Crystal Structure of Bis(triphenylphosphoranylidene)methane [Hexaphenylcarbodiphosphorane, $Ph_3P{:}C{:}PPh_3$] †

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The structure of the title compound has been determined. The crystals are monoclinic with a = 15·362, b = 9·483, c = 20·054 Å, β = 95° 6′, Z = 4, space group $C2$. 3292 Visually estimated X-ray reflections were refined to R 8·88%. There are two crystallographically independent molecules, each possessing a two-fold axis. The P=C=P angle is 143·8° in one of these molecules and 130·1° in the other. The results are compared with those obtained for related species, including the isoelectronic cation $Ph_3P{=}\overset{+}{N}{=}PPh_3$ and the cumulene ylides.

In the gas phase the C=C=C chain in allene is linear, and the geometry of the molecule is conventionally explained in terms of π,π-bonding. Vinylideneamines, containing the C=C=N group, often show anomalous values for the angle at the nitrogen atom, or for the length of the C=N bond, or for both. The C=C=N angle varies from 172 to 180°.[1-4] A current determination of the structure of a carbodi-imide, containing the N=C=N group, gives normal angles at the nitrogen atoms and an N=C=N angle of 170°.[5] In an iminoborane, containing the $B\underline{\leftarrow}N{=}C$ group, the angle at the nitrogen is 170°.[6] It thus appears that, if the three atoms in the chain are confined to the first short period, lattice forces can cause deviations from linearity of up to *ca.* 10°. However, this departure from linearity becomes more pronounced when a phosphorus atom is incorporated in the chain of doubly bonded atoms: $Ph_3P{:}C{:}C{:}S$ and $Ph_3P{:}C{:}C{:}O$ have P=C=C angles of 168·0 and 145·5° respectively.[7,8] The $P{=}\overset{+}{N}{=}P$ group has an angle of *ca.* 140° at the nitrogen atom.[9,10] Hexaphenylcarbodiphosphorane, containing the P=C=P group, presents a further opportunity of studying molecules containing adjacent double bonds. A preliminary account has already appeared.[11]

EXPERIMENTAL

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, β = 95° 6′(3′), U = 2909·9 Å^3, 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_α radiation, λ = 1·5418 Å, μ = 15·4 cm^{-1}.

The crystals grew in the form of yellow diamond-shaped plates and were very susceptible to moisture. They were sealed in Lindemann glass capillaries under nitrogen for exposure to X-rays. Intensities were collected from equi-inclination Weissenberg photographs of the h0—8l and 0—13kl layers and estimated visually. 3301 independent reflexions were assigned non-zero intensity and were corrected for Lorentz and polarization effects, but not for absorption. The intensities were placed on the same scale through common reflections. It was noticeable that the reflections with l odd were significantly weaker than those with l even.

Structure Determination and Refinement.—Direct methods, applied at various stages in the analysis, failed to provide a solution to the phase problem for the reasons detailed below. Attention was, therefore, turned to the Patterson map. Figure 1 shows the $u,0,w$ section contoured at arbitrary intervals. In order to satisfy the distribution of peaks, the two independent phosphorus atoms in the asymmetric unit must have approximately the same y co-ordinates. There is, however, an ambiguity, since the vector set satisfies two fundamentally different arrangements: (i) the two phosphorus atoms may belong to one molecule, in which case molecules are related in pairs by a two-fold axis and the molecules have no crystallographic symmetry requirements; and (ii) the phosphorus atoms may belong to different molecules in which case the unit cell contains two crystallographically independent molecules each with a two-fold axis. The X-ray analysis shows that (ii) is the correct solution.

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† Reprints not available.

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[7] J. J. Daly, *J. Chem. Soc.* (*A*), 1967, 1913.

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[10] L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7312, 7327.

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There is, moreover, a second feature which complicates the analysis. The large peak at $0,0,\frac{1}{2}$ indicates the presence of many atoms related by pseudo-translational symmetry of *ca.* $z/2$, suggesting the existence of pseudo-two-fold axes at $z = \frac{1}{4}$ and $\frac{3}{4}$ in addition to the two-fold axes required by the space group. This is also in agreement with the observed intensity distribution. The final structure revealed that *ca.* 60% of the scattering material had this relationship.

The two phosphorus atoms and four carbon atoms were located from the Patterson map and used to phase a Fourier synthesis. One phosphorus atom was fixed at $y = 0$ and the other set initially at $y = 0$. However, no satisfactory trial structure could be found, and attention was turned to the $h0l$ projection for which the ambiguity is reflected in the phases but not in the magnitudes of the structure factors. A satisfactory solution was found, and refinement of the $h0l$ data (346 planes) reduced R to 22·8% with a single isotropic thermal factor. Once the x and z co-ordinates were fixed, it proved possible to resolve the three-dimensional ambiguity from packing considerations. Full-matrix least-squares refinement (894 planes) of the trial structure reduced R to 10·5%. Refinement was continued with the full data set, with anisotropic thermal factors for the phosphorus atoms, and with individual isotropic thermal factors for the carbon atoms. At R 9·8% hydrogen atoms were introduced at calculated positions, new positions being obtained at the beginning of each refinement cycle. Nine low-order planes which appeared to be affected by extinction were eliminated during the refinement, and the final R was 8·88% for 3292 reflections. In the later stages of the refinement it was necessary for computational reasons to refine each molecule independently, but the final cycle was completed with both molecules refined together, the mean shift to σ ratio being 0·021 for all parameters.

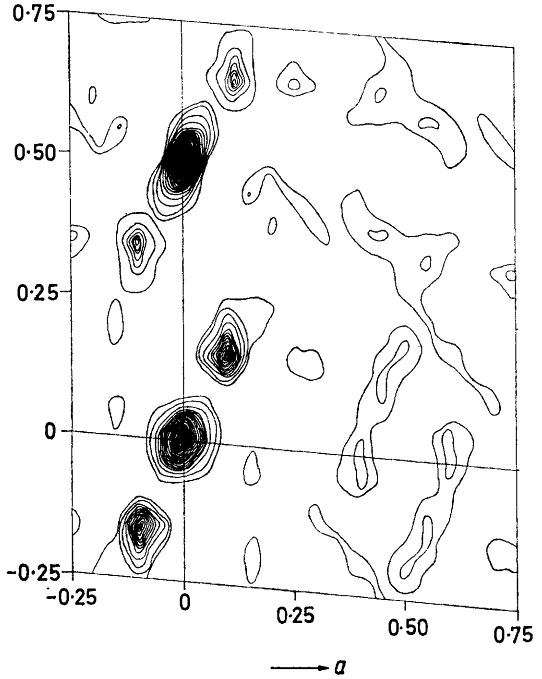

FIGURE 1 $u,0,w$ section of the Patterson map. Contours at arbitrary intervals

The weighting scheme[12] was $w = 1/(35{\cdot}3 + F_o + 0{\cdot}03782F_o^2)$ with the constants chosen from an analysis of the variance. Scattering factors[13] were used in which the imaginary part ($\Delta f''$) was set equal to zero. Friedel's law was assumed in the data reduction, and no attempt was made to determine the absolute configuration.

RESULTS

The final fractional co-ordinates, anisotropic and isotropic temperature factors, with their estimated standard deviations given as units in the last place, are listed in Tables 1 and 2. The thermal factors are, in general, very similar for the two independent molecules. The motion of the phosphorus atoms is close to isotropic. The thermal factors of the carbon atoms of the phenyl groups increase as their distance from the phosphorus atom increases, as expected. No correction for thermal motion has been applied to the bond lengths and angles.

An analysis of the agreement between observed and calculated structure factors is given in Table 3. The planes with l odd are significantly weaker than those with l even

TABLE 1

(*a*) Final fractional co-ordinates ($\times 10^4$) for the heavier atoms with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
P(1)	5428(1)	5000	0729(1)
P(2)	4617(1)	5346(2)	4296(1)
C(1)	5000	4466(11)	0000
C(2)	5000	4620(10)	5000
C(11)	6467(4)	5960(7)	0761(3)
C(12)	6459(5)	7337(9)	0527(4)
C(13)	7241(5)	8033(11)	0471(4)
C(14)	8027(6)	7368(11)	0636(4)
C(15)	8048(6)	6006(11)	0863(4)
C(16)	7256(4)	5281(9)	0909(3)
C(21)	5673(4)	3463(7)	1270(3)
C(22)	5926(5)	3571(9)	1946(4)
C(23)	6092(6)	2394(11)	2326(5)
C(24)	6021(5)	1047(11)	2041(4)
C(25)	5760(6)	0938(12)	1380(5)
C(26)	5596(5)	2128(9)	0989(4)
C(31)	4758(4)	6111(7)	1224(3)
C(32)	3842(4)	6039(8)	1087(3)
C(33)	3297(5)	6837(9)	1456(4)
C(34)	3647(5)	7703(9)	1958(4)
C(35)	4543(5)	7813(9)	2094(4)
C(36)	5091(4)	7016(8)	1725(3)
C(41)	5358(4)	6532(7)	3907(3)
C(42)	5424(5)	7940(9)	4103(4)
C(43)	6089(6)	8786(12)	3887(5)
C(44)	6682(6)	8245(12)	3472(5)
C(45)	6612(6)	6850(11)	3274(4)
C(46)	5939(4)	6009(8)	3480(3)
C(51)	4334(4)	3971(2)	3664(3)
C(52)	4004(4)	4335(9)	3010(3)
C(53)	3773(5)	3268(10)	2556(4)
C(54)	3877(6)	1887(10)	2730(4)
C(55)	4190(5)	1539(11)	3384(4)
C(56)	4439(5)	2572(9)	3845(4)
C(61)	3591(4)	6358(7)	4296(3)
C(62)	3048(4)	6024(8)	4797(3)
C(63)	2255(6)	6739(11)	4806(4)
C(64)	2006(7)	7725(12)	4332(5)
C(65)	2560(6)	8100(12)	3859(5)
C(66)	3354(5)	7378(10)	3837(4)

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[12] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, London, 1961, p. 32.

[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17; D. T. Cromer and J. T. Waber, *ibid.*, p. 104.

TABLE 1 (*Continued*)

(*b*) Final fractional co-ordinates ($\times 10^4$) for the hydrogen atoms. Each atom is assigned the same number as the carbon atom to which it is attached. The temperature factor for the hydrogen atoms was refined as a single parameter and has the value U 0·0560(6) Å^2

Atom	x/a	y/b	z/c
H(12)	5845	7859	0397
H(13)	7234	9095	0298
H(14)	8631	7915	0590
H(15)	8668	5495	0994
H(16)	7261	4208	1076
H(22)	5989	4590	2169
H(23)	6284	2501	2843
H(24)	6158	0109	2337
H(25)	5694	−0086	1164
H(26)	5402	2027	0470
H(32)	3567	5355	0697
H(33)	2599	6772	1351
H(34)	3222	8310	2244
H(35)	4812	8506	2485
H(36)	5785	7091	1829
H(42)	4964	8364	4426
H(43)	6144	9867	4042
H(44)	7198	8906	3306
H(45)	7073	6428	2954
H(46)	5879	4935	3319
H(52)	3927	5427	2863
H(53)	3518	3532	2058
H(54)	3701	1078	2367
H(55)	4258	0460	3528
H(56)	4700	2295	4346
H(62)	3238	5225	5167
H(63)	1830	6495	5182
H(64)	1389	8245	4340
H(65)	2372	8911	3500
H(66)	3782	7630	3461

TABLE 2

(*a*) Anisotropic vibrational amplitudes (10^4 Å^2) for the phosphorus atoms in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hl^*c^*U_{13})]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
P(1)	271(6)	243(8)	243(6)	1(5)	15(5)	5(5)
P(2)	262(6)	252(8)	243(6)	−1(5)	−7(5)	25(5)

(*b*) Isotropic vibrational amplitudes (10^4 Å^2) for the carbon atoms

Atom	U	Atom	U	Atom	U
C(1)	354(18)	C(26)	495(17)	C(51)	307(12)
C(2)	313(16)	C(31)	317(12)	C(52)	437(15)
C(11)	319(12)	C(32)	389(13)	C(53)	508(17)
C(12)	473(16)	C(33)	496(17)	C(54)	552(20)
C(13)	592(20)	C(34)	487(17)	C(55)	575(20)
C(14)	573(19)	C(35)	455(16)	C(56)	435(15)
C(15)	592(20)	C(36)	380(13)	C(61)	341(12)
C(16)	444(15)	C(41)	349(13)	C(62)	429(14)
C(21)	316(12)	C(42)	492(17)	C(63)	587(20)
C(22)	495(17)	C(43)	658(23)	C(64)	673(23)
C(23)	609(21)	C(44)	646(23)	C(65)	686(24)
C(24)	567(19)	C(45)	584(20)	C(66)	514(17)
C(25)	637(22)	C(46)	416(14)		

$\left[\sum_{1663} F(l\ \text{even})/\sum_{1629} F(l\ \text{odd}) = 1{\cdot}47\right]$, consistent with the pseudo-symmetry previously discussed. The group of planes with l even contains the strongest planes and therefore, reasonably, gives the lower R. A Table of observed and calculated structure factors is published in Supplementary Publication No. SUP 20290 (31 pp., 1 microfiche).†

The labelling of atoms and phenyl groups is shown in Figure 2; atoms of the primed phenyl groups are referred to in the text as 2′,3′, . . ., and are related to 2,3, . . ., by a two-fold axis. Bond lengths and angles are listed in Table 4. The mean C–C length (1·385 Å) is slightly less than the standard value (1·394 Å).[14] The co-ordination round each phosphorus atom is approximately tetrahedral. The mean C–P–C angle (103·8°) is less than the average C=P–C angle (114·7°), a feature in common with other compounds containing the $Ph_3P{=}C$ group.[7,8,15–20]

TABLE 3

(*a*) R as a function of the magnitude of F_o and of sin θ

$10F_o/F_o$ (max.) *	No.	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	R
0·00—0·37	281	1383	1223	27·63
0·37—0·50	269	2111	1844	19·77
0·50—0·61	263	2612	2341	17·68
0·61—0·72	270	3219	2981	13·56
0·72—0·83	263	3674	3464	11·64
0·83—0·95	262	4190	4120	9·85
0·95—1·08	279	5085	4958	9·94
1·08—1·25	262	5467	5362	8·58
1·25—1·43	243	5852	5875	8·74
1·43—1·67	228	6303	6361	7·19
1·67—2·05	235	7831	7922	7·33
2·05—2·80	216	9164	9221	6·76
2·80—10·0	221	15,850	15,776	4·99
10 sin θ				
0·0—4·0	229	11,733	11,361	6·71
4·0—5·0	216	7540	7435	6·61
5·0—6·0	327	9920	9899	6·87
6·0—6·7	300	8209	8276	7·86
6·7—7·3	307	6426	6446	10·11
7·3—7·9	358	6386	6394	10·38
7·9—8·4	337	5584	5530	10·72
8·4—8·9	369	5860	5630	10·03
8·9—9·4	405	5788	5364	12·16
9·4—10·0	444	5293	5113	12·22
All	3292	72,745	71,453	8·88

* F_o (max.) 179·97.

(*b*) R as a function of parity of indices and special sub-groups

Group	No.	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	R
$h + k + l = 2n$	1663	43,242	42,786	8·16
$h + k + l = 2n + 1$	1629	29,502	28,667	9·94
$h + k = 2n$	3292	72,745	71,453	8·88
$h + k = 2n + 1$	0	0	0	
$k + l = 2n$	1653	37,123	36,450	8·86
$k + l = 2n + 1$	1639	35,622	35,003	8·91
$h + l = 2n$	1653	37,123	36,450	8·86
$h + l = 2n + 1$	1639	35,622	35,003	8·91
$h = 2n$	1736	37,915	37,316	9·25
$h = 2n + 1$	1556	34,829	34,137	8·48
$k = 2n$	1736	37,915	37,316	9·25
$k = 2n + 1$	1556	34,829	34,137	8·48
$l = 2n$	1663	43,242	42,786	8·16
$l = 2n + 1$	1629	29,502	28,667	9·94
ggg	880	22,767	22,549	8·48
ggu	856	15,147	14,766	10·40
uug	783	20,474	20,236	7·80
uuu	773	14,354	13,900	9·46
0*kl*	131	3864	3652	9·15
*h*0*l*	342	8144	8039	10·34
*hk*0	98	3112	3043	7·55

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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[18] P. J. Wheatley, *J. Chem. Soc.*, 1965, 5785.

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[20] G. Chioccola and J. J. Daly, *J. Chem. Soc.* (*A*), 1968, 568.

The mean P–C(Ph) lengths in the two molecules (1·832 and 1·837 Å) are slightly greater than those found in *P*-phenyl ylides (mean 1·79—1·83 Å),[7,8,17-20] and also in molecules containing the $Ph_3P{:}\overset{+}{N}{:}PPh_3$ cation (mean 1·78—1·81 Å).[9,10] All these lengths are somewhat less than the value found in Me_3P.[21] The P=C lengths (1·629 and 1·633 Å) are the shortest reported for *P*-phenyl ylides (1·648—1·745 Å hitherto) and are less than the sum of the covalent radii of doubly bonded phosphorus and carbon atoms (1·665 Å).[22] A comparison of bond lengths in related compounds is given in Table 5.

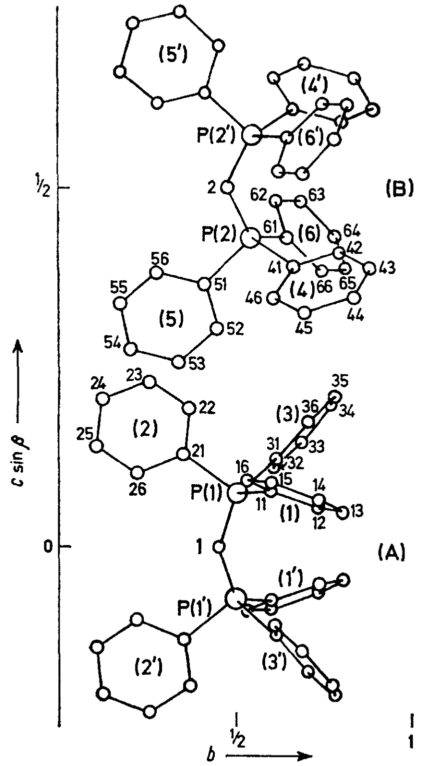

FIGURE 2 Projection down *a* of the asymmetric unit and the two-fold equivalent giving the labelling of the atoms and phenyl groups

The most interesting and striking feature of the molecular geometry is the P=C=P angle which is 143·8° in one molecule and 130·1° in the other.

Table 6 gives equations for some least-squares planes in terms of orthogonal axes and deviations of atoms from these planes. P(1) lies only 0·010 Å from the Ph(2) plane, but deviations of the phosphorus atoms are very significant for all other planes (0·046—0·298 Å). Least-squares planes were also calculated for the central P=C=P groups together with the Ph(2) and Ph(2′) or Ph(5) and Ph(5′) phenyl groups. The maximum deviations (0·145 and 0·046 Å, respectively) tend to be smaller than the deviations of the phosphorus atoms from the planes of the other phenyl groups. The orientation of Ph(2),(2′) and Ph(5),(5′) are the most favourable for overlap of the π systems of the phenyl groups and the central P=C=P group. There is, however, no diminution of the P–Ph(2),(5) distances which might be considered to confirm such conjugation.

TABLE 4

(*a*) Bond lengths (Å) with estimated standard deviations

Molecule (A)		Molecule (B)	
P(1)–C(1)	1·629(3)	P(2)–C(2)	1·633(4)
P(1)–C(11)	1·833(6)	P(2)–C(41)	1·823(6)
P(1)–C(21)	1·835(6)	P(2)–C(51)	1·844(6)
P(1)–C(31)	1·827(6)	P(2)–C(61)	1·845(6)
Mean P–C(Ph)	1·832	Mean P–C(Ph)	1·837
C(11)–C(12)	1·388(10)	C(41)–C(42)	1·393(10)
C(12)–C(13)	1·384(11)	C(42)–C(43)	1·397(12)
C(13)–C(14)	1·376(12)	C(43)–C(44)	1·385(12)
C(14)–C(15)	1·369(13)	C(44)–C(45)	1·383(14)
C(15)–C(16)	1·408(11)	C(45)–C(46)	1·396(11)
C(16)–C(11)	1·381(9)	C(46)–C(41)	1·383(9)
C(21)–C(22)	1·381(10)	C(51)–C(52)	1·407(9)
C(22)–C(23)	1·362(12)	C(52)–C(53)	1·385(11)
C(23)–C(24)	1·400(13)	C(53)–C(54)	1·361(13)
C(24)–C(25)	1·353(12)	C(54)–C(55)	1·395(11)
C(25)–C(26)	1·384(12)	C(55)–C(56)	1·377(11)
C(26)–C(21)	1·387(10)	C(56)–C(51)	1·381(10)
C(31)–C(32)	1·411(8)	C(61)–C(62)	1·398(8)
C(32)–C(33)	1·389(10)	C(62)–C(63)	1·395(11)
C(33)–C(34)	1·372(10)	C(63)–C(64)	1·363(13)
C(34)–C(35)	1·382(10)	C(64)–C(65)	1·376(13)
C(35)–C(36)	1·392(9)	C(65)–C(66)	1·402(12)
C(36)–C(31)	1·385(9)	C(66)–C(61)	1·363(10)
Mean C–C	1·384	Mean C–C	1·386

(*b*) Bond angles (°) and estimated standard deviations

Molecule (A)		Molecule (B)	
P(1)=C(1)=P(1′)	143·8(6)	P(2)=C(2)=P(2′)	130·1(6)
C(11)–P(1)–C(21)	104·0(3)	C(41)–P(2)–C(51)	105·1(3)
C(11)–P(1)–C(31)	103·1(3)	C(41)–P(2)–C(61)	104·2(3)
C(21)–P(1)–C(31)	103·5(3)	C(51)–P(2)–C(61)	102·6(3)
Mean C–P–C	103·5	Mean C–P–C	104·0
C(1)=P(1)–C(11)	117·8(2)	C(2)=P(2)–C(41)	116·1(2)
C(1)=P(1)–C(21)	109·2(4)	C(2)=P(2)–C(51)	109·9(3)
C(1)=P(1)–C(31)	117·7(2)	C(2)=P(2)–C(61)	117·4(2)
Mean C=P–C	114·9	Mean C=P–C	114·5
P(1)–C(11)–C(12)	118·3(5)	P(2)–C(41)–C(42)	120·2(5)
P(1)–C(11)–C(16)	121·4(5)	P(2)–C(41)–C(46)	120·4(5)
P(1)–C(21)–C(22)	123·1(6)	P(2)–C(51)–C(52)	120·7(5)
P(1)–C(21)–C(26)	118·7(5)	P(2)–C(51)–C(56)	119·0(5)
P(1)–C(31)–C(32)	117·9(5)	P(2)–C(61)–C(62)	116·5(5)
P(1)–C(31)–C(36)	124·2(4)	P(2)–C(61)–C(66)	123·1(5)
Mean P–C–C	120·6	Mean P–C–C	120·0
C(11)–C(12)–C(13)	119·6(7)	C(41)–C(42)–C(43)	120·0(7)
C(12)–C(13)–C(14)	120·8(9)	C(42)–C(43)–C(44)	120·7(9)
C(13)–C(14)–C(15)	120·4(9)	C(43)–C(44)–C(45)	119·2(9)
C(14)–C(15)–C(16)	119·2(8)	C(44)–C(45)–C(46)	120·2(8)
C(15)–C(16)–C(11)	120·4(7)	C(45)–C(46)–C(41)	120·9(7)
C(16)–C(11)–C(12)	119·5(6)	C(46)–C(41)–C(42)	118·9(6)
C(21)–C(22)–C(23)	120·7(8)	C(51)–C(52)–C(53)	118·9(7)
C(22)–C(23)–C(24)	121·0(8)	C(52)–C(53)–C(54)	121·1(8)
C(23)–C(24) -C(25)	118·4(9)	C(53)–C(54)–C(55)	119·4(8)
C(24)–C(25)–C(26)	121·0(9)	C(54)–C(55) -C(56)	120·9(8)
C(25)–C(26)–C(21)	120·7(7)	C(55)–C(56)–C(51)	119·2(7)
C(26)–C(21)–C(22)	118·2(7)	C(56)–C(51)–C(52)	120·3(6)
C(31)–C(32)–C(33)	120·5(6)	C(61)–C(62)–C(63)	118·4(7)
C(32)–C(33)–C(34)	120·1(7)	C(62)–C(63)–C(64)	121·0(8)
C(33)–C(34)–C(35)	120·5(7)	C(63)–C(64)–C(65)	120·4(9)
C(34)–C(35)–C(36)	119·5(7)	C(64)–C(65)–C(66)	119·2(10)
C(35)–C(36)–C(31)	121·4(6)	C(65)–C(66)–C(61)	120·4(7)
C(36)–C(31)–C(32)	118·0(6)	C(66)–C(61)–C(62)	120·4(6)
Mean C–C–C	120·0	Mean C–C–C	120·0

Table 7(*a*) compares torsion angles for several molecules. The zero reference point is taken as the P=C bond for

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[21] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 1958, **29**, 914.

[22] L. Pauling, 'Nature of the Chemical Bond,' 1st edn., Cornell University Press, Ithaca, New York, 1948.

molecules containing the $Ph_3P{=}C$ group, and the phosphorus lone-pair, the P=N bond, or the P–C bond for the others. Molecules in which there are six phenyl groups have similar orientations of these groups. It is also reported that four other structures containing the $Ph_3P{:}\overset{+}{N}{:}PPh_3$ cation and crystallizing in different systems show this feature.[10] $Ph_3P{:}CH_2$, $Ph_3P{:}C{:}C{:}O$, and $Ph_3P{:}C{:}C{:}S$ form a group which have torsion angles different from those above but similar within themselves. These observations suggest that the molecular geometry is not primarily governed by packing forces.

TABLE 5

Bond lengths (Å) in comparable molecules

Molecule	P=C	P–C(Ph)	Mean P–C(Ph)
$Ph_3P{:}C(Cl){\cdot}C(O){\cdot}Ph$ [a]	1·736(14)	1·798—1·822(13)	1·807
$Ph_3P{:}C(I){\cdot}C(O){\cdot}Ph$ [b]	1·71(5)	1·77—1·82(6)	1·79
$Ph_3P{:}C{:}C{:}O$ [c]	1·648(7)	1·793—1·815(6)	1·805
$Ph_3P{:}C{:}C{:}S$ [d]	1·677(8)	1·783—1·804(7)	1·795
$Ph_3P{:}CH_2$ [e]	1·661(8)	1·811—1·839(15)	1·823
$(Ph_3P)_2C{:}C(NPh)_2$ [f]	1·726(2) [g]	1·804—1·823(6)	1·813
$Ph_3P{:}C{:}PPh_3$ [h]	1·629(3) 1·633(4)	1·823—1·845(6)	1·834

[a] Ref. 15. [b] Ref. 16. [c] Ref. 8. [d] Ref. 7. [e] Ref. 17. [f] Ref. 23. [g] No single resonance structure can be written for this molecule. [h] This work.

TABLE 6

Least-squares planes in terms of orthogonal axes,* and in square brackets deviations (Å) of relevant atoms from the planes

Plane	Atoms	Equation
Ph(1)	C(11)—(16)	$0{\cdot}0877x' - 0{\cdot}3237y' - 0{\cdot}9421z' = -2{\cdot}3860$
		[(C11) −0·015, C(12) 0·005, C(13) 0·002, C(14) 0·000, C(15) −0·010, C(16) 0·018, P(1) 0·200]
Ph(2)	C(21)—(26)	$0{\cdot}9796x' + 0{\cdot}0325y' - 0{\cdot}1985z' = 7{\cdot}9170$
		[C(21) 0·001, C(22) −0·001, C(23) −0·005, C(24) 0·010, C(25) −0·009, C(26) 0·004, P(1) −0·010]
Ph(3)	C(31)—(36)	$0{\cdot}0845x' + 0{\cdot}7454y' - 0{\cdot}6612z' = 3{\cdot}3111$
		[C(31) −0·009, C(32) 0·004, C(33) 0·005, C(34) −0·009, C(35) 0·004, C(36) 0·005, P(1) −0·046]
Ph(4)	C(41)—(46)	$-0{\cdot}5340x' + 0{\cdot}2740y' - 0{\cdot}7999z' = -8{\cdot}5547$
		[C(41) −0·013, C(42) 0·004, C(43) 0·004, C(44) −0·002, C(45) −0·008, C(46) 0·015, P(2) −0·298]
Ph(5)	C(51)—(56)	$0{\cdot}9576x' + 0{\cdot}0040y' - 0{\cdot}2879z' = 3{\cdot}6616$
		[(51) −0·003, C(52) 0·000, C(53) −0·005, C(54) 0·012, C(55) −0·015, C(56) 0·011, P(2) −0·053]
Ph(6)	C(61)—(66)	$0{\cdot}3922x' + 0{\cdot}6958y' + 0{\cdot}6016z' = 11{\cdot}2340$
		[C(61) 0·012, C(62) −0·007, C(63) −0·011, C(64) 0·025, C(65) 0·002, C(66) 0·002, P(2) 0·062]
Ph(2,2′)	C(21)—(26), P(1), C(1), P(1′), C(21′)—(26′)	$0{\cdot}9586x' - 0{\cdot}2847z' = 7{\cdot}3631$
Ph(5,5′)	C(51)—(56), C(2), P(2), P(2′), C(51′)—(56′)	$0{\cdot}9592x' - 0{\cdot}2829z' = 3{\cdot}6867$

* $x' = x + z\cos\beta$; $y' = y$; $z' = z\sin\beta$.

The difference between the largest and smallest torsion angles may be regarded as a measure of the departure of the Ph_3P groups from three-fold symmetry, and it is seen that the deviations (64 and 83°) in hexaphenylcarbodiphosphorane are the largest found in these compounds.

TABLE 7

(*a*) Torsion angles (°) defined as C=P–C–C or N=P–C–C

Molecule	Torsion angles		
Ph_3P [a]	56	24	29
$Ph_3P{:}C(H)SO_2{\cdot}C_6H_4Me$ [a]	59	35	45
$Ph_3P{:}C{:}C{:}O$ [a]	55	19	41
$Ph_3P{:}C{:}C{:}S$ [a]	62	8	40
$Ph_3P{:}CH_2$ [b]	57 56	17 13	46 49
$[(Ph_3P)_2N]^+[Cr_2(CO)_{10}I]^-$ [c,d]	77	17	33
$(Ph_3P)_2C{:}C(NPh)_2$ [e,d]	70	14	36
$Ph_3P{:}C{:}PPh_3$ [f]	73 85	9 2	23 23

[a] J. J. Daly, *Perspectives in Structural Chem.*, 1970, **3**, 165. [b] Ref. 17. [c] Ref. 10. [d] Calculated from quoted co-ordinates. [e] Ref. 23. [f] This work.

(*b*) Torsion angles (°) defined as C–P–P–C in hexaphenylcarbodiphosphorane

C(11)–P(1)–P(1′)–C(31′)	5·5
C(21)–P(1)–P(1′)–C(21′)	8·3
C(31)–P(1)–P(1′)–C(11′)	5·5
C(41)–P(2)–P(2′)–C(61′)	6·3
C(51)–P(2)–P(2′)–C(51′)	7·7
C(61)–P(2)–P(2′)–C(41′)	6·3

The torsion angles given in Table 7(*b*) show that the two Ph_3P groups in each molecule of hexaphenylcarbodiphosphorane are almost in the eclipsed configuration. These values would all be zero for ideal eclipsed geometry.

Intramolecular contacts are summarized in Table 8.

TABLE 8

Number of intramolecular contacts <4·0 Å

Contact	Molecule (A)	Molecule (B)	Shortest
P · · · P	1 (3·097)	1 (2·961)	
P · · · C (as. un.)	12	12	2·769
P · · · C (2-fold)	0	6	3·772
C(Ph) · · · C(Ph) (as. un.)	36	30	2·866
C(Ph) · · · C(Ph) (2-fold)	8	16	3·442
C(central) · · · C(Ph)	14	14	2·849
P · · · H (as. un.)	12	12	2·865
P · · · H (2-fold)	6	4	3·376
C · · · H (as. un.)	74	66	2·552
C · · · H (2-fold)	24	26	2·974
H · · · H (as. un.)	24	32	2·429
H · · · H (2-fold)	10	12	2·159

TABLE 9

Number of van der Waals contacts

Contact	Molecule (A)	Molecule (B)	Maximum search (Å)	Shortest (Å)
P · · · P	0	0	4·0	
P · · · C	0	0	4·0	
P · · · H	4	4	3·9	3·368
C · · · C	66	70	4·0	3·588
C · · · H	108	106	3·7	2·616
H · · · H	74	66	3·4	2·175

Those shown as asymmetric unit contacts (as. un.) are within each half of either molecule (A) or (B). The two-fold contacts occur between the symmetry related halves of each molecule. The difference in the P=C=P angles

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[23] F. K. Ross, W. C. Hamilton, and F. Ramirez, personal communication.

is reflected in the number of P · · · C contacts <4·0 Å due to the two-fold axis. Similarly the number of short C(Ph) · · · C(Ph) contacts due to the two-fold axis is greater for molecule (B) which has the smaller angle.

The number of van der Waals contacts (Table 9) is similar for the two molecules. The packing of the molecules is shown in Figures 3 and 4. The crystal structure consists of alternate layers of (A) and (B) molecules whose centres are separated by $z/2$.

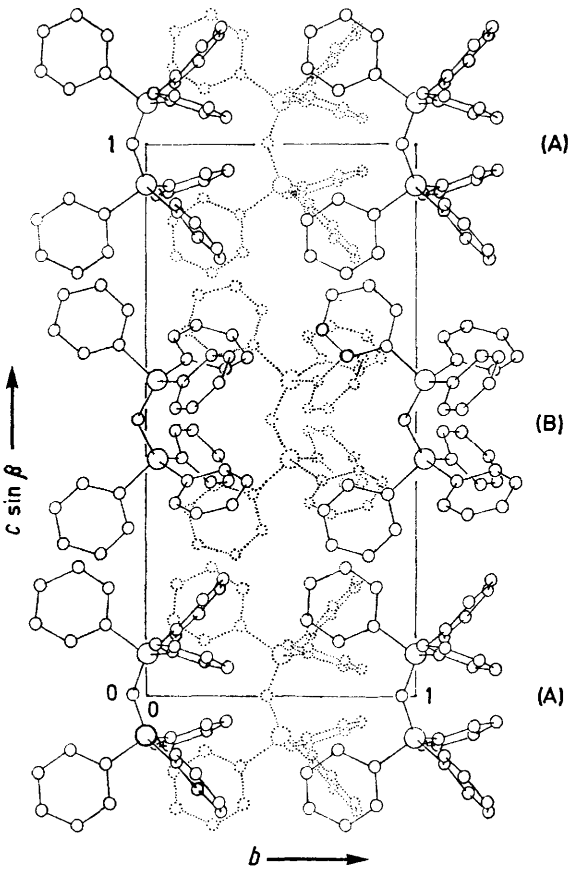

FIGURE 3 Projection down *a*. Molecules due to C-centering shown dotted

DISCUSSION

The primary purpose of this analysis was the determination of the P=C=P angle. We expected this angle to be substantially less than 180°, but we did not expect to find two independent molecules with P=C=P angles differing by 13·7°, and we find this difference hard to understand or rationalize. The general invariance of molecular geometry of this and analogous molecules to packing arrangement suggests that intermolecular forces do not play a dominant part in determining the molecular geometry. An examination of the non-bonded contacts in hexaphenylcarbodiphosphorane shows that the short contacts are more numerous on the ' closed ' angle side of the P=C=P group, suggesting that these specific contacts are not responsible for the departure of the chain from linearity, but rather that the values adopted for the P=C=P angles determine the contact distances. We can only conclude that the bending of the P=C=P chain is electronic in origin, arising from the overlap of the phosphorus *d* orbitals with the π-electronic system of the chain,[24] and can offer no explanation for the disparity of the P=C=P angles in the two molecules.

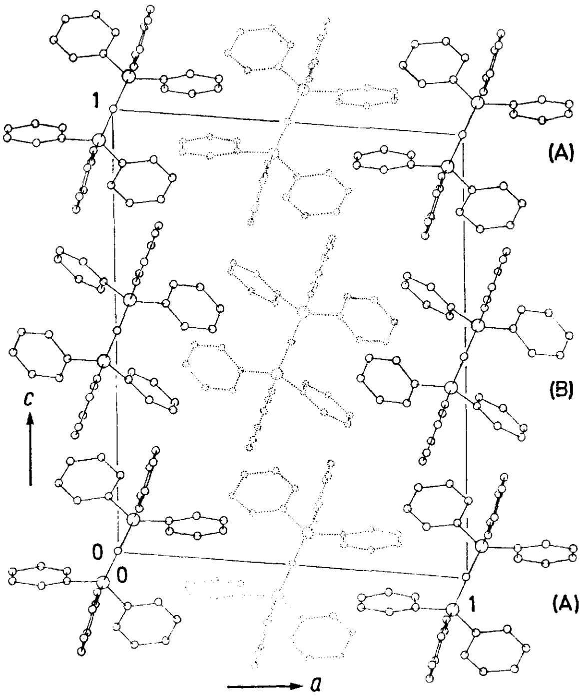

FIGURE 4 Projection down *b*. Molecules due to C-centering shown dotted

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[1/1939 *Received, 21st October*, 1971]

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[24] H. H. Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.