)–P(1)–C(13)	98.0(4)	O(7)–C(8)–C(13)	124.0(6)
C(1)–P(1)–C(14)	100.7(4)	C(8)–C(9)–C(10)	118.9(8)
C(13)–P(1)–C(14)	101.3(4)	C(9)–C(10)–C(11)	121.1(8)
P(1)–C(1)–C(2)	119.4(6)	C(10)–C(11)–C(12)	119.1(8)
P(1)–C(1)–C(6)	123.5(6)	C(11)–C(12)–C(13)	121.7(7)
C(2)–C(1)–C(6)	117.7(7)	P(1)–C(13)–C(8)	123.4(5)
C(1)–C(2)–C(3)	122.2(8)	P(1)–C(13)–C(12)	119.0(6)
C(2)–C(3)–C(4)	119.7(9)	C(8)–C(13)–C(12)	117.5(7)
C(3)–C(4)–C(5)	120.0(8)	P(1)–C(14)–C(15)	117.9(6)
C(4)–C(5)–C(6)	119.1(7)	P(1)–C(14)–C(19)	123.4(6)
C(5)–C(6)–O(7)	113.2(7)	C(15)–C(14)–C(19)	118.7(7)
C(5)–C(6)–O(1)	122.0(6)	C(14)–C(15)–C(16)	120.3(7)
C(1)–C(6)–O(7)	124.8(5)	C(15)–C(16)–C(17)	120.9(8)
C(6)–C(7)–C(8)	122.3(5)	C(16)–C(17)–C(18)	119.3(7)
O(7)–C(8)–C(9)	114.4(7)	C(17)–C(18)–C(19)	119.7(7)
C(9)–C(8)–C(13)	121.6(6)	C(18)–C(19)–C(14)	121.1(7)

We thank Dr. K. Chui for providing the diffractometer intensity data.

[5/2034 *Received, 17th October,* 1975]

---

[8] J. J. Daly, *J. Chem. Soc.*, 1964, 3799.