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The Molecular and Crystal Structure of $(PCF_3)_4$

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Crystals of $(PCF_3)_4$ are tetragonal, with 2 molecules in a unit cell of symmetry $P4_2/nmc$ and lattice constants $a = 10{\cdot}100$, $c = 6{\cdot}397$ Å. The required molecular symmetry is $\bar{4}2m$.

Fourier and least squares refinement on 226 visually-estimated intensities were used to obtain optimum values for the nine positional and eighteen thermal parameters. The value of R is 8%. The bond distances found are: $P–P = 2{\cdot}213 \pm 0{\cdot}005$, $P–C = 1{\cdot}867 \pm 0{\cdot}014$, average $C–F = 1{\cdot}335 \pm 0{\cdot}015$ Å (corrected for libration). The four-membered phosphorus ring is far from planar, having bond angles of 84·7° and torsion angles of 34°. The remaining molecular quantities are compared with those in other phosphorus and trifluoromethyl compounds.

Introduction

Relatively few compounds containing a phosphorus–phosphorus bond were known until the recent work of Mahler & Burg (1957, 1958) and of Kuchen & Buchwald (1956). The tetramer and pentamer of PCF_3, hereafter referred to as the tetramer and pentamer respectively, prepared by Mahler & Burg, represent the first case in which the experimental evidence pointed to a phosphorus ring system. The confirmation of the phosphorus ring system and an investigation of the geometry of the ring together with its attached trifluoromethyl groups is therefore of interest. The crystal structure determination of the tetramer was begun shortly after its preparation and characterization by Mahler & Burg, but the work was subject to numerous interruptions. The structure determination of the pentamer has very recently been described by Spencer & Lipscomb (1961).

Experimental

The tetramer is a slightly volatile solid which melts at 66° under its own vapor pressure. The colorless crystals can be prepared in various crystal habits depending on the method of preparation. Crystals grown by condensing the gaseous material into thin-walled capillaries always present [100] or [110] parallel to the capillary axis. Crystals grown by sublimation in a tube containing a small amount of carbon dioxide formed as needles elongated along [001]. Both types of crystal habit were subsequently used in the collection of the intensity data.

The following Weissenberg photographs ($Cu\,K\alpha$, $\lambda = 1{\cdot}5418$ Å) were taken: zero to fourth layer about [100], zero to seventh layer about [110], and zero to fourth layer about [001]. A total of 226 independent reflections was observed. The Laue symmetry is $4/mmm(D_{4h})$. The systematic absences $(hk0)$ when $h+k = 2n+1$ and (hhl) when $l = 2n+1$ indicate that the probable space group is $P4_2/nmc(D_{4h}^{15})$. The unit cell has dimensions $a = 10{\cdot}100 \pm 0{\cdot}020$ Å and $c = 6{\cdot}397 \pm 0{\cdot}015$ Å. The density calculated for two molecules per unit cell is 2·00 g.cm.$^{-3}$. The only density datum available is that of the liquid at its melting point, where Mahler (1958) found the value 1·54 g.cm.$^{-3}$. The calculated density of the pentamer (Spencer & Lipscomb, 1961) is 2·12 g.cm.$^{-3}$ at -100 °C.

With two molecules per unit cell, the required molecular symmetry is $\bar{4}2m(D_{2d})$. One of the two sets of eight-fold positions of the space group, $8f$, is eliminated for placement of the phosphorus, carbon, and eight of the fluorine atoms because it requires, among other objectionable features, a P–C–F bond angle of 180°. Positions $8g$, $(0, x, z)$ etc., point symmetry m, must therefore accommodate these atoms, with the remaining sixteen fluorine atoms in the general position $16h$. The number of positional parameters to be determined is thus nine.

Determination of the structure

A Patterson section, $P(u, v, 0)$, gave 0·152 as the value of the x-coordinate for the phosphorus atom, and a Patterson line $P(0{\cdot}152, 0{\cdot}152, w)$, gave a value for z of 0·066. These parameters give a puckered four-membered phosphorus ring. Of the two possible directions for the phosphorus–carbon bond relative to the ring, one is eliminated because it places the trifluoromethyl groups impossibly close together ($C\cdots C$ is 1·4 Å for a P–P–C angle of 90°). The other alternative allows two possible orientations of the fluorine atoms relative to the phosphorus–carbon skeleton.

It then was assumed that the phosphorus–carbon and carbon–fluorine distances were 1·83 Å and 1·36 Å, and that the P–P–C and P–C–F angles were 90° and 109°. On the basis of the above assumptions, the

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Table 1. *Observed and calculated structure factors*

Values shown are 10 F_o and 10 F_c. Minus sign on F_o signifies 'less than'

h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	n	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c
0	2	0	297	287	1	9	1	114	-106	1	1	2	665	711	7	10	2	97	-85	7	9	3	101	-102	6	7	4	85	71	0	9	6	-18	78
0	4	0	-00	-13	1	10	1	113	-116	1	2	2	452	493	8	8	2	73	54	7	10	3	-13	1	6	8	4	-40	34	1	1	6	103	-107
0	6	0	725	825	1	11	1	-55	35	1	3	2	386	-374	0	1	3	373	386	0	0	4	211	-212	6	9	4	88	-97	1	2	6	-63	39
0	3	0	376	349	1	12	1	79	64	1	4	2	237	-194	0	2	3	355	-335	0	1	4	341	-379	7	7	4	-40	43	1	3	6	-54	36
0	10	0	-36	7	2	3	1	234	-166	1	5	2	154	165	0	3	3	242	-235	0	2	4	-31	-25	7	8	4	78	-41	1	4	6	170	-174
0	12	0	134	131	2	4	1	166	-144	1	6	2	-45	-48	0	4	3	284	-283	0	3	4	331	-329	0	1	5	112	111	1	5	6	-58	-10
1	1	0	388	417	2	5	1	166	-143	1	7	2	300	306	0	5	3	446	458	0	4	4	-67	-34	0	2	5	453	-436	1	6	6	-45	-16
1	3	0	225	231	2	6	1	-54	5	1	8	2	106	-96	0	6	3	-49	33	0	5	4	274	-265	0	3	5	80	58	1	7	6	76	-76
1	5	0	433	425	2	7	1	185	187	1	9	2	-63	-25	0	7	3	202	211	0	6	4	-54	7	0	4	5	378	-381	1	8	6	-36	-7
1	7	0	320	348	2	8	1	-49	43	1	10	2	87	-82	0	8	3	-76	68	0	7	4	-54	7	0	5	5	-72	7	2	2	6	-49	-27
1	9	0	-35	13	2	9	1	131	-136	1	11	2	-63	-7	0	9	3	-76	-30	0	8	4	-52	34	0	6	5	-54	26	2	3	6	99	-83
1	11	0	-31	-10	2	10	1	-63	47	1	12	2	-36	44	0	10	3	191	-199	0	9	4	159	-171	0	7	5	-49	0	2	4	6	68	62
1	13	0	55	89	2	11	1	120	-111	2	2	2	111	85	0	11	3	-54	-5	0	10	4	-81	-10	0	8	5	-67	65	2	5	6	-49	21
2	2	0	1081	1303	2	12	1	-45	22	2	3	2	314	-279	1	2	3	241	206	0	11	4	123	-134	0	9	5	-54	13	2	6	6	-58	-47
2	4	0	463	-460	3	4	1	614	-571	2	4	2	429	-397	1	3	3	250	-215	1	1	4	-58	15	1	2	5	106	-97	2	7	6	82	99
2	6	0	102	106	3	5	1	375	-385	2	5	2	246	242	1	4	3	-49	-11	1	2	4	308	-312	1	3	5	344	-338	2	8	6	-31	-12
2	8	0	46	-57	3	6	1	132	-130	2	6	2	151	144	1	5	3	279	-285	1	3	4	-45	29	1	4	5	-63	45	3	3	6	82	88
2	10	0	240	-251	3	7	1	161	169	2	7	2	169	-153	1	6	3	134	128	1	4	4	422	-397	1	5	5	95	-78	3	4	6	-54	33
2	12	0	-45	-5	3	8	1	-67	11	2	8	2	-54	45	1	7	3	120	117	1	5	4	99	-103	1	6	5	-54	28	3	5	6	-45	46
3	3	0	1211	-1512	3	9	1	61	57	2	9	2	-54	41	1	8	3	52	48	1	6	4	-54	-53	1	7	5	-49	-17	3	6	6	134	131
3	5	0	395	-413	3	10	1	228	-243	2	10	2	109	-87	1	9	3	104	-92	1	7	4	100	96	1	8	5	-45	-30	3	7	6	-49	-6
3	7	0	89	-80	3	11	1	-63	16	2	11	2	-54	52	1	10	3	-58	19	1	8	4	-49	0	1	9	5	79	-85	4	4	6	137	136
3	9	0	212	-224	3	12	1	-45	-41	2	12	2	-36	-7	1	11	3	147	-121	1	9	4	-58	-2	1	10	5	-31	-7	4	5	6	63	50
3	11	0	147	-139	4	5	1	204	-210	3	3	2	403	-360	2	3	3	434	-467	1	10	4	173	-166	2	3	5	-67	-52	4	6	6	-40	3
4	4	0	240	-218	4	6	1	392	396	3	4	2	74	-65	2	4	3	204	-204	1	11	4	-31	-19	2	4	5	54	-36	4	7	6	102	147
4	6	0	-31	-13	4	7	1	118	119	3	5	2	186	-182	2	5	3	-49	-14	2	2	4	140	138	2	5	5	-58	12	4	8	6	-22	22
4	8	0	55	51	4	8	1	-67	-61	3	6	2	376	379	2	6	3	151	135	2	3	4	137	-129	2	6	5	185	167	5	5	6	-40	16
4	10	0	186	-222	4	9	1	185	-193	3	7	2	-72	64	2	7	3	97	85	2	4	4	-49	10	2	7	5	-63	-46	5	6	6	99	81
4	12	0	-40	-26	4	10	1	-49	-20	3	8	2	108	96	2	8	3	146	142	2	5	4	-54	-14	2	8	5	64	83	5	7	6	-22	-19
5	5	0	274	248	4	11	1	115	-129	3	9	2	177	-181	2	9	3	-49	-31	2	6	4	-67	32	2	9	5	-36	-22	6	6	6	47	-62
5	7	0	196	195	4	12	1	-36	-22	3	10	2	-49	-31	2	10	3	109	-87	2	7	4	235	227	2	10	5	-27	48	0	1	7	158	-155
5	9	0	140	-136	5	6	1	-63	21	3	11	2	128	-125	2	11	3	-45	-38	2	8	4	-49	20	3	4	5	85	-12	0	2	7	101	-89
5	11	0	57	-55	5	7	1	-54	-43	3	12	2	-36	-31	3	4	3	256	-234	2	9	4	-45	6	3	5	5	183	181	0	3	7	-49	-9
6	6	0	134	125	5	8	1	62	62	4	4	2	532	-513	3	5	3	157	146	2	10	4	-58	-38	3	6	5	-58	-28	0	4	7	119	-130
6	8	0	175	178	5	9	1	-63	-5	4	5	2	265	255	3	6	3	107	101	2	11	4	-31	20	3	7	5	200	216	0	5	7	70	-69
6	10	0	-27	-36	5	10	1	118	-124	4	6	2	-49	22	3	7	3	282	264	3	3	4	-49	44	3	8	5	-58	7	0	6	7	-31	-7
7	9	0	-27	36	5	11	1	-36	34	4	7	2	212	208	3	8	3	148	-143	3	4	4	122	104	3	9	5	-36	-15	1	2	7	-54	-4
7	11	0	-22	1	6	7	1	340	291	4	8	2	143	-146	3	9	3	-49	-49	3	5	4	-54	-42	3	10	5	-13	-3	1	3	7	133	-136
8	8	0	51	81	6	8	1	-54	40	4	9	2	85	74	3	10	3	73	-86	3	6	4	275	263	4	5	5	106	85	1	4	7	-49	-2
0	1	1	737	735	6	9	1	-58	13	4	10	2	127	-144	3	11	3	-49	9	3	7	4	-76	12	4	6	5	141	151	1	5	7	-36	20
0	2	1	1005	1156	6	10	1	-49	56	4	11	2	-49	4	4	5	3	210	-179	3	8	4	188	193	4	7	5	-54	12	1	6	7	55	-65
0	3	1	262	253	6	11	1	-36	-14	4	12	2	-22	-40	4	6	3	185	189	3	9	4	-45	-22	4	8	5	92	97	2	3	7	118	105
0	4	1	346	-318	7	8	1	175	173	5	5	2	144	-154	4	7	3	72	-71	3	10	4	-36	50	4	9	5	-40	0	2	4	7	-40	47
0	5	1	-45	-43	7	9	1	-45	35	5	6	2	186	174	4	8	3	184	188	3	11	4	-22	-32	5	6	5	-67	-7	2	5	7	-36	15
0	6	1	173	-189	7	10	1	-40	-14	5	7	2	140	143	4	9	3	-67	-64	4	4	4	143	-146	5	7	5	94	110	2	6	7	60	68
0	7	1	465	454	0	0	2	278	-327	5	8	2	-63	28	4	10	3	41	-55	4	5	4	118	112	5	8	5	-40	9	3	4	7	102	102
0	8	1	129	126	0	1	2	335	355	5	9	2	-67	-25	4	11	3	79	-78	4	6	4	-54	-15	5	9	5	-27	36	3	5	7	-31	-59
0	9	1	122	107	0	2	2	415	415	5	10	2	66	-56	5	6	3	239	202	4	7	4	230	225	6	7	5	-49	-16	3	6	7	-22	15
0	10	1	-76	28	0	3	2	1173	-1300	5	11	2	46	-59	5	7	3	138	138	4	8	4	-63	13	6	8	5	-27	28	4	5	7	-36	26
0	11	1	-67	11	0	4	2	111	103	6	6	2	346	351	5	8	3	-58	5	4	9	4	-58	10	0	0	6	-54	-30	0	0	8	100	-108
0	12	1	-54	28	0	5	2	196	-196	6	7	2	87	-54	5	9	3	-63	23	4	10	4	32	-53	0	1	6	-63	-12	0	1	8	-36	15
1	2	1	77	45	0	6	2	357	337	6	8	2	90	103	5	10	3	-49	-32	5	5	4	-54	-5	0	2	6	-54	-51	0	2	8	-27	-37
1	3	1	374	-337	0	7	2	-45	0	6	9	2	-54	63	5	11	3	-18	37	5	6	4	86	61	0	3	6	178	-179	1	1	8	47	-57
1	4	1	196	-157	0	8	2	186	187	6	10	2	-54	-13	6	7	3	119	114	5	7	4	-49	13	0	4	6	-72	16	1	2	8	-27	32
1	5	1	87	35	0	9	2	156	-139	6	11	2	59	-67	6	8	3	-45	-21	5	8	4	95	100	0	5	6	104	-100	2	2	8	-18	22
1	6	1	404	389	0	10	2	-72	-35	7	7	2	161	169	6	9	3	-45	33	5	9	4	-54	-10	0	6	6	71	-66					
1	7	1	149	152	0	11	2	115	-90	7	8	2	-67	31	6	10	3	105	-113	5	10	4	-36	71	0	7	6	-40	-33					
1	8	1	237	254	0	12	2	-45	39	7	9	2	-40	35	7	8	3	69	46	6	6	4	-49	28	0	8	6	-45	-31					

coordinates of the carbon and fluorine atoms were calculated for the two different models. In the first model the fluorine atom on the mirror plane was directed toward the center of the phosphorus ring. The second model was related to the first by a rotation of 180° around the phosphorus–carbon bond.

McWeeny (1951) scattering factors for diamond carbon and fluorine, and Viervoll & Øgrim (1949) scattering factor for phosphorus were used in calculating structure factors for both models. The agreement obtained for the first model was clearly superior, and refinement was started with this conformation. It should be noted that in the correct model the orientation about the phosphorus–carbon bonds is such that the carbon–fluorine bonds are more nearly staggered with respect to the phosphorus–phosphorus bonds than in the incorrect model.

Refinement of the structure

The scale factor and an isotropic temperature factor were obtained from the structure factor calculations in the usual way. A three-dimensional Fourier was calculated by the use of only those structure factors whose signs could be assigned with some degree of confidence. New values for the coordinates were obtained and the procedure was twice repeated. The value of R was 23% at this stage.

A least-squares refinement, including anisotropic temperature factors, was then carried out on SWAC (Sparks *et al.*, 1956), by the use of a program which refines both positional and thermal parameters, and uses the full matrix. Seven cycles of least-squares were carried out. The final shifts were smaller than the standard errors calculated from the inverse matrix. The fairly large number of cycles was required because of an initial error in weighting which slowed convergence.

The final set of structure factors is listed in Table 1. The final R value for the observed reflections, including several reflections which obviously suffered from ex-

Table 2. *Refinement of positional parameters*

				Least squares		
		Initial	Fourier	Sixth	Seventh	σ
P	x	0·152	0·1474	0·1476	0·1475	0·0003
	z	−0·066	−0·0532	−0·0533	−0·0529	0·0005
C	x	0·282	0·2590	0·2534	0·2536	0·0013
	z	0·158	0·1852	0·1856	0·1859	0·0025
F_{I}	x	0·193	0·1988	0·1948	0·1943	0·0010
	z	0·337	0·3651	0·3715	0·3706	0·0013
F_{II}	x	0·338	0·3329	0·3304	0·3304	0·0008
	y	0·111	0·1063	0·1045	0·1048	0·0008
	z	−0·152	−0·1842	−0·1857	−0·1851	0·0013
R		34%	23%	8%		

Table 3. *Thermal parameters*

		B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	B_{ij}	0·0073	0·0093	0·0220		−0·0023	
	σ	0·0003	0·0003	0·0007		0·0009	
C	B_{ij}	0·0097	0·0106	0·0349		0·0092	
	σ	0·0013	0·0014	0·0045		0·0042	
F_I	B_{ij}	0·0172	0·0299	0·0283		−0·0148	
	σ	0·0012	0·0018	0·0023		0·0030	
F_{II}	B_{ij}	0·0217	0·0272	0·0656	−0·0223	0·0335	−0·0064
	σ	0·0010	0·0012	0·0030	0·0036	0·0030	0·0019

tinction, is 8·0%. The progress of the refinement of the positional parameters is presented in Table 2, and the final temperature factors in Table 3. The standard deviations were obtained from the diagonal elements of the inverse matrix. The temperature factors were converted to the mean displacements and direction cosines given in Table 4.

Table 4. *Principal axis parameters of the atomic vibration ellipsoids*

Atom	i	$(\bar{r}_i^2)^{\frac{1}{2}}$	q_{ia}	q_{ib}	q_{ic}
P	1	0·220	0	1	0
	2	0·217	−0·3782	0	0·9257
	3	0·190	−0·9257	0	−0·3782
C	1	0·283	−0·4499	0	−0·8931
	2	0·234	0	1	0
	3	0·206	−0·8931	0	0·4499
F_I	1	0·393	0	1	0
	2	0·320	−0·8744	0	0·4853
	3	0·213	−0·4853	0	−0·8744
F_{II}	1	0·461	0·6218	−0·5761	0·5306
	2	0·358	0·0157	0·6865	0·7269
	3	0·221	0·7830	0·4437	−0·4359

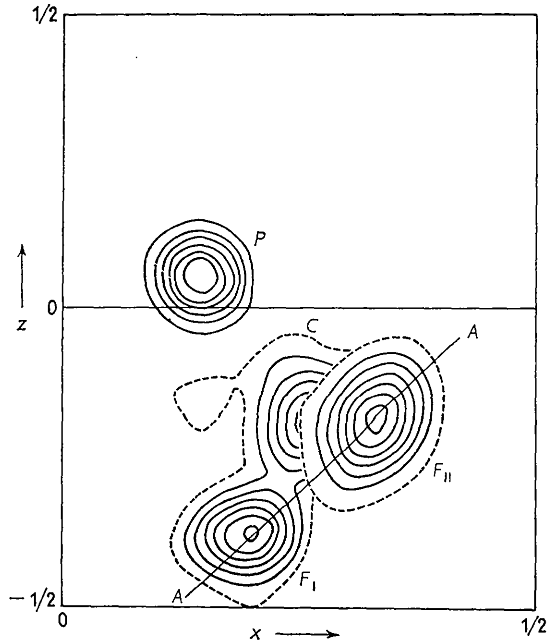

Fig. 1. Sections of $\varrho(x, y, z)$ at $y=0$ and $y=0·1$. Contours on the phosphorus atom at 4, 8, ... e.Å^{-3}, and the other atoms at 0 (dashed), 1, 2, ... e.Å^{-3}. (The third phosphorus atom of the CF_3 group lies directly below F_{II} at $y=-0·1$.)

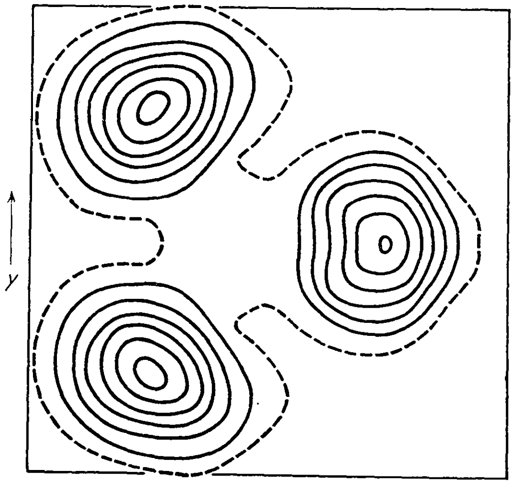

Fig. 2. Section of $\varrho(x, y, z)$ through the plane of the three fluorine atoms. The trace of this plane is the line AA in Fig. 1.

The three-dimensional electron density function was then calculated with the phases as given by parameter set seven. Fig. 1 is the section $(x, 0, z)$ with the section through F_{II} parallel to (010) superimposed. This composite drawing shows that the thermal vibrations of the phosphorus atom are almost isotropic but that the fluorine atoms are vibrating anisotropically, with the maximum displacement approximately perpendicular to the carbon–fluorine bond. The electron density section through the three fluorine atoms of the CF_3 group is presented in Fig. 2. The trace of this plane is indicated by the line AA in Fig. 1. The anisotropic nature of the thermal motions of the fluorine atoms is easily seen in this section. The anisotropies are in agreement with the value of B_{ij} obtained by least squares.

Discussion

Intramolecular distance and angles are presented in Table 5. The intermolecular contacts are shown in Fig. 3. The phosphorus–phosphorus bond distance of 2·213 ± 0·005 Å is in good agreement with the phosphorus–phosphorus distances of 2·21 ± 0·02 Å

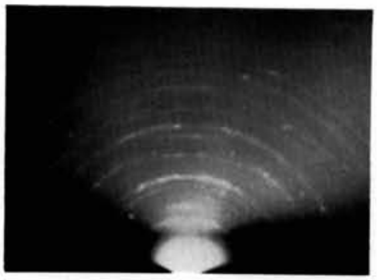

Fig. 1. Electron diffraction from compressed CsCl; surface slightly etched.

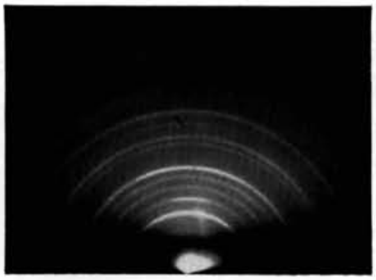

Fig. 2. Electron diffraction from compressed TlCl; surface slightly etched.

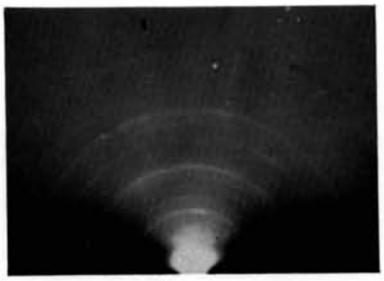

Fig. 3. Electron diffraction from compressed NH_4Cl; surface as compressed.

reported in P_4 by Maxwell, Henricks & Mosley (1935), of 2·21 ± 0·06 Å in P_2I_4 by Leung & Waser (1956), of 2·20 and 2·21 ± 0·01 Å in P_4S_5 by van Houten & Wiebenga (1957), of 2·240 and 2·246 ± 0·01 Å in P_4S_3 by Leung *et al.* (1957), of 2·21 ± 0·01 Å in 1,2-dimethyl-1,2-diphenyldiphosphine disulfide by Wheatley (1960), of 2·20 and 2·17 Å in black phosphorus by Hultgren, Gingrich & Warren (1935), and of 2·223 ± 0·007 Å in $(PCF_3)_5$ by Spencer & Lipscomb (1961). It is noteworthy that the P–P bond distance is sensibly the same in all of these substances where widely different types of *s–p–d* or *π–σ* combinations would be invoked by others in discussions of the nature of the bonding.

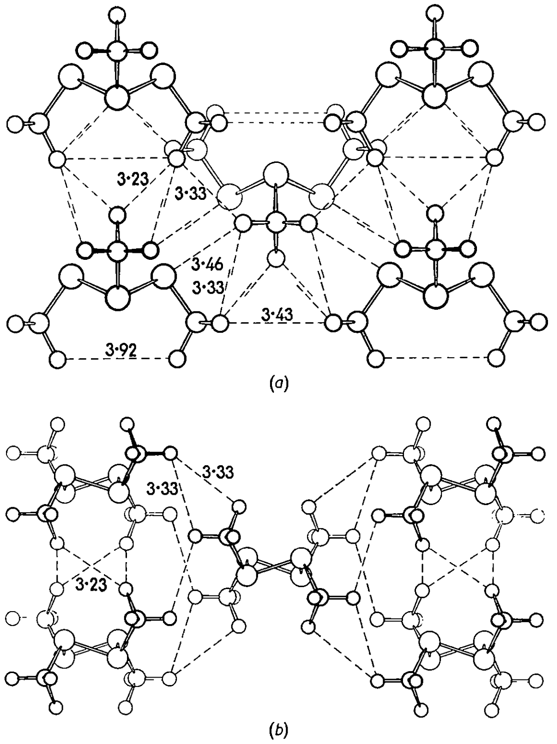

Fig. 3. The structure projected on: (*a*) (010), (*b*) (110).

The observed distance of 1·867 ± 0·014 Å for the phosphorus–carbon bond is slightly longer than the average value of 1·837 ± 0·012 Å* found by Hamilton (1955) in $[(CH_3)_2PBH_2]_3$ but the difference of 0·030 Å is not significant. Bartell (1960) and Bartell & Brockway (1960) reported 1·847, 1·853, and 1·858 Å, all ± 0·003 Å for the phosphorus–carbon bonds in $(CH_3)_3P$, $(CH_3)_2PH$, and CH_3PH_2, respectively. The average value of 1·906 ± 0·020 Å found in the pentamer by Spencer & Lipscomb (1961) is slightly longer, but not significantly so. A significantly longer phosphorus–carbon distance of 1·937 ± 0·017 Å was found by Bowen (1954) in $(CF_3)_3P$.

The two carbon–fluorine bond distances of 1·326 ±

Table 5. *Intramolecular distances and angles*

	d (Å)	*σ* (Å)		*d* (Å)
P–P	2·213	0·005	$P \cdots P'$	2·980
P–C	1·867	0·014	$F_I \cdots F_I'$	3·925
$C–F_I$	1·326 (1·340)*	0·018	$P' \cdots F_I$	3·194
$C–F_{II}$	1·313 (1·331)	0·010	$P' \cdots F_{II}$	3·470
∠ P–P′–P	84·7°		$\angle P–C–F_{II}$	109·6°
∠ P′–P–C	97·8		$\angle F_I–C–F_{II}$	105·7
$\angle P–C–F_I$	118·1		$\angle F_{II}–C–F_{II}$	107·5

P–P–P–P torsion angle: 34°.

* Parenthetical values include libration correction.

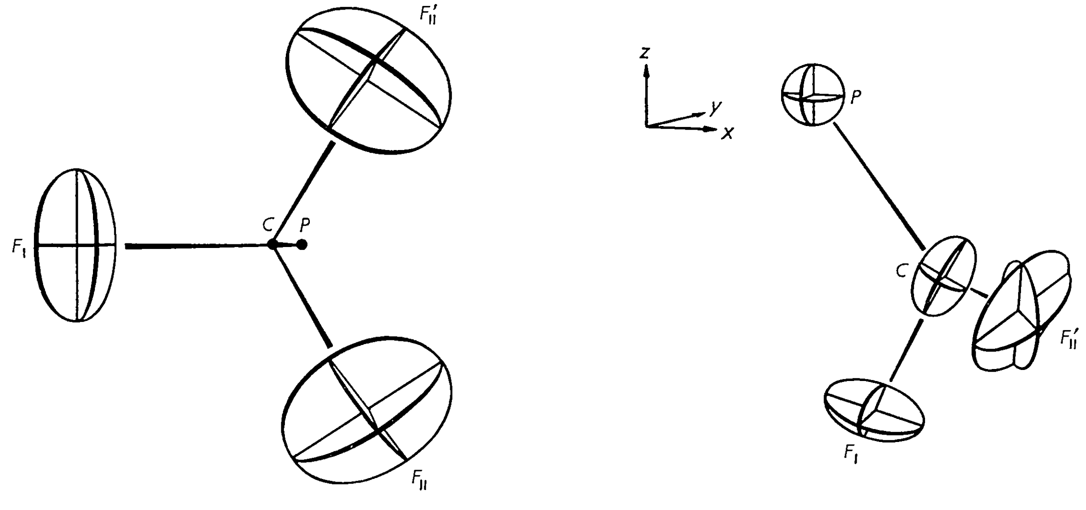

Fig. 4. Two perspective views of the vibration ellipsoids. The axes of the ellipsoids shown are proportional to the respective values of $(\overline{r^2})^{\frac{1}{2}}$, but are not on the same scale as the bond lengths.

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* The much smaller value of 0·007 Å given by Hamilton for the standard deviation of this bond length is the standard error of the mean as calculated from the standard errors of the individual values used to calculate that mean This kind of calculation ignores the scatter among those values. We feel that the standard error as calculated from the deviations of the individual values from the mean is a much more meaningful quantity.

0·018 Å and 1·313 ± 0·010 Å are not significantly different. After correction for libration (Cruickshank, 1956), the two lengths are 1·340 and 1·331 Å. These carbon–fluorine bond lengths are in satisfactory agreement with the average value of 1·334 ± 0·004 Å found in numerous polyfluorides (Sutton *et al.*, 1958).

Several views of the atomic vibration ellipsoids are shown in Fig. 4. One of the valency angles at the carbon atom, namely, $P{-}C{-}F_{I}$, is much larger than the others (Table 5), a condition which may result from $P \cdots F_{I}$ repulsion, although a similar condition was not observed in the pentamer (Spencer & Lipscomb, 1961), where the bond angles at the carbon atoms show considerable scatter.

Fig. 5 depicts packing drawings of the molecule, and shows its approximately spherical nature. The high degree of shielding of the phosphorus and carbon atoms by the fluorine atoms is evident. The volatility of this moderately high molecular weight compound may result from the fluorine-like exterior and high symmetry, both of which limit the intermolecular interactions to van der Waals forces.

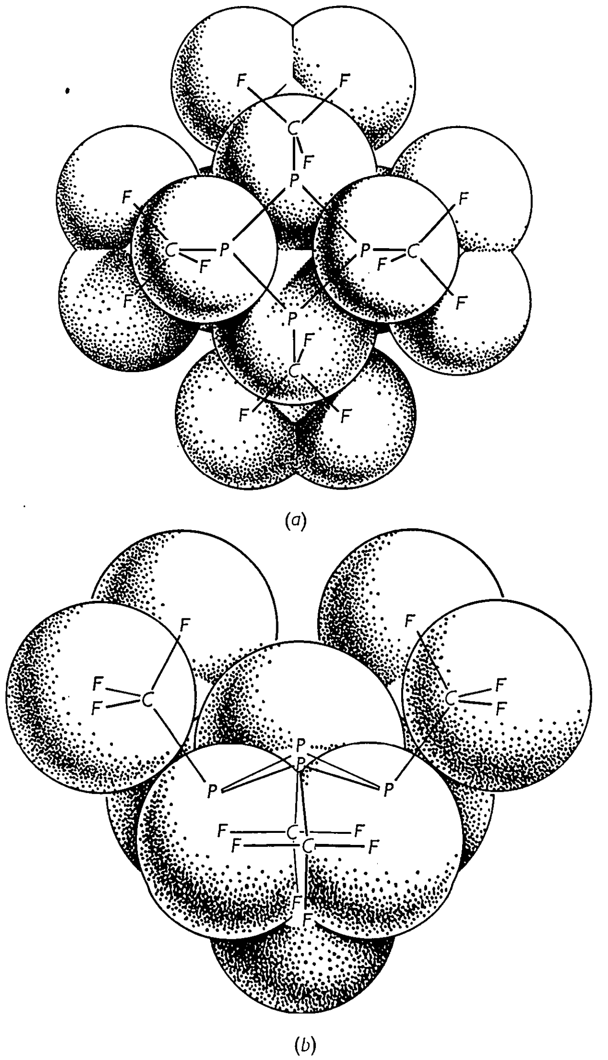

Fig. 5. Two packing drawings of the (PCF$_3$)$_4$ molecule: (*a*) View down the 4-fold inversion axis. The peripheral atoms and the two uppermost atoms are fluorine; only two of the phosphorus atoms (which have larger diameters) show to any extent, the other two phosphorus atoms and the carbon atoms are largely hidden. (*b*) View along one of the mirror planes.

Also evident in Fig. 5 is the fact that the intramolecular $F \cdots F$ distance (of 3·925 Å) in the mirror plane is much longer than one corresponding to a van der Waals contact. (A packing radius of 1·55 Å for the fluorine atoms was used in the preparation of these figures. This value is 0·20 Å greater than that suggested by Pauling (1960, p. 260), as discussed below.) The non-planarity of the phosphorus ring is accordingly *not* a consequence of steric repulsion between the trifluoromethyl groups. Three changes in the molecular quantities which *do* occur when a planar four-membered ring, with sides equal to 2·213 Å, is distorted to give the observed system are: (1) decrease of the cross-ring $P \cdots P$ distances from 3·130 to 2·980 Å, (2) decrease of the P–P–P bond angles from 90° to 84·6°, and (3) increase of the P–P–P–P torsion angles from 0° to 34°. It should be noted that cross-ring repulsion, which has been invoked in the discussion of the abnormally long bonds in four-membered rings of carbon atoms by Dunitz & Schomaker (1952), apparently is not an important factor in the case of four-membered phosphorus rings, since the phosphorus–phosphorus distance in the tetramer is not significantly different from those in the (less strained) pentamer, and probably not different from those in black phosphorus, although a refinement of this latter structure is to be desired. It seems likely that the non-planarity of the ring in the tetramer is due largely to relief of Pitzer (torsion) strain, the equilibrium conformation being attained by a balance between the energy loss due to increase of the torsion angles from 0° and the energy gain due to bond angle deformation plus a small amount, perhaps, of $P \cdots P$ repulsion.

Fig. 3 shows the fact that all intermolecular contacts less than 4·0 Å involve the fluorine atoms. This observation is not surprising if one considers the van der Waals model of the molecule given in Fig. 5. If one assumes that the shortest fluorine $\cdots$ fluorine intermolecular distances represent van der Waals contacts, the Pauling value of 1·35 Å for the van der Waals radius should be increased to about 1·55 Å. Atoji & Lipscomb (1954) made a similar observation in connection with their study of crystalline hydrogen fluoride. The larger van der Waals radius is consistent with values observed in the covalently-bonded fluorine compounds listed by them.

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The Crystal Structure of Tosyl-L-prolyl-L-hydroxyproline monohydrate

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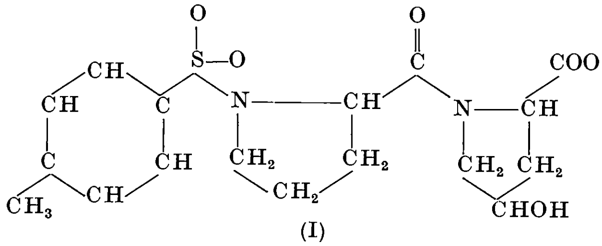
The structure of the synthetic peptide tosyl-L-prolyl-L-hydroxyproline, $C_{17}H_{22}O_6N_2S.H_2O$, has been determined to establish the stereochemical configuration of the sequence—pro-hypro—and to determine the feasibility of using sulphur as the 'heavy-atom' and the tosyl system as a marker group for the analysis of compounds of comparable complexity. The compound crystallizes in the monoclinic space group $P2_1$ with

$$a=6\cdot291,\ b=7\cdot689,\ c=19\cdot640\ \text{Å};\ \beta=99°\ 27\cdot5',\ Z=2\ .$$

Intensity data were collected for 0–5 layers about the b-axis. With generalized Patterson functions $P_K(u, w)$, the sulphur atom and a few others on the same y level were located. Subsequent image-seeking operations on modulus generalized Patterson functions and on the zero-layer Patterson distribution indicated the molecular structure which, with the aid of models of the component units—tosyl, proline and hydroxyproline—was established by ϱ_o and $\Delta\varrho$ projections. The y parameters were fixed by three-dimensional ϱ_o (and ϱ_c) syntheses.

It has been established from hydrolysis studies of collagen and gelatin (Schroeder *et al.*, 1954; Kroner *et al.*, 1955) that the proline and hydroxyproline components of these substances occur commonly in the sequence -gly-pro-hypro- and this sequence is now generally accepted in discussing model structures of collagen and gelatin (Rich & Crick, 1955; Cowan & Gavin, 1955; Ramachandran & Kartha, 1955). The structure analysis of a peptide involving the sequence -pro-hypro- seemed therefore to be of interest, insofar as the knowledge of the steric relationships in it might be of some assistance for further developments of these models. We had available for this purpose the synthetic peptide tosyl-L-prolyl-L-hydroxyproline (Beecham, 1957)—$C_{17}H_{22}O_6N_2S$ (I)—and this substance



(I)

because of its p-toluene-sulphonyl (tosyl) group,