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# The Molecular and Crystal Structure of $(PC_6H_{11})_4$

By J. C. J. Bart*

*Monsanto Research S. A., Eggbühlstrasse* 36, *Zurich, Switzerland*

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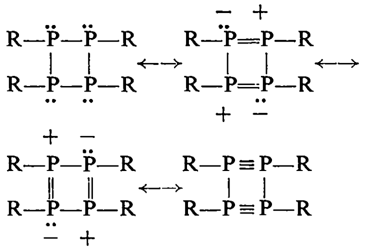
A tetragonal modification of tetracyclohexylcyclotetraphosphine, $(PC_6H_{11})_4$, has been subjected to an X-ray analysis. The unit cell, of symmetry $P\bar{4}2_1c$ and lattice constants $a=10{\cdot}158$, $c=12{\cdot}695$ Å, contains 2 molecules. The required molecular symmetry is $\bar{4}$, but in fact approximates $\bar{4}2m$ ($D_{2d}$). The structural parameters were obtained by Patterson methods and refinement of the three-dimensional diffractometer data was carried out by a block-diagonal least-squares procedure. The final $R$ value is 0·034. The bond distances are P–P $=2{\cdot}224\pm0{\cdot}002$, P–C $=1{\cdot}874\pm0{\cdot}002$, C–C(average) $=1{\cdot}521\pm0{\cdot}004$ Å. As in $(PCF_3)_4$ the four-membered phosphorus ring is not planar; P–P–P bond angles are 85·5° with P–P–P–P torsional angles of 31·4°. The cyclohexane ring has the chair configuration with phosphorus occupying an equatorial position. The bond angles in the cyclohexane ring (average 111·5°) are in full agreement with electron diffraction data and recent work on the total molecular strain energy functions in cycloalkanes.

## Introduction

The existence of relatively few pure compounds containing a phosphorus four-membered ring is known with certainty. At present several facts indicate that many aliphatic cyclopolyphosphines which were supposed to have a cyclotetraphosphine structure are more complex and exist as $(PR)_n$, with $n=4,5$ (Maier, 1967). For the cyclohexyl derivative the tetrameric structure in solution has been found to be plausible (Issleib & Seidel, 1960), by determination of the molecular weight, as well as in the crystalline state [preliminary investigations of Siegel (1963) and Daly & Maier (1965)].

As to the nature of the P–P bonding it is of interest to note that in all previously studied phosphorus ring-compounds an essentially equal P–P distance has been found, which corresponds to a single bond. Several tetrameric alkylphosphines, $(RP)_4$, have been studied. The ring configurations are not known but nuclear magnetic resonance spectra indicate a cyclic structure and ultraviolet spectra suggest a high degree of electron delocalization between the lone pair on one phosphorus atom and the vacant 3*d*-orbital of the neighbouring phosphorus atom (Henderson, Epstein & Seichter, 1963; Mahler & Burg, 1957, 1958) with formation of $p_\pi-d_\pi$ bonds. Formally the following types of resonance structures can be written:



Support for this view comes from chemical reactions, such as addition reactions, which involve the lone pairs of the phosphorus atoms, and lead to the destruction of the cyclophosphine ring, or to rather unstable adducts.

Several of the observations made and the fact that aliphatic substituted cyclopolyphosphines are non-basic in nature, are not consistent with the observed P–P distances (Henderson, Epstein & Seichter, 1963). Complexes of $(cyclo\text{-}C_6H_{11}P)_4$ with copper(I)-halides have been studied recently (Hicks & Dean, 1965). With $Fe(CO)_5$, $(cyclo\text{-}C_6H_{11}P)_4[Fe(CO)_4]_2$ is formed (Issleib & Keil, 1964) where the cyclotetraphosphine ring is supposed to be sandwiched by the two Fe-atoms.

## Experimental

Two crystalline modifications of tetracyclohexylcyclotetraphosphine, both tetragonal, have been observed during previous investigations. One of these, described by Siegel (1963) is the same as used in the present X-ray structure determination. The other modification, described by Daly & Maier (1965) crystallizes as thin needles elongated along [*c*] in the space group $P4_2/n$ with $a=15{\cdot}33$ and $c=5{\cdot}63$ Å. With two molecules of $(cyclo\text{–}C_6H_{11}P)_4$ in the unit cell, the required molecular symmetry here is $\bar{4}$.

$(PC_6H_{11})_4$ was prepared by Professor K. Issleib from the reaction of a primary phosphine with the corresponding organophosphonous dihalide. Colourless crystals suitable for intensity measurements could readily be grown by a slow cooling procedure from benzene solution. Although the crystal habit largely depends on the solvent, the same modification ($P\bar{4}2_1c$) was always obtained. No success was met with in trying to grow sufficiently thick needles of the $P4_2/n$ form. Tetracyclohexylcyclotetraphosphine is stable in air and light, but under the influence of X-rays the crystals display a rather pronounced red-violet colour. No influence on the X-ray intensities was detected over the whole period

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* Present address: Montecatini-Edison S. p. A. Research Laboratory, 20021 Bollate, Milano, Italy.

of measurements. The coloured crystals give a strong paramagnetic signal; the effect is the subject of further study.

A small crystal was used to determine the cell constants from precession photographs, recorded with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The crystallographic constants of the polymorphic form studied, together with some experimental details are given in Table 1.

Table 1. *Crystallographic and experimental constants of* ($cyclo$-$C_6H_{11}P)_4$

$C_{24}H_{44}P_4$, $M = 456{\cdot}5$, m.p. 219–220°

| | |
|---|---|
| $a = b = 10{\cdot}158$ Å | $\sigma(a) = 0{\cdot}004$ Å |
| $c = \;\; 12{\cdot}695$ | $\sigma(c) = 0{\cdot}005$ |

Systematic absences: $hhl$ for $l = 2n+1$; $h00$ for $h = 2n+1$
Spacegroup $P\bar{4}2_1c$

$V = 1310{\cdot}0$ Å$^3$; $d$(calc) ($n = 2$) $= 1{\cdot}157$ g.cm$^{-3}$;
$F(000) = 496$
$\mu$(Mo $K\alpha$) $= 2{\cdot}97$ cm$^{-1}$
Crystal faces: {011} and {111}

Oscillation angle:

| | |
|---|---|
| $0kl - 7kl$ | 2·5° |
| $8kl - 12kl$ | 3·5 |

Intensities were collected on a linear Hilger–Watts automatic diffractometer (Arndt & Phillips, 1961), equipped with a scintillation-counter with pulse height discrimination. The radiation was Mo $K\alpha$ which was monochromatized by the use of balanced filters. The data were collected as reciprocal lattice sections perpendicular to [100] up to $\theta = 25°$ from a prismatic crystal of approximate cross-section $0{\cdot}35 \times 0{\cdot}5$ mm$^2$. Each reflexion was measured twice with both filters, by a one-minute oscillation-motor. That part of reciprocal space was covered for which $h, k$ and $l$ are positive. The average $\Delta I_o$ was estimated as 3%. Scale factors between sets of layers recorded with different oscillation angles (Table 1) were established by the ratio of the observed intensity of a number of suitable reflexions, scanned in both ranges. The intensities varied from 1 to 90,000. The background counts were included in the normal manner. A threshold intensity $I_t$ was established by taking twice the maximum number of counts of a set of space-group absent reflexions. A few reflexions with negative counts were attributed the value $\frac{1}{2}I_t$. Corresponding $F(hkl)$ and $F(khl)$, obtained from different layers, were averaged, yielding 872 independent reflexions. From an analysis of $|F_{\text{obs}}|$ and $F|_{\text{calc}}|$ at the end of the refinement it was not thought necessary to reject any weak reflexion.

The reflexion data were corrected for the Lorentz-polarization factor, but not for absorption. An approximate scale factor was obtained from structure factor calculations. With two molecules per unit cell, the required molecular symmetry is $\bar{4}$, as in the $P4_2/n$ modification. Positions 8($e$) (*International Tables for X-ray Crystallography*, 1952) accommodate the atoms.

## Structure determination and refinement

The coordinates of the phosphorus atoms were deduced from a Patterson function $P(uvw)$. Part of the cyclohexane ring was easily recognizable as P–C vectors. More accurate parameters for the carbon positions were obtained from a three-dimensional electron-density distribution, based on all structure factors calculated with the phosphorus contribution only ($R = 0{\cdot}40$). This improved $R(= \Sigma\ |kF_o - |F_c||/kF_o)$ to 0·27. A least-squares refinement, using the block-diagonal approximation, was then started with an assumed overall temperature factor and Cruickshank's (1961) weighting scheme. Thermal anisotropy was introduced at $R = 0{\cdot}09$ together with the hydrogen atoms at positions which had been calculated in the usual way. Subsequently the very strong reflexions 002, 013 and 112 were removed from the calculations as it was feared that they were subject to extinction effects or otherwise of too low intensity. At $R = 0{\cdot}042$ the hydrogen parameters were allowed to refine.

In this stage the Cruickshank scheme, $w = 1/(5{\cdot}0 + |F_o| + 0{\cdot}03|F_o|^2)$, prevented further refinement. The $\Delta F$ of the weakly observed plane (220) gave disproportionate contributions to the normal equation matrices for most of the atoms. The influence of the plane was reduced by multiplication of the Cruickshank weights by $(|F_o|/|F_{\min}|)^2$ for reflexions with $|F_o| < |F_{\min}|$ . $|F_{\min}|$ was chosen as 5·0 (absolute scale), from inspection of the analysis of $\Sigma\ w\Delta^2/n$ against the magnitude of $|F_o|$. Refinement was continued accordingly until the shifts were random. Final $R = 0{\cdot}034$, with $R'(= \Sigma\ w|\Delta|^2/\Sigma\ wF_o^2) = 0{\cdot}0017$.

Throughout the calculations planes with $3|F_c| \leq |F_o|$ were omitted from the least-squares totals; in the last cycle 15 planes were subject to this restriction. With the least-squares program used it was necessary to refine the H atoms anisotropically together with the other atoms. Constant values over the whole range were reached for $\Sigma\ w\Delta^2/n$ as a function of $|F_o|$ and $\sin^2\theta/\lambda^2$, except for the strongest reflexions and those with the lowest $\sin^2\theta/\lambda^2$. The atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962).

## Results

The labelling of the atoms, as used in this study, is given in Fig. 1 and Table 2 (for the hydrogen atoms). The final coordinates and their estimated standard deviations (in Å) in the asymmetric unit, all referred to the axes $a, b, c$ of the tetragonal cell, are listed in Table 2; the thermal parameters are given in Table 3. The e.s.d.'s were calculated with expression 6.4.3 (6) of *International Tables for X-ray Crystallography* (1959), and not increased arbitrarily as no unobserved reflexions were excluded. A list of the observed and final calculated structure factors may be obtained from the author. Planes preceded by an asterisk were omitted from the least-squares totals because of their low calculated amplitude. It may be noted that all these reflexions are of weak intensity or are unobserved, with $I=\frac{1}{2}I_t$. More informative are Tables 4 and 5 where the structure factors are examined in terms of the magnitude of $|F_{obs}|$ and the $R$ index as a function of the parity of the indices. The weakest planes show poor agreement between $|F_{obs}|$ and $|F_{calc}|$, but their $\Sigma\,|\Delta|/N$ value is not outstanding.

The thermal parameters for the heavy atom are nearly isotropic and rather lower than for the carbon atoms. The motion of the cyclohexane-ring atoms is anisotropic. As expected the smallest $U_{ij}$ are found for the C(1) atom directly attached to the polyphosphine ring, with increasing values for atoms further away in the cyclohexane ring.

Table 2. *Final atomic coordinates in* Å

Standard deviations are given as units of the last decimal place.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| P | 4·1233 (05) | 6·2472 (05) | 6·0349 (05) |
| C(1) | 3·3575 (23) | 7·1748 (22) | 7·4719 (22) |
| C(2) | 1·8405 (25) | 7·1010 (27) | 7·3742 (28) |
| C(3) | 1·1566 (29) | 7·9447 (31) | 8·4431 (31) |
| C(4) | 1·6417 (29) | 9·3785 (28) | 8·4312 (28) |
| C(5) | 3·1553 (31) | 9·4444 (29) | 8·5449 (30) |
| C(6) | 3·8358 (24) | 8·6256 (24) | 7·4596 (27) |
| H(1)[C(1)*a*]* | 3·569 (32) | 6·865 (30) | 8·291 (23) |
| H(2)[C(2)*e*] | 1·446 (27) | 6·105 (38) | 7·396 (31) |
| H(3)[C(2)*a*] | 1·650 (24) | 7·435 (27) | 6·535 (28) |
| H(4)[C(3)*e*] | 0·179 (28) | 7·872 (31) | 8·314 (27) |
| H(5)[C(3)*a*] | 1·483 (32) | 7·569 (32) | 9·267 (27) |
| H(6)[C(4)*e*] | 1·237 (27) | 9·990 (36) | 9·170 (30) |
| H(7)[C(4)*a*] | 1·422 (27) | 9·768 (35) | 7·602 (24) |
| H(8)[C(5)*e*] | 3·448 (30) | 10·333 (33) | 8·526 (32) |
| H(9)[C(5)*a*] | 3·441 (29) | 9·075 (29) | 9·389 (27) |
| H(10)[C(6)*e*] | 4·822 (33) | 8·700 (30) | 7·546 (32) |
| H(11)[C(6)*a*] | 3·648 (28) | 9·064 (25) | 6·557 (26) |

* Denotes the carbon atom to which the hydrogen is attached, with indication of its *a*(xial) or *e*(quatorial) position.

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

| | $R$ |
|---|---|
| $h+k+l=2n$ | 0·031 |
| $h+k+l=2n+1$ | 0·040 |
| $h+k=2n$ | 0·035 |
| $h+k=2n+1$ | 0·033 |
| $k+l=2n$ | 0·034 |
| $k+l=2n+1$ | 0·034 |
| $h+l=2n$ | 0·032 |
| $h+l=2n+1$ | 0·035 |
| $h=2n$ | 0·035 |
| $h=2n+1$ | 0·032 |
| $k=2n$ | 0·032 |
| $k=2n+1$ | 0·036 |
| $l=2n$ | 0·035 |
| All planes | 0·034 |

Table 3. *Thermal parameters* (Å$^2$) *in the form*

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

Standard deviations, in brackets, in units of the last decimal place.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{12}$ | $2U_{23}$ | $2U_{13}$ |
|---|---|---|---|---|---|---|
| P | 0·0326 (02) | 0·0323 (02) | 0·0395 (02) | 0·0040 (04) | 0·0010 (05) | 0·0015 (05) |
| C(1) | 0·0370 (11) | 0·0328 (10) | 0·0441 (10) | 0·0100 (18) | −0·0011 (19) | 0·0009 (19) |
| C(2) | 0·0381 (11) | 0·0480 (13) | 0·0701 (15) | −0·0070 (21) | −0·0250 (27) | 0·0180 (25) |
| C(3) | 0·0454 (14) | 0·0563 (15) | 0·0795 (18) | 0·0016 (26) | −0·0249 (30) | 0·0406 (29) |
| C(4) | 0·0551 (15) | 0·0458 (14) | 0·0679 (15) | 0·0298 (26) | −0·0129 (27) | 0·0197 (28) |
| C(5) | 0·0584 (15) | 0·0434 (13) | 0·0714 (16) | −0·0008 (25) | −0·0299 (26) | 0·0121 (29) |
| C(6) | 0·0422 (12) | 0·0367 (11) | 0·0666 (15) | −0·0043 (20) | −0·0102 (23) | 0·0128 (25) |
| H(1) | 0·039 (21) | 0·020 (17) | 0·015 (12) | −0·022 (33) | −0·017 (26) | 0·003 (28) |
| H(2) | 0·002 (14) | 0·111 (32) | 0·072 (22) | 0·065 (36) | −0·080 (48) | 0·071 (34) |
| H(3) | 0·006 (13) | 0·030 (15) | 0·049 (19) | 0·015 (25) | −0·024 (32) | 0·031 (30) |
| H(4) | −0·008 (13) | 0·057 (20) | 0·078 (19) | −0·009 (29) | −0·053 (38) | 0·051 (32) |
| H(5) | 0·101 (29) | 0·011 (16) | 0·036 (18) | −0·035 (38) | −0·036 (31) | −0·001 (40) |
| H(6) | 0·018 (17) | 0·034 (20) | 0·091 (21) | 0·035 (36) | −0·012 (46) | −0·026 (38) |
| H(7) | 0·005 (15) | 0·068 (26) | 0·031 (15) | 0·035 (36) | −0·029 (37) | 0·031 (28) |
| H(8) | 0·015 (20) | 0·011 (18) | 0·102 (24) | 0·000 (31) | −0·037 (42) | 0·021 (41) |
| H(9) | 0·031 (18) | 0·048 (18) | 0·044 (18) | 0·103 (31) | −0·107 (32) | 0·042 (31) |
| H(10) | 0·022 (23) | 0·031 (19) | 0·069 (22) | 0·019 (34) | −0·052 (38) | −0·001 (41) |
| H(11) | 0·038 (17) | 0·004 (14) | 0·047 (17) | 0·060 (25) | −0·014 (30) | 0·037 (31) |

Table 4. *Analysis of* $F_{obs}$ *and* $F_{calc}$ *as a function of the magnitude of* $F_{obs}$

All figures are on an absolute scale.

| Range of $\lvert F_o\rvert$ | $\Sigma\,\lvert F_o\rvert$ | $\Sigma\,\lvert F_c\rvert$ | $\Sigma\,\lvert\Delta\rvert$ | $N$ | $R$ | $\Sigma\,\lvert\Delta\rvert/N$ |
|---|---|---|---|---|---|---|
| 0 – 4·0 | 455·40 | 416·14 | 85·04 | 187 | 0·187 | 0·45 |
| 4·0– 8·0 | 1581·64 | 1573·33 | 56·07 | 261 | 0·035 | 0·21 |
| 8·0–12·0 | 1490·01 | 1488·51 | 29·82 | 154 | 0·020 | 0·19 |
| 12·0–16·0 | 1346·44 | 1342·74 | 29·96 | 98 | 0·022 | 0·31 |
| 16·0–20·0 | 889·68 | 887·67 | 19·55 | 50 | 0·022 | 0·39 |
| 20·0–24·0 | 747·00 | 737·49 | 19·97 | 34 | 0·027 | 0·59 |
| 24·0–28·0 | 673·39 | 665·68 | 13·05 | 26 | 0·019 | 0·50 |
| 28·0–32·0 | 482·75 | 475·80 | 12·31 | 16 | 0·025 | 0·77 |
| > 32·0 | 1964·38 | 1960·59 | 61·13 | 43 | 0·031 | 1·42 |

The values for the hydrogen atoms are probably not meaningful.

## Discussion

### *Bond lengths and angles*

Intramolecular distances and angles, uncorrected for thermal motion, are given in Table 6, together with the standard deviations, calculated from the e.s.d. of the positional parameters. These $\sigma$ values are to be considered as the lower limit. The standard deviations in the C–C bond lengths due to the estimated standard deviations in the cell-dimensions are relatively unimportant, but the $\sigma$(P–P) has been increased for this reason. The phosphorus–phosphorus bond length is 2·224 ± 0·002 Å, in agreement with distances observed in other compounds involving this bond. Numerous compounds containing P–P bonds are listed in Table 7 in order of decreasing ring-size $P_n$. Bearing in mind the limits of error in the various investigations the values for the P–P lengths are within a rather short range, in spite of the different valency states of phosphorus and the nature of the attached groups. Exceptions are $\alpha$-$P_4S_7$ and $(OC)_3Ni(P\mathit{Ph}_2)_2Ni(CO)_3$ which are both seriously strained, although in $\beta$-$P_4S_7$ the P–P length is not significantly different from others. As already pointed out by Palenik & Donohue (1962) cross-ring repulsion, leading to long bonds in cyclobutane and its derivatives, is not an important factor in the case of four-membered phosphorus rings. The cross-ring P---P distance in the puckered ring (3·019 Å) is smaller than it would have been in a planar ring (3·145 Å). Not even mentioned in the Table are numerous metallic polyphosphides, such as $Ni_5P_4$ (Elfström, 1965), $CuP_2$ (Olofsson, 1965), and others, where tetrahedrally coordinated

Table 6. *Bond lengths and angles*

Standard deviations, in brackets, are in units of the last decimal place.

| | | | |
|---|---|---|---|
| P–P′ | 2·224 (2) Å | P′–P–P″ | 85·47 (6) ° |
| P–C(1) | 1·874 (2) | P′–P–C(1) | 102·83 (10) |
| | | P″–P–C(1) | 102·61 (10) |
| C(1)–C(2) | 1·522 (4) | Average P–P–C | 102·72 |
| C(1)–C(6) | 1·528 (3) | | |
| C(2)–C(3) | 1·524 (4) | P–C(1)–C(2) | 109·52 (16) |
| C(3)–C(4) | 1·514 (4) | P–C(1)–C(6) | 109·63 (16) |
| C(4)–C(5) | 1·519 (4) | Average P–C–C | 109·58 |
| C(5)–C(6) | 1·520 (4) | | |
| Average C–C | 1·521 | P–C(1)–H(1) | 115·5 (19) |
| C(1)–H(1) | 0·90 (3) | C(1)–C(2)–C(3) | 112·05 (22) |
| C(2)–H(2) | 1·07 (3) | C(2)–C(3)–C(4) | 112·03 (24) |
| C(2)–H(3) | 0·92 (3) | C(3)–C(4)–C(5) | 111·09 (24) |
| C(3)–H(4) | 0·99 (3) | C(4)–C(5)–C(6) | 111·66 (24) |
| C(3)–H(5) | 0·96 (3) | C(5)–C(6)–C(1) | 111·44 (21) |
| C(4)–H(6) | 1·04 (3) | C(6)–C(1)–C(2) | 110·95 (20) |
| C(4)–H(7) | 0·94 (3) | Average C–C–C | 111·54 |
| C(5)–H(8) | 0·94 (3) | | |
| C(5)–H(9) | 0·97 (3) | H(2)—C(2)–H(3) | 106·3 (24) |
| C(6)–H(10) | 0·99 (3) | H(4)—C(3)–H(5) | 114·8 (25) |
| C(6)–H(11) | 1·02 (3) | H(6)—C(4)–H(7) | 106·9 (25) |
| Average C–H | 0·98 | H(8)—C(5)–H(9) | 106·7 (26) |
| | | H(10)–C(6)–H(11) | 103·2 (24) |
| | | Average H–C–H | 107·6 |
| C(1)–C(2)–H(2) | 114·3 (18) ° | | |
| C(1)–C(2)–H(3) | 104·2 (17) | | |
| C(3)–C(2)–H(2) | 109·5 (18) | | |
| C(3)–C(2)–H(3) | 110·1 (17) | | |
| C(2)–C(3)–H(4) | 108·2 (17) | | |
| C(2)–C(3)–H(5) | 103·4 (19) | | |
| C(4)–C(3)–H(4) | 112·7 (17) | | |
| C(4)–C(3)–H(5) | 105·5 (19) | | |
| C(3)–C(4)–H(6) | 115·3 (17) | | |
| C(3)–C(4)–H(7) | 109·0 (18) | | |
| C(5)–C(4)–H(6) | 108·0 (18) | | |
| C(5)–C(4)–H(7) | 106·2 (18) | | |
| C(4)–C(5)–H(8) | 110·6 (20) | | |
| C(4)–C(5)–H(9) | 110·1 (17) | | |
| C(6)–C(5)–H(8) | 110·9 (20) | | |
| C(6)–C(5)–H(9) | 106·6 (17) | | |
| C(5)–C(6)–H(10) | 110·0 (19) | | |
| C(5)–C(6)–H(11) | 108·5 (15) | | |
| C(1)–C(6)–H(10) | 112·4 (19) | | |
| C(1)–C(6)–H(11) | 111·0 (15) | | |
| C(6)–C(1)–H(1) | 105·1 (19) | | |
| C(2)–C(1)–H(1) | 106·1 (18) | | |
| Average C–C–H | 109·0 | | |

phophorus atoms are present with P–P distances of about 2·20 Å as well, suggesting $sp^3$ bonds.

A 2.20 Å value is predicted for the P–P single bond by the covalent radii table (Pauling, 1962). The length of the P–P bond in $(PC_6H_{11})_4$ is essentially the same as most of the values collected in Table 7. If any electron delocalization in the cyclotetraphosphine ring exists, it does not seem to shorten the P–P length appreciably. The 1·874 ± 0·002 Å distance for the phosphorus–carbon bond is longer than the values of 1·847, 1·853, 1·858Å (all ± 0·003Å) obtained by Bartell (1960) and Bartell & Brockway (1960) from electron diffraction data for the P–C(alkyl) bonds in $(CH_3)_3P$, $(CH_3)_2PH$ and $CH_3PH_2$, respectively. A slightly different value (1·841 ± 0·003 Å) is reported by Lide & Mann (1958) for the P–C bond in $(CH_3)_3P$ from microwave data. Using the same technique Kojima, Breig & Lin (1961) determined a 1·863 Å P–C bond in $CH_3PH_2$.

The P–C length in $(PC_6H_{11})_4$ is closer to the value of 1·867 Å (± 0·014 Å) determined by Palenik & Donohue (1962) for the phosphorus–carbon bond in $(PCF_3)_4$, by Spencer & Lipscomb (1961) in the corresponding pentamer (average 1·906 ± 0·020 Å) and by Bowen (1954) in another fluoro-derivative, $(CF_3)_3P$ (1·937 ± 0·017 Å). From the last three values is appears that adjacent bonds involving atoms of high electronegativity influence the P–C bonds. The P–C bond in $(PC_6H_{11})_4$ is significantly larger than in the *aromatic* cyclopolyphosphines $(PC_6H_5)_5$ and $(PC_6H_5)_6$, for which Daly (1964, 1965, 1966*a*) reports 1·843 Å. Although one is tempted to ascribe the effect at least partly to the difference in covalent radii for $sp^2$ and $sp^3$ carbon atoms, this fits in less well with the data of the methylphosphines as quoted above.

The phosphorus atoms have a pyramidal environment. In comparison with non-cyclic phosphines and larger ($n = 5,6$) cyclopolyphosphines the angles are greatly distorted. Because of the lone-pair electrons on the trivalent phosphorus atoms, the bonds in phosphines may have varying amounts of $sp^3$ character and in general show bond angles between 90° and tetrahedral values. In the (cyclo)polyphosphines the molecular configuration may be influenced to some extent by a $\pi$-bonding system, in which the role of the *d*-orbitals has been considered. In contrast to $p_\pi - p_\pi$ carbon systems, where planarity is required for resonance, the geometry of the *d*-orbitals allows some $\pi$-binding in a *bent* ring (Craig, 1959; Paddock 1962), as suggested for $(PC_6H_{11})_4$. Attempts have been made to relate the geometry of the orbital system to the molecular configuration (Mahler & Burg, 1958). The treatment which involves delocalization of the lone-pair electrons to occupy molecular orbitals extending over the whole P–P bonded system explains the ultraviolet absorptions of $(CF_3P)_4$ better than it fits the bands observed with the alkylcyclopolyphosphines.

The P–P–P valency angles in the puckered ring are rather small (85·5°) and can be compared with 84·7° in $(PCF_3)_4$ and 90° in a planar four-membered ring. The P–P–P–P torsional angles are 31·4° [34° in $(PCF_3)_4$] as opposed to 0° in a planar structure. A P–P–P–S ring of similar shape is found in $P_4S_5$. A pre-

Table 7. P–P *bond lengths*

| Compound | P–P bond length (Å) | Reference |
|---|---|---|
| $(PC_6H_5)_6$[a] | 2·237 (3) | Daly (1965) |
| $(PC_6H_5)_6$[b] | 2·220–2·241 (5) | Daly (1966*a*) |
| $(PO_2)_6^{6-}$ | 2·20* | Weiss (1960) |
| P (black) | 2·224–2·244 (3) | Brown & Rundqvist (1965) |
| P (violet) | 2·219* | Thurn & Krebs (1966) |
| $(EtP)_5Mo(CO)_4$ | 2·21 (3) | Bush, Cook & Woodward (1967) |
| $(PC_6H_5)_5$ | 2·207–2·223 (5) | Daly (1964) |
| $(PCF_3)_5$ | 2·202–2·252 (7) | Spencer & Lipscomb (1961) |
| $(PCF_3)_4$ | 2·213 (5) | Palenik & Donohue (1962) |
| $(PC_6H_{11})_4$ | 2·224 (2) | Present study |
| $P_4$ gas | 2·21 (2) | Maxwell, Hendricks & Mosely (1935) |
| $P_4Se_3$ | 2·23–2·26 (3) | Keulen & Vos (1959) |
| $P_4S_3$ | 2·223–2·246 (10) | Leung *et al.* (1957) |
| $P_4S_5$ | 2·24–2·26 (1) | Vos, Olthof, Van Bolhuis & Botterweg (1965) |
| $C_6H_4(PC_6H_5)_3$ | 2·209 (3) | Daly (1966*b*) |
| $\alpha P_4S_7$ | 2·326 (7) | Vos, Olthof, Van Bolhuis & Botterweg (1965) |
| $\beta P_4S_7 \simeq P_4S_{6\cdot5}$ | 2·26 (2) | Dixon, Einstein & Penfold (1965) |
| $P_4S_3I_2$ | 2·20* (4) | Wright & Penfold (1959) |
| $P_2I_4$ | 2·21 (6) | Leung & Waser (1956) |
| $(NH_4)_2H_2P_2O_6$ | 2·170 (3) | Wilson & McGeachin (1964) |
| $(OC)_3Ni(PPh_2)_2-Ni(CO)_3$ | 2·277 (4) | Mais, Owston, Thompson & Wood (1967) |
| $(OC)_4Fe(PMe_2)_2-Fe(CO)_4$ | 2·231 (7) | Jarvis, Mais, Owston & Thompson (1968) |
| $(Me_2PS)_2$ | 2·18 | Pedone & Sirigu (1967) |
| $(Et_2PS)_2$ | 2·22 (1) | Dutta & Woolfson (1961) |
| $(MePhPS)_2$ | 2·21 (1) | Wheatley (1960) |

* Average. [a] Trigonal. [b] Triclinic.
All from crystal structure determinations, except $P_4$ (electron diffraction).

liminary X-ray study of $(EtP)_4W(CO)_4$, suggests that this compound has a cyclotetraphosphine-ring (Bush, Cook & Woodward, 1967). In $(PCF_3)_5$ and $(PC_6H_5)_5$ where the cyclopentaphosphine rings are both nonplanar [probably as the result of bond angle requirements of the trivalent phosphorus ($\angle$P–P–P 94–108°), and steric requirements of the substituents], P–P–P–P torsional angles ranging from 18° to 58° and from 2° to 61° respectively, are found with an average value of about 38° in both cases. Similarly in $(PC_6H_5)_6$ the P–P–P bond angles are about 95° with P–P–P–P torsional angles of 84°, the molecule assuming a chair conformation with phenyl-groups occupying the equatorial positions. Recently another cyclopentaphosphine, $(EtP)_5Mo(CO)_4$, has been described (Bush *et al.*, 1967).

The P–P–C angles in $(PC_6H_{11})_4$ (average 102·7°) are normal compared to the range of values found in similar compounds: $(PCF_3)_4$, 97·8°; $(PCF_3)_5$, 94·2–107·8°; $(PC_6H_5)_5$, 96·4–109·8°; $(PC_6H_5)_6$, 97·1–99·2 (trigonal) and 96·5–100·1° (triclinic). There is no difference between the two P–C–C angles in contrast to the usual observation in the case of a *phenyl* group attached to a trivalent phosphorus atom.

The average C–C bond is 1·521 Å, with a mean C–C–C angle of 111·54°, close to the 1·533 ± 0·002 Å value in n-alkanes (Bartell & Kohl, 1963) and shorter than in diamond. Thermal motion correction, which is not expected to be high, would slightly increase the observed value for the C–C length. The estimated variances $s^2=\sum_{i=1}^{n}(\bar{x}-x_i)^2/(n-1)$ for the C–C and C–C–C bond data give $s$ values slightly higher than the e.s.d. values, namely $s=0·005$ Å (e.s.d. 0·004 Å) and $s=0·43°$ (e.s.d. = 0·23°) respectively. The individual values do not deviate significantly from the means. The C–C–C–C torsional angles in the sequence C(1)–C(2)–C(3)–C(4), C(2)–C(3)–C(4)–C(5), *etc.* are −53·9°, 54·2°, −55·3°, 55·7°, −54·5°, and 53·6° (average of the moduli 54·5°), as compared with −60°, 60°,. . ., in the case of the classical cyclohexane ring with tetrahedral angles. Our results for a substituted cyclohexane ring are in full agreement with the electron-diffraction data for $C_6H_{12}$ in the chair conformation. Davis & Hassel (1963) report here C–C–C bond angles of 111·55 ± 0·15° and C–C lengths of 1·528 ± 0·005 Å.

In recent calculations on the conformations of cycloalkanes, Bixon & Lifson (1967) have abandoned the tetrahedral angle as the zero-strain value of bond angles. Instead they choose the experimental value of the C–C–C angle of the n-alkanes [112·7° (Bartell & Kohl, 1963)] as the zero-strain angle, and assume that the deviations from this angle, as found in cycloalkanes, are imposed by the closing of the ring. Our results support the values predicted by Bixon & Lifson for the bond angles of the chair conformation in cyclohexane (111·5°; torsional angles of 54·7°). Intermolecular interactions which may distort the equilibrium conformation are probably not important in $(PC_6H_{11})_4$, as was checked by the calculation of the intermolecular distances. The cyclohexane ring which is slightly flatter than that based on the tetrahedral angle gives a better interpretation for various physical and chemical experimental results, such as infrared, nuclear magnetic resonance and kinetic data (Wohl, 1964).

The individual C–H bond lengths and C–C–H and H–C–H angles are close to the average value of 0·98 Å, 109·0° and 107·6° respectively. In all these cases the $s$ values are about 60% higher than the e.s.d.

## *Molecular geometry*

The cyclotetraphosphine ring is puckered (see Fig. 2) and of the antipyramidal type with symmetry (required crystallographically) $\bar{4}$. In $(PCF_3)_4$ a very similar ring structure is observed with symmetry $\bar{4}2m$. In $(PC_6H_{11})_4$ the puckering is slightly less pronounced than in $(PCF_3)_4$, as can be seen from the smaller separation of the P atoms of the ring in the direction [**c**], 0·625 and 0·677 Å, the larger cross-ring P- - - P distance, 3·019 and 2·980 Å, and from the differences in P–P–P bond and P–P–P–P torsional angles, as already mentioned above.

Raman spectra of liquid cyclopolyphosphines $(RP)_4$, have been interpreted in terms of a ring with $D_{2d}$ symmetry (Amster, Colthup & Henderson, 1963), on the assumption that they are pure cyclotetraphosphines. The first assumption was based on the structure determination of $(PCF_3)_4$ and is now further supported by $(PC_6H_{11})_4$. Little alkyl-alkyl interaction was detected with R = Et, n-Pr, i-Pr, and i-Bu, and the phosphorus ring vibrations were not affected greatly by varying the alkyl group.

As opposed to a puckered $P_4$-ring, a characteristic of the phosphides $CoP_3$, $NiP_3$, $RhP_3$, $PdP_3$ and $IrP_3$, which have the skutterudite ($CoAs_3$) type structure (Oftedal, 1928), is the existence of a crystallographically required *planar* four-membered ring of P atoms, which need not be square. The analysis of $RhP_3$ (Rundqvist & Hede, 1960) is of limited accuracy only and gives P–P = 2·3 ± 0·1 Å. Covalent bonding is indicated by the short P–P distance and the tetrahedral configuration

Table 8. *Non-bonded intramolecular distances* (Å)

| | | | |
|---|---|---|---|
| H(1)—H(5) | 2·41 | P–H(2) | 3·01 |
| H(5)—H(9) | 2·47 | P–H(3) | 2·79 |
| H(9)—H(1) | 2·47 | P–H(10) | 2·97 |
| H(3)—H(7) | 2·58 | P–H(11) | 2·90 |
| H(7)—H(11) | 2·56 | P–C(2) | 2·781 |
| H(11)–H(3) | 2·58 | P–C(6) | 2·787 |
| H(2)—H(4) | 2·36 | P——P′ | 3·019 |
| H(4)—H(6) | 2·52 | P——C(1″) | 3·206 |
| H(6)—H(8) | 2·33 | P——C(1‴) | 3·211 |
| H(8)—H(10) | 2·35 | P——H(1″) | 3·21 |
| | | P——H(1‴) | 3·24 |
| | | P——H(2″) | 3·25 |
| | | P——H(10‴) | 3·15 |
| | | C(2)–H(10‴) | 3·21 |
| | | C(6)–H(2″) | 3·14 |
| | | H(2)–H(10‴) | 2·59 |
| | | H(2)–H(11‴) | 2·78 |

of two phosphorus and two Rh atoms around each P atom. In a recent accurate determination of the isostructural $IrAs_3$ (Kjekshus & Pedersen, 1961) such a planar ring of four As atoms has been found.

The most interesting intramolecular contacts are presented in Table 8. The cyclohexyl groups alternate above and below the phosphorus ring. No interactions between the substituent groups are found, in full accordance with similar results for $(PCF_3)_4$. This would also be true for the planar polyphosphine ring, so that its non-planarity is not caused by steric repulsions. The characteristics of the tetramer-ring are probably connected with bond angle and torsional angle requirements.

As can be seen from Fig. 1 the overall configuration of the molecule is quite symmetrical and close to $\bar{4}2m$ ($D_{2d}$), just as in $(PCF_3)_4$, where this symmetry is required crystallographically. To achieve this symmetry the moduli of the torsional angles P‴–P–C(1)–C(2) and P″–P–C(1)–C(6), 77·7° and –72·2° respectively, where P‴ and P″ are the neighbours of P on the side of C(2) and C(6) respectively, should be equal. The distance of C(4) from the weighted least-squares plane ($w=Z$) through the atoms C(1), P, P′, C(1′) is 0·07 Å. The four carbon atoms C(2), C(3), C(5), and C(6) show maximum deviation of 0·007 Å to their mean plane $0\cdot4065X-0\cdot5805Y+0\cdot7056Z=1\cdot8224$, where $X, Y, Z$ are the orthogonal coordinates in Å. The cyclotetraphosphine ring is considerably shielded by the atoms C(1), C(2), C(6), the axial H(1) and the hydrogen atoms in the equatorial positions, attached to C(2) and C(6).

The cyclohexane rings are in the chair configuration with the phosphorus atoms occupying an equatorial position, just as in the only other compound with P-cyclohexane units which has been described: $NiCl_2\cdot 2P(C_6H_{11})_3$ (Bellon, Albano, Bianco, Pompa & Scatturin, 1963).

It was not possible to detect any significant bending of the axial C–H bonds away from the principal ring axis. Such a small inclination should be a direct consequence of a flattened cyclohexane ring and would be roughly of the order of 3°, which is only about $1\cdot5\sigma$ for the C–C–H bond angles. The axial H---H interactions across the ring are about 2·50 Å (Table 8), well above twice the van der Waals radius of hydrogen.

### *Packing arrangement*

Figs. 1 and 2 show the packing scheme. Molecules at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ differ slightly in orientation This is necessary in order to prevent too short contacts between the equatorial hydrogen atoms H(6) at C(4), in molecules related by a translation over [110]. The separation is now H(6)---H(6′) = 2·50 Å (corresponding C---C distance of 3·64 Å). Without this orientational difference the space-group would have been $I\bar{4}2m$. The stacking of the molecules is along [001]. The arrangement is such that the cyclohexane rings of symmetry-related molecules are in contact mainly through short H---C and H---H distances. The peripheral equatorial H(6) atom gives the only short P---H distance of 3·31 Å; the corresponding P---C distance is 3·98 Å. All intermolecular contacts within the upper limit of the sum of the van der Waals radii plus 0·4 Å were calculated. Of the 16 independent contacts the shortest in each category of atom are: P---P, none; P---C, 3·98; P---H, 3·31; C---C, 3·64; C---H, 3·12; H---H, 2·50 Å. As no distances were found appreciably shorter than the sum of the interatomic radii, the molecules are packed by ordinary van der Waals forces.

With the external surface of the molecules consisting almost entirely of hydrogen atoms, the shortest H---H distance is considerably longer than twice the van der Waals radius of hydrogen, determined by Kitaigorodskii (1961). The difference may be due to the shorter C–H length (0·98 Å) as compared with the assumption made by Kitaigorodskii (1·08 Å). The van der Waals radius of the methylene group (1·82 Å) conforms with the usually accepted value.

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

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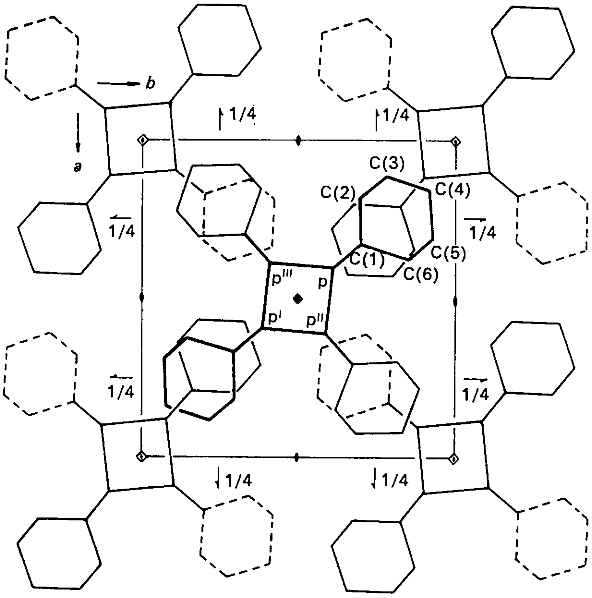

Fig. 1. The structure of $(PC_6H_{11})_4$ projected on (001). The labelling of the atoms, as used in the analysis, is indicated.

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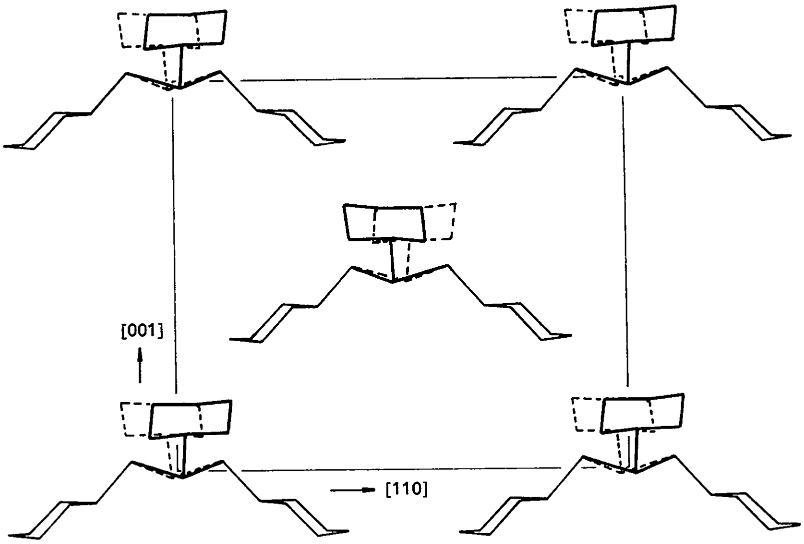

Fig.2. The structure of $(PC_6H_{11})_4$ projected on $(1\bar{1}0)$.

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# The Crystal and Molecular Structure of 1:2,5:6-Dibenzanthraquinone

By R. F. Entwistle,* J. Iball, W. D. S. Motherwell and B. P. Thompson

*Department of Chemistry, The University, Dundee, Scotland*

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The crystal structure of 1:2,5:6-dibenzanthraquinone has been determined by the use of the weighted reciprocal lattice to determine the molecular orientation, and by a trial-and-error computer program, to determine the molecular position in the unit cell. The crystals are orthorhombic with $a=28\cdot54$, $b=3\cdot85$, $c=12\cdot90$ Å and the space group is $Pca2_1$ with four molecules per unit cell. The atomic coordinates and anisotropic temperature parameters have been refined by the least-squares method, to a final $R$ value of 0·0965 for 1354 observed reflexions. The standard deviations of the coordinates are approximately 0·008 Å. The molecular structure consists of two planar naphthalene portions with an angle of 14·1° between the normals to the planes.

## Introduction

The interest in 1:2,5:6-dibenzanthraquinone (DBAQ, Fig. 1) arose because of its relationship to the carcinogenic compound 1:2,5:6-dibenzanthracene, although DBAQ shows no biological activity itself. It was also of interest to determine how much the DBAQ molecule departs from planarity, and to compare the results with the molecules of 5-methyl- and 2′-methyl-1:2-benzanthraquinones, which have a similar close approach of a quinone oxygen atom to the 1′ carbon and hydrogen atoms. These latter compounds show little deviation from planarity (Ferrier & Iball, 1963*a*,*b*) though there is some evidence of steric repulsion within the molecules.

## Experimental

Early attempts to determine the structure with two-dimensional methods had given reasonable atomic coordinates in the (010) plane but no satisfactory three-dimensional coordinates were obtained. It was decided therefore to collect full three-dimensional data and the compound was recrystallized from dimethylformamide, which, of the many solvents tried, gave the largest crystals in the form of orange needles. The unit cell was measured by calibration of zero-layer Weissenberg photographs with NaCl powder lines, and the crystal density was measured by flotation in a density gradient column. The cell is orthorhombic with

$a=28\cdot54\pm0\cdot02$, $b=3\cdot85\pm0\cdot005$, $c=12\cdot90\pm0\cdot01$ Å
Cell volume $=1417$ Å$^3$;
Observed density $=1\cdot443\pm0\cdot003$ g.cm$^{-3}$;
Calculated density $=1\cdot441$ with 4 molecules per unit cell.

The systematic absences were $h0l$ absent when $h$ is odd, and $0kl$ absent when $l$ is odd. The space group

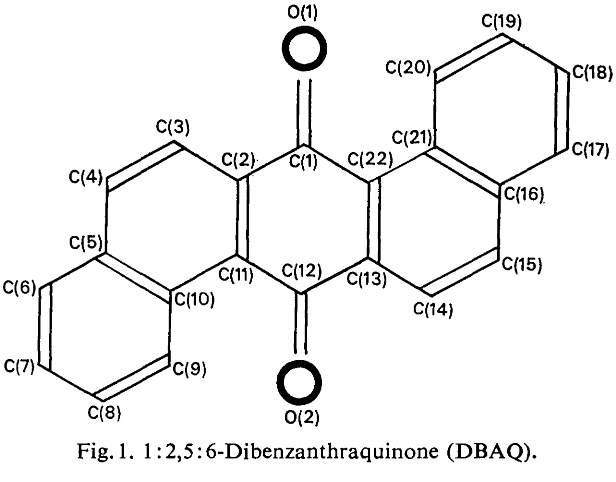

Fig. 1. 1:2,5:6-Dibenzanthraquinone (DBAQ).

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* Present address: Physics Department, University of Otago, New Zealand.