

The Crystal and Molecular Structure of Bis(diphenylphosphino)acetylene

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A three-dimensional X-ray diffraction analysis of the structure of bis(diphenylphosphino)acetylene, $(C_6H_5)_2PC\equiv CP(C_6H_5)_2$, has been carried out. The crystals are monoclinic, space group $P2_1/n$ with $a = 14.709$, $b = 8.166$, $c = 17.836$ Å, $\beta = 95^\circ 13'$, $Z = 4$. The parameters determined earlier by Brinkel were refined by a block-diagonal least-squares method with 2717 intensities collected with a Hilger-Watts linear diffractometer. The hydrogen atoms were included in the calculations. The final R value, including all reflexions, was 0.061 ($R' = 0.0064$). The molecule has the expected pyramidal configuration about both phosphorus atoms, but in view of the asymmetric orientation of the benzene rings about the P-C bonds, possesses no symmetry. π -Interaction between the phosphorus atoms and the acetylenic group has been advanced to account for the geometry of the molecule. The torsion angle between the directions of the polar axes of the phosphorus lone-pair orbitals is approximately 90° . Bond lengths and angles do not differ significantly in the two equivalent parts of the molecule. The mean $>P-C(Ph)$ and $>P-C\equiv$ bond lengths are 1.832 and 1.765 Å respectively, and include an angle of 101.1° (e.s.d. 0.004 Å and 0.2°). All benzene rings are essentially planar with some significant in- and out-of-plane bendings of the exocyclic bonds. The packing arrangement is described.

Introduction

Chemical evidence (Hartmann, Beermann & Czempik, 1956) suggests that the reactivity of bis(diphenylphosphino)acetylene, $(C_6H_5)_2PC\equiv CP(C_6H_5)_2$, may be affected by the interaction between the phosphorus atom, the acetylene group and the organic substituents, as well as by the polarity of the $>P-C\equiv$ bond (inductive effect) and molecular geometry (mesomeric effect). In order to study the reactivity of the free-electron pair at the hetero-atom and the specific interactions in the molecule, accurate knowledge of the nature of the phosphorus-acetylene bond and of the geometry of the molecule is highly desirable.

The determination of the structure of bis(diphenylphosphino)acetylene in the solid state has been reported recently (Mootz & Brinkel, 1961; Brinkel, 1964). Because of overlap and lack of computer facilities the parameters obtained by Brinkel, using two-dimensional data for two projections, were insufficient to reveal the details of the structure with the required precision. In particular the large difference in the P-C \equiv bond lengths (1.78 and 1.89 Å) seemed to be rather peculiar. As special interest exists in the distribution of valencies around the phosphorus atoms and in the values for the P-acetylene bond distance, refinement of the structure of this tertiary phosphine has now been carried out by the least-squares method, with three-dimensional data.

Experimental

Suitable crystals, obtained by recrystallization from a mixture of ethanol and chloroform, were kindly sup-

plied by Dr L. Maier. The cell dimensions were re-determined from precession photographs, recorded with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and are listed in Table 1, together with other crystallographic constants. For computational reasons we preferred space group $P2_1/n$ instead of the former $P2_1/c$ (Brinkel). Brinkel's transformed cell constants, given in brackets in Table 1, compare nicely with the present ones, although c differs by about 3σ .

Table 1. Crystallographic and experimental data of $(C_6H_5)_2PC\equiv CP(C_6H_5)_2$

	$C_{26}H_{20}P_2$,	$M = 394.4$,	m.p. 85°
a	14.709 (14.728) Å		$\sigma(a)$ 0.009 Å
b	8.166 (8.161)		$\sigma(b)$ 0.005
c	17.836 (17.805)		$\sigma(c)$ 0.009
β	$95^\circ 13'$ ($95^\circ 22'$)		$\sigma(\beta)$ $10'$

Systematic absences: $h0l$ for $h+l$ odd; $0k0$ for k odd

Space group $P2_1/n$

$V = 2133.5$ Å³;

$d(\text{obs}) = 1.23$ g.cm⁻³ (20.5°) (Brinkel)

$d(\text{calc}) (n=4) = 1.228$ g.cm⁻³

$F(000) = 824$

$\mu(\text{Mo}K\alpha) = 2.15$ cm⁻¹

Oscillation angle

$h0l-h5l$ 3°

$h6l-h9l$ 4°

The data were collected with a needle-shaped crystal round $[b]$, of approximate cross section 0.5×0.2 mm, showing $\{001\}$, $\{101\}$ and $\{10\bar{1}\}$. The intensities were recorded with Mo $K\alpha$ radiation on a Hilger-Watts diffractometer (Arndt & Phillips, 1961) equipped with balanced filters and a scintillation counter with pulse height discrimination. A one minute oscillation motor was used, and each of the over 4500 independent re-

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flexions was measured twice with each filter in position, up to a value of $\theta = 25^\circ$. The average ΔF_o was estimated as 2%. The background counts were low and were included as usual; the intensities varied from 1 to 150,000. All intensities with less than 5 counts per measurement were rejected as having an insignificant value and they were not further used in the analysis.

The reflexion data (3332 terms) were corrected for the Lorentz-polarization factor, but not for absorption. A scale factor was obtained by comparison with Brinkel's list of structure factors on an absolute scale.

Refinement

Brinkel's parameters (P_{21}/c) were transformed to the P_{21}/n axial system used in the present analysis, in accordance with *International Tables*, Vol. I (§4.9). Refinement started straight away and was carried out with the Cruickshank (1961) weighting scheme $w = 1/(6.0 + |F_o| + 0.05|F_o|^2)$ and a program that employs the block-diagonal approximation, minimizing $\Sigma w(|F_o| - |F_c|)^2$. The atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962).

At $R[\Sigma |kF_o - |F_c||/\Sigma kF_o] = 0.135$ anisotropic refinement was started which reduced R to 0.115. Hydrogen positions were calculated under the usual assumptions and were included in the refinement ($R = 0.091$). A comparison of kF_o and F_c during this stage indicated extinction effects (the five strongest reflexions were corrected accordingly) and showed an unreasonably high R value (0.34) for the about 450 weakest reflexions. The significance limit of the observed reflexions was raised to 12 counts and the remaining 2717 terms could readily be refined to $R = 0.069$. A final drop in R to 0.061 was subsequently obtained in two least-squares cycles with anisotropic temperature factors for all atoms, including hydrogen. $R'[\Sigma w|\Delta|^2/\Sigma wF_o^2] = 0.0064$ could not be further reduced. The maximum drift was 0.4σ and 0.7σ for the heavy and light atoms respectively.

During the calculations no contributions to the least-squares totals were made by planes with $3|F_c| \leq F_o$; 8 planes were thus rejected in the last cycle.

Constant values over the whole range were reached for $\Sigma w\Delta^2/n$ as a function of $|F_o|$ and $\sin^2 \theta/\lambda^2$, indicating that satisfactory weighting had been applied.

Results

Brinkel's solution of the phase problem has been confirmed. The details of the structure have now been worked out to a greater accuracy. For consistency with Brinkel the same numbering of the atoms was adopted [Fig. 1(a)]: the hydrogen atoms have the same labelling as the carbon atoms to which they are attached. The final atomic coordinates and anisotropic temperature factors, with their standard deviations, all referred to the axes a, b, c , of the monoclinic cell, are listed in Tables

2 and 3. Table 4(a)* gives the observed and calculated structure factors. Planes preceded by an asterisk were omitted from the least-squares totals because of low calculated amplitudes. More informative is Table 4(b), which examines the structure factors in terms of the index of the layer (k) and magnitude of F_{obs} , and Table 5, which analyses the R value as a function of the parity of the indices. R increases slightly towards the higher layers, probably as the result of geometrical factors and the decrease in the magnitude of the average intensity. Although the contribution of the weak reflexions to $\Sigma|\Delta|$ is still high in comparison to the stronger F_{obs} their $\Sigma|\Delta|/N$ -value is normal.

Table 2. Final atomic coordinates (Å)

Standard deviations are given as units in the last place

	x	y	z
P(1)	-3.1989 (10)	2.2158 (09)	1.0125 (09)
P(2)	1.1112 (09)	1.8694 (09)	3.3640 (09)
C(1)	-1.5593 (39)	2.1557 (36)	1.8331 (37)
C(2)	-0.4708 (38)	1.9902 (35)	2.4369 (36)
C(3)	0.6065 (34)	2.0576 (30)	5.0677 (33)
C(4)	1.4381 (37)	2.7552 (38)	5.9972 (37)
C(5)	1.0980 (41)	2.9399 (42)	7.2970 (38)
C(6)	-0.0846 (44)	2.4324 (42)	7.6716 (38)
C(7)	-0.9233 (46)	1.7443 (49)	6.7490 (45)
C(8)	-0.5811 (43)	1.5535 (43)	5.4560 (39)
C(9)	-4.1680 (34)	2.2594 (31)	2.4746 (33)
C(10)	-5.3443 (41)	1.5384 (44)	2.4112 (41)
C(11)	-6.1234 (45)	1.5057 (52)	3.4825 (48)
C(12)	-5.7194 (44)	2.1993 (42)	4.6349 (44)
C(13)	-4.5449 (46)	2.9086 (44)	4.7263 (42)
C(14)	-3.7660 (39)	2.9581 (39)	3.6537 (37)
C(15)	1.4066 (29)	0.0623 (30)	3.2414 (30)
C(16)	2.1201 (34)	-0.5991 (34)	4.2987 (35)
C(17)	2.4379 (40)	-1.9356 (35)	4.1678 (44)
C(18)	2.0579 (40)	-2.6259 (36)	3.0011 (45)
C(19)	1.3518 (41)	-1.9626 (37)	1.9476 (42)
C(20)	1.0316 (36)	-0.6250 (37)	2.0562 (33)
C(21)	-3.2898 (33)	3.9538 (32)	0.4250 (29)
C(22)	-4.3803 (39)	4.3133 (38)	-0.4661 (35)
C(23)	-4.5142 (41)	5.6010 (42)	-0.9533 (36)
C(24)	-3.5633 (46)	6.5515 (40)	-0.5615 (41)
C(25)	-2.4853 (48)	6.2037 (42)	0.3121 (50)
C(26)	-2.3313 (40)	4.9124 (41)	0.7966 (40)
H(4)	2.275 (33)	3.169 (42)	5.725 (29)
H(5)	1.695 (40)	3.493 (40)	8.007 (38)
H(6)	-0.328 (37)	2.479 (41)	8.557 (44)
H(7)	-1.753 (37)	1.331 (43)	7.014 (37)
H(8)	-1.150 (38)	0.971 (42)	4.793 (31)
H(10)	-5.626 (47)	0.837 (47)	1.604 (42)
H(11)	-7.013 (41)	1.026 (40)	3.356 (42)
H(12)	-6.272 (40)	2.218 (41)	5.354 (36)
H(13)	-4.301 (46)	3.435 (46)	5.543 (43)
H(14)	-2.860 (36)	3.425 (44)	3.631 (36)
H(16)	2.370 (34)	-0.105 (32)	5.210 (32)
H(17)	3.014 (40)	-2.495 (43)	4.996 (44)
H(18)	2.332 (38)	-3.498 (35)	2.933 (38)
H(19)	1.008 (44)	-2.505 (41)	1.107 (41)
H(20)	0.569 (40)	-0.188 (38)	1.259 (38)
H(22)	-5.123 (44)	3.699 (40)	-0.565 (44)
H(23)	-5.388 (39)	5.900 (29)	-1.615 (30)
H(24)	-3.590 (39)	7.467 (43)	-0.917 (44)
H(25)	-1.849 (42)	6.942 (38)	0.610 (43)
H(26)	-1.525 (34)	4.718 (33)	1.381 (35)

* Owing to its length Table 4(a) has been omitted from this paper. A copy may be obtained from the author on request.

The thermal parameters of the heavy atoms are only slightly anisotropic, without pronounced motions in any specific direction. The values for the hydrogen atoms seem to be reasonable; a few refined towards a slightly negative U_{33} . As the molecule does not seem to be rigid no attempt has been made to correct for apparent atomic displacements caused by thermal motion (Cruickshank, 1956).

Discussion

Bond lengths and angles

Fig. 1 and Tables 6 and 7 show the final bond data and list the mean values of chemically equivalent bonds

and angles. Standard deviations of the individual measurements, calculated from the e.s.d. of the positional parameters, are given in Table 7 for the various types of bonds and valence angles. The estimated variance in the bond distances and angles, defined as $s^2 = [\sum_{i=1}^n (\bar{x} - x_i)^2 / (n-1)]$, and calculated for C-C, C-H, P-C \equiv and P-C distances and C-C-H and C-C-C angles, gives s values slightly higher than the corresponding e.s.d. values, except in the last case, where $s = 0.82^\circ$ (to be compared with an e.s.d. of 0.37°).

The average P-C \equiv length is 1.765 \AA (e.s.d. 0.0038 \AA) with no deviations from the mean. This result differs quite considerably from Brinkel's values and seems more reasonable. Recently Mootz & Sassmannshausen

Table 3. Thermal parameters (\AA^2) in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$

Standard deviations are appended in brackets as units in the last place.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
P(1)	0.0639 (05)	0.0529 (05)	0.0477 (05)	0.0073 (08)	0.0052 (08)	0.0055 (08)
P(2)	0.0546 (05)	0.0459 (04)	0.0529 (05)	0.0017 (08)	0.0056 (07)	0.0184 (08)
C(1)	0.0687 (22)	0.0645 (21)	0.0512 (18)	0.0323 (36)	0.0107 (33)	0.0163 (33)
C(2)	0.0619 (20)	0.0638 (21)	0.0541 (19)	0.0249 (34)	0.0212 (33)	0.0242 (32)
C(3)	0.0547 (18)	0.0463 (16)	0.0508 (17)	0.0012 (30)	-0.0096 (28)	0.0136 (28)
C(4)	0.0623 (22)	0.0587 (20)	0.0613 (21)	0.0046 (34)	-0.0031 (34)	-0.0012 (35)
C(5)	0.0747 (25)	0.0794 (26)	0.0540 (21)	0.0053 (42)	-0.0169 (38)	-0.0158 (36)
C(6)	0.0838 (27)	0.0776 (25)	0.0531 (21)	0.0127 (43)	-0.0143 (38)	0.0198 (38)
C(7)	0.0811 (29)	0.1036 (34)	0.0704 (26)	-0.0400 (51)	-0.0204 (48)	0.0537 (44)
C(8)	0.0791 (26)	0.0862 (27)	0.0568 (22)	-0.0499 (45)	-0.0285 (41)	0.0304 (38)
C(9)	0.0574 (19)	0.0502 (18)	0.0495 (18)	0.0037 (30)	0.0172 (29)	0.0084 (29)
C(10)	0.0703 (25)	0.0832 (27)	0.0661 (24)	-0.0279 (43)	0.0196 (42)	-0.0059 (39)
C(11)	0.0731 (27)	0.0978 (32)	0.0886 (31)	-0.0384 (48)	0.0297 (52)	0.0293 (47)
C(12)	0.0792 (27)	0.0795 (26)	0.0730 (25)	0.0320 (43)	0.0383 (42)	0.0504 (42)
C(13)	0.0927 (29)	0.0791 (27)	0.0642 (24)	0.0120 (46)	-0.0244 (42)	0.0361 (43)
C(14)	0.0687 (23)	0.0670 (23)	0.0601 (21)	-0.0171 (37)	-0.0202 (35)	0.0231 (36)
C(15)	0.0427 (16)	0.0452 (16)	0.0494 (17)	-0.0022 (26)	0.0006 (27)	0.0153 (27)
C(16)	0.0560 (20)	0.0537 (18)	0.0571 (20)	0.0076 (32)	0.0012 (32)	-0.0084 (31)
C(17)	0.0672 (23)	0.0522 (19)	0.0838 (27)	0.0199 (36)	0.0082 (37)	0.0143 (40)
C(18)	0.0715 (24)	0.0475 (18)	0.0952 (30)	0.0058 (37)	-0.0008 (39)	0.0556 (43)
C(19)	0.0735 (24)	0.0614 (21)	0.0723 (24)	-0.0256 (37)	-0.0415 (37)	0.0503 (39)
C(20)	0.0645 (21)	0.0646 (20)	0.0436 (17)	-0.0087 (34)	-0.0087 (31)	0.0209 (30)
C(21)	0.0601 (19)	0.0526 (17)	0.0343 (15)	0.0114 (30)	0.0064 (27)	0.0086 (27)
C(22)	0.0735 (24)	0.0638 (22)	0.0540 (20)	0.0107 (37)	-0.0016 (34)	-0.0061 (36)
C(23)	0.0771 (25)	0.0800 (25)	0.0480 (19)	0.0371 (42)	0.0217 (37)	-0.0013 (35)
C(24)	0.0959 (30)	0.0655 (23)	0.0666 (24)	0.0181 (44)	0.0326 (39)	0.0377 (44)
C(25)	0.0894 (31)	0.0660 (24)	0.0919 (32)	-0.0263 (44)	0.0281 (44)	-0.0001 (50)
C(26)	0.0691 (24)	0.0721 (23)	0.0678 (24)	-0.0295 (40)	0.0264 (39)	-0.0221 (38)
H(4)	0.041 (21)	0.110 (31)	-0.012 (16)	0.084 (44)	-0.045 (37)	0.031 (31)
H(5)	0.070 (28)	0.052 (27)	0.045 (24)	-0.027 (48)	0.041 (44)	-0.058 (44)
H(6)	0.022 (23)	0.076 (27)	0.098 (33)	-0.086 (40)	-0.041 (53)	0.022 (45)
H(7)	0.055 (24)	0.086 (29)	0.019 (22)	-0.010 (46)	-0.080 (42)	0.043 (37)
H(8)	0.074 (25)	0.088 (28)	-0.001 (17)	-0.124 (43)	0.039 (36)	0.032 (34)
H(10)	0.109 (36)	0.080 (33)	0.044 (26)	-0.064 (62)	0.018 (50)	0.067 (53)
H(11)	0.085 (31)	0.049 (25)	0.074 (29)	-0.005 (48)	-0.097 (47)	0.089 (48)
H(12)	0.048 (28)	0.098 (32)	0.019 (20)	-0.018 (52)	0.011 (43)	0.005 (40)
H(13)	0.094 (33)	0.088 (33)	0.056 (30)	-0.072 (57)	-0.046 (56)	0.044 (53)
H(14)	0.036 (21)	0.125 (31)	0.034 (23)	-0.142 (41)	-0.069 (45)	0.010 (35)
H(16)	0.040 (23)	0.017 (18)	0.025 (21)	-0.061 (35)	-0.055 (33)	-0.064 (39)
H(17)	0.062 (27)	0.079 (30)	0.075 (31)	0.095 (45)	0.000 (54)	0.053 (47)
H(18)	0.054 (26)	0.037 (21)	0.056 (26)	0.008 (40)	-0.037 (39)	-0.023 (44)
H(19)	0.094 (32)	0.047 (28)	0.040 (28)	-0.036 (51)	-0.018 (48)	-0.051 (50)
H(20)	0.067 (28)	0.056 (24)	0.046 (26)	0.032 (44)	-0.093 (40)	-0.046 (46)
H(22)	0.094 (29)	0.066 (26)	0.101 (32)	-0.153 (45)	-0.038 (49)	-0.127 (52)
H(23)	0.085 (26)	0.008 (17)	-0.003 (16)	0.022 (35)	-0.005 (28)	-0.010 (36)
H(24)	0.048 (26)	0.077 (30)	0.069 (32)	-0.041 (51)	-0.004 (58)	-0.009 (48)
H(25)	0.070 (28)	0.021 (22)	0.080 (32)	0.040 (44)	-0.005 (45)	0.006 (52)
H(26)	0.031 (22)	0.032 (20)	0.048 (24)	-0.028 (35)	-0.013 (37)	-0.069 (39)

Table 4(b).

(i) Analysis of F_{obs} and F_{calc} as a function of the layer-index

All figures are on absolute scale.

k	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	N	R	$\Sigma \Delta /N$
0	5548.94	5553.91	300.07	241	0.054	1.25
1	7624.81	7595.21	433.34	413	0.057	1.05
2	6364.22	6169.56	400.40	409	0.063	0.98
3	5595.62	5437.57	349.07	395	0.062	0.88
4	4538.78	4541.22	262.20	358	0.058	0.73
5	3703.21	3703.95	210.34	301	0.057	0.70
6	2532.30	2512.04	174.26	242	0.069	0.72
7	1526.94	1493.86	118.30	179	0.077	0.66
8	1008.89	989.94	86.35	129	0.086	0.67
9	354.93	352.73	36.88	50	0.104	0.74
All	38798.64	38349.99	2371.21	2717	0.061	0.87

(ii) Analysis of F_{obs} and F_{calc} as a function of the magnitude of F_{obs}

All figures are on absolute scale

Range of $ F_o $	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	N	R	$\Sigma \Delta /N$
0.0-6.0	2851.72	2680.03	401.59	586	0.141	0.69
6.0-12.0	9156.32	9082.67	654.07	1078	0.071	0.61
12.0-18.0	7135.31	7125.72	360.21	487	0.050	0.74
18.0-24.0	4280.51	4252.30	209.31	206	0.049	1.02
24.0-30.0	2996.41	2968.78	143.75	112	0.048	1.28
30.0-36.0	2663.91	2662.02	129.09	82	0.048	1.57
36.0-42.0	2022.19	1979.72	86.25	52	0.043	1.66
42.0-48.0	1249.54	1193.84	69.62	28	0.056	2.49
48.0-54.0	1023.88	995.89	62.43	20	0.061	3.12
54.0-60.0	740.99	713.24	34.11	13	0.046	2.62
>60.0	4677.86	4695.78	220.78	53	0.047	4.17

Table 5. Analysis of R as a function of the parity of the indices

	R
$h+k+l=2n$	0.062
$h+k+l=2n+1$	0.060
$h+k=2n$	0.060
$h+k=2n+1$	0.062
$k+l=2n$	0.062
$k+l=2n+1$	0.060
$h+l=2n$	0.057
$h+l=2n+1$	0.068
$h=2n$	0.060
$h=2n+1$	0.063
$k=2n$	0.061
$k=2n+1$	0.061
$l=2n$	0.060
$l=2n+1$	0.062
All planes	0.061

(1967) have reported exactly the same length (1.765 ± 0.010 Å) for the P-C \equiv bond in tris(phenylethynyl)-phosphine. The value compares well with that found by Emerson & Britton (1964) for a similar kind of bond in P(CN)₃ (average value 1.788 Å; e.s.d. 0.028 Å).

Part of the difference in length with respect to P-C bond lengths in aromatic and aliphatic phosphines can be accounted for by the smaller covalent radius of an sp carbon atom. With Pauling (1962) and Bent (1961) one calculates 1.79 Å for P-C (sp). As in molecules where phosphorus is surrounded by *four* ligands in an approximately tetrahedral arrangement, some π -bonding might occur between suitable ligand orbitals

and the phosphorus orbitals $d_{x^2-y^2}$ and d_{z^2} . The small additional experimentally observed shortening of P-C \equiv may be caused by such an interaction. The π -orbital system can be a double one as two of the five $3d$ orbitals can be used simultaneously. An analysis of the proton nuclear magnetic resonance spectra of ethynylphosphines supports the presence of $3d$ -orbital participation in the P-C \equiv bond in these compounds (Drenth & Rosenberg, 1967). In phosphorus tricyanide a pure single P-C \equiv bond is present, according to a study of the vibration spectra (Goubeau, Haerberle & Ulmer, 1961).

The P-C(*aryl*) bond lengths compare well with each other and do not deviate significantly from their average 1.832 Å. This value is in good agreement with others (Table 8). P-C(*alkyl*) bond lengths tend, in general, to be slightly longer. The observed trend mainly represents the increase in atomic radius going from an sp^2 to an sp^3 carbon atom.

This study alone does not provide much evidence for conjugation between the phenyl groups and the phosphorus atom. In spite of the different orientation of phenyl group IV no effect on the length of P(1)-C(21) is observed. The unsymmetrical geometry of this acetylenic phosphine as compared with the corresponding arsine (Mootz, 1962) cannot readily be ascribed to an asymmetrical opportunity for mesomeric stabilization involving the benzene rings, as suggested by Brinkel. In the arsenic analogue the existence of mesomeric systems is described by Mootz. The resulting blockage

of the free-electron pair on As should account for the non-oxidizability of this compound. Jaffé (1952, 1954) and Rao, Ramachandran, Jah, Samosekhara & Rajakumar (1959) have observed that the phenyl derivatives of the Vb elements in the trivalent state exhibit only one strong absorption band ($n \rightarrow \pi^*$) in the ultraviolet without fine structure. They conclude that the unshared p electrons in the trivalent atom derivatives participate

in resonance interaction with the π -electrons of the benzene system. Charrier, Simonnin, Chodkiewicz & Cadiot (1964) do not exclude intervention of the $3d$ orbitals of phosphorus to account for the strong variation to weaker field of the chemical shift observed from aliphatic to aromatic α -acetylenic phosphines. This is in accordance with their ultraviolet spectral studies. Probably variation of the electronegativity of the sub-

Table 6. C-H bond lengths and C-C-H bond angles

C(4)-H(4)	0.99 Å	C(10)-H(10)	1.09 Å
C(5)-H(5)	1.04	C(11)-H(11)	1.01
C(6)-H(6)	0.94	C(12)-H(12)	0.95
C(7)-H(7)	0.99	C(13)-H(13)	0.98
C(8)-H(8)	1.02	C(14)-H(14)	1.02
C(16)-H(16)	1.05 Å	C(22)-H(22)	0.96 Å
C(17)-H(17)	1.12	C(23)-H(23)	1.09
C(18)-H(18)	0.92	C(24)-H(24)	0.98
C(19)-H(19)	1.03	C(25)-H(25)	1.00
C(20)-H(20)	0.99	C(26)-H(26)	0.97
C(3)-C(4)-H(4)	119.9°	C(9)-C(10)-H(10)	122.4°
C(5)-C(4)-H(4)	119.0	C(11)-C(10)-H(10)	115.7
C(4)-C(5)-H(5)	122.3	C(10)-C(11)-H(11)	117.9
C(6)-C(5)-H(5)	117.7	C(12)-C(11)-H(11)	122.2
C(5)-C(6)-H(6)	122.9	C(11)-C(12)-H(12)	120.0
C(7)-C(6)-H(6)	117.6	C(13)-C(12)-H(12)	119.7
C(6)-C(7)-H(7)	120.5	C(12)-C(13)-H(13)	118.6
C(8)-C(7)-H(7)	118.8	C(14)-C(13)-H(13)	120.7
C(7)-C(8)-H(8)	121.2	C(13)-C(14)-H(14)	126.6
C(3)-C(8)-H(8)	118.2	C(9)-C(14)-H(14)	113.4
C(15)-C(16)-H(16)	120.3°	C(21)-C(22)-H(22)	117.0°
C(17)-C(16)-H(16)	119.9	C(23)-C(22)-H(22)	120.7
C(16)-C(17)-H(17)	121.5	C(22)-C(23)-H(23)	121.2
C(18)-C(17)-H(17)	117.5	C(24)-C(23)-H(23)	118.6
C(17)-C(18)-H(18)	118.5	C(23)-C(24)-H(24)	123.0
C(19)-C(18)-H(18)	122.3	C(25)-C(24)-H(24)	117.5
C(18)-C(19)-H(19)	118.5	C(24)-C(25)-H(25)	116.4
C(20)-C(19)-H(19)	120.7	C(26)-C(25)-H(25)	122.4
C(19)-C(20)-H(20)	117.4	C(25)-C(26)-H(26)	117.2
C(15)-C(20)-H(20)	122.6	C(21)-C(26)-H(26)	122.7

Table 7. Mean values and estimated standard deviations

(i) Bond lengths			
	Average	σ^*	
> P-C (sp^2)	$\langle 1.832 \text{ Å} \rangle$	0.0033 Å	
> P-C (sp)	$\langle 1.765 \rangle$	0.0038	
-C≡C-	1.207	0.0052	
C=C	$\langle 1.381 \rangle$	0.0056	
C-H	$\langle 1.01 \rangle$	0.040	
(ii) Bond angles			
	Average	σ^*	
C-P-C	$\langle 101.08 \rangle$	0.16°	
P-C=C	$\langle 118.34 \rangle$ and $\langle 122.77 \rangle$	0.26	
P-C≡C	$\langle 174.65 \rangle$	0.35	
C-C-C	$\langle 120.00 \rangle$	0.37	
C-C-H	$\langle 119.8 \rangle$	2.3	
(iii) Phenyl groups			
	Ring I	Ring II	Ring III
$\langle \text{C}=\text{C} \rangle$	1.378 Å	1.380 Å	1.384 Å
$\langle \text{C}-\text{H} \rangle$	1.00	1.01	1.02
$\langle \angle \text{C}-\text{C}-\text{C} \rangle$	120.00°	120.00°	120.00°
$\langle \angle \text{C}-\text{C}-\text{H} \rangle$	119.8	119.7	119.9
	Ring IV		
	1.380 Å		1.00
	120.00°		119.7

* e.s.d. of the individual values.

stituent group is a more important effect (Charrier, Chodkiewicz & Cadiot, 1966).

The C≡C length (1.207 Å) is close to the standard (Sutton, 1965) triple bond value (1.204 ± 0.002 Å). All carbon atoms of the phenyl groups conform well to regular hexagons. The individual bond lengths [Fig. 1(a)] do not deviate significantly from the means (Table 7). The average C–C length in the phenyl groups however, is lower than the standard value (1.394 Å), probably as the result of thermal motion. Also the individual C–H distances (Table 6) compare very well with the average value 1.01 Å. The average C–C–C bond angle in all rings is 120.0°, with some significant deviations for the angles at the carbon atoms directly attached to phosphorus. Only around C(14) the C–C–H angles deviate by about 3σ from the mean value (Tables 6 and 7).

For tertiary phosphines sp^3 hybridization is assumed, with the free electron pair occupying one of the four equivalent valences. As the bond angles around the phosphorus atom are not different from those observed in other aromatic derivatives of trivalent phosphorus, its hybridization state is expected to be the same. The average C–P–C angle is 101.1°, although the angles appear to split into two groups, depending upon the precise state of the carbon atoms. The angle formed by the P–C(Ph) bonds is significantly larger than the one between P–C(Ph) and P–C≡. Literature values of C–P–C angles are 102.1–104.0° (± 0.2) in $(C_6H_5)_3P$ (Daly, 1964a), 99.1° (± 0.2) in $(CH_3)_3P$ (Lide & Mann, 1958) and 100.7° (± 0.5) in $(C_6H_5C≡C)_3P$ (Mootz & Sassmannshausen, 1967). In phosphine, in the absence of steric repulsion, the H–P–H angle is only slightly greater than 93° (Burrus, Jache & Gordy, 1954), which is close to the theoretical value for p bonding. It is not known whether the flattening of the system in PR_3 is on account of a change in the hybridization of the P atoms, as a result of certain π -bonding interactions in the molecule, or caused by steric repulsions. It has been

noticed (Bent, 1961) that, in the absence of obvious steric effects, the valence angle R–P–R appears to be correlated with the electronegativity of R.

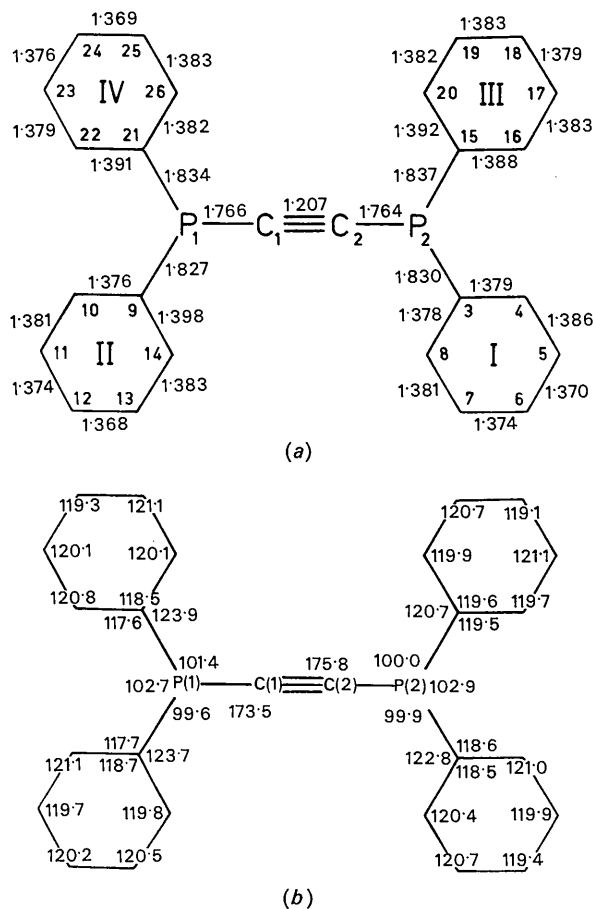


Fig. 1. (a) Bond lengths of bis(diphenylphosphino)acetylene (Å). The labelling of the atoms is indicated. (b) Bond angles of $(C_6H_5)_2PC≡CP(C_6H_5)_2$ in degrees.

Table 8. P–C bond lengths

Compound	P–C (aryl)	Method	Reference
1,2,3-Triphenyl-1,2,3-triphosphindane	1.825 (0.008) Å	XR	Daly (1966b)
$P(C_6H_5)_3$	1.828 (0.003)	XR	Daly (1964a)
$(PC_6H_5)_5$	1.843 (0.014)	XR	Daly (1964b)
$(PC_6H_5)_6$ (trigonal)	1.843 (0.012)	XR	Daly (1966a)
$(PC_6H_5)_6$ (trigonal)	1.843 (0.007)	XR	Daly (1965)
$P(C_6H_5)_2(C_6H_4Br)$	1.83	XR	Kuhn & Plieth (1966)
	P–C (alkyl)		
$(CH_3)_3P$	1.841 (0.003) Å	MW	Lide & Mann (1958)
$(CH_3)_3P$	1.847 (0.003)	ED	Bartell & Brockway (1960)
$(CH_3)_2PH$	1.853 (0.003)	ED	Bartell (1960)
CH_3PH_2	1.858 (0.003)	ED	Bartell (1960)
$(PC_6H_{11})_4$	1.874 (0.002)	XR	Bart (1969)
$(PCF_3)_4$	1.867 (0.014)	XR	Palenik & Donohue (1962)
$(PCF_3)_5$	1.906 (0.020)	XR	Spencer & Lipscomb (1961)
$P(CF_3)_3$	1.937 (0.017)	ED	Bowen (1954)

The P-C≡C angles are somewhat different from 180°. The P-C≡C-P part of the molecule is bent twice, giving it a slight *trans*-like aspect. Similar deviations from 180° were found in P(CCC₆H₅)₃ (Mootz & Sassmannshausen), P(CN)₃ (Emerson & Britton, 1964), As(CN)₃ (Emerson & Britton, 1963) and (CH₃)₂AsCN (Camerman & Trotter, 1963). In the latter three cases it is a likely possibility that non-linearity at the carbon atoms is a consequence of a non-linear intermolecular interaction of the type C≡N...P(As).

The P-C≡C bond angles differ significantly from 120° [see Fig. 1(b) and Table 7]. The systematic difference in the two P-C≡C angles from a trivalent phosphorus atom to a phenyl group has been noted before in the polyphenylcyclophosphines (Daly, 1964*a,b*, 1965, 1966*a*) as well as in 1,2,3-triphenyl-1,2,3-triphosphaindane (Daly, 1966*b*). The distortion was described there in terms of an attraction between the lone pair on the phosphorus atom and the hydrogen atom closest to the lone pair, provided that the lone pair occupies an approximately tetrahedral position with respect to the other phosphorus valences. For the present case a simple explanation may be found in the non-bonded intramolecular distances of the *ortho* carbon and hydrogen atom towards the central part of the molecule (see Table 9). The observed distortions are such that the largest angle is found at the side where the *ortho* carbon atom is nearest to the *sp* carbon atoms. The differences in P-C≡C angular values for rings I to IV are 4.2°, 6.0°, 1.2° and 6.2° ($\sigma=0.26^\circ$). It is remarkable that for ring III, where the smallest discrepancy is found, the only large and significant out-of-plane deviation of the exocyclic P-C is observed.

Apart from the non-bonded intramolecular distances mentioned above no other remarkable features were found. The set of most important contacts of less than 4.0 Å is given in Table 9.

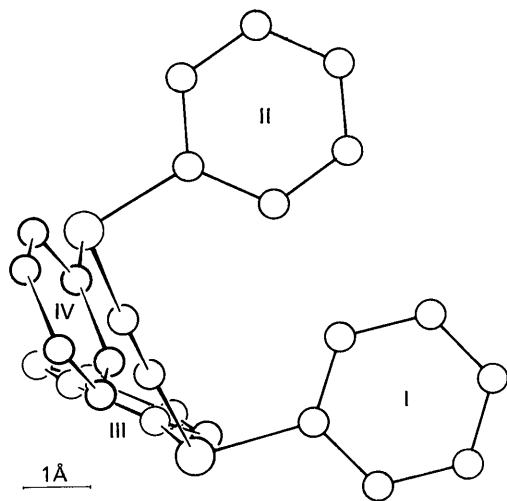


Fig. 2. Bis(diphenylphosphino)acetylene. The molecule is viewed perpendicular to the least-squares plane of ring I.

Table 9. Non-bonded intramolecular distances

P(1)—C(10)	2.75 Å	P(2)—C(4)	2.77 Å
P(1)—C(14)	2.85	P(2)—C(8)	2.83
P(1)—C(22)	2.77	P(2)—C(16)	2.80
P(1)—C(26)	2.85	P(2)—C(20)	2.81
P(1)—H(10)	2.90	P(2)—H(4)	2.85
P(1)—H(14)	2.88	P(2)—H(8)	2.92
P(1)—H(22)	2.80	P(2)—H(16)	2.91
P(1)—H(26)	3.02	P(2)—H(20)	2.96
C(1)—C(14)	3.09	C(2)—C(8)	3.06
C(1)—C(26)	3.02	C(2)—C(20)	3.06
C(1)—H(14)	2.64	C(2)—H(8)	2.71
C(1)—H(26)	2.60	C(2)—H(20)	2.73
H(14)—H(26)	3.01	H(4)—H(16)	3.32
	H(8)—H(14)	3.15	

Geometry of the molecule

The molecule possesses a pyramidal configuration around both phosphorus atoms. The benzene rings have unequal rotations about the P-C bonds and the molecule therefore has no symmetry, which no doubt leads to a finite dipole moment. In the crystal all approach to molecular symmetry is destroyed, possibly as a result of the requirements of overlap of the *d* orbitals of the phosphorus atoms with the mutually perpendicular π orbitals of the acetylenic group. The two acetylenic orbitals may combine with the same type of *d* orbitals on each phosphorus atom. We were not able to detect C≡C absorption in the infrared using the potassium bromide pressed disk technique. On the other hand, Voskuil (1963) reports a 2085 cm⁻¹ frequency for (t-Bu)₂P-C≡C-P(t-Bu)₂, from which he concludes that the molecule lacks symmetry because of steric hindrance.

A few interesting torsion angles are: C(3) P(2) P(1) C(9) 5.7°; C(3)P(2)P(1)C(21) 99.4°; C(15)P(2)P(1)C(9) 99.1° and C(15)P(2)P(1)C(21) 155.8°. Accordingly the torsion angle between the directions of the polar axes of the lone pair orbitals is approximately 90°. It is felt that the geometry as determined might well be a characteristic property of the molecule, which is not caused by casual packing effects in the crystalline state. It would be of interest to study the chelating properties of this ditertiary phosphine, especially in view of its geometry.

The molecular configuration can best be seen in Fig. 2, where one is looking down the normal to ring I. This projection requires transformation of a set of orthogonal axes (a_0, b_0, c_0), defined in Table 10, to another orthogonal set (a_1, b_1, c_1) such that [c_1] coincides with the normal to the least-squares plane through ring I, [b_1] is perpendicular to [c_1] and [c_0] while [a_1] is perpendicular to [b_1] and [c_1]. The transformed coordinates (x_1, y_1, z_1) then are

$$x_1 = -\frac{ln}{q} x_0 - \frac{mn}{q} y_0 + qz_0$$

$$y_1 = -\frac{m}{q} x_0 - \frac{l}{q} y_0$$

$$z_1 = -lx_0 + my_0 + nz_0$$

Table 10. *Weighted least-squares equations in their normal form of the mean planes through groups of atoms and deviations of the atoms from these planes (Å) according to Schomaker et al.*

(i) Equation: $lX_0 + mY_0 + nZ_0 = p$, where X_0, Y_0, Z_0 are orthogonal coordinates in Å, which are related to the monoclinic coordinates in the following way:

$$X_0 = X + Z \cos \beta$$

$$Y_0 = Y$$

$$Z_0 = Z \sin \beta$$

Plane	l	m	n	p
Ring I	-0.4411	0.8524	-0.2809	0.2740
Ring II	-0.4718	0.8052	-0.3593	3.0047
Ring III	-0.8972	-0.2556	0.3601	0.1443
Ring IV	-0.5836	0.2493	0.7729	3.2491

(ii) Deviations from the planes

Ring I		Ring II		Ring III		Ring IV	
	Δ		Δ		Δ		Δ
C(3)	-0.002*	C(9)	0.002*	C(15)	0.005*	C(21)	0.006*
C(4)	0.003*	C(10)	-0.004*	C(16)	-0.001*	C(22)	-0.001*
C(5)	-0.001*	C(11)	0.000*	C(17)	-0.002*	C(23)	-0.003*
C(6)	-0.002*	C(12)	0.005*	C(18)	0.002*	C(24)	0.002*
C(7)	0.003*	C(13)	-0.007*	C(19)	0.002*	C(25)	0.005*
C(8)	-0.001*	C(14)	0.003*	C(20)	-0.005*	C(26)	-0.009*
P(2)	0.023	P(1)	-0.030	P(2)	-0.138	P(1)	0.003
H(4)	0.052	H(10)	-0.181	H(16)	0.050	H(22)	0.198
H(5)	0.037	H(11)	0.074	H(17)	-0.011	H(23)	0.038
H(6)	-0.067	H(12)	0.055	H(18)	-0.052	H(24)	-0.048
H(7)	-0.046	H(13)	0.046	H(19)	0.079	H(25)	0.063
H(8)	-0.088	H(14)	-0.040	H(20)	-0.053	H(26)	-0.046

The atoms denoted by asterisks determine the plane.

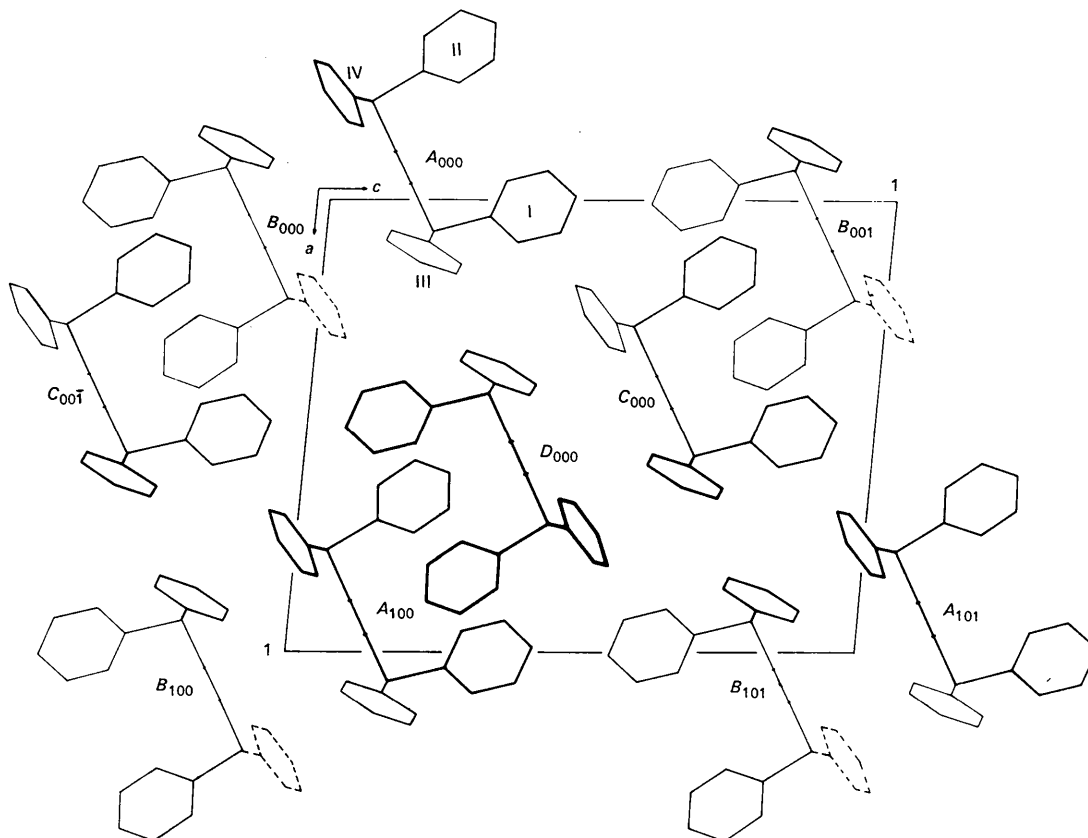


Fig. 3. [010] projection of the structure of bis(diphenylphosphino)acetylene.

where $q^2 = 1 - n^2$, and l , m , and n are the direction cosines, referred to a_0 , b_0 , c_0 , of the normal to the least-squares plane. It is seen that rings I and II are in *cis* position with respect to P--P, with a rotation around the P--C bonds, giving a perpendicular distance of 2.95 Å between their almost parallel planes. (Angle ring I/II = $5^\circ 28'$). Rings III and IV are in a *trans* configuration. The angles between the planes of the rings are: I-III = $85^\circ 36'$, I-IV = $75^\circ 22'$, II-III = $84^\circ 57'$, II-IV = $78^\circ 33'$, III-IV = $42^\circ 33'$. The angles of the P--P direction with the rings I to IV are $35^\circ 41'$, $40^\circ 12'$, $35^\circ 27'$ and $8^\circ 6'$, respectively.

The carbon atoms show no significant deviations from the mean planes (Table 10); among the hydrogen atoms only H(10) and H(22) are considerably out of these planes. The P--C bonds, except P(1)--C(21), are slightly tilted out of the planes of the benzene rings: the deviations of P(1) from ring II and P(2) from rings I and III are significant (Table 10). Especially the latter deviation is quite large (0.138 Å) and outstanding with respect to the others.

Packing arrangement

The packing arrangement is illustrated in the *b*-axis projection (Fig. 3). The symbols *A*, *B*, *C*, *D* are used to designate molecules with coordinates x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ and $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ respectively. In this notation $B_{\alpha\beta\gamma}$ stands for fractional coordinates $\alpha - x, \beta - y, \gamma - z$. The molecules are stacked along the *b* axis such that the protruding rings III and IV contact with molecules shifted along [0 $\bar{1}$ 0] and [010]. Molecules of *D* type are in a position which allows a reasonably dense stacking of the rings I and II of *A* type molecules without directly superimposing the rings. The same holds of course for the packing of *B* and *C* molecules. Rings III and IV of *A*, *B* and *C*, *D* type molecules, related by the centres of symmetry at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ respectively, are pointing in the same direction. All intermolecular contacts, arbitrarily limited at the sum of the interatomic radii plus 0.4 Å up to a maximum of 4.1 Å, were calculated. Of the 106 independent van der Waals contacts within these limits the shortest ones for each category of atom are: P--P none; P--C 3.64; P--H 3.10; C--C 3.67; C--H 2.75; H--H 2.44 Å. The molecules are packed by ordinary van der Waals forces.

All the calculations were performed on an Elliott 803B computer with the aid of the programming system devised by Daly, Stephens & Wheatley.

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