Table 3. *Internal rotation angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)–C(3)–C(4)	69·7 (3)	O(1)–C(1)–C(2)–C(3)	−137·5 (3)	C(6)–N(1)–C(7)–C(8)	−178·3 (2)
C(2)–C(3)–C(4)–C(5)	−176·1 (2)	O(2)–C(1)–C(3)–C(3)	42·2 (3)	N(1)–C(7)–C(8)–C(9)	−168·4 (2)
C(3)–C(4)–C(5)–C(6)	−177·2 (2)			C(7)–C(8)–C(9)–C(10)	169·9 (2)
C(4)–C(5)–C(6)–C(7)	−175·8 (2)	C(6)–N(1)–C(7)–O(3)	1·9 (4)	C(8)–C(9)–C(10)–C(11)	−175·5 (2)
C(5)–C(6)–N(1)–C(7)	169·8 (2)	O(3)–C(7)–C(8)–C(9)	11·4 (4)	C(9)–C(10)–C(11)–C(12)	170·4 (2)
				C(10)–C(11)–C(12)–N(2)	−173·8 (2)

molecules at both ends by N(2)H(23)···O(1) [2·775 (2) Å] hydrogen bonds to form an infinite chain of molecules along the *a* axis. Each molecule is also connected, by hydrogen bonds between amido groups at the middle part of the molecule {N(1)H(11)···O(3) [2·902 (3) Å]}, to the molecules above and below along the *b* axis. A wavy sheet of parallel molecules is thus formed. These sheets stack parallel to one another along the *c* axis, and are on one side bonded by an N(2)H(22)···O(2) [2·694 (2) Å] hydrogen bond and on the other by two hydrogen bonds N(2)-H(24)···O(*W*) [2·930 (2) Å] and O(*W*)H(*W*1)···O(1) [2·634 (2) Å] *via* a water molecule. The water molecules of crystallization themselves are connected by a weak O(*W*)H(*W*2)···O(*W*) [2·923 (3) Å] hydrogen bond along the *b* axis.

Under the combined influences of heat and high vacuum, the existence of crystalline water probably increases the vapor pressure in the reaction vessel appreciably, which controls the vaporization of water molecules released by the polycondensation and affects the solid-state conversion of the present dimer molecule to Nylon 6. This is consistent with the fact that the solid-state polycondensation of the ε-aminocaproic acid hardly takes place if the crystal is sealed in a small ampoule.

Computations throughout the study were carried out on an ACOS series 77 NEAC System 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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Tetra-*tert*-butylcyclotetraphosphane, $[PC(CH_3)_3]_4$

By Willis Weigand, A. W. Cordes and Paul N. Swepston

Department of Chemistry, University of Arkansas, Fayetteville, AR 72701, *USA*

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Abstract. $C_{16}H_{36}P_4$, monoclinic, $P2_1/c$, $a = 9{\cdot}391$ (1), $b = 14{\cdot}029$ (2), $c = 16{\cdot}854$ (2) Å, $\beta = 95{\cdot}80$ (1)°, $V = 2196$ Å^3, $Z = 4$, D_o (by flotation in $ZnCl_2$ solution) = 1·08, D_c = 1·07 Mg m^{-3}. The central P_4 ring is non-planar with P–P distances of 2·212 (2) Å and P–P–P–P torsion angles of 24·5°. The *tert*-butyl groups are on alternate sides of the ring such that the molecule very nearly possesses $\bar{4}2m$ symmetry. The final R was 0·037 for the 1981 observed reflections.

Introduction. The crystal structures of four cyclopolyphosphane molecules have been reported: the tetramer $(PCF_3)_4$ (Palenik & Donohue, 1962), pentamers $(PCF_3)_5$ (Spencer & Lipscomb, 1961, 1962) and $(PPh)_5$ (Daly, 1964) and the hexamer $(PPh)_6$ (Daly, 1965, 1966). The present paper reports the structure of $[PC(CH_3)_3]_4$ which was determined in order to study the effects of the bulky *tert*-butyl groups on the phosphorus ring conformation and, through

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comparison with $(PCF_3)_4$, to evaluate the effect of substituent-group electronegativity on the structure of the tetramer ring.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$)

$$B_{eq} = \tfrac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac\cos\beta).$$

	x	*y*	*z*	B_{eq}* (Å²)
P(1)	1641 (1)	401 (1)	7801 (1)	4·53 (3)
P(2)	3043 (1)	57 (1)	6855 (1)	4·44 (3)
P(3)	1245 (1)	−783 (1)	6262 (1)	4·48 (3)
P(4)	459 (1)	−923 (1)	7458 (1)	4·79 (3)
C(1)	2759 (4)	82 (3)	8766 (2)	5·7 (2)
C(2)	3541 (6)	−862 (4)	8743 (3)	7·5 (3)
C(3)	1751 (7)	67 (5)	9414 (3)	8·9 (3)
C(4)	3842 (7)	890 (5)	8905 (4)	9·3 (4)
C(5)	3058 (4)	1175 (2)	6236 (2)	5·0 (2)
C(6)	4096 (5)	1858 (3)	6697 (3)	6·6 (2)
C(7)	1621 (5)	1646 (4)	6050 (3)	7·0 (2)
C(8)	3675 (7)	868 (4)	5464 (3)	8·2 (3)
C(9)	2055 (4)	−1978 (3)	6079 (2)	5·4 (2)
C(10)	2912 (8)	−1849 (4)	5359 (4)	9·3 (3)
C(11)	3037 (5)	−2381 (4)	6784 (3)	7·1 (3)
C(12)	817 (6)	−2670 (3)	5886 (3)	7·4 (3)
C(13)	−1469 (4)	−531 (3)	7278 (2)	5·8 (2)
C(14)	−1993 (6)	−411 (5)	8110 (4)	8·7 (3)
C(15)	−2249 (5)	−1355 (4)	6837 (4)	7·8 (3)
C(16)	−1715 (5)	379 (4)	6798 (4)	7·8 (3)
H(C2)	285 (5)	−135 (3)	871 (3)	
H′(C2)	420 (4)	−91 (3)	829 (3)	
H″(C2)	406 (5)	−96 (3)	916 (3)	
H(C3)	99 (5)	−44 (3)	926 (3)	
H′(C3)	108 (5)	69 (3)	941 (3)	
H″(C3)	222 (5)	−12 (3)	987 (3)	
H(C4)	432 (5)	80 (3)	933 (3)	
H′(C4)	451 (5)	90 (3)	842 (3)	
H″(C4)	321 (5)	149 (3)	900 (2)	
H(C6)	503 (5)	158 (3)	676 (2)	
H′(C6)	420 (5)	242 (3)	641 (2)	
H″(C6)	370 (5)	201 (3)	717 (3)	
H(C7)	167 (4)	218 (3)	576 (3)	
H′(C7)	93 (5)	116 (3)	572 (3)	
H″(C7)	115 (5)	185 (3)	650 (3)	
H(C8)	473 (5)	68 (3)	563 (3)	
H′(C8)	379 (4)	144 (3)	524 (3)	
H″(C8)	303 (5)	49 (3)	516 (3)	
H(C10)	326 (5)	−240 (3)	528 (3)	
H′(C10)	219 (5)	−168 (4)	497 (3)	
H″(C10)	377 (4)	−138 (3)	557 (3)	
H(C11)	384 (5)	−193 (3)	693 (2)	
H′(C11)	338 (4)	−303 (3)	663 (2)	
H″(C11)	251 (5)	−247 (3)	720 (3)	
H(C12)	120 (4)	−331 (3)	571 (2)	
H′(C12)	12 (5)	−241 (3)	548 (3)	
H″(C12)	24 (5)	−274 (3)	637 (3)	
H(C14)	−145 (5)	14 (3)	842 (3)	
H′(C14)	−297 (5)	−23 (3)	792 (3)	
H″(C14)	−193 (5)	−96 (3)	832 (3)	
H(C15)	−208 (4)	−197 (3)	714 (2)	
H′(C15)	−196 (4)	−142 (3)	629 (3)	
H″(C15)	−313 (5)	−124 (3)	680 (3)	
H(C16)	−131 (5)	91 (3)	697 (3)	
H′(C16)	−146 (5)	29 (3)	625 (3)	
H″(C16)	−263 (5)	53 (3)	677 (3)	

* All hydrogen atoms were refined with isotropic $B = 5{\cdot}0$ Å².

$[PC(CH_3)_3]_4$ was produced *via* the reaction of *tert*-butyllithium with PCl_3 in pentane to give *tert*-butylPCl_2, which was subsequently reduced with Mg using tetrahydrofuran as the solvent. The compound was crystallized by slow cooling of a diethyl ether–ethanol solution. The crystal used for all data collection had opposing external faces parallel to the (100), (010), (011), and $(01\bar{1})$ planes at face-to-center distances of 0·21, 0·18, 0·15, and 0·15 mm, respectively. A least-squares refinement of 17 values of $2\sin\theta/\lambda$ for 2θ values > 75° ($\lambda = 1{\cdot}5405$ Å) gave the cell constants listed above. $P2_1/c$ symmetry was determined by preliminary Weissenberg photographs.

Intensities were measured using Ni-filtered Cu $K\alpha$ radiation and a manual GE XRD-5 diffractometer. A θ–2θ scan (2θ max = 100°) at 2° min^{-1} over 2° was used, with 10 s background counts taken at the beginning and end of each scan. Three standard reflections monitored every 3 h indicated general crystal and electronic stability. The μ value for the crystal was 3·035 mm^{-1}; an absorption correction gave a range of correction factors of 0·64 to 0·70. Of the 2248 unique reflections measured, 1981 had intensities greater than 3σ and the latter were used for structure solution and refinement.

Table 2. *Intramolecular distances* (Å) *and angles* (°) *not involving* H *atoms*

P(1)–P(2)	2·213 (1)
P(2)–P(3)	2·211 (1)
P(3)–P(4)	2·212 (1)
P(4)–P(1)	2·210 (1)
P(1)–P(3)	3·058 (1)
P(2)–P(4)	3·048 (1)
P(1)–C(1)	1·890 (4)
P(2)–C(5)	1·881 (4)
P(3)–C(9)	1·879 (4)
P(4)–C(13)	1·887 (4)
C(1)–C(2)	1·517 (7)
C(1)–C(3)	1·511 (7)
C(1)–C(4)	1·524 (8)
C(5)–C(6)	1·521 (6)
C(5)–C(7)	1·507 (6)
C(5)–C(8)	1·531 (7)
C(9)–C(10)	1·527 (8)
C(9)–C(11)	1·532 (6)
C(9)–C(12)	1·523 (6)
C(13)–C(14)	1·533 (8)
C(13)–C(15)	1·520 (7)
C(13)–C(16)	1·514 (7)
C–H average	0·96
C–H range	0·82–1·07

Torsion angles

P(1)–P(2)–P(3)–P(4)	−24·49 (4)
P(2)–P(3)–P(4)–P(1)	24·52 (4)
P(3)–P(4)–P(1)–P(2)	−24·50 (4)
P(4)–P(1)–P(2)–P(3)	24·52 (4)
C–P–P–C (average)	±127·8 (8)
P–P–P–C (average)	±128 (1)
P–P–C–C (average)	±76 (3)
	±166 (4)
	±45 (3)

P(2)–P(1)–P(4)	87·12 (5)
P(1)–P(2)–P(3)	87·46 (4)
P(2)–P(3)–P(4)	87·11 (5)
P(3)–P(4)–P(1)	87·49 (4)
P(1)–P(2)–C(5)	104·6 (1)
P(2)–P(1)–C(1)	104·0 (1)
P(2)–P(3)–C(9)	104·2 (1)
P(3)–P(4)–C(13)	103·4 (1)
P(1)–C(1)–C(2)	114·4 (3)
P(1)–C(1)–C(3)	106·5 (3)
P(1)–C(1)–C(4)	105·0 (3)
P(2)–C(5)–C(6)	106·6 (3)
P(2)–C(5)–C(7)	115·1 (3)
P(2)–C(5)–C(8)	104·9 (3)
P(3)–C(9)–C(10)	106·1 (3)
P(3)–C(9)–C(11)	115·2 (3)
P(3)–C(9)–C(12)	106·9 (3)
P(4)–C(13)–C(14)	106·1 (3)
P(4)–C(13)–C(15)	105·2 (3)
P(4)–C(13)–C(16)	115·0 (3)
C(2)–C(1)–C(3)	110·2 (4)
C(2)–C(1)–C(4)	109·6 (4)
C(3)–C(1)–C(4)	110·9 (4)
C(6)–C(5)–C(7)	110·1 (3)
C(7)–C(5)–C(8)	110·8 (4)
C(6)–C(5)–C(8)	109·2 (4)
C(10)–C(9)–C(11)	109·2 (4)
C(10)–C(9)–C(12)	111·1 (4)
C(11)–C(9)–C(12)	108·4 (4)
C(14)–C(13)–C(15)	110·0 (4)
C(14)–C(13)–C(16)	110·2 (4)
C(15)–C(13)–C(16)	110·1 (4)
C–C–H average	109
H–C–H average	110
C–C–H range	97–120
H–C–H range	100–124

The structure was solved by direct methods using *MULTAN*80 (Main, Germain, Declercq & Woolfson, 1980). The initial E map yielded an incorrect position for the tetraphosphorus ring, which led to uninterpretable Fourier maps in the search for the C positions. A re-calculation of the E values using a preformed P_4 unit as part of the scattering factor calculation led to the correct solution, which was related to the false solution by a translation of the z coordinates. The C atoms were then located on subsequent difference maps. The initial positions of the 36 H atoms were also determined from difference maps and their refinement was included in the full-matrix least-squares treatment. The final refinement included anisotropic thermal parameters for P and C and fixed isotopic thermal parameters of $B = 5{\cdot}0$ Å^2 for the H atoms. Neutral-atom scattering factors were used and anamolous-dispersion corrections were made for P. The weighting scheme employed was $w = 1/(2F_{\rm min} + F_o + 2F_o^2/F_{\rm max})$. The final cycle gave an R of 0·037, $R_w = 0{\cdot}052$, a standard deviation of an observation of unit weight of 0·53, and no parameter shifts greater than $0{\cdot}11\sigma$. A lack of correlation of $\Delta F/\sigma$ with either F or θ indicated the weighting scheme was satisfactory. Table 1 gives positional parameters and Table 2 gives intramolecular bond distances and angles not involving hydrogen, and selected torsion angles.*

Discussion. The structure of the molecule consists of a tetraphosphorus central ring which is non-planar, with the exocyclic groups oriented such that each *tert*-butyl group and the P atom to which it is attached lie on opposite sides of the central best plane, as shown in Fig. 1. The molecule has no crystallographically imposed symmetry, but it approaches point symmetry $\bar{4}2m$. All the P and C atoms are within 0·09 Å of a $\bar{4}2m$ model (0·03 Å or 5σ average displacement), and the 36 H atoms are all within 0·22 Å (0·11 Å or 3σ average displacement) of this idealized geometry. This symmetry, which is crystallographically imposed on the $(PCF_3)_4$ molecule in its crystals, is best shown by the view of Fig. 2.

The four crystallographically independent P—P distances average 2·212 (2) Å,† which is in agreement with the remarkably constant value found in all previously characterized polyphosphanes (including tetramers, pentamers, and hexamers, of CF_3 and/or phenyl substituents) (Donohue, 1962). The average P—C bond distance of 1·884 (8) Å is equal to the value found in both the PCF_3 tetramer and pentamer, another somewhat surprising fact in view of the large difference in the group electronegativities of the trifluoromethyl and the *tert*-butyl groups. The main consequence of the $CF_3/C(CH_3)_3$ electronegativity difference is the expected contraction of the X—C—X and P—C—X angles in the CF_3 derivative.

The only intramolecular distance which indicates a relatively short non-bonded contact in these tetramers is that between the P atoms and the 'internal' H (or F) atoms of the substituent groups on the adjacent P atoms (see Fig. 3). This P···H contact averages 2·9 (1) Å, a distance equal to the sum of the 1·0 Å van der Waals radius for H (Baur, 1972) and the 1·9 Å value for P (Pauling, 1960); the corresponding P···F contact in $(PCF_3)_4$ is 3·19 (8) Å where the van der Waals value is 3·25 Å. These contacts account for the staggered arrangement of the CX_3 groups with respect to the P_4 ring and the larger PCX angle for the internal X group: For the *tert*-butyl derivative the internal PCC angles average 114·9 (5)° while the PCC angles that go to the methyl groups external to the ring average 106 (1)°, and a similar distortion exists [118·1 (7) and 109·6 (7)°] in the trifluoro molecule.

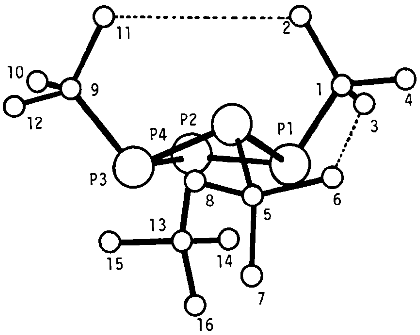

Fig. 1. A general view of the molecule. The unlabelled atoms are C atoms.

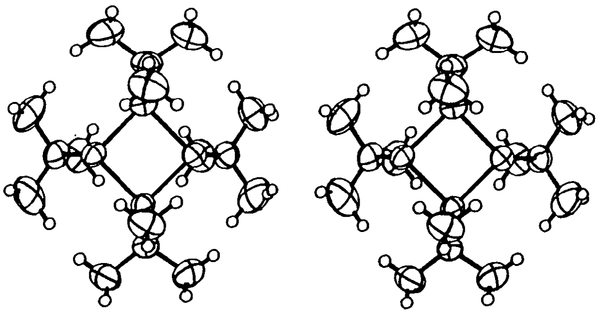

Fig. 2. A stereoview of the molecule parallel to the approximate $\bar{4}$ axis.

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* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36041 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Throughout this paper the numbers in parentheses are estimated standard deviations of the least significant figure for experimental values singly determined, and indicate the range of values for the least significant figure for values which represent averages.

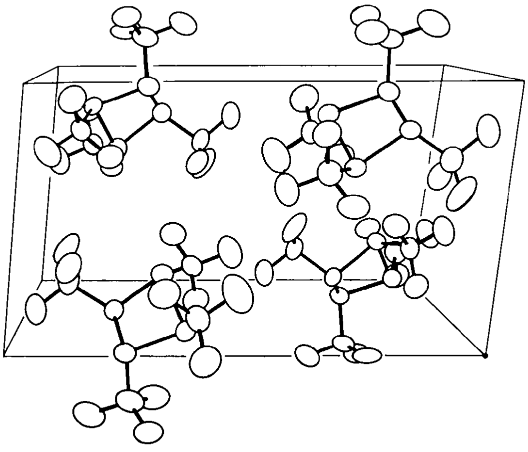

Fig. 3. Packing diagram, with z horizontal, x vertical, y perpendicular to the page, and the origin (shown by the black dot) of the cell in the front, lower, righthand corner.

The P_4 ring of the *tert*-butyl tetramer is less puckered than the trifluoromethyl tetramer: the PPPP torsion angles average 24·51 (2)° *vs* 34·0 (1)° for $(PCF_3)_4$, the average PPP bond angle is 87·30 (9)° compared to 84·6 (1)° for the fluoro derivative, and the P atoms are displaced 0·240 (1) Å from the best plane whereas this displacement is 0·338 (3) Å for $(PCF_3)_4$. The dihedral angle formed by the two PPP planes is 145·0 (1)° for the *tert*-butyl compound and 131·1 (1)° for the fluoro compound. Although the closest cross-ring and adjacent-group H···H contacts (shown by dotted lines in Fig. 1) in $(PC_4H_9)_4$ at 2·69 (6) and 2·66 (6) Å are considerably longer than the van der Waals contact of 2·0 Å (Baur, 1972), they are apparently important in determining the ring conformation. Using experimental values for P—P, P—C, and C—Me distances and P—P—C, P—C—C, and C—C—C angles, calculations show that the amount of ring puckering in the P_4 ring has little effect on the short P—H distance discussed above but greatly affects the cross-ring and adjacent-group methyl–methyl contacts of the types indicated by the dotted lines in Fig. 1. Increased ring puckering shortens the C(2)···C(11)-type cross-ring contact and lengthens the adjacent-group contact of the type C(2)···C(4). These two types of contacts are equal in the experimental structure at the 24·51° PPPP torsion angles. This equalization of substituent-group contacts is also the case for the corresponding F···F contacts in the CF_3 tetramer, where these contacts are also 0·7 Å greater than the sum of the van der Waals radii. Thus, assuming that the bond distances and angles within the P—C—X systems correspond to unstrained values, the balancing of the rather long cross-ring and adjacent-group substituent distances can account for the difference in the P_4 ring puckering of the two tetramer rings.

The packing of $[PC(CH_3)_3]_4$, shown in Fig. 3, does not involve any intermolecular H···H contacts of less than 2·45 (6) Å; consequently crystal packing is not considered a source of molecular distortion.

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