

## Crystal Structure of Methanetetraylbis(triphenylphosphorane) (Hexaphenylcarbodiphosphorane)

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**Summary** An X-ray determination of the crystal structure of methanetetraylbis(triphenylphosphorane) (hexaphenylcarbodiphosphorane) shows that the angle at the central carbon atom is not  $180^\circ$ , but is  $145^\circ$  and  $131^\circ$  in the two independent molecules in the unit cell.

EVIDENCE already exists that the angle in a system  $X=C=C$  is not  $180^\circ$  provided that X is an atom with vacant  $d$  orbitals.<sup>1,2</sup> In the system  $P=N=P$  the angle adopts a value of about  $140^\circ$ .<sup>3-5</sup> We have investigated the structure of hexaphenylcarbodiphosphorane,  $Ph_3P=C=PPh_3$ , to discover whether the same unexpected feature also occurs in the  $P=C=P$  system.

*Crystal data:*  $C_{37}H_{30}P_2$ .  $M = 536.6$ , monoclinic,  $a = 15.362$  (9),  $b = 9.483$  (12),  $c = 20.054$  (8) Å,  $\beta = 95^\circ 6'$  (3'),  $U = 2909.9$  Å<sup>3</sup>,  $D_m = 1.205$ ,  $Z = 4$ ,  $D_c = 1.225$ ,  $F(000) = 1128$ . Space group  $C2/m$ ,  $Cm$ , or  $C2$  (from absences),  $C2$  (from statistics); Cu- $K_\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu = 15.4$  cm<sup>-1</sup>.

A sample of the compound was kindly supplied by Prof. Ramirez. Additional material was synthesized by a method based on those used by Ramirez<sup>6</sup> and Matthews.<sup>7</sup> Crystals were grown from diglyme and mounted in Lindemann glass capillaries. Intensities were collected from equi-inclination Weissenberg photographs of the  $h0l-h8l$  and  $0kl-13kl$  layers and estimated visually. 3301 independent reflexions were assigned non-zero intensity.

Direct methods failed to provide a solution to the crystal structure because of pseudo-symmetry, but a trial structure

was obtained from a three-dimensional Patterson synthesis which served to locate the phosphorus and some of the carbon atoms. The positions of the remaining carbon atoms were found from successive Fourier syntheses. Least-squares refinement with isotropic thermal factors for the phosphorus and central carbon atoms, and an overall isotropic thermal factor for the rest of the carbon atoms has currently reduced  $R$  to 11.4%.

There are two crystallographically independent molecules in the unit cell, each possessing a two-fold axis. The two molecules approximate to enantiomorphic forms but there are significant differences between the two, the most striking of which is in the value of the  $P=C=P$  angle, the very feature of primary concern to us. Values of some of the more interesting lengths and angles in the two molecules are given in the Table.

TABLE

Length (Å)/angle (°)	Molecule A	Molecule B
P=C	1.624	1.624
P-C (av.)	1.833	1.837
P=C=P	145.3	131.4
C=P-C (av.)	114.8	114.4

Refinement is continuing, and full structural details will be presented later.

We thank Dr. G. M. Sheldrick for computer programmes and the S.R.C. for financial support.

(Received, March 29th, 1971; Com. 424.)

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