# Crystal and Molecular Structure of 1-Benzylphosphole by *X*-Ray Analysis

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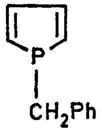
Molecular dimensions for the title compound have been established by single-crystal *X*-ray analysis from photographic data. Crystals are orthorhombic, space group *Pbca* with $a = 17{\cdot}62(2)$, $b = 14{\cdot}60(2)$, $c = 7{\cdot}67(1)$ Å, $Z = 8$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R$ 0·073 over 1351 independent observed reflexions. Comparison of the molecular dimensions with those of other heteroaromatic compounds is made. The phosphole ring has a non-planar geometry, and the mean P–C(phosphole) length of 1·783(5) Å is consistent with the interpretation that some electron delocalisation is present in the ring.

ACCURATE determinations of molecular dimensions form an important basis for discussions on relationships between structure and reactivity. For the five-membered heterocyclic group of compounds a number of microwave spectral studies have provided such structural information for furan,[1] pyrrole,[2] and thiophen,[3] and the dimensions of these lend support to the theory that electron delocalisation (aromaticity) occurs to varying degrees in these systems. The phosphorus analogue, phosphole, with its potential aromaticity is also of considerable interest, but no synthetic procedure to this compound has yet been devised although routes to a number of simple derivatives have been developed.[4] For two of these derivatives, 1-methyl-[5] and 1-phenyl-phosphole,[6] n.m.r. spectroscopic studies provide data consistent with the interpretation that some delocalisation is present in the phosphole ring. Furthermore, a series of n.m.r. studies of pyramidal inversion at phosphorus in some phosphole derivatives[7] have been interpreted as evidence for nonplanarity of the phosphole ring in the ground state, with increased electron delocalisation occurring in the planar transition-state. In view of these results it was clearly desirable that the accurate molecular geometry of a simple phosphole be established in order to compare the dimensions with those of the other heteroaromatics and to determine the detailed shape of the ring. The synthesis of 1-benzylphosphole (I), a low-melting solid, provided a suitable crystalline derivative which we have subjected to single crystal *X*-ray analysis. A preliminary account of this work has appeared.[8]



(I)

EXPERIMENTAL

Crystals of 1-benzylphosphole, m.p. 34—34·5 °C, were obtained from a melt; those used for the data collection were sealed in a thin-walled capillary.

*Crystal Data.*—$C_{11}H_{11}P$, $M = 174{\cdot}2$, Orthorhombic, $a = 17{\cdot}62(2)$, $b = 14{\cdot}60(2)$, $c = 7{\cdot}67(1)$ Å, $U = 1973$ Å$^3$, $Z = 8$, $D_c = 1{\cdot}172$, $F(000) = 736$. Space group *Pbca* ($D_{2h}^{15}$) from systematic absences. Cu-$K_\alpha$ radiation, $\lambda = 1{\cdot}542$ Å; $\mu$(Cu-$K_\alpha$) = 19·6 cm$^{-1}$.

*Crystallographic Measurements.*—Unit cell dimensions were evaluated from precession photographs taken with Mo-$K_\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Intensity data were recorded by means of equi-inclination multiple-film Weissenberg photography, and were visually estimated by comparison with a calibrated intensity strip. Corrections for spot-shape, Lorentz, polarisation, and rotation factors were applied, and 1351 independent non-zero structure amplitudes were derived from the intensity estimates.

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[8] P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, 1970, **92**, 5779.

*Structure Analysis.*—Initial co-ordinates for the phosphorus atom were determined from the three-dimensional Patterson map. Structure factors based on the phosphorus atom alone were evaluated and $R$ was 0·57. Approximate co-ordinates for the carbon atoms were obtained from a phosphorus-phased three-dimensional $F_o$ electron-density distribution. Inclusion of the eleven carbon atoms along with the phosphorus atom in a second structure-factor calculation resulted in $R$ 0·34.

The positional and isotropic thermal parameters of the carbon and phosphorus atoms were refined by five rounds of full-matrix least-squares calculations which reduced $R$ to 0·16. Then followed four least-squares cycles during which the carbon and phosphorus atoms were allowed to assume anisotropic thermal parameters, and these decreased $R$ to 0·108. A difference electron-density map showed peaks in positions close to those expected for the hydrogen atoms, and contributions from these were included in the next structure-factor calculation for which $R$ was 0·100. Refinement was continued with variation of the positional parameters of all atoms, anisotropic thermal parameters for the carbon and phosphorus atoms, and isotropic thermal parameters for the hydrogen atoms. The refinement converged in four cycles to a final $R$ of 0·073.

Theoretical atomic scattering factors taken from ref. 9 were used in all the structure-factor calculations. The weighting scheme employed in the least-squares refinement was $\sqrt{w} = 1$ when $|F_o| \leqslant 12{\cdot}0$ and $\sqrt{w} = 12{\cdot}0/|F_o|$ when $|F_o| > 12{\cdot}0$ with $\Sigma w\Delta^2$, $\Delta = |F_o| - |F_c|$, being minimised. The adequacy of the weighting scheme was confirmed by an analysis of $\langle w\Delta^2 \rangle$ values within ranges of $|F_o|$ and sin θ.

## RESULTS AND DISCUSSION

Final atomic co-ordinates and thermal parameters, together with their estimated standard deviations, are in Table 1; interatomic distances and angles are given in Table 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20737 (10 pp., 1 microfiche).* A view of the molecule and the atomic numbering scheme are shown in Figure 1 while the arrangement of molecules in the crystal is illustrated by Figure 2. The crystal contains discrete 1-benzylphosphole molecules separated by van der Waals distances, and the shortest P · · · P separation of 4·34 Å is between molecules related by the $c$-glide plane.

In order to define the shape of the phosphole ring, the least-squares planes through selected groups of atoms were evaluated, and the displacements of some atoms from these planes are recorded in Table 3. The root-mean-square deviation of the phosphole ring atoms from the plane calculated through atoms P(1)–C(5) is 0·049 Å these five atoms cannot be considered coplanar. The corresponding value in 1,2,5-triphenylphosphole[10] is reported to be 0·041 Å, and consequently the ring is similarly non-planar in that compound also. Omission of the phosphorus atom from the derivation of plane ($B$), root-mean-square deviation 0·0018 Å, indicates

TABLE 1

Fractional atomic co-ordinates and thermal parameters with estimated standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ | $B/\text{Å}^2$ |
|---|---|---|---|---|
| P | 0·35280(7) | 0·68055(7) | 0·07263(15) | * |
| C(2) | 0·4467(3) | 0·6835(3) | 0·1595(6) | * |
| C(3) | 0·4945(3) | 0·6389(3) | 0·0524(6) | * |
| C(4) | 0·4576(3) | 0·5915(3) | −0·0884(5) | * |
| C(5) | 0·3816(3) | 0·6005(3) | −0·0895(5) | * |
| C(6) | 0·2949(2) | 0·6145(3) | 0·2314(5) | * |
| C(7) | 0·3271(2) | 0·5242(2) | 0·2903(5) | * |
| C(8) | 0·3071(2) | 0·4435(3) | 0·2065(6) | * |
| C(9) | 0·3365(3) | 0·3602(3) | 0·2683(7) | * |
| C(10) | 0·3857(3) | 0·3600(3) | 0·4106(7) | * |
| C(11) | 0·4049(3) | 0·4394(3) | 0·4902(6) | * |
| C(12) | 0·3769(2) | 0·5208(3) | 0·4299(5) | * |
| H(2) | 0·463(2) | 0·720(3) | 0·267(6) | 4·1(10) |
| H(3) | 0·547(3) | 0·633(3) | 0·067(6) | 3·8(10) |
| H(4) | 0·492(3) | 0·560(4) | −0·174(7) | 5·3(13) |
| H(5) | 0·344(3) | 0·574(4) | −0·180(7) | 5·7(13) |
| H(6α) | 0·251(3) | 0·610(3) | 0·165(6) | 4·7(10) |
| H(6β) | 0·289(3) | 0·660(3) | 0·333(6) | 4·5(11) |
| H(8) | 0·268(2) | 0·452(3) | 0·106(5) | 3·1(9) |
| H(9) | 0·317(4) | 0·312(4) | 0·188(10) | 9·6(20) |
| H(10) | 0·408(4) | 0·304(4) | 0·449(10) | 10·9(22) |
| H(11) | 0·435(2) | 0·444(3) | 0·603(6) | 4·8(11) |
| H(12) | 0·384(3) | 0·576(4) | 0·487(7) | 7·1(14) |

* For these atoms anisotropic thermal parameters in the form $B \sin^2 \theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$ were used with parameters:

| | $10^5b_{11}$ | $10^5b_{22}$ | $10^4b_{33}$ | $10^5b_{12}$ | $10^4b_{13}$ | $10^4b_{23}$ |
|---|---|---|---|---|---|---|
| P | 486(4) | 521(4) | 231(2) | 172(8) | 14(2) | 54(2) |
| C(2) | 516(16) | 450(16) | 237(8) | −136(29) | 26(6) | −23(6) |
| C(3) | 461(15) | 518(18) | 275(9) | −143(29) | 26(7) | 21(7) |
| C(4) | 582(17) | 543(18) | 196(7) | −100(31) | 50(6) | 13(6) |
| C(5) | 602(18) | 702(22) | 152(7) | −104(37) | −7(6) | 32(7) |
| C(6) | 377(13) | 642(20) | 223(8) | 140(30) | 16(6) | 16(7) |
| C(7) | 268(9) | 524(16) | 153(6) | −35(23) | 23(4) | 6(5) |
| C(8) | 416(4) | 642(21) | 244(8) | −145(31) | 12(6) | −38(7) |
| C(9) | 646(20) | 599(21) | 394(12) | −277(35) | 125(8) | −51(8) |
| C(10) | 545(17) | 740(23) | 379(11) | 402(36) | 107(8) | 127(8) |
| C(11) | 465(16) | 906(26) | 238(8) | 188(38) | 16(7) | 109(8) |
| C(12) | 404(13) | 664(21) | 173(7) | 25(30) | 8(7) | 17(7) |

TABLE 2

Interatomic distances (Å) and angles (deg.), with estimated standard deviations in parentheses

($a$) Bond lengths

| | | | |
|---|---|---|---|
| P–C(2) | 1·786(5) | C(7)–C(8) | 1·386(5) |
| P–C(5) | 1·780(4) | C(7)–C(12) | 1·385(5) |
| P–C(6) | 1·858(4) | C(8)–C(9) | 1·405(6) |
| C(2)–C(3) | 1·343(6) | C(9)–C(10) | 1·390(7) |
| C(3)–C(4) | 1·438(6) | C(10)–C(11) | 1·353(7) |
| C(4)–C(5) | 1·343(7) | C(11)–C(12) | 1·365(6) |
| C(6)–C(7) | 1·506(5) | Mean C–H | 0·96 |

($b$) Valency angles

| | | | |
|---|---|---|---|
| C(2)–P–C(5) | 90·7(2) | C(6)–C(7)–C(8) | 120·5(3) |
| C(2)–P–C(6) | 106·1(2) | C(6)–C(7)–C(12) | 120·2(3) |
| C(5)–P–C(6) | 105·9(2) | C(8)–C(7)–C(12) | 119·3(3) |
| P–C(2)–C(3) | 109·9(3) | C(7)–C(8)–C(9) | 119·0(4) |
| C(2)–C(3)–C(4) | 114·1(4) | C(8)–C(9)–C(10) | 119·7(4) |
| C(3)–C(4)–C(5) | 114·1(4) | C(9)–C(10)–C(11) | 120·5(4) |
| P–C(5)–C(4) | 110·1(3) | C(10)–C(11)–C(12) | 120·1(4) |
| P–C(6)–C(7) | 116·4(3) | C(7)–C(12)–C(11) | 121·4(4) |

($c$) Some non-bonded distances

| | | | |
|---|---|---|---|
| C(2) · · · C(7) | 3·29 | C(5) · · · C(7) | 3·26 |

($d$) Intermolecular separations <3·6 Å

| | | | |
|---|---|---|---|
| C(4) · · · C($4^{\text{I}}$) | 3·35 | C(3) · · · C($4^{\text{I}}$) | 3·48 |

The Roman numeral superscript I refers to transformation of the co-ordinates of Table 1 to $1 - x$, $1 - y$, $-z$.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[9] 'International Tables for $X$-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[10] W. P. Ozbirn, R. A. Jacobson, and J. C. Clardy, *Chem. Comm.*, 1971, 1062.

that atoms C(2)—(5) are coplanar and the phosphorus atom is significantly displaced by 0·208 Å from this plane. This result contrasts with the situation in pyrrole [2] where it has been found necessary to assume $C_{2v}$ molecular symmetry in order to explain the microwave spectrum. Also in contrast to the geometry at the pyrrole nitrogen atom, where the nitrogen proton is in the ring plane, the methylene carbon atom of 1-benzylphosphole is 1·357 Å from the C(2)—(5) plane and the displacement is to the opposite side of the plane from the phosphorus atom. Thus the phosphorus atom retains a pyramidal geometry in the phosphole ring.

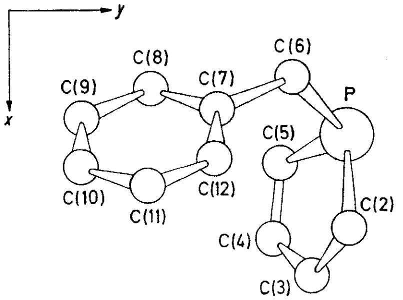


FIGURE 1 Conformation of 1-benzylphosphole

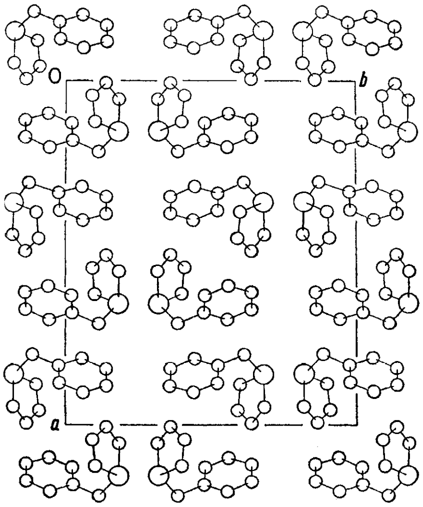


FIGURE 2 The crystal structure, viewed in projection along the *c* axis

TABLE 3

Displacements (Å) of atoms from selected planes

Plane (*A*): P, C(2)—(5)

P 0·059, C(2) −0·060, C(3) 0·032, C(4) 0·028, C(5) −0·058

Plane (*B*): C(2)—(5)

C(2) −0·001, C(3) 0·002, C(4) −0·002, C(5) 0·002, P 0·208, C(6) −1·357

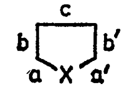
Plane (*C*): C(6)—(12)

C(6) −0·018, C(7) 0·007, C(8) 0·013, C(9) −0·013, C(10) −0·010, C(11) −0·008, C(12) 0·019, P 1·630, C(2) 2·504, C(5) 2·678

Molecular dimensions for pyrrole, thiophen, furan and cyclopentadiene [11] derived from microwave studies are compared in Table 4 together with those of the phosphole ring from the present analysis. Significant differences exist between b and c bond lengths in each of these molecules, with the phosphole ring distances being most similar to the corresponding cyclopentadiene values. For a completely delocalised diene system the carbon–carbon bond lengths would be expected to be equal and so, using the b — c differences as a measure of delocalisation, pyrrole is the most aromatic, followed by thiophen, furan, and phosphole. It should be recognised that the order of aromaticity is dependent upon the criteria employed to measure it, *e.g.* ring current, chemical reactivity, u.v. spectroscopy.[12] In common with the other heterocyclopentadienes listed, there is a highly significant (Δ/σ *ca.* 14) reduction in the 1-benzylphosphole carbon–heteroatom ring distance from the value of 1·84 Å calculated using the sum of the appropriate single-bond covalent radii,[13,14] the extent of the contraction (Δ −0·06 Å) being similar to the corresponding decreases in the other heteroaromatics, pyrrole (Δ −0·07 Å), thiophen (Δ −0·07 Å), and furan (Δ −0·04 Å). It is generally accepted that these latter decreases indicate different degrees of π-electron delocalisation in these molecules. Dewar and Rona [15] have shown that π-like delocalisation involving the lone electron-pair of an $sp^3$-hybridised nitrogen atom and carbon atom $2p$ orbitals can result in a resonance interaction of *ca.* 0·80 of that derived from an $sp^2$-hybridised (planar) nitrogen atom. A similar treatment is applicable to the phosphorus lone-pair of 1-benzylphosphole. The mean P–C(phosphole) bond length [1·786(5) Å] is entirely consistent with the presence of some delocalisation of the phosphorus lone-pair into the ring and concomitant increase in P–C bond-order from unity, for it is intermediate bebetween the calculated P–C($sp^2$) single-bond length

TABLE 4

Molecular dimensions for heterocyclopentadienes and cyclopentadiene



| | Bond lengths †/Å | | | Bond angles/deg. | | |
|---|---|---|---|---|---|---|
| X | *a* | *b* | *c* | *a-a′* | *a-b* | *b-c* |
| NH [a] | 1·370(1·44) | 1·382 | 1·417 | 109·8 | 107·7 | 107·4 |
| O [b] | 1·362(1·40) | 1·361 | 1·431 | 106·6 | 110·7 | 106·0 |
| S [c] | 1·714(1·78) | 1·370 | 1·423 | 92·2 | 111·5 | 112·4 |
| $PCH_2Ph$ [d] | 1·783(1·84) | 1·343 | 1·438 | 90·7 | 110·0 | 114·1 |
| $CH_2$ [e] | 1·509(1·51) | 1·342 | 1·469 | 102·8 | 109·3 | 109·4 |

† Values in parentheses are the sums of the single-bond covalent radii taken from refs. 12 and 13. [a] Ref. 2. [b] Ref. 1. [c] Ref. 3. [d] Present work. [e] Ref. 11.

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[12] See *e.g.*, G. Del Re in E. D. Bergmann and B. Pullman, eds., 'Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity,' Israel Academy of Sciences, Jerusalem, 1971, Proc. Jerusalem Symposia Quantum Chem. and Biochem. III, p. 76, and references therein.

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(1·84 Å) and the P–C length [1·743(5) Å] in the planar phosphorus analogue of pyridine, 2,6-dimethyl-4-phenylphosphorinan,[16] where a six $\pi$-electron delocalised system is assumed to be present and a P–C bond order of 1·5 has been suggested. On the other hand, the bond lengths at phosphorus in 1-benzylphosphole contrast with the corresponding distances reported recently for 1,2,5-triphenylphosphole[10] where the mean P–C distance is 1·822 Å with no significant shortening of the ring bonds. We interpret this result as being indicative of the fact that in this compound the coplanarity of the C(2) and C(5) phenyl substituents and the ring atoms C(2)—(5) provide an alternative path for delocalisation not involving the phosphorus atom. It would appear, therefore, that while this phosphole with its phenyl substituents represents a poorer model than 1-benzylphosphole for the study of electron delocalisation in the parent phosphole, the results do indicate that P–C distances in phosphole derivatives are very sensitive to the nature of the substituents at the phosphorus atom and in the phosphole ring. Moreover, these results suggest that conclusions relating to delocalisation in phosphole rings but derived from substituted phospholes should be accepted with reservation. Clearly further studies of other related simple phospholes are desirable in order to obtain some correlation between the nature of substituent, substitution pattern, and phosphole ring dimensions.

The mean C–C length (1·382 Å) and the mean C–C–C angle (120·0°) in the phenyl ring are normal.[17] The phenyl ring carbon atoms and the methylene carbon atom, C(6), are coplanar (Table 3), and the dihedral angle between the C(6)—(12) plane and the C(2)—(5) plane is 60°. The P–C($sp^3$) and C($sp^2$)–C($sp^2$) bond lengths [1·858(4) and 1·506(5) Å] agree well with their expected values.[17,18] In order to reduce non-bonded intramolecular interactions between the phenyl and phosphole rings the P–C(6)–C(7) angle is enlarged significantly to 116·4(3)° from the normal tetrahedral value (109·5°).

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[3/475 *Received, 2nd March,* 1973]

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