As with many other nitro compounds and other types of derivative (Trotter, 1960), these dimensions indicate that there is no 'resonance' involving excited structures.

The bond distances and angles in the six-membered ring vary widely and haphazardly, many of the variations being too large to be real. It is considered that part at least of this variation is the result of errors in positional parameters due to the inadequacy of the block diagonal least-squares approximation, or perhaps of the weighting system, used in the present refinement. It would have been very useful to repeat the refinement using either full-matrix least-squares or differential syntheses for comparison of the results, but we did not have computational facilities for carrying out these refinements. It is considered that the finer details of the bond-length variations in the benzene ring are still obscure. The mean C–C distance is 1·38 Å.

Intermolecular dimensions

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation *c* is 3·46 Å. The shorter lateral contacts are illustrated in Fig. 3.

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The Molecular and Crystal Structure of $(PCF_3)_5$

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Visual estimates of 2078 reflections obtained from a single crystal at −100 °C. indicated four molecules of $(PCF_3)_5$ in a unit cell of symmetry $P2_1/n$ and having parameters

$$a = 9{\cdot}87,\ b = 9{\cdot}78,\ c = 16{\cdot}67\ \text{Å};\ \beta = 103°\ 0'.$$

The sterically distorted P_5 ring shows also one short P · · · F interaction of 3·04 Å.

Average distances are P–P = 2·223 ± 0·007, P–C = 1·91 ± 0·02 and C–F = 1·35 ± 0·03 Å. The P–P–P angles vary from 94·6 to 107·5 ± 0·4°. Values of

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}18 \quad \text{and} \quad r = \Sigma w||F_o|^2 - |F_c|^2|^2/\Sigma w F_o^4 = 0{\cdot}14$$

do not include the anisotropic thermal motions of the P_5 ring along x and the torsional oscillations of CF_3 and the P–C bonds.

Introduction

Recognition of the ability of the CF_3 group to stabilize unusual molecular and valence structures had led to the recent preparation of many new compounds in recent years. Among these are some new fluorocarbon–phosphorus compounds, and especially the two new ring compounds $(PCF_3)_4$ and $(PCF_3)_5$ (Mahler & Burg, 1958). The nature of the P–P bond in small rings, the role of the unshared pairs on P in the valence structures, and especially the not-directly bonded P · · · P interactions were of interest. In particular, the unshared pair might play a role in stabilizing the ring structure in several possible ways. Also, a comparison of the structures of $(PCF_3)_5$ and $(AsCH_3)_5$ (Burns & Waser, 1957) is of interest because CF_3 is larger than CH_3 and P is smaller than As, thus increasing the steric effects greatly.

Experimental

A sample of $(PCF_3)_5$, pentakis-(trifluoromethyl)-cyclopentaphosphine, was distilled in vacuum into thin-walled pyrex capillaries about 0·3 mm. in diameter. A single crystal, m.p. −33 °C., was grown in the usual way (Reed & Lipscomb, 1953; Lipscomb, 1957) and maintained at −100 °C. Precession photographs were taken using Mo $K\alpha$ radiation at a precession angle of 25° of the zero levels of the $\{0kl\}$, $\{hk0\}$, $\{hkh\}$, $\{\bar{h}kh\}$, $\{hk2h\}$, $\{\bar{h}k2h\}$, $\{3hkh\}$ and $\{\bar{h}k4h\}$ zones, the first four upper levels about the [100] axis, and the first two upper levels about the [001] axis. Equi-inclination Weissenberg photographs were taken using Cu $K\alpha$ radiation of the zero and first four upper levels about the [010] axis. Intensities were estimated visually by comparison with timed intensity scales prepared from reflections from the same $(PCF_3)_5$ single crystals. Absorption and extinction corrections were not made on the data obtained with Mo $K\alpha$ radiation; however, an empirical correction, $2/(2+\sin^2\theta)$, of the rough general form of the absorption and secondary extinction correction was found to improve the correlation of the data obtained with Cu $K\alpha$ radiation with the data obtained with Mo $K\alpha$ radiation. A detailed study of this correlation has resulted in a computer program for placing all intensities from all levels onto a single scale (Spencer, 1960). A total of 1492 independent reflections were obtained from the precession photographs, and the addition of reflections from the Weissenberg photographs brought the total to 2078 independent reflections.

Structure determination

The unit cell is monoclinic with parameters

$$a=9\cdot87\pm0\cdot014,\quad b=9\cdot78\pm0\cdot013,\quad c=16\cdot67\pm0\cdot056\text{ Å};$$
$$\beta=103°\ 0'\pm10'.$$

Systematic absences of $h0l$ reflections when $h+l$ is odd and of $0k0$ when k is odd indicate C_{2h}^5–$P2_1/n$ as the probable space group. The assumption of four molecules in general positions seems most reasonable, since the molecule can hardly be expected to be centrosymmetric, and since the resulting calculated density of 2·12 g.cm.$^{-3}$ is a reasonable value (Mahler & Burg, 1958).

A three dimensional Patterson function

$$P''(u,v,w)=AP'(u,v,w)+BP(u,v,w)$$

was calculated, where $P(u,v,w)$ is the usual sharpened Patterson function and $P'(u,v,w)$ is the 'gradient' sharpened Patterson function (Jacobson, Wunderlich & Lipscomb, 1959).

$$P'(u,v,w)$$
$$=\int\nabla\varrho(x,y,z)\,.\,\nabla\varrho(x+u,y+v,z+w)\,V\,dx\,dy\,dz$$
$$=(4\pi^2/V)\sum_{hkl}(4\sin^2\theta/\lambda^2)|F_{hkl}|^2\exp 2\pi i\,(hu+kv+lw)\,.$$

The $|F_{hkl}|^2$ are the usual sharpened coefficients; $|F_{hkl}|^2=\hat{f}^{\,-2}F_o^2\exp(\beta'\sin^2\theta/\lambda^2)$, where $\hat{f}=\sum_i f_i/\sum_i Z_i$, and β', chosen as 2 Å^2, is the artificial temperature factor. Values of $A=1/(4\pi^2)$ and $B=1/6$ were chosen in order to sharpen individual peaks as much as we dared without introducing appreciable negative regions around the peaks in the function $P''(u,v,w)$. Intervals of $a/80$, $b/40$ and $c/80$ were chosen.

The analysis of this Patterson function, greatly facilitated by the use of this sharpening procedure, yielded the P_5 ring, which was then placed in the unit cell by a thorough check of all intermolecular P · · · P interactions. A three dimensional electron density map, $\varrho_1(x,y,z)$, was then computed from the largest 600 reflections with signs as given by the P atoms only. The P atoms ranged from 190 to 230 in arbitrary units, and were shifted by 0·1 Å or less from their assumed positions; of the 56 other peaks above 30, only six (F_1 at height 34, F_2 at 72, F_4 at 66, F_4' at 50, F_4'' at 31 and F_5 at 76) satisfied the criteria that they were 2·4 to 2·8 Å from a P atom, more than 2·8 Å from any other P atom, and gave P · · · F vectors which checked throughout the Patterson function.

Atom C_4, bonded to F_4, F_4' and F_4'', was then added to this list, although it did not appear in $\varrho_1(x,y,z)$, and the coordinates of these 12 known atoms were

Table 1. *Final atomic parameters and their probable errors in fractions of the cell edges*

Atom	x	y	z	B (Å^2)
P_1	0·1203	0·2622	0·2046	1·84 ± 0·09
P_2	−0·0659	0·2655	0·0997	1·31 ± 0·08
P_3	−0·2108	0·1865	0·1759	1·59 ± 0·08
P_4	−0·1138	−0·0099	0·2231	1·64 ± 0·09
P_5	0·1015	0·0635	0·2652	1·86 ± 0·09
C_1	0·2404	0·1985	0·1404	3·11 ± 0·45
C_2	−0·1070	0·4553	0·1131	2·39 ± 0·35
C_3	−0·3577	0·1236	0·0905	2·40 ± 0·37
C_4	−0·0847	−0·1141	0·1305	2·30 ± 0·34
C_5	0·0767	0·1376	0·3674	2·20 ± 0·35
F_1	0·2559	0·2922	0·0841	3·37 ± 0·27
F_1'	0·2168	0·0783	0·1024	3·03 ± 0·24
F_1''	0·3738	0·1879	0·1915	3·82 ± 0·32
F_2	−0·0956	0·4953	0·1933	2·68 ± 0·22
F_2'	−0·0082	0·5301	0·0860	3·32 ± 0·27
F_2''	−0·2303	0·4821	0·0721	3·92 ± 0·29
F_3	−0·4420	0·2295	0·0609	2·72 ± 0·23
F_3'	−0·4356	0·0327	0·1194	2·82 ± 0·23
F_3''	−0·3197	0·0680	0·0223	2·26 ± 0·21
F_4	−0·0457	−0·0397	0·0699	2·21 ± 0·21
F_4'	0·0196	−0·2019	0·1576	4·40 ± 0·32
F_4''	−0·1969	−0·1824	0·0973	3·45 ± 0·26
F_5	−0·0195	0·2321	0·3619	2·93 ± 0·24
F_5'	0·0491	0·0380	0·4149	3·49 ± 0·27
F_5''	0·1998	0·1945	0·4078	3·05 ± 0·24

Average probable errors of atomic coordinates are ±0·005 Å for P, ±0·022 Å for C and ±0·014 Å for F.

Table 2. *Intramolecular bond distances*

P_1-P_2	2·233 ± 0·007 Å	C_1-F_1	1·346 ± 0·029 Å
P_2-P_3	2·252 ± 0·007	C_1-F_1'	1·331 ± 0·029
P_3-P_4	2·212 ± 0·007	C_1-F_1''	1·401 ± 0·030
P_4-P_5	2·202 ± 0·007	C_2-F_2	1·373 ± 0·025
P_5-P_1	2·218 ± 0·008	C_2-F_2'	1·374 ± 0·026
Average	2·223 ± 0·017* Å	C_2-F_2''	1·281 ± 0·026
		C_3-F_3	1·351 ± 0·025
P_1-C_1	1·873 ± 0·026	C_3-F_3'	1·334 ± 0·025
P_2-C_2	1·925 ± 0·022	C_3-F_3''	1·387 ± 0·025
P_3-C_3	1·891 ± 0·022	C_4-F_4	1·369 ± 0·024
P_4-C_4	1·924 ± 0·022	C_4-F_4'	1·338 ± 0·027
P_5-C_5	1·916 ± 0·022	C_4-F_4''	1·305 ± 0·025
Average	1·906 ± 0·020* Å	C_5-F_5	1·314 ± 0·025
		C_5-F_5'	1·322 ± 0·025
		C_5-F_5''	1·368 ± 0·025
		Average	1·346 ± 0·032* Å

* Standard deviation of individual bond distances from average.

Table 3. *Bond angles*

$P_1-P_2-P_3$	94·6 ± 0·3°	$F_3-C_3-P_3$	119·5 ± 1·7
$P_2-P_3-P_4$	105·1 ± 0·3	$F_3'-C_3-P_3$	112·3 ± 1·7
$P_3-P_4-P_5$	107·2 ± 0·3	$F_3''-C_3-P_3$	125·1 ± 1·7
$P_4-P_5-P_1$	96·6 ± 0·3	$F_4-C_4-P_4$	108·9 ± 1·7
$P_5-P_1-P_2$	107·5 ± 0·3	$F_4'-C_4-P_4$	93·1 ± 1·7
Average	102·2°	$F_4''-C_4-P_4$	125·0 ± 1·7
		$F_5-C_5-P_5$	99·1 ± 1·7
$C_1-P_1-P_5$	86·1 ± 0·8°	$F_5'-C_5-P_5$	104·3 ± 1·7
$C_1-P_1-P_2$	94·7 ± 0·8	$F_5''-C_5-P_5$	125·0 ± 1·7
$C_2-P_2-P_1$	95·2 ± 0·8		
$C_2-P_2-P_3$	102·4 ± 0·8	$F_1'-C_1-F_1$	106 ± 2°
$C_3-P_3-P_2$	100·4 ± 0·8	$F_1''-C_1-F_1'$	114 ± 2
$C_3-P_3-P_3$	110·1 ± 0·8	$F_1-C_1-F_1''$	115 ± 2
$C_4-P_4-P_3$	99·9 ± 0·8	$F_2'-C_2-F_2$	107 ± 2
$C_4-P_4-P_5$	114·8 ± 0·8	$F_2'-C_2-F_2$	112 ± 2
$C_5-P_5-P_4$	115·9 ± 0·8	$F_2''-C_2-F_2$	127 ± 2
$C_5-P_5-P_1$	93·4 ± 0·8	$F_3'-C_3-F_3$	107 ± 2
		$F_3''-C_3-F_3'$	94 ± 2
$F_1-C_1-P_1$	99·4 ± 1·7	$F_3-C_3-F_3''$	94 ± 2
$F_1'-C_1-P_1$	118·7 ± 1·7	$F_4'-C_4-F_4$	119 ± 2
$F_1''-C_1-P_1$	103·7 ± 1·7	$F_4''-C_4-F_4'$	118 ± 2
$F_2-C_2-P_2$	108·6 ± 1·7	$F_4-C_4-F_4''$	95 ± 2
$F_2'-C_2-P_2$	102·2 ± 1·7	$F_5'-C_5-F_5$	122 ± 2
$F_2''-C_2-P_2$	106·4 ± 1·7	$F_5''-C_5-F_5'$	95 ± 2
		$F_5-C_5-F_5''$	114 ± 2

Table 4

Final agreement factors, *R*		Final agreement factors, *R*, as a function of sin *θ*	
Category of reflection	*R*	Range of sin *θ*	*R*
All planes	0·18	0·00–0·40	0·13
$h+k+l$ odd	0·18	0·40–0·50	0·14
$h+k$ odd	0·18	0·50–0·60	0·18
$k+l$ odd	0·18	0·60–0·70	0·18
$h+l$ odd	0·19	0·70–0·75	0·19
h odd	0·16	0·75–0·80	0·18
k odd	0·18	0·80–0·85	0·20
l odd	0·19	0·85–0·90	0·21
$hk0$	0·16	0·90–0·95	0·24
$0kl$	0·12	0·95–1·50	0·31
$h0l$	0·20		

used to calculate the signs of coefficients for a second map $\varrho_2(x, y, z)$. Two new atoms, F_5' and F_5'', were found at about one-third of their expected height, even though one P atom had been entered accidentally with incorrect coordinates. Correction of this error, and addition of these two new atoms then led to $\varrho_3(x, y, z)$ in which all observed reflections were included, and in which all remaining atoms were then found and later rechecked by search for their vectors in Patterson space. An electron density map $\varrho_4(x, y, z)$ in which all atoms were included showed all atoms at their proper relative heights, but with a large number of additional maxima at about one-half of the height of the carbon atom. Later, a difference map which was identically zero everywhere led to the discovery that, owing to a misunderstanding between us and the Computer, all coefficients in all of our electron density maps were identical. The proper signs had, however, been used in all computations. The fact that our original Patterson function had been computed with the proper coefficients does suggest that the experimental data are not completely irrelevant in a structure determination. After the least-squares analysis, which confirmed the structure, a final difference electron density map shown in Fig. 1 and a final electron density map of the molecule shown in Fig. 2 indicated no spurious effects other than those attributed to thermal motion.

Three cycles of three dimensional least-squares analysis using the full matrix were carried out with variation of all distance parameters and a single separate temperature factor constant *B* for each atom. Successive values of *r* (see abstract) = 0·39, 0·17, and 0·14 were obtained, and the final parameters listed in Table 1 were found. The standard deviations were computed from the full matrix. Bond distances are shown in Table 2, bond angles in Table 3, agreement factors for various classes of reflections in Table 4. and the comparison of F_o and F_c in Table 5.

Although refinement of this structure with isotropic temperature factors is complete, the difference electron density map around the five-membered ring (Fig. 1) clearly indicates crystal vibrations preferentially along the *a* axis. In addition, there are clear indications of torsional oscillation of the CF_3 group about the P–C bond, as shown by positive arc-shaped regions (not shown here) up to 1·5 e.Å^{-3} with corresponding negative regions on either side around the F atoms. No conclusions could readily be drawn concerning the anisotropy of thermal motion about the C atoms, however. The maximum and minimum electron densities not attributable to the residues of an atom were between $-\frac{1}{2}$ and $\frac{1}{2}$ e.Å^{-3} in the difference map. In the electron density map itself (Fig. 2) the highest peak

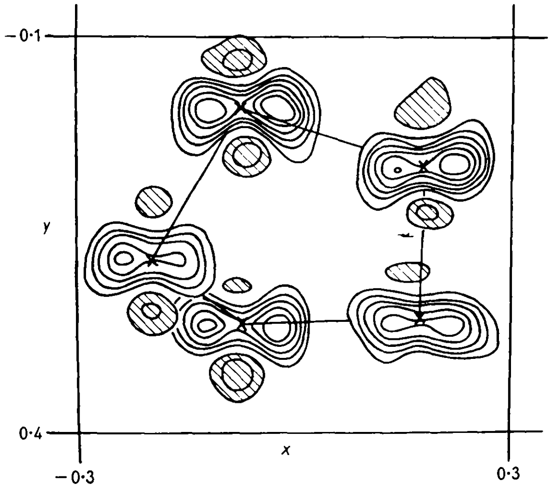

Fig. 1. Final three-dimensional difference electron density map projected on (100) showing sections through the centers of the phosphorus atoms only. Contours are drawn at 0·25, 0·5, 1·0, 1·5, and 2·0 e.Å^{-3}. Negative regions, shown as cross-hatched areas, are toroidal-shaped in three dimensions around the positive regions.

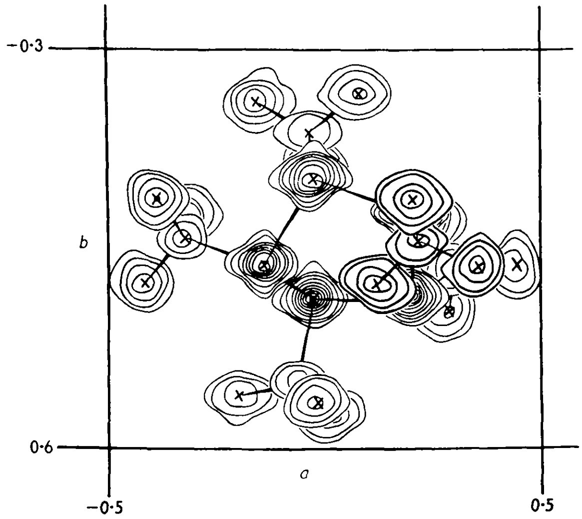

Fig. 2. Final three-dimensional electron density map projected on (100) showing sections through the center of each atom. Contours are drawn at 1, 2, 4, 6, etc. e.Å^{-3}.

which does not represent an atom is at 1·5 e.Å^{-3}, but there are negative regions in the neighborhood of P atoms as low as −2·5 e.Å^{-3}. Thus it is clear that refinement with the use of anisotropic thermal parameters would improve the agreement shown in Tables 4 and 5, perhaps markedly, but out primary interest here is the molecular structure, and we felt that the additional information to be gained by further refinement did not justify the large amount of computing time that would be required.

Results and discussion

The five-membered ring is widely distorted from a planar configuration (Fig. 3). Although the average P–P–P angle of 102·2° is nearly normal (Wright & Penfold, 1959), there appear to be two kinds of angles here. Thus P_1–P_2–P_3 is 94·7° and P_4–P_5–P_1 is 96·6°, while the remaining three angles average to 106·6°. The CF_3 groups would be as widely separated as possible if they lie on alternate sides of the ring on adjacent P atoms, but in a five membered ring this regularity is not possible, and so the CF_3 groups on P_3 and P_4 lie on the same side of the ring. These two CF_3 groups are in widely different positions relative to the ring. In addition to the distortion of the ring, there is a further displacement of the $C_3F_3F_3'F_3''$ group from the $C_4F_4F_4'F_4''$ group such that the angles C_3–P_3–P_4 of 110·1° and C_3–P_3–P_2 of 100·4° are far from equal. Another steric aspect of the CF_3 orientation is that these groups attached to P_1, P_2 and P_5 are oriented such that one of the F atoms of each is equidistant from the two P atoms adjacent to the P to which the CF_3 is bonded, but the overcrowded situation of the CF_3 groups on P_3 and P_4 is such that similar orientations cannot occur.

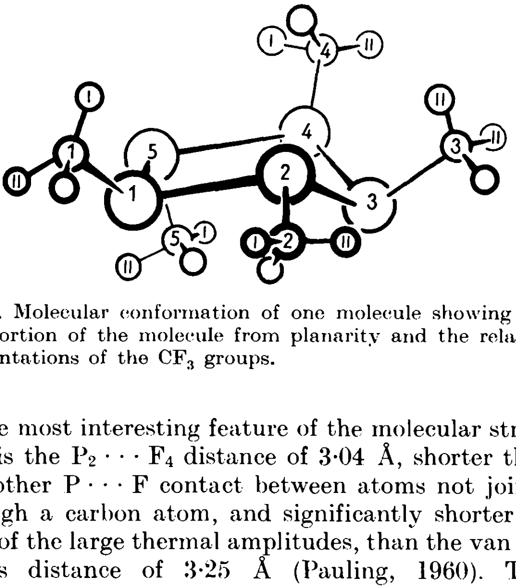

Fig. 3. Molecular conformation of one molecule showing the distortion of the molecule from planarity and the relative orientations of the CF_3 groups.

The most interesting feature of the molecular structure is the $P_2 \cdots F_4$ distance of 3·04 Å, shorter than any other $P \cdots F$ contact between atoms not joined through a carbon atom, and significantly shorter, in view of the large thermal amplitudes, than the van der Waals distance of 3·25 Å (Pauling, 1960). This $C_4F_4F_4'F_4''$ group is bent toward the center of the ring and towards P_2 such that angles of C_4–P_4–$P_5 = 114·8°$ and C_4–P_4–$P_3 = 99·9°$ occur. Further details of the structure reflect this interaction. The P_2–P_3 bond of 2·252 Å and the P_2–P_1 bond of 2·234 Å are significantly longer than the other three P–P bonds which average to 2·211 Å, thus suggesting that the electron pairs participate in the ring bonds except on P_2 where some interaction with F_4 occurs; but this interpretation is not unique, and neglects possible change in the hybridization which may be important on account of the distortions of bond angles. We are not at all sure as to whether a charge transfer or electrostatic

Table 5. *Observed and calculated structure factors*

h k ℓ	F_o	F_c
0,0,0		960
2	62	43-
4	202	207-
6	185	167-
8	40	35-
10	106	102
12	33	31
16	29	23-
18	14	1
0,1,1	31	28
2	63	82-
3	17	13-
4	20	19
5	41	38
6	105	93-
7	54	55
8	45	42
10	47	42
11	25	19-
12	71	68-
13	18	12-
14	22	17
18	13	15
19	13	11
20	11	15-
0,2,1	95	94-
2	20	19
4	114	104
6	106	87-
8	40	41
9	12	6-
10	23	21-
13	37	33-
14	22	22
15	10	9
17	8	6-
18	11	13
19	5	5-
20	29	37-
0,3,1	61	55-
2	61	56
3	66	71
4	13	16-
5	24	22-
6	92	66
8	87	79-
9	76	71
10	32	22-
11	60	50-
12	26	25-
15	15	5
17	13	14-
19	11	15
0,4,0	216	219
1	20	15-
2	26	25-
3	28	27-
4	27	17-
5	54	51-
6	71	70-
7	90	66
8	55	49-
9	19	17-
10	51	47
11	25	25-
12	19	12-
13	30	30-
14	24	24
15	25	25-
16	22	19-
17	15	13
18	14	10
19	14	16
0,5,1	40	43-
2	40	43-
3	51	46-
4	30	30-
5	93	66
6	30	29
7	26	16
8	14	16
9	25	24-
10	29	25-
11	52	46-
12	56	56-
13	21	19
14	39	31
15	26	16-
16	14	13-
17	43	40
0,6,1	12	16-
2	22	27-
3	11	10
6	21	25
8	44	41-
9	35	31-
11	11	12
12	19	14
13	13	13-
15	19	16
0,7,1	13	9-
2	32	27
3	13	20-
4	59	54
6	31	27
7	47	45-
8	91	82-
9	71	63
11	25	24-
13	21	23
14	37	24
15	24	26-
0,8,1	12	10-
3	15	11-
5	20	19
6	20	15-
9	18	16
10	29	21
11	13	18-
12	47	42-
13	17	14-
0,9,1	21	26-
4	11	12-
5	13	7
8	28	27
9	20	12
10	16	13-
11	50	43-
0,10,1	44	50
2	12	13-
3	24	23-
5	11	13
6	27	21
8	14	15-
9	12	14-
0,11,1	25	24
2	15	12
3	37	41-
0,12,2	20	20-
1,0,1	59	50
3	24	23-
5	37	24
9	21	18
11	43	42
13	14	10
15	19	23-
17	26	29-
19	54	59
21	30	18-
$\bar{1}$,0,3	119	130-
5	23	12
7	116	109-
9	11	13
11	51	50
13	35	35-
1,1,0	45	45
1	43	40-
2	34	28-
3	44	39
4	41	32
5	20	21
6	27	21-
7	93	72
9	22	19-
11	27	19-
14	68	59
15	43	39-
16	28	22-
17	34	39
18	24	27
20	30	22-
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Table 5 (*cont.*)

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$\overline{12}$,4,2	11	22
$\overline{12}$,5,2	14	14

description is preferable, or even whether these interpretations are truly distinct, but a final, though possibly not significant effect is the slight lengthening of C_4–P_4 and C_2–P_2. Whatever the precise valence interpretation there are still other indications that atom F_4 is interacting with P_2. The isotropic temperature factor of F_4 is considerably smaller than the average for all F atoms (Table 1), and similarly the lowest temperature factor for all P atoms is that of P_2. It may be that refinement with the use of anisotropic temperature factors would provide further evidence concerning this interesting interaction. It may be possible to sort out the various attractive and steric interactions in this molecule on a quantitative basis, especially when molecular constants are available on $(PCF_3)_4$ and on the related simpler molecules, $P_2(CF_3)_4$ and $P(CF_3)_3$.

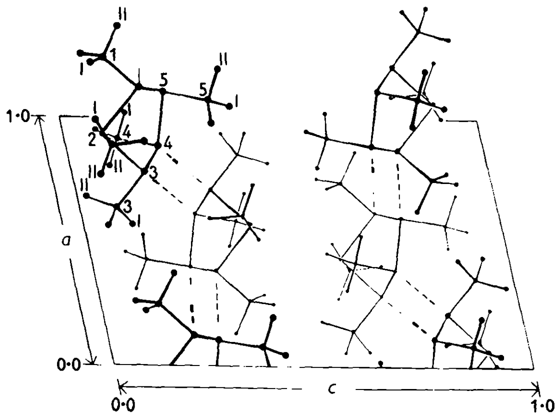

Fig. 4. Projection of one unit cell along the *b* axis. Broken lines indicate short intermolecular P · · · P contacts. These contacts extend in infinite chains along the *b* axis, as is shown by ending the broken lines where they pass into the unit cell above or below. Numerals indicate phosphorus atoms and carbon atoms, and primes indicate fluorine atoms.

The crystal structure, projected along *b*, is shown in Fig. 4. Most of the intermolecular contacts are normal distances between F atoms, but the few P · · · P contacts between atoms in different molecules are significant aspects of the bonding in the solid and are indicated by broken lines. The $P_1 \cdots P_5$ contacts of 3·98 Å and the $P_3 \cdots P_4$ contacts of 4·00 Å extend these P · · · P interactions as infinite chains along the *b* axis, the direction along which the crystals tend to grow most readily. These distances are just over twice the van der Waals radius of 1·9 Å, by an amount about equal to the thermal amplitudes of vibration. The liquid itself shows a very marked tendency to supercool to form a glass at low temperatures. This glass crystallized at −80° within a day or two, and more rapidly at higher temperatures. The barrier responsible for the supercooling is not understood, nor is it completely clear whether the molecules have a fixed geometry or strong associations in the liquid, but we suggest that nuclear magnetic resonance studies of P^{31} or F^{19} in the liquid or in solutions as a function of temperature might provide interesting results.

The large difference of the melting points of $(PCF_3)_5$ (−33 °C.) and $(PCF_3)_4$ (66·3 °C.) (Mahler & Burg, 1958) is of interest in view of the expected high symmetry of the tetramer, which is being studied elsewhere by similar methods (Donohue & Palenik, 1959). Other details of the comparison of these two cyclic molecules will also be of interest.

Comparison of the structure of $(PCF_3)_5$ with that of $(AsCH_3)_5$ (Burns & Waser, 1957) shows that the five-membered ring of As atoms is far less distorted than the P_5 ring. This result is not surprising, since the relative sizes of the ring atoms and the substituent groups are reversed in these two compounds. Finally, the H atom is not so electronegative as the F atom, and hence an anomalous interaction such as the short P · · · F contact across the ring in $(PCF_3)_5$ would not be expected in $(AsCH_3)_5$.

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