Crystal and Molecular Structure of 1,2,5-Triphenylphosphole†

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Summary The molecular structure of 1,2,5-triphenylphosphole ($C_{22}H_{17}P$) has been determined by single crystal X-ray diffraction techniques in order to assess possible electron delocalization.

IN recent years conflicting interpretations have been offered for thermo-chemical and spectroscopic data concerning the character of the phosphole ring.[1] Consequently we have determined the molecular structure of 1,2,5-triphenylphosphole ($C_{22}H_{17}P$) to investigate possible electron delocalization.

Weissenberg photographs of the clear yellow needles and systematic absences of $0k0$ reflections showed that the space group is monoclinic, $P2_1$, with two molecules per unit cell; $a = 12{\cdot}129(2)$ Å $b = 5{\cdot}926(4)$, $c = 12{\cdot}678(2)$ Å, and $\beta = 115{\cdot}84(4)°$.

Data were collected on a fully automated Hilger–Watts four circle diffractometer using Ni-filtered Cu-K_α (1·5418 Å) radiation. The unique reflections with $\theta < 55°$ were corrected for background and Lorentz and polarisation effects. 1126 Reflections were judged observed.

A trial model was obtained by standard Patterson and electron density syntheses. Using full-matrix least-squares techniques, nonhydrogen atom positions were refined anisotropically and hydrogen atom positions isotropically until R reached a minimum of 0·057.

The Figure illustrates the molecular structure. All P–C bonds are the same length and there is no significant shortening of P–C bonds in the phosphole ring. The average P–C bond length of 1·822 Å agrees well with the average P–C (sp^2) single bond length reported for $Ph_3P{=}CH_2$ (1·823 Å)[2] and the P–C (phenyl) bond length in triphenylphosphine (1·828 Å).[3] The co-ordination about P suggests sp^3 hybridization. The C(2)–P(1)–C(18) and C(5)–P(1)–C(18) bond angles are essentially tetrahedral, 104·4 and 106·2°, respectively. The angle between the least-squares plane of the phosphole ring and the P(1)–C(18) bond is 116·1°. The C(2)–C(3), C(3)–C(4), and C(4)–C(5) bond distances are 1·348, 1·440, and 1·351 Å, respectively, typical butadiene distances. The heterocyclic ring appears to be nonplanar, deviations from its least-squares plane being P(1), 0·048; C(2), −0·053; C(3), 0·031; C(4), 0·019; and C(5), −0·045 Å. In addition the average bond lengths and bond angles in the phenyl substituents are 1·384(9) Å and 119·9(9)°, respectively, with no significant variation from independent ring averages. All the structural evidence indicates that the heterocyclic ring exhibits little if any electron delocalization.

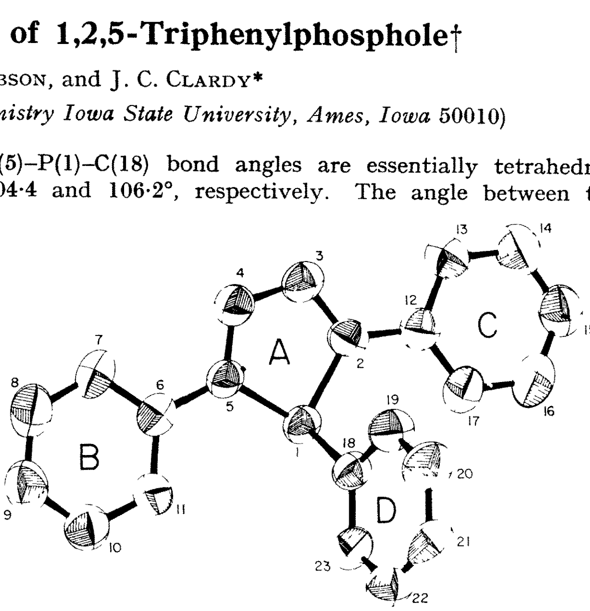

FIGURE. *Final* X-*ray model of* 1,2,5-*triphenylphosphole with* 50% *probability vibrational ellipsoids. Atom* 1 *is the phosphorus and atoms* 2—23 *are carbon.*

(*Received, September* 28*th*, 1970; *Com.* 1651.)

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† Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, 1969, **91**, 3308; W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 1442.

[2] J. C. J. Bart, *Angew. Chem.*, 1968, **80**, 697; *J. Chem. Soc.* (*B*), 1969, 350.

[3] J. J· Daly, *J. Chem. Soc.*, 1964, 3799.