

The Crystal and Molecular Structure of 1,1-Dimethyl-2,4,6-triphenylphosphabenzene

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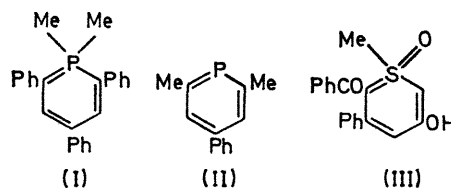
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Summary The structure of 1,1-dimethyl-2,4,6-triphenylphosphabenzene, $C_{25}H_{23}P$, has been determined by X-ray methods and the molecule contains an almost planar heterocyclic ring with a $P \cdots C$ bond length of 1.754 Å.

THE 1,1-dimethyl-2,4,6-triphenylphosphabenzene molecule (I) contains a novel heterocyclic ring wherein the phosphorus atom is formally quinevalent with ten electrons in its valence shell. We have determined the structure of (I) to see if the heterocyclic ring is planar with equal C-C bond lengths and equal P-C bond lengths as in (II)¹ or if the ring is nonplanar with unequal C-C bond lengths as in (III)².

The crystals of (I) ($C_{25}H_{23}P$) were prepared by a method described previously.³ They are orange-red in colour and are triclinic, space group $P\bar{1}$ with $a = 12.840(10)$, $b = 9.463(8)$, $c = 10.039(9)$ Å, $\alpha = 67.41(12)$, $\beta = 106.45(12)$, $\gamma = 68.57(12)^\circ$, $U = 1002.0$ Å³, $Z = 2$. Diffractometer measurements gave 1868 planes with significant intensity. The structure was determined by Patterson and Fourier methods and refined by least-squares with individual

anisotropic temperature factors. The current R factor is 0.094 and the hydrogen atoms have been ignored.



The Figure shows the molecule projected on to the weighted ($w =$ atomic number) least-squares plane of the heterocyclic ring; the molecule has roughly the symmetry 2 (C_2). The heterocyclic ring is almost planar but some of the deviations from the weighted least-squares plane are significant. These deviations are: P, -0.019 ; C(1), 0.055 ; C(2), -0.020 ; C(3), -0.027 ; C(4), 0.024 ; C(5), 0.016 Å; the standard deviations of the atomic co-ordinates are 0.002 Å for P and 0.007 for C(1)—C(5). The P-C bond lengths in the ring (average 1.754 Å) are slightly, but not significantly, longer than those found in (II) (average 1.743 Å) and they

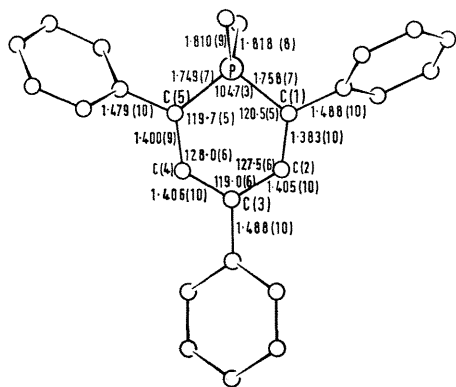


FIGURE. The 1,1-dimethyl-2,4,6-triphenylphosphabenzene molecule projected on to the weighted ($w = \text{atomic number}$) least-squares plane through the heterocyclic ring. The more important lengths and angles are shown with standard deviations in parentheses.

lie between the values observed⁴ for P-C (1.823 Å) and P=C (1.661 Å) in $\text{Ph}_3\text{P}=\text{CH}_2$. The C-C bond lengths in the heterocyclic ring do not differ significantly from one another and have an average value of 1.399 Å, close to the values observed in benzene⁵ (1.397 Å), pyridine⁶ (1.394 Å), and in (II)¹ (1.388 Å). The ring angle at the phosphorus atom (104.7°) is not very different from that found in (II) (102.4°) and the ring angles at C(2) and C(4) expand to 127.7° so that the ring is almost planar.

Thus the heterocyclic ring is quite similar to that found in (II) and shows only small deviations from the shape expected when a delocalised π -electron system is present. The bonding in the ring between phosphorus and carbon is formally analogous to that between phosphorus and nitrogen in the phosphonitrilics $(\text{PNX}_2)_3$ except that there are no lone-pair electrons on the carbon atoms which might contribute to the π -bonding.

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¹ J. C. J. Bart and J. J. Daly, *Angew. Chem.*, 1968, **80**, 843.

² C. Tamura, S. Sato, and Y. Kishida, *Tetrahedron Letters*, 1968, 2739.

³ G. Märkl, *Tetrahedron Letters*, 1968, 3611.

⁴ J. C. J. Bart, *J. Chem. Soc. (B)*, 1969, 356.

⁵ A. Langseth and B. P. Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350.

⁶ B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1958, **2**, 361.