889. *The Crystal and Molecular Structure of a Trigonal Form of Phosphobenzene B*, $(PC_6H_5)_6$

By J. J. Daly

Crystalline phosphobenzene B is polymorphic. The structure of one of these forms has been determined. The axes of the trigonal unit cell are $a = 13{\cdot}026$, $c = 11{\cdot}547$ Å; the space group is $P\bar{3}c1$ and the required molecular symmetry is $\bar{3}$ (C_{3i}). The molecule is hexameric, $(PC_6H_5)_6$, with a six-membered ring of phosphorus atoms in the chair form with phenyl groups occupying the equatorial positions.

The existence of at least three polyphosphines of formula $(PC_6H_5)_n$ is well established.[1,2] The structure of one of them, phosphobenzene A, has been determined [3,4] and it is known to be pentameric in the solid state $(PC_6H_5)_5$. Various values for n in phosphobenzene B (m. p. 190°) have been suggested, the highest from other methods, chiefly in solution, being four. In the solid state, the trigonal form of phosphobenzene B is hexameric ($n = 6$). Three other crystalline forms of this compound are known to exist and have been described.[2,3] This Paper describes the structure of the trigonal modification.

Experimental

$C_{36}H_{30}P_6$. $M = 648{\cdot}5$. Trigonal. $a = 13{\cdot}026$, $c = 11{\cdot}547$ Å. $U = 1696{\cdot}8$ Å^3. $Z = 2$. $D_c = 1{\cdot}269$, $D_m = 1{\cdot}265$ g./c.c. Space group $P\bar{3}c1$ (D_{3d}, No. 165). The cell constants were determined from precession photographs recorded with Cu-K_α radiation. Recrystallisation from tetrahydrofuran gave at least two crystalline forms in one batch, one triclinic [2] and one trigonal. The trigonal crystals were in the form of hexagonal prisms elongated along c; many of these crystals exhibit twinning, which superimposes the *hkil* and the *khil* spectra, and this superposition, when the twins are of the same size, gives the reciprocal lattice the apparent symmetry $6/mmm$. The true Laue symmetry is $\bar{3}m$, in which the intensities *hkil* and *khil* are not necessarily equal. The relative size of the twins could be estimated by comparing the intensities of the $13\bar{4}1$ and $31\bar{4}1$ diffraction spectra; these intensities were in the ratio 1 : 1600 for the crystal used in the analysis. The crystals are quite stable to the atmosphere but turn milky on exposure to X-rays. The intensities were measured with the aid of a Hilger and Watts automatic linear diffractometer.[5] Balanced filters were used with Mo-K_α radiation; results were recorded up to $\theta \sim 27°$. The oscillation axis was c and 1397 independent intensities were measured: of these 518 were adjudged to be weak enough to be classified as unobserved, leaving 879 planes with which the analysis was carried out. The intensities were converted into $|F_o|$ values and, in the initial stages, the layers were assumed to be on the same relative scale; the layers were rescaled later ($R = 0{\cdot}20$) by equating $\Sigma|F_o|$ to $\Sigma|F_c|$ for each value of l. The systematic absences were *hh*0*l* absent for l odd, and so the possible space groups were $P\bar{3}c1$ and $P3c1$ with required molecular symmetries $\bar{3}(C_{3i})$ or $32(D_3)$ for the former and $3(C_3)$ for the latter.

Determination of the Structure and Refinement

The $N(z)$ test,[6] though not strictly applicable in view of the probable centric distribution of the heavy phosphorus atoms, was applied to the intensity values. The results (see Table 1)

[1] H. Köhler and A. Michaelis, *Chem. Ber.*, 1877, **10**, 807; Th. Weil, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, 1952, **35**, 616; J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, 1957, **22**, 385; W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2296; F. Pass and H. Schindlbauer, *Monatsh.*, 1959, **90**, 148; L. Horner, H. Hoffmann, and P. Beck, *Chem. Ber.*, 1958, **91**, 1583; P. R. Bloomfield and K. Parvin, *Chem. and Ind.*, 1959, 541; W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 1963, **85**, 2462; E. Wiberg, M. Van Gehman, and G. Müller-Schiedmeyer, *Angew. Chem.*, 1963, **75**, 814.

[2] J. J. Daly and L. Maier, *Nature*, 1965, in the press.

[3] J. J. Daly and L. Maier, *Nature*, 1964, **203**, 1167.

[4] J. J. Daly, *J.*, 1964, 6147.

[5] U. W. Arndt and D. C. Phillips, *Acta Cryst.*, 1961, **14**, 807.

[6] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

were encouraging, as the values fitted closely to the error function expected from a centric distribution of atoms. The space group $P\bar{3}c1$ was accordingly accepted provisionally and refinement in it was successful.

Since the molecule possesses $\bar{3}$ symmetry, it is only necessary to determine the position of one phosphorus atom and one phenyl group. The position of the phosphorus atom was found from a three-dimensional sharpened Patterson synthesis. The X and Y co-ordinates of C1 and C4 were then estimated from a model, leaving the orientation of the phenyl group

TABLE 1

Results of $N(z)$ test

Z	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
$(PPh)_6$ $N(z)$	26·0	36·0	44·0	49·5	52·0	57·0	62·0	64·0	67·0	69·0
erf$(z/2)^2$ (centric)	24·8	34·5	41·9	47·4	52·1	56·1	59·7	62·3	65·7	68·3
1-exp$(-z)$ (acentric) ...	9·5	18·1	25·9	33·0	39·4	45·1	50·3	55·1	59·3	63·2

undetermined, and the three atoms were then used to calculate the electron density of the [c]-axis projection. This map showed the positions of the four remaining carbon atoms and structure factors were again calculated: $R(hk0)$ was 0·25 at this stage. The model was then used to estimate the Z co-ordinates of the light atoms and a three-dimensional least-squares refinement was started. The trial structure was refined successfully till R (for 879 planes) had fallen to 0·072 and R' (for 876 planes) to 0·0066; the hydrogen atoms were ignored.

$$R = \Sigma|\Delta|/\Sigma|F_o|;\ R' = \Sigma\, w\Delta^2/\Sigma\, wF_o^2$$

Anisotropic temperature factors were applied to each atom in the form

$$\exp -\ 2\pi^2\,\Sigma(h^2a^{*2}\,U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13}).$$

A constant weight was applied to all observed structure factors; planes were not included in the least squares totals or R' if $3|F_c|$ was less than $|F_o|$ and there were three such planes in the final least-squares cycle. Refinement was stopped when the maximum drift was less than 0·2 of the corresponding standard deviation. The calculations were carried out on our Elliott 803B computer by using the programming system of Daly, Stephens, and Wheatley.[7]

RESULTS AND DISCUSSION

The results of the analysis are summarised in Tables 2—5. The atomic co-ordinates and standard deviations are given in Table 2, the thermal parameters and standard

TABLE 2

Co-ordinates and standard deviations in Å (hexagonal axes)

	X	Y	Z		X	Y	Z
P	1·4680(17)	2·1429(18)	0·5918(14)	C3	3·9021(90)	5·6974(89)	−2·1322(96)
				C4	4·9128(90)	6·8729(82)	−1·2103(114)
C1	2·8002(66)	3·9949(65)	−0·2198(62)	C5	4·8555(105)	6·6381(94)	0·1442(108)
C2	2·8141(78)	4·2354(78)	−1·6049(69)	C6	3·7800(85)	5·1792(86)	0·6507(87)

TABLE 3

Thermal parameters and standard deviations in Å² (hexagonal axes)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
P ...	0·0452(8)	0·0489(8)	0·0411(6)	0·0491(14)	−0·0093(13)	−0·0048(12)
C1 ...	0·0407(31)	0·0429(32)	0·0708(38)	0·0416(53)	−0·0131(56)	0·0000(56)
C2 ...	0·0668(43)	0·0574(41)	0·0758(45)	0·0606(72)	0·0386(69)	0·0402(71)
C3 ...	0·0746(52)	0·0699(51)	0·1318(72)	0·0841(89)	0·0645(96)	0·0707(98)
C4 ...	0·0654(49)	0·0471(42)	0·2145(109)	0·0609(78)	0·0310(108)	0·0310(118)
C5 ...	0·0917(65)	0·0529(45)	0·1648(97)	0·0316(92)	−0·0137(103)	−0·0328(126)
C6 ...	0·0658(47)	0·0659(46)	0·1055(60)	0·0481(78)	−0·0519(86)	−0·0352(86)

[7] J. J. Daly, F. S. Stephens, and P. J. Wheatley, Monsanto Research S.A., 1963, *Final Report No.* 52.

deviations in Table 3, the bond lengths and angles with their standard deviations in Table 4, and the final values of F_o, F_c, and Δ are listed in Table 5. The [*c*]-axis projection of the molecule in Figure 1 shows the labelling of the atoms and some non-bonded intramolecular distances: Figure 2 represents the packing of the molecules in the unit cell.

TABLE 4

Bond lengths (in Å) and angles (in degrees) with their corresponding standard deviations

P–P	2·237(5)	P–C1–C2	123·13(51)
P–C1	1·843(7)	P–C1–C6	115·14(53)
C1–C2	1·405(10)	C6–C1–C2	121·70(65)
C2–C3	1·417(12)	C1–C2–C3	118·70(69)
C3–C4	1·437(13)	C2–C3–C4	117·93(80)
C4–C5	1·371(14)	C3–C4–C5	122·79(89)
C5–C6	1·405(13)	C4–C5–C6	118·61(90)
C6–C1	1·400(11)	C5–C6–C1	120·20(78)
Average C–C	1·406(20) *	Average C–C–C	119·99(199) *

* Standard deviation of individual values from the average.

P′–P–P″ 94·58(9); P′–P–Cl 97·05(22); P″–P–Cl 99·92(22)

The successful refinement in the space group $P\bar{3}c1$ shows that the molecule has symmetry $\bar{3}$ (C_{3i}) with a six-membered ring of phosphorus atoms in the chair form: to each phosphorus atom is attached one phenyl group in what, by analogy with cyclohexane, may be described as the equatorial position. A six-membered ring of phosphorus atoms

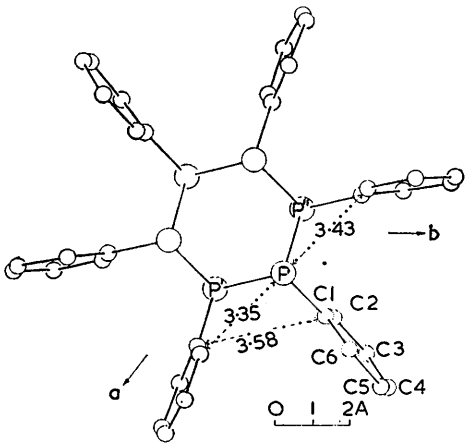

FIGURE 1. The [*c*]-axis projection of the molecule showing the labelling of the atoms and some non-bonded intramolecular contacts

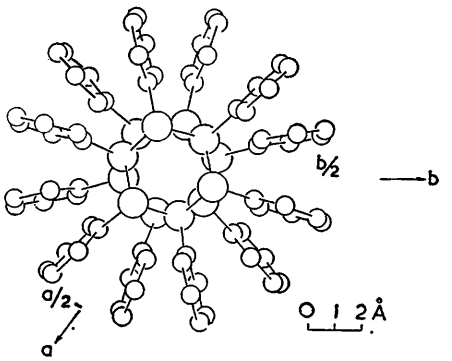

FIGURE 2. Packing in the unit cell: the [*c*]-axis projection

is not common, and has been found previously only in elemental black phosphorus [8] and in the inorganic salt [9] $(CsPO)_6,xH_2O$; in the latter case, the phosphorus atoms are bonded to two oxygen atoms as well as to two phosphorus atoms. In the $(PO_2)_6$ ion the average P–P–P–P torsion angle is 68·6°, while the average P–P–P angle is 105·6°; the phosphorus ring (in the chair form) is therefore much flatter than that found in $(PC_6H_5)_6$.

[8] R. Hultgren, N. S. Gingrich, and B. E. Warren, *J. Chem. Phys.*, 1935, **3**, 351.
[9] J. Weiss, *Z. anorg. u. allgem. Chem.*, 1960, **306**, 30.

TABLE 5

h	k	l	$100F_o$	$100F_c$	100Δ	h	k	l	$100F_o$	$100F_c$	100Δ
1	1	0	-969	-786	-183	2	11	1	984	1046	-62
2	0	0	-1235	-1030	-205	2	12	1	604	722	-118
2	1	0	992	709	283	3	1	1	7198	6594	604
2	2	0	-6105	-5356	-749	3	2	1	5674	5391	283
3	0	0	-8511	-7876	-635	* 3	3	1	299	42	257
3	1	0	1098	458	640						
3	2	0	-3673	-3395	-278	3	4	1	-1641	-1269	-372
3	3	0	-3522	-3140	-382	3	5	1	-4676	-4622	-54
4	0	0	-10612	-10269	-343	3	6	1	-5307	-5292	-15
4	1	0	-601	-507	-94	3	7	1	-2283	-2287	4
4	2	0	1657	1303	354	3	8	1	1205	1134	71
4	3	0	2012	2116	-104	3	10	1	2040	2094	-54
4	4	0	2382	2195	187	3	11	1	1059	1071	-12
5	0	0	-6663	-6372	-291	4	1	1	6083	5824	259
5	2	0	5415	5140	275	4	2	1	2479	2187	292
5	3	0	3695	3635	60	4	3	1	-1072	-698	-374
5	4	0	2115	1985	130	4	4	1	414	553	-139
5	5	0	-1725	-1821	96	4	5	1	-873	-762	-111
6	0	0	888	1102	-214	4	6	1	-515	-548	33
6	1	0	376	351	25	4	7	1	1800	1762	38
6	2	0	3539	3582	-43	4	8	1	-536	-233	-305
6	3	0	1361	1264	97	4	9	1	585	403	182
6	4	0	-1495	-1664	169	5	1	1	555	590	-35
6	5	0	-487	-484	-3	5	2	1	7217	6938	279
6	6	0	-1942	-2084	142	5	3	1	3779	3529	250
7	0	0	838	730	108	5	4	1	2338	2246	92
7	1	0	-1012	-1109	97	5	6	1	943	873	70
7	2	0	-666	-692	26	5	7	1	1133	1235	-102
7	5	0	-1532	-1709	177	5	10	1	-795	-704	-91
7	6	0	-1657	-1834	177	5	11	1	-1007	-1190	183
8	1	0	-2229	-2592	363	6	1	1	659	717	-58
8	2	0	-1228	-1378	150	6	2	1	4141	3986	155
8	3	0	-597	-710	113	6	3	1	3502	3642	-140
8	4	0	451	549	-98	6	4	1	-515	-512	-3
9	0	0	-920	-988	68	6	5	1	712	663	49
9	1	0	516	591	-75	6	6	1	1543	1434	109
9	2	0	-1567	-1621	54	6	7	1	1050	1182	-132
9	3	0	1251	1422	-171	6	9	1	-547	-528	-19
9	4	0	1189	1316	-127	6	10	1	-1243	-1322	79
9	5	0	558	364	194	7	1	1	627	497	130
10	1	0	-1058	-964	-94	7	2	1	2473	2592	-119
10	3	0	1287	1326	-39	7	3	1	1361	1245	116
10	4	0	1446	1594	-148	7	4	1	-1260	-1356	96
10	5	0	1159	1158	1	7	5	1	1076	863	213
11	0	0	-1214	-1297	83	7	7	1	480	543	-63
11	2	0	1272	1346	-74	7	9	1	-550	-700	150
11	3	0	1351	1387	-36	8	1	1	-428	-364	-64
11	4	0	1121	1201	-80	8	2	1	-623	-791	168
12	0	0	-897	-1055	158	8	3	1	-685	-621	-64
14	0	0	-547	-583	36	8	6	1	539	522	17
14	1	0	-608	-857	249	9	1	1	-567	-557	-10
1	1	1	-3750	-3678	-72	9	2	1	-2583	-2672	89
1	2	1	-9119	-8923	-196	9	3	1	-1159	-1108	-51
1	3	1	567	790	-223	9	4	1	-601	-493	-108
1	4	1	-1185	-1268	83	10	1	1	-1691	-1671	-20
1	5	1	1038	1131	-93	10	2	1	-2625	-2687	62
1	6	1	-2555	-2599	44	10	3	1	-1212	-1395	183
1	7	1	-3376	-3478	102	10	5	1	570	672	-102
1	8	1	-1879	-1908	29	10	6	1	827	929	-102
1	9	1	529	441	88	11	1	1	-1540	-1646	106
1	10	1	657	767	-110	11	2	1	-1173	-1306	133
1	11	1	1203	1186	17	11	3	1	-1361	-1510	149
2	1	1	11176	12412	-1236	11	4	1	539	630	-91
2	2	1	-2112	-1407	-705	11	5	1	1053	1154	-101
2	3	1	-1712	-1834	122	12	2	1	-622	-499	-123
2	4	1	-2029	-2020	-9	13	4	1	616	301	315
2	5	1	-5920	-5915	-5	0	1	2	3060	3644	-584
2	6	1	-4419	-4110	-309	0	2	2	-321	-176	-145
2	7	1	-5024	-5128	104	0	3	2	-2257	-1902	-355
2	8	1	463	531	-68	0	4	2	3193	2702	491
2	10	1	1359	1331	28	0	5	2	1318	923	395

TABLE 5 (*Continued*)

	h	*k*	*l*	$100F_o$	$100F_c$	100Δ	*h*	*k*	*l*	$100F_o$	$100F_c$	100Δ
	0	6	2	-549	-380	-169	7	0	2	-1208	-1093	-115
	0	7	2	-1462	-1389	-73	7	1	2	659	651	8
	0	8	2	-760	-875	115	7	2	2	2452	2504	-12
	0	9	2	-2317	-2293	-24	7	3	2	1179	1045	134
	0	10	2	1975	1803	172	7	4	2	-461	-638	177
	0	11	2	-448	-301	-147	7	6	2	-1280	-1278	-2
	0	14	2	-1313	-1379	68	7	7	2	-831	-972	141
	0	15	2	-1072	-1284	212	7	9	2	-700	-815	115
	1	0	2	10360	12536	-2176	8	0	2	1081	1036	45
	1	1	2	2246	2051	195	8	1	2	-1013	-993	-20
*	1	2	2	-388	-123	-265	8	2	2	-397	-302	-95
							8	3	2	-887	-817	-70
	1	3	2	3194	3148	46	8	4	2	437	407	30
	1	4	2	925	1034	-109	8	5	2	-873	-843	-30
	1	5	2	-519	-562	43	9	0	2	-665	-796	131
	1	7	2	-370	-353	-17	9	1	2	-1582	-1619	37
	1	8	2	-2514	-2379	-135	9	2	2	-1780	-1872	92
	1	9	2	819	803	16	9	3	2	512	482	30
	1	13	2	-616	-705	89	9	4	2	857	849	8
	1	14	2	-1056	-1058	2	9	5	2	593	734	-141
	2	0	2	3737	3314	423	10	0	2	-1064	-1111	47
	2	1	2	-5146	-4851	-295	10	1	2	-1165	-1307	142
	2	2	2	-3691	-3724	33	10	2	2	-1032	-1069	37
	2	4	2	997	1211	-214	10	3	2	1154	1322	-168
	2	5	2	3474	3252	222	10	4	2	1306	1554	-248
	2	6	2	1168	1150	18	10	5	2	640	701	-61
	2	7	2	-2797	-2693	-104	11	0	2	-660	-808	148
	2	8	2	-1829	-1910	81	11	1	2	-868	-755	-113
	2	9	2	897	895	2	11	3	2	862	849	13
	2	10	2	848	1019	-171	11	4	2	649	959	-310
	2	11	2	784	876	-92	11	6	2	579	452	127
	2	13	2	-596	-483	-113	12	0	2	-1185	-1125	-60
	3	0	2	-5245	-5795	550	1	1	3	2346	2026	320
	3	1	2	-4595	-4718	123	1	2	3	1518	1374	144
	3	2	2	-4738	-4325	-413	1	3	3	1954	1751	203
	3	4	2	2589	2444	145	1	4	3	-746	-700	-46
	3	5	2	1179	1230	-51	1	5	3	524	418	106
	3	6	2	-495	-544	49	1	6	3	-3901	-3890	-11
	3	7	2	-1573	-1491	-82	1	7	3	-3104	-3096	-8
	3	9	2	1585	1688	-103	1	8	3	-1469	-1376	-93
	3	10	2	1203	1318	-115	1	10	3	-850	-813	-37
	3	11	2	1159	1280	-121	2	1	3	1263	1500	-237
	4	0	2	-12339	-12714	375	2	2	3	3916	3753	163
	4	1	2	-5554	-5139	-415	2	3	3	5612	5283	329
	4	2	2	-1442	-1287	-155	2	5	3	-2023	-2157	134
	4	3	2	2144	2096	48	2	6	3	-4204	-4034	-170
	4	4	2	2057	1924	133	2	7	3	-5128	-5103	-25
	4	5	2	2084	1938	146	2	8	3	-1902	-1895	-7
	4	6	2	-965	-877	-88	2	9	3	-735	-857	122
	4	8	2	-877	-888	11	2	11	3	680	596	84
	4	9	2	1321	1243	78	2	12	3	518	601	-83
	4	10	2	949	897	52	2	14	3	571	356	215
	4	11	2	1310	1127	183	3	1	3	3028	3100	-72
	4	12	2	542	515	27	3	2	3	7091	6807	284
	5	0	2	-6929	-6649	-280	3	3	3	-677	-379	-298
	5	1	2	2180	1898	282	3	4	3	-1544	-1618	74
	5	2	2	3555	3503	52	3	5	3	-2417	-2396	-21
	5	3	2	2419	2267	152	3	6	3	-2895	-2776	-119
	5	4	2	1865	1875	-10	3	7	3	-2766	-2770	4
	5	5	2	-1254	-1235	-19	3	8	3	568	402	166
	5	6	2	-838	-719	-119	3	10	3	565	412	153
	5	7	2	-1732	-1666	-66	4	1	3	5074	4919	155
	5	11	2	674	640	34	4	2	3	1215	1279	-64
	6	0	2	911	737	174	4	4	3	706	600	106
	6	1	2	1289	1385	-96	4	5	3	-1107	-1086	-21
	6	2	2	4120	3926	194	4	6	3	-570	-568	-2
	6	3	2	1711	1684	27	4	7	3	1275	1220	55
	6	4	2	-784	-865	81	4	8	3	608	664	-56
	6	5	2	-1186	-1158	-28	5	1	3	3298	3287	11
	6	6	2	-1091	-1096	5	5	2	3	3268	3262	6
	6	7	2	-1481	-1491	10	5	3	3	1321	1274	47

TABLE 5 (*Continued*)

h	*k*	*l*	$100F_o$	$100F_c$	100Δ	*h*	*k*	*l*	$100F_o$	$100F_c$	100Δ
5	4	3	830	725	105	2	10	4	948	885	63
5	6	3	2211	2266	-55	3	0	4	-4817	-4044	-573
5	7	3	2280	2304	-24	3	1	4	-5527	-5079	-448
5	8	3	662	686	-24	3	2	4	-1616	-1788	170
5	11	3	-608	-753	145	3	3	4	290	357	-67
6	4	3	1156	1203	-47	3	5	4	-922	-898	-24
6	5	3	2058	2221	-163	3	6	4	-1163	-1240	77
6	6	3	2694	2609	85	3	7	4	-1446	-1339	-107
6	7	3	2023	2146	-123	3	9	4	1113	1092	21
6	9	3	-798	-940	142	3	10	4	905	928	-23
6	10	3	-796	-846	50	4	0	4	-9326	-9664	338
7	1	3	-862	-788	-74	4	1	4	-4976	-4987	11
7	2	3	-763	-742	-21	4	2	4	-1344	-1281	-63
7	5	3	1526	1594	-68	4	3	4	1735	1837	-102
7	6	3	1457	1541	-84	4	4	4	394	387	7
7	7	3	981	1049	-68	4	6	4	-1061	-924	-137
7	8	3	-893	-987	94	4	7	4	-1055	-1186	131
7	9	3	-747	-808	61	4	9	4	1261	1166	95
8	1	3	-877	-865	-12	4	11	4	622	501	121
8	2	3	-1295	-1276	-19	5	0	4	-3580	-3440	-140
8	3	3	-1356	-1438	82	5	1	4	-1446	-1519	73
8	4	3	-480	-474	-6	5	3	4	2625	2600	25
8	5	3	567	524	43	5	4	4	698	685	13
8	6	3	527	421	106	5	5	4	-391	-329	-62
8	7	3	-533	-277	-256	6	0	4	1050	1024	26
8	8	3	-515	-564	49	6	1	4	1006	992	14
9	1	3	-2072	-2261	189	6	2	4	3167	3056	111
9	2	3	-2714	-2820	106	6	3	4	2303	2283	20
9	3	3	-807	-736	-71	6	7	4	-552	-624	72
9	8	3	-605	-606	1	6	8	4	-770	-707	-63
10	1	3	-1845	-1990	145	7	0	4	1757	1739	18
10	2	3	-1728	-1857	129	7	1	4	2318	2333	-15
10	3	3	-845	-870	25	7	2	4	2581	2522	59
11	1	3	-1310	-1362	52	7	3	4	443	407	36
11	2	3	-1293	-1330	37	7	4	4	417	484	-67
11	3	3	-798	-649	-149	7	6	4	-596	-548	-48
0	1	4	5521	5243	278	8	0	4	691	778	-87
0	2	4	6027	5902	125	8	4	4	513	322	191
0	3	4	2908	2373	535	8	9	4	-623	-556	-67
0	4	4	8827	8592	235	9	0	4	-882	-1048	166
0	5	4	1480	1715	-235	9	1	4	-1102	-1114	12
0	6	4	-2249	-2115	-134	9	2	4	-952	-824	-128
0	7	4	-1786	-1838	52	9	3	4	-582	-650	68
0	8	4	-1529	-1699	170	9	5	4	633	685	-52
0	9	4	-734	-622	-112	10	0	4	-1029	-1150	121
0	10	4	2393	2241	152	10	1	4	-1306	-1253	-53
0	11	4	1480	1626	-146	10	2	4	-1062	-885	-177
0	13	4	-1252	-1257	5	11	0	4	-1760	-1967	207
0	14	4	-1044	-1094	50	11	1	4	-1113	-1173	60
1	0	4	-279	-310	31	13	0	4	885	924	-39
1	1	4	679	690	-11	13	1	4	773	777	-4
1	2	4	341	352	-11	14	0	4	1044	1245	-201
1	3	4	2688	2769	-81	14	1	4	637	592	45
1	4	4	5377	5017	360	1	1	5	3875	3835	40
1	5	4	1029	1320	-291	1	2	5	230	210	20
1	7	4	-1911	-1874	-37	1	3	5	874	978	-104
1	8	4	-1634	-1580	-54	1	4	5	951	1063	-112
1	9	4	689	547	142	1	5	5	344	357	-13
1	10	4	1489	1352	137	1	6	5	-446	-416	-30
1	11	4	622	664	-42	1	7	5	-986	-1109	123
1	13	4	-743	-677	-66	1	8	5	-1221	-1196	-25
1	14	4	-888	-927	39	1	9	5	-1217	-1296	79
2	0	4	-4638	-4505	-133	1	10	5	-1105	-997	-108
2	1	4	-2139	-2013	-126	1	12	5	-504	-395	-109
2	2	4	-1410	-1431	21	2	1	5	2979	2926	53
2	3	4	1290	1013	277	2	2	5	5354	5328	26
2	4	4	1442	1643	-201	2	3	5	4519	4308	211
2	5	4	888	981	-93	2	4	5	968	1067	-99
2	6	4	-1370	-1387	17	2	5	5	720	528	192
2	7	4	-2188	-2229	41	2	6	5	-2551	-2540	-11
2	9	4	1166	1129	37	2	7	5	-2798	-2743	-55

TABLE 5 (*Continued*)

h	*k*	*l*	$100F_o$	$100F_c$	100Δ	*h*	*k*	*l*	$100F_o$	$100F_c$	100Δ
2	8	5	-1623	-1686	-135	1	5	6	1150	1060	90
2	9	5	-1590	-1625	35	1	6	6	-1382	-1229	-153
2	10	5	-752	-797	45	1	7	6	-1928	-1902	-26
2	11	5	-622	-567	-55	1	8	6	-801	-797	-4
3	1	5	1936	1746	188	1	9	6	1497	1496	1
3	2	5	5230	4980	250	1	10	6	1280	1361	-81
3	3	5	1940	1941	-1	1	11	6	882	747	135
3	4	5	513	400	113	2	0	6	-3857	-3833	-24
3	6	5	-2092	-2160	68	2	1	6	-490	-782	292
3	7	5	-1416	-1309	-107	2	2	6	1726	1742	-16
3	8	5	-880	-992	112	2	3	6	2217	2247	-30
3	9	5	-1033	-1113	80	2	4	6	943	758	185
3	10	5	-818	-661	-157	2	5	6	-873	-864	-9
3	12	5	539	709	-170	2	6	6	-1147	-1038	-109
4	1	5	1521	1434	87	2	7	6	-1344	-1388	44
4	2	5	2820	2695	125	2	9	6	622	555	67
4	3	5	-683	-648	-35	2	10	6	532	618	-86
4	4	5	-1085	-1061	-24	2	12	6	-532	-416	-116
4	5	5	-711	-773	62	3	0	6	-3927	-4062	135
4	7	5	1073	1170	-97	3	1	6	-1480	-1472	-8
5	2	5	-1281	-1329	48	3	3	6	-1148	-1080	-68
5	3	5	-1403	-1220	-183	3	4	6	-882	-761	-121
5	5	5	1315	1377	-62	3	5	6	-1327	-1084	-243
5	6	5	2941	3081	-140	3	6	6	-1885	-1972	87
5	7	5	1810	1827	-17	3	7	6	-1036	-1041	5
5	8	5	897	780	117	3	9	6	619	472	147
6	1	5	-1723	-1614	-109	4	0	6	-3896	-3663	-233
6	2	5	-1919	-1848	-71	4	1	6	-2936	-2803	-133
6	3	5	-1105	-1025	-80	4	2	6	-1899	-2032	133
6	4	5	553	426	127	4	3	6	-810	-880	70
6	5	5	1529	1511	18	4	4	6	-1543	-1419	-124
6	6	5	2373	2380	-7	4	5	6	-1780	-1753	-27
6	7	5	1998	1901	97	4	6	6	-472	-417	-55
7	1	5	-1559	-1500	-59	4	8	6	549	714	-165
7	2	5	-2797	-2756	-41	4	10	6	-698	-544	-154
7	3	5	-1616	-1714	98	5	0	6	-3621	-3569	-52
7	5	5	1460	1448	12	5	1	6	-2021	-1922	-99
7	6	5	1899	1922	-23	5	2	6	654	626	28
7	7	5	588	773	-185	5	3	6	954	968	-14
7	8	5	-599	-606	7	5	4	6	-469	-348	-121
7	9	5	-565	-628	63	5	6	6	448	610	-162
8	1	5	-1269	-1101	-168	5	9	6	-691	-804	113
8	2	5	-2596	-2712	116	6	0	6	654	814	-160
8	3	5	-1065	-1088	23	6	1	6	1503	1632	-129
8	4	5	816	802	14	6	2	6	1804	1845	-41
8	5	5	885	913	-28	6	3	6	1717	1740	-23
8	8	5	-859	-917	58	6	5	6	498	657	-159
9	1	5	-1576	-1600	24	7	0	6	1371	1250	121
9	2	5	-1758	-1821	63	7	1	6	651	562	89
9	7	5	-861	-867	6	7	2	6	972	952	20
10	1	5	-1114	-1283	169	7	3	6	747	672	75
10	2	5	-798	-808	10	7	4	6	1007	967	40
10	6	5	-545	-447	-98	7	5	6	795	800	-5
11	1	5	-743	-706	-37	8	0	6	1030	934	96
0	1	6	-143	-685	542	8	1	6	882	891	-9
0	2	6	802	996	-194	8	6	6	547	392	155
0	3	6	4522	4656	-134	8	7	6	648	595	53
0	4	6	5583	5712	-129	9	0	6	464	687	-223
0	5	6	2497	2528	-31	9	2	6	-801	-638	37
0	6	6	-403	-325	-78	9	3	6	-824	-823	-1
0	7	6	-2035	-2040	5	10	1	6	-1082	-1103	21
0	8	6	-1563	-1795	232	10	2	6	-926	-931	5
0	9	6	1414	1627	-213	10	3	6	-906	-937	31
0	10	6	2142	2193	-51	11	0	6	-1411	-1539	128
0	11	6	1209	1210	-1	11	1	6	-798	-751	-47
0	13	6	-810	-625	-185	11	2	6	-504	-407	-97
1	0	6	-3283	-3378	95	13	0	6	1125	1118	7
1	1	6	-1962	-1884	-78	13	1	6	1044	993	51
1	2	6	1651	1738	-87	1	1	7	608	520	88
1	3	6	4756	4820	-64	1	2	7	318	709	-391
1	4	6	5031	4742	289	1	3	7	1267	1281	-14

TABLE 5 (*Continued*)

h	*k*	*l*	$100F_o$	$100F_c$	100Δ	*h*	*k*	*l*	$100F_o$	$100F_c$	100Δ
1	4	-7	1295	1167	128	1	1	8	-1697	-1922	225
1	5	-7	2486	2442	44	1	2	8	682	494	188
1	6	-7	1726	1798	-72	1	3	8	4796	4706	90
1	7	-7	-422	-629	207	1	4	8	2674	2561	113
1	8	-7	-717	-727	10	1	6	8	-833	-821	-12
1	9	-7	-486	-542	56	1	-7	8	-815	-831	16
1	10	-7	-1121	-999	-122	1	9	8	1455	1279	176
1	11	-7	-995	-1075	80	1	10	8	929	850	79
1	12	-7	-672	-652	-20	2	0	8	-957	-857	-100
2	1	-7	1584	1240	344	2	2	8	2512	2598	-86
2	2	-7	2642	2745	-103	2	3	8	2260	2233	27
2	3	-7	1711	1607	104	2	4	8	-605	-641	36
2	4	-7	2885	2879	6	2	5	8	-627	-783	156
2	5	-7	1894	1911	-17	2	6	8	-795	-824	29
2	-7	-7	-411	-496	85	2	-7	8	-1469	-1414	-55
2	8	-7	-991	-903	-88	2	9	8	-726	780	-54
2	9	-7	-1748	-1712	-36	3	1	8	839	673	166
2	10	-7	-1234	-1237	3	3	2	8	524	462	62
2	11	-7	-997	-1009	12	3	3	8	-698	-587	-111
3	1	-7	2324	2405	-81	3	4	8	-1215	-1273	58
3	2	-7	2644	2654	-10	3	5	8	-1719	-1579	-140
3	3	-7	1220	1137	83	3	6	8	-1500	-1329	-171
3	4	-7	596	446	150	4	0	8	-776	-635	-141
3	8	-7	-1090	-1157	67	4	1	8	-1238	-1266	28
3	9	-7	-1251	-1278	27	4	2	8	-1511	-1436	-75
4	1	-7	1859	2092	-233	4	3	8	-1423	-1359	-64
4	3	-7	-1841	-1834	-7	4	4	8	-2268	-2139	-129
4	4	-7	-440	-457	17	4	5	8	-1145	-1014	-131
4	6	-7	1012	945	67	4	6	8	561	543	18
4	-7	-7	1036	1062	-24	4	-7	8	891	794	97
4	9	-7	-510	-588	78	4	9	8	-649	-667	18
5	1	-7	-2324	-2332	8	*5	0	8	-452	-119	-333
5	2	-7	-2592	-2854	262						
5	3	-7	-900	-818	-82	5	3	8	-1154	-1177	23
5	5	-7	896	984	-88	5	4	8	-1053	-985	-68
5	6	-7	1559	1666	-107	5	6	8	804	763	41
5	-7	-7	851	1031	-180	5	9	8	-931	-803	-128
6	1	-7	-2239	-2202	-37	6	0	8	914	798	116
6	2	-7	-2596	-2678	82	6	2	8	604	551	53
6	3	-7	-2355	-2333	-22	6	5	8	764	733	31
6	4	-7	-1131	-1177	46	6	6	8	752	683	69
6	5	-7	916	870	46	6	-7	8	579	489	90
6	6	-7	1771	1766	5	-7	0	8	-1212	-1121	-91
6	-7	-7	1408	1468	-60	-7	2	8	989	919	70
-7	1	-7	-2278	-2283	5	-7	3	8	654	604	50
-7	2	-7	-2933	-2949	16	-7	4	8	1137	976	161
-7	3	-7	-1624	-1669	45	-7	5	8	983	902	81
-7	5	-7	1191	1152	39	-7	6	8	792	664	128
-7	6	-7	1244	1330	-86	8	0	8	764	525	239
8	1	-7	-1437	-1545	108	8	1	8	1021	1081	-60
8	2	-7	-1475	-1406	-69	9	0	8	865	754	111
8	4	-7	1023	1027	-4	9	1	8	483	438	45
8	-7	-7	-813	-775	-38	9	2	8	-579	-538	-41
8	8	-7	-555	-540	-15	9	3	8	-567	-663	96
9	1	-7	-796	-933	137	10	2	8	-871	-889	18
9	2	-7	-568	-460	-108	10	3	8	-862	-765	-97
9	3	-7	526	682	-156	11	2	8	-691	-412	-279
9	4	-7	530	532	-2	1	3	9	1041	1009	32
9	6	-7	-772	-809	37	1	4	9	1301	1353	-52
11	2	-7	529	236	293	1	5	9	2642	2415	227
12	2	-7	619	530	89	1	6	9	1425	1356	69
0	1	8	-3439	-3620	181	1	9	9	-510	-225	-285
0	2	8	-1359	-1580	221	1	10	9	-816	-922	106
0	3	8	2970	2951	19	1	11	9	-880	-922	42
0	4	8	4961	4831	130	2	1	9	-489	-581	92
0	5	8	1700	1500	200	2	2	9	945	1093	-148
0	7	8	-1472	-1298	-174	2	3	9	923	751	172
0	9	8	1616	1684	-68	2	4	9	1806	1693	113
0	10	8	1428	1196	232	2	5	9	2358	2120	238
0	11	8	631	611	20	2	6	9	1706	1599	107
1	0	8	-3303	-3856	553	2	7	9	862	813	49

TABLE 5 (*Continued*)

h	*k*	*l*	$100F_o$	$100F_c$	100Δ	*h*	*k*	*l*	$100F_o$	$100F_c$	100Δ
2	9	9	-752	-731	-21	5	6	10	913	882	31
2	10	9	-1079	-1098	19	5	1	10	-640	-568	-72
3	1	9	362	416	-54	6	5	10	701	665	36
3	2	9	601	410	191	6	6	10	792	816	-24
3	3	9	-1091	-1070	-21	6	7	10	601	547	54
3	4	9	622	603	19	7	0	10	-536	-612	76
3	5	9	1719	1695	24	8	2	10	571	504	67
3	6	9	1494	1512	-18	9	1	10	627	607	20
3	7	9	547	440	107	1	1	11	-441	-545	104
3	9	9	-747	-772	25	1	2	11	-344	-364	20
4	1	9	623	564	59	1	4	11	484	464	20
4	2	9	-1888	-1666	-222	1	5	11	943	846	97
4	3	9	-1587	-1549	-38	1	6	11	1211	1131	80
4	4	9	646	448	198	1	7	11	1091	1112	-21
4	5	9	795	807	-12	1	8	11	594	571	23
4	6	9	850	737	113	2	1	11	-732	-666	-66
5	1	9	-1356	-1223	-133	2	2	11	-555	-547	-8
5	2	9	-2350	-2312	-38	2	4	11	435	517	-82
5	3	9	-1269	-1289	20	2	5	11	1660	1514	146
5	6	9	588	426	162	2	6	11	1836	1797	39
6	1	9	-1910	-1701	-209	2	7	11	1162	1287	-125
6	2	9	-3092	-2915	-177	2	8	11	619	506	113
6	3	9	-2069	-1902	-167	3	1	11	-679	-748	69
6	4	9	-839	-750	-89	3	2	11	-978	-1099	121
6	6	9	712	737	-25	3	3	11	-798	-753	-45
6	7	9	588	619	-31	3	4	11	631	731	-100
7	1	9	-1659	-1560	-99	3	5	11	1590	1519	71
7	2	9	-2023	-1894	-129	3	6	11	1310	1264	46
7	3	9	-564	-716	152	4	1	11	-541	-618	77
8	1	9	-883	-814	-69	4	2	11	-1153	-1220	67
8	3	9	519	553	-34	4	3	11	-975	-942	-33
8	4	9	568	538	30	4	5	11	786	720	66
9	2	9	813	745	68	5	1	11	-763	-836	73
9	3	9	861	954	-93	5	2	11	-1556	-1545	-11
10	2	9	830	754	76	5	3	11	-1220	-1213	-7
11	2	9	665	687	-22	6	1	11	-916	-838	-78
0	1	10	-2774	-3683	909	6	2	11	-1215	-1300	85
0	2	10	-1269	-1370	81	6	3	11	-657	-786	129
0	3	10	928	1041	-113	7	1	11	-550	-446	-104
0	4	10	2245	2032	213	7	2	11	-518	-539	21
0	6	10	-622	-479	-143	9	2	11	961	896	65
0	8	10	798	927	-129	0	1	12	-1737	-1954	217
0	9	10	564	644	-80	0	2	12	-917	-896	-21
1	0	10	-3020	-3406	386	0	4	12	-532	-513	-19
1	1	10	-1215	-1264	49	0	7	12	579	385	194
1	2	10	287	297	-10	0	8	12	645	702	-57
1	3	10	2026	2001	25	1	0	12	-1229	-1599	370
1	4	10	974	937	37	1	1	12	-617	-648	31
1	5	10	-746	-639	-107	1	4	12	-532	-464	-68
1	6	10	-487	-498	11	1	5	12	-575	-562	-13
1	9	10	605	520	85	1	7	12	680	596	84
2	1	10	977	1103	-126	1	8	12	605	536	69
2	2	10	1440	1329	111	2	0	12	339	381	-42
2	3	10	1231	1087	144	2	1	12	746	807	-61
2	5	10	-997	-1029	32	2	2	12	743	736	7
2	6	10	-784	-724	-60	2	4	12	-512	-484	-28
3	0	10	1521	1505	16	2	5	12	-689	-585	-104
3	1	10	1442	1451	-9	2	7	12	565	582	-17
3	2	10	876	805	71	3	0	12	1642	1704	-62
3	4	10	-1321	-1236	-85	3	1	12	1775	1763	12
3	5	10	-1012	-1037	25	3	2	12	822	821	1
4	0	10	1469	1621	-152	3	4	12	-723	-640	-83
4	1	10	1090	1126	-36	3	5	12	-637	-330	-307
4	3	10	-1342	-1254	-88	4	0	12	2341	2371	-30
4	4	10	-1621	-1626	5	4	1	12	1546	1460	86
4	7	10	565	459	106	4	3	12	-900	-809	-91
5	0	10	1540	1605	-65	4	4	12	-968	-778	-190
5	2	10	-1033	-921	-112	5	0	12	1270	1269	1
5	3	10	-1439	-1475	36	5	2	12	-503	-577	74
5	4	10	-1004	-1028	24	5	3	12	-1081	-964	-117
5	5	10	571	238	333	6	2	12	-714	-655	-59

TABLE 5 (*Continued*)

h	*k*	*l*	$100F_o$	$100F_c$	100Δ	*h*	*k*	*l*	$100F_o$	$100F_c$	100Δ
6	3	12	-555	-588	33	4	1	13	-657	-568	-129
7	0	12	-536	-460	-76	4	2	13	-908	-836	-72
7	1	12	-663	-500	-163	5	1	13	-599	-503	-96
1	1	13	-302	-392	90	0	2	14	-613	-699	86
1	2	13	-541	-542	1	0	3	14	-932	-918	-14
1	3	13	-509	-578	69	0	4	14	-1249	-1095	-154
1	6	13	796	772	24	1	2	14	-504	-395	-109
2	1	13	-620	-639	19	1	3	14	-776	-671	-105
2	2	13	-931	-992	61	1	4	14	-870	-838	-32
2	3	13	-715	-834	119	2	0	14	321	503	-182
2	5	13	665	678	-13	2	1	14	608	609	-1
2	6	13	1157	1060	97	3	0	14	1221	1250	-29
3	1	13	-649	-652	3	3	1	14	1122	1073	49
3	2	13	-948	-1010	62	4	0	14	1436	1342	94
3	3	13	-601	-556	-45	4	1	14	857	843	14

Some molecular quantities in $(PC_6H_5)_6$ and $(PC_6H_5)_5$ are compared in Table 6. Although the P–P bond length found here (2·237 ± 0·003 Å) is not significantly different from the average P–P length in $(PC_6H_5)_5$ (2·217 ± 0·006 Å), it is interesting to note that the same situation occurs for arsenomethane [10] $(AsCH_3)_5$ and arsenobenzene [11] $(AsC_6H_5)_6$, where the As–As bond length is greater by 0·028 Å in the six-membered ring than in the five. The similarity of the six-membered phosphorus ring found here to the six-membered arsenic ring in arsenobenzene [11] is striking: the bond angles are 94·6 and 100·0° (average), respectively, and the torsion angels are 85·0 and 89° (average), respectively.

The P–C bond length found here does not differ significantly from that found in triphenylphosphorus,[12] but the bond angles at the phosphorus atom are much larger in $(PC_6H_5)_3$, where they are essentially equal and average 103·0°.

TABLE 6

Comparison of molecular quantities in $(PC_6H_5)_6$ and $(PC_6H_5)_5$

	$(PC_6H_5)_6$		$(PC_6H_5)_5$	
	Range	Average	Range	Average
P–P	—	2·237(3)	2·207—2·223	2·217(6) *
P–P–P	—	94·6(1)	94·1—107·2	100·0(54) *
|P–P–P–P|	—	85·0	2·2—60·6	38·1
P–C	—	1·843(7)	1·828—1·858	1·843(14) *
P–P–C	97·1(2) and 99·9(2)	98·5	96·4—109·8	102·0(40) *
P–C–C	123·1(5) and 115·1(5)	119·6	114·5—125·5	120·2(42) *
C–C	1·371—1·437	1·406(20) σ	1·372—1·440	1·403(26) *
C–C–C	117·9—122·8	120·0(20) *	117·0—123·7	120·0(14) *

* Standard deviation of individual values from the average.

The carbon atoms of the phenyl group do not deviate significantly from a plane regular hexagon of side 1·397 Å. However, the U_{33} thermal parameter is rather high for some of the atoms, particularly C4 and C5. This may be real and due, for example, to slight disorder, but it is difficult in this case to see why the thermal parameters of atom C6 are not particularly big. Another possibility is that there is an unidentified systematic error in the intensity measurements.

The departures of the molecule from symmetry $\bar{3}m$ (D_{3d}) are not great. To achieve this symmetry both P–C–C angles should be equal (they differ by 2·8°), the phenyl ring should be parallel to the [*c*]-axis (it makes an angle of 5·6° with *c*) and the phosphorus atom should be coplanar with the phenyl ring (the displacement is 0·03 Å).

There are 9 independent Van der Waals contacts of less than 4·0 Å; the two shortest are

[10] J. H. Burns and J. Waser, *J. Amer. Chem. Soc.*, 1957, **79**, 859.
[11] K. Hedberg, E. W. Hughes, and J. Waser, *Acta Cryst.*, 1961, **14**, 369.
[12] J. J. Daly, *J.*, 1964, 3799.

C · · · C contacts both of 3·46 Å; there are no contacts of less than 4 Å involving the phosphorus atom. If we ignore contacts within a phenyl group and those that subtend a bond angle, then there are three non-bonded intramolecular contacts of less than 3·6 Å; these are illustrated in Figure 1.

It seems possible that the monoclinic and rhombohedral forms [3] of $(PC_6H_5)_6$, in which the required molecular symmetry forbids the boat conformation, differ from the trigonal form mainly in the orientation of the phenyl rings about the P–C bonds; the triclinic modification [2] however is not known to be restricted to the chair form by symmetry.

I thank Dr. L. Maier who prepared the crystals and determined the density and with whom I have had many helpful discussions.

MONSANTO RESEARCH S.A., BINZSTRASSE 39,
8045 ZURICH, SWITZERLAND.

[*Received, December 21st,* 1964.]