

The Crystal Structure of Compounds with (P-N)_n rings. VI. * Fluoropentachlorocyclotriphosphazene

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(Received 25 November 1968)

Fluoropentachlorocyclotriphosphazene crystallizes in space group *Pnma* or *Pn2₁a* with cell dimensions $a=14.289$, $b=12.777$ and $c=6.038$ Å. There are four molecules in the unit cell. A molecule consists of a (P-N)₃ ring with two halogen atoms attached to each of the phosphorus atoms. For both possible space groups least-squares refinements lead to the conclusion that the fluorine atom is distributed over the halogen positions. In the centrosymmetric space group *Pnma* models with different fluorine distributions were investigated. The *R* indices for these models range from 0.043 to 0.037 for 506 reflexions. The P-halogen bond lengths appear to be highly dependent on the assumed distribution, unlike the P-N bonds and valence angles. The ring is planar; the ring bond lengths and chemically equivalent angles are equal within experimental error. Average values and standard deviations of the individual values are: P-N, 1.563 Å, s.d. 0.007 Å; N-P-N, 118.5°, s.d. 0.5°; Hal-P-Hal, 100.5°, s.d. 0.2°; N-P-Hal, 108.9°, s.d. 0.4°.

Introduction

Trimeric cyclophosphazene compounds so far investigated by X-ray diffraction are N₃P₃Cl₆ (Wilson & Carroll, 1960; Giglio, 1960), N₃P₃F₆ (Dougill, 1963), N₃P₃Br₆ (Giglio & Puliti, 1967), and N₃P₃Cl₄(C₆H₅)₂ and N₃P₃(C₆H₅)₄Cl₂ (Mani, Ahmed & Barnes, 1965, 1966 respectively). N₃P₃Br₆, for which an approximate structure has been determined, is being refined in our laboratory.

In all cases the molecule consists of a (P-N)₃ ring with two halogen atoms, or phenyl groups, attached to the phosphorus atoms (Fig. 1). In each of the molecules N₃P₃F₆, N₃P₃Cl₆ and N₃P₃Br₆ the P-N bond lengths are equal (Table 1); average values are 1.560, 1.59 (Wilson & Carroll, 1960) and 1.59 Å respectively. There is a tendency for the P-N bond lengths to become shorter with increasing electronegativity of the exocyclic ligands, in agreement with theory (Craig & Zauli, 1962). The inequality of the P-N bonds within each of the non-uniformly substituted molecules N₃P₃Cl₄(C₆H₅)₂ and N₃P₃(C₆H₅)₄Cl₂ may also be ascribed to the influence of the ligands.

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The X-ray diffraction study of N₃P₃Cl₅F was undertaken to see how substitution of one of the chlorine atoms in N₃P₃Cl₆ by a fluorine atom would affect the lengths of the endocyclic bonds.

Experimental

A sample of N₃P₃Cl₅F was kindly sent to us by Professor N.L. Paddock. The compound is one of the products of the reaction of hexachlorocyclotriphosphazene with potassium fluoride and sulphur dioxide (Allen, Barnard, Emsley, Paddock & White, 1963); the melting point is 50°C. The sample appeared to contain some crystals suitable for X-ray work. They were colourless prisms, which decomposed rapidly in moist air; the crystals were therefore mounted in glass capillaries. For the collection of the intensity data a crystal with dimensions of approximately 0.36 × 0.24 × 0.50 mm was selected.

The unit-cell dimensions of fluorohexachlorocyclotriphosphazene, given in Table 2, were obtained with the automatic Nonius diffractometer. The compound is orthorhombic. Laue symmetry and systematic absences indicate as possible space groups *Pn2₁a* (33) and *Pnma* (62) without and with an inversion centre respectively.

Table 1. P-N bond lengths and standard deviations in trimeric cyclophosphazene compounds

	P(1)-N(2)	P(2)-N(2)	P(2)-N(1)
N ₃ P ₃ F ₆ *	1.546 (0.011) Å	1.563 (0.012) Å	1.572 (0.008) Å
N ₃ P ₃ Cl ₆ *	1.61 (0.017)	1.57 (0.017)	1.60 (0.011)
N ₃ P ₃ Br ₆ *	1.60 (0.033)	1.60 (0.045)	1.55 (0.035)
N ₃ P ₃ Cl ₄ (C ₆ H ₅) ₂ †	1.615 (0.005)	1.555 (0.005)	1.578 (0.005)
N ₃ P ₃ (C ₆ H ₅) ₄ Cl ₂ †	1.556 (0.009)	1.609 (0.008)	1.578 (0.008)

* The molecule lies on a mirror plane in the unit cell. The numbering refers to Fig. 1.

† Molecule at general position; mean values of corresponding bonds are given.

Table 2. *Crystallographic data*

	$N_3P_3Cl_5F$	$N_3P_3Cl_6$
<i>a</i>	14.289 (0.02) Å	14.15 (0.02) Å
<i>b</i>	12.777 (0.02)	12.99 (0.02)
<i>c</i>	6.038 (0.01)	6.19 (0.01)
Space group	<i>Pnma</i> or <i>Pn2₁a</i>	<i>Pnma</i>
<i>Z</i>	4	4

The intensities of all 656 independent reflexions with $\theta \leq 22^\circ$ were measured on the Nonius diffractometer with Zr filtered Mo radiation by the moving-crystal moving-counter method. Attenuation filters were used to keep deviations from linearity below 1%. The intensi-

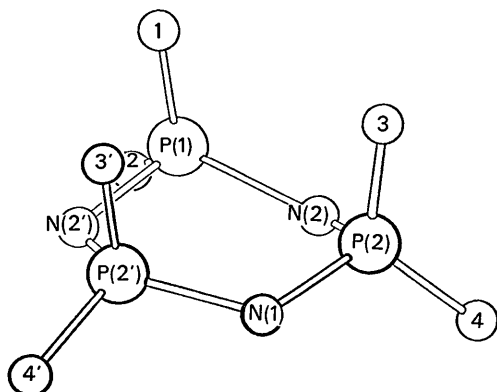


Fig. 1. The $N_3P_3Hal_6$ molecule. The halogen atoms are numbered 1 to 4.

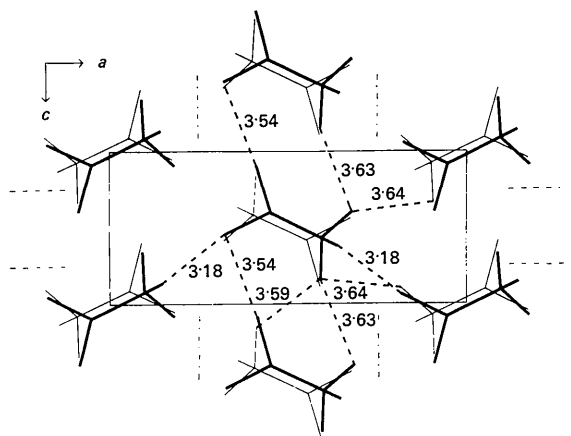


Fig. 2. [010] projection of the structure showing the shortest intermolecular distances (in Å). The heavily outlined molecules possess a (pseudo) mirror plane at $y = \frac{1}{4}$, those lightly outlined, at $y = -\frac{1}{4}$.

ties were corrected for Lorentz and polarization effects. The method of Busing & Levy (1957) was used for the calculation of the absorption corrections [$\mu(Mo) = 1.68 \text{ mm}^{-1}$].

Structure determination

Approximate structure

Comparison of the crystallographic data of $N_3P_3Cl_5F$ with those of $N_3P_3Cl_6$ (Table 2) suggests that the two compounds are isomorphous. We therefore started the structure determination by assuming *Pnma* to be the correct space group for $N_3P_3Cl_5F$. This choice was supported by statistical tests on a centre of symmetry (Howells, Phillips & Rogers, 1950; Ramachandran & Srinivasan, 1959).

In *Pnma* the four molecules in the unit cell lie in special positions, *viz.* on mirror planes. It was initially thought that one of the halogen atoms on the mirror plane [Hal(1) or Hal(2) in Fig. 1] would be a fluorine atom. An *F*(obs) Fourier synthesis of the 506 stronger reflexions to which signs obtained from $N_3P_3Cl_6$ were given showed, however, that the electron densities at the four non-equivalent halogen positions did not differ much (Table 3, row 1). It therefore seemed likely that the fluorine atom was randomly distributed over the halogen atom positions.

Refinement with equal halogen atoms

During the least-squares refinements described below, 150 reflexions with low statistical weights (smaller than 10 per cent of the average weight calculated for the reflexions on the basis of counting statistics) were not taken into account; the remaining 506 reflexions were given unit weight. This seems to be reasonable as at the end of the refinement the value of $\langle (\Delta F)^2 \rangle$, which was calculated in a number of $|F|$ -intervals, appeared to be nearly independent of $|F|$. A program written for the Tr4 computer by Palm and Peterse according to Cruickshank's (1961) block diagonal approximation was used. The scattering factors were taken from Moore's (1963) Table.

First an anisotropic least-squares refinement was carried out in which all halogen atoms were supposed to be equal; the scattering factor of chlorine was used for these atoms. The residual *R* amounted to 4.3%. The parameters obtained for this model (model *A*) are listed in Tables 4 and 5. In Table 6 the observed and calculated structure factors are compared. Table 7, column 1, gives the bond lengths and valence angles; the calculated standard deviations are based on the standard deviations of the coordinates (Table 4).

Table 3. *Comparison of the maximum electron densities, average B values ($= 8\pi^2 \overline{U_{ii}}$) and P-Hal distances for the non-equivalent halogen atoms*

	Hal(1)	Hal(2)	Hal(3)	Hal(4)
Maximum electron density ($e \cdot \text{Å}^{-3}$)	20.8	18.6	16.5	18.0
<i>B</i> (average) (Å^2)	6.3	7.5	8.9	8.3
P-Hal (Å)	1.969	1.949	1.899	1.936

The supposition that fluorine is distributed over the six halogen positions is confirmed by two facts: (a) the average temperature factors for the halogen atoms do not show large differences (Table 3); (b) all P-Hal distances are between the values 1.97₅ Å, observed by Wilson & Carroll (1960) in N₃P₃Cl₆, and 1.52 Å in N₃P₃F₆. As a result of this disorder the structure could not be determined accurately. Below we shall describe some attempts to improve the model obtained for the molecule.

Table 4. Model A. Fractional atomic coordinates and standard deviations*

	x	y	z
P(1)	0.4470 (2)	0.2500	0.4116 (5)
P(2)	0.5966 (1)	0.3567 (2)	0.5792 (4)
N(1)	0.6448 (6)	0.2500	0.6303 (20)
N(2)	0.4982 (4)	0.3551 (5)	0.4650 (12)
Hal(1)	0.3228 (2)	0.2500	0.5523 (6)
Hal(2)	0.4106 (3)	0.2500	0.1005 (6)
Hal(3)	0.5903 (2)	0.4348 (2)	0.8463 (5)
Hal(4)	0.6818 (2)	0.4420 (2)	0.4068 (5)

* The standard deviations listed in parentheses are the values calculated by the least-squares program.

Models with symmetry m

(1) If the distribution of fluorine over the halogen positions is supposed to be random, each halogen consists of $\frac{5}{6}$ Cl and $\frac{1}{6}$ F (model B). A least-squares refinement was carried out in which the statistically distributed fluorine atom was taken into account. Each $\frac{1}{6}$ F was located at 1.52 Å from the phosphorus atom on the P-Hal bond and was given an isotropic temperature factor with B equal to $8\pi^2$ times the mean U_{ii} value for the corresponding $\frac{5}{6}$ Cl. Coordinates and thermal parameters of P, N and $\frac{5}{6}$ Cl were refined. After each cycle the parameters of $\frac{1}{6}$ F were adjusted. The R index decreased to 4.0%.

(2) The electron densities, average thermal parameters of the halogen atoms and the P-Hal bond lengths in model A (Table 3) suggest, however, that the distribution of fluorine is not completely random. Starting from the P-Hal bond lengths in Table 3 we calculated the distribution of fluorine for which all P-Cl bonds have the same length, assuming P-F to be 1.52 Å. Use was made of the fact that each halogen position Hal(i) in Table 4 is the centre of mass of x_i fluorine and

(1 - x_i) chlorine atoms. Fluorine occupancy factors of 0.026, 0.108, 0.279 and 0.154 were obtained (model C). With these values an anisotropic least-squares refinement was carried out with the use of the same positional and thermal conditions for fluorine as before: R decreased to 3.7%.

It may be noted that the positions of the chlorine atoms are correlated to the distribution of the fluorine atoms. Several models would be possible, each resulting in the same R index. This proved to be true in a least-squares refinement of the occupancy factors of chlorine and fluorine, which was independently carried out by Mrs E.W.M. Rutten-Keulemans, by a full-matrix least-squares program. The method followed by her for the introduction of the restrictions concerning the total amount of chlorine and fluorine in the molecule is described in the *Appendix*. The resultant values for the fluorine occupancy factors were 0.096, 0.149, 0.239 and 0.140.

To test whether a non-random fluorine distribution is in better agreement with the experimental data than a random distribution, with the unit weighting scheme, we consider the hypothesis that a random distribution of fluorine describes the structure correctly (Hamilton, 1965). There are three variables in this hypothesis, namely the number of occupancy factors to be chosen for an irregular distribution; the number of degrees of freedom is $506 - 3 = 503$. The weighted R values, $R_w = [\sum w_i (\Delta F)^2 / \sum w_i F_{obs}^2]^{1/2}$, with $w = 1$, are 3.70 and 3.47% for models B and C respectively; $\mathcal{R} = R_B/R_C = 1.078$. Hamilton's table shows $\mathcal{R}_{3,503,0.00} = 1.013$. On the 0.5% significance level we can conclude that model C is a better approximation to the structure than model B.

Asymmetric models

In the models discussed so far the molecule was assumed to have a mirror plane, as required for space group $Pnma$. If, however, the space group is $Pn2_1a$ rather than $Pnma$, the N₃P₃Cl₅F molecule does not lie on a mirror plane and the fluorine occupancy factors need not be equal for Hal(3) and Hal(3') and for Hal(4) and Hal(4'). To test whether the need to assume a distribution of fluorine over different positions is a result of a wrong choice of space group, least-squares refinements in space group $Pn2_1a$ were done in which Hal(3') and Hal(4') respectively were considered to be entirely fluorine. The best agreement with the observed intensi-

Table 5. Model A. Thermal parameters ($\times 10^4$) of the temperature factor:

$$\exp\{-2\pi^2[h^2a^*2U_{11} + k^2b^*2U_{22} + l^2c^*2U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{31}]\}.$$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
P(1)	363 (15)	599 (19)	603 (19)	0	0	-148 (31)
P(2)	437 (10)	558 (13)	779 (15)	-105 (22)	-6 (26)	-228 (23)
N(1)	509 (56)	702 (69)	1204 (97)	0	0	-672 (125)
N(2)	470 (30)	544 (40)	970 (52)	37 (64)	120 (88)	-310 (72)
Hal(1)	460 (16)	982 (26)	934 (25)	0	0	166 (38)
Hal(2)	904 (25)	1175 (31)	733 (24)	0	0	-198 (43)
Hal(3)	1223 (22)	1020 (22)	1097 (21)	-193 (38)	-237 (41)	-247 (38)
Hal(4)	813 (16)	1035 (21)	1250 (23)	-460 (32)	161 (40)	245 (36)

Table 6. Model A. Observed and calculated structure factors ($\times 10$)

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
2	0	0	398	358	9	1	1	245	245	5	10	1	159	151	6	11	0	-167	-166
4	0	0	-1483	-1514	10	1	1	165	157	4	11	1	114	126	2	12	0	75	47
6	0	0	-322	-311	11	1	1	-202	-203	5	11	1	-103	-99	2	13	0	324	301
8	0	0	-691	-738	12	1	1	122	122	6	11	1	72	73	1	0	1	1514	1404
10	0	0	716	712	13	1	1	-213	-214	7	11	1	-115	-119	2	0	1	1251	1251
12	0	0	512	528	1	2	1	-658	-551	2	12	1	68	61	3	0	1	-308	-291
14	0	0	-337	-306	2	2	1	-371	-328	5	12	1	64	73	4	0	1	1726	1748
2	1	0	-438	-413	3	2	1	-204	-227	0	13	1	-104	-94	5	0	1	1096	1121
4	1	0	67	44	4	2	1	108	134	1	13	1	118	127	6	0	1	-438	-443
6	1	0	726	699	5	2	1	133	148	2	13	1	-113	-105	7	0	1	196	175
8	1	0	511	513	6	2	1	-158	-149	0	0	2	1361	1379	8	0	1	-669	-660
12	1	0	-228	-230	8	2	1	-148	-147	1	0	2	-561	-930	9	0	1	-265	-261
14	1	0	-203	-214	9	2	1	159	159	2	0	2	119	94	10	0	1	52	28
2	2	0	-661	-632	11	2	1	91	91	3	0	2	108	76	11	0	1	306	407
4	2	0	54	34	0	3	1	578	617	5	0	2	404	394	13	0	1	-159	-157
6	2	0	112	115	1	3	1	-763	-745	6	0	2	296	290	14	0	1	102	97
8	2	0	62	40	2	3	1	994	980	7	0	2	-337	-323	0	1	1	175	185
10	2	0	203	195	3	3	1	447	492	8	0	2	-259	-239	1	1	1	-314	-300
2	3	0	-2685	-2735	4	3	1	-345	-366	9	0	2	386	386	2	1	1	-164	-145
4	3	0	-401	-391	5	3	1	236	232	10	0	2	265	248	3	1	1	-495	-424
6	3	0	-495	-491	6	3	1	-1048	-1036	12	0	2	159	172	4	1	1	-512	-490
8	3	0	434	439	7	3	1	-215	-211	13	0	2	-210	-200	5	1	1	195	187
10	3	0	665	690	8	3	1	55	36	14	0	2	-131	-131	6	1	1	-133	-121
12	3	0	-353	-357	9	3	1	213	212	1	1	2	178	162	7	1	1	760	747
0	4	0	418	431	10	3	1	114	110	2	1	2	202	216	8	1	1	184	165
2	4	0	-475	-433	13	3	1	-68	-92	3	1	2	-525	-517	6	10	1	63	52
4	4	0	-192	-169	1	4	1	-444	-423	4	1	2	-48	-41	4	6	2	-66	-64
6	4	0	349	338	3	4	1	-487	-452	5	1	2	-564	-543	5	6	2	-144	-142
8	4	0	-628	-631	4	4	1	181	195	6	1	2	261	249	6	6	2	-140	-138
10	4	0	-581	-594	5	4	1	612	621	8	1	2	222	218	7	6	2	-274	-265
12	4	0	-112	-116	6	4	1	153	149	9	1	2	257	255	8	6	2	308	320
14	4	0	-76	-36	7	4	1	81	79	10	1	2	-137	-139	9	6	2	-444	-446
2	5	0	257	215	8	4	1	153	138	11	1	2	306	323	10	6	2	132	152
4	5	0	816	801	9	4	1	-721	-722	12	1	2	-81	-83	11	6	2	116	110
8	5	0	-311	-305	10	4	1	90	87	13	1	2	77	85	1	7	2	-164	-170
12	5	0	94	84	11	4	1	-336	-346	0	2	2	-729	-716	2	7	2	-205	-216
0	6	0	-1148	-1164	12	4	1	-168	-173	1	2	2	-546	-571	3	7	2	373	369
2	6	0	224	209	13	4	1	-121	-117	2	2	2	-282	-283	4	7	2	98	101
4	6	0	337	314	14	4	1	-121	-133	3	2	2	-405	-416	6	7	2	-131	-120
6	6	0	-48	-42	0	5	1	-257	-254	4	2	2	171	167	8	7	2	-84	-77
8	6	0	616	623	1	5	1	178	178	5	2	2	-108	-105	10	7	2	121	108
10	6	0	179	196	3	5	1	809	764	6	2	2	131	138	11	7	2	-225	-219
2	7	0	-697	-698	4	5	1	42	28	7	2	2	-197	-197	0	8	2	377	392
4	7	0	-94	-76	5	5	1	397	373	8	2	2	134	134	1	8	2	351	367
6	7	0	-293	-287	6	5	1	81	69	9	2	2	47	33	2	8	2	194	196
10	7	0	297	298	7	5	1	-325	-311	11	2	2	67	55	3	8	2	377	361
12	7	0	-88	-71	8	5	1	219	213	12	2	2	-91	-92	4	8	2	-108	-106
2	8	0	348	357	9	5	1	-185	-181	1	3	2	-700	-736	5	8	2	130	112
6	8	0	-139	-136	1	6	1	286	303	2	3	2	-478	-489	6	8	2	-117	-111
12	8	0	65	42	2	6	1	-231	-221	3	3	2	911	909	9	8	2	-166	-141
6	9	0	346	344	3	6	1	404	369	4	3	2	226	222	1	9	2	238	246
8	9	0	167	173	4	6	1	-502	-476	5	3	2	-90	-73	2	9	2	-51	-39
10	9	0	-66	-77	5	6	1	-724	-718	6	3	2	-238	-243	3	9	2	-284	-292
2	10	0	-218	-216	9	6	1	549	550	10	3	2	200	207	4	9	2	-81	-78
4	10	0	272	265	11	6	1	210	211	11	3	2	-404	-395	5	9	2	-294	-291
6	10	0	95	92	12	6	1	125	144	12	3	2	-108	-94	1	6	3	-86	-95
8	10	0	179	161	13	6	1	254	138	1	4	2	-366	-397	6	6	3	160	149
10	10	0	-159	-162	0	7	1	37	90	2	4	2	-309	-308	7	6	3	-85	-96
2	11	0	144	149	1	7	1	-259	-264	3	4	2	-348	-342	8	6	3	-87	-84
6	11	0	-140	-151	2	7	1	290	289	5	4	2	173	178	9	6	3	-87	-84

Table 6 (cont.)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
6	9	2	159	169	1	7	3	-122	-125	1	9	4	54	49
7	9	2	-116	-115	2	7	3	292	287	3	9	4	-127	-135
8	9	2	121	133	3	7	3	-76	-69	4	9	4	-69	-54
9	9	2	181	168	6	7	3	-305	-303	5	9	4	-115	-106
10	9	2	-54	-39	9	7	3	72	69	0	10	4	162	161
0	10	2	-315	-333	1	8	3	-63	-61	3	10	4	-168	-179
1	10	2	55	41	2	8	3	334	339	1	0	5	-161	-201
2	10	2	-57	-61	4	8	3	178	181	2	0	5	-80	-75
3	10	2	-175	-181	5	8	3	172	154	3	0	5	107	105
5	10	2	-131	-140	6	8	3	72	69	4	0	5	132	126
7	10	2	124	129	7	8	3	89	74	6	0	5	-70	-44
1	11	2	86	83	8	8	3	-103	-100	7	0	5	67	85
3	11	2	82	71	1	9	3	67	71	9	0	5	110	95
5	11	2	57	82	2	9	3	-137	-133	1	1	5	122	138
7	11	2	-81	-73	3	9	3	68	63	2	1	5	-108	-111
1	0	3	612	606	4	9	3	-145	-169	3	1	5	115	120
2	0	3	499	508	1	10	3	-102	-103	4	1	5	-82	-98
4	0	3	1309	1308	2	10	3	-155	-174	6	1	5	90	31
5	0	3	-231	-232	4	10	3	-345	-336	7	1	5	-158	-175
6	0	3	-270	-258	2	11	3	51	51	9	1	5	-137	-144
7	0	3	-113	-128	4	11	3	97	99	2	2	5	-79	-64
8	0	3	-512	-510	0	0	4	-729	-720	3	2	5	127	127
9	0	3	204	194	2	0	4	-164	-157	4	2	5	-184	-178
11	0	3	222	240	3	0	4	519	532	8	2	5	106	90
12	0	3	-76	-76	4	0	4	331	343	9	2	5	-78	-78
0	1	3	-77	-77	5	0	4	340	281	0	3	5	-140	-126
1	1	3	140	137	6	0	4	325	306	1	3	5	95	105
2	1	3	-291	-294	7	0	4	-372	-360	2	3	5	51	46
3	1	3	-106	-119	8	0	4	227	204	7	3	5	156	119
4	1	3	-373	-357	10	0	4	-79	-31	2	4	5	-125	-133
5	1	3	-139	-146	1	1	4	171	174	3	4	5	-60	-81
7	1	3	161	137	2	1	4	73	80	4	4	5	66	71
8	1	3	150	143	3	1	4	-272	-298	5	4	5	-174	-180
10	1	3	199	210	4	1	4	-156	-164	7	4	5	-75	-72
12	1	3	154	159	5	1	4	-285	-290	8	4	5	57	37
1	2	3	112	125	7	1	4	-72	-70	0	5	5	-167	-156
2	2	3	-529	-539	9	1	4	118	123	2	5	5	-86	-83
3	2	3	105	103	10	1	4	-70	-53	3	5	5	-144	-135
4	2	3	-289	-295	11	1	4	252	247	4	5	5	133	135
5	2	3	-271	-265	2	2	4	169	172	5	5	5	-130	-138
6	2	3	-140	-136	5	2	4	-94	-112	6	5	5	220	205
7	2	3	-82	-78	6	2	4	-139	-158	2	6	5	148	145
8	2	3	63	75	7	2	4	-93	-99	5	6	5	159	151
9	2	3	71	60	9	2	4	-63	-52	6	6	5	-70	-60
10	2	3	79	78	10	2	4	-97	-75	2	8	5	97	76
11	2	3	-74	-92	1	3	4	132	140	0	0	6	-260	-252
0	3	3	185	168	2	3	4	420	413	3	0	6	106	78
1	3	3	-336	-345	3	3	4	221	225	4	0	6	69	69
2	3	3	701	711	4	3	4	272	268	4	1	6	-73	-68
3	3	3	-388	-387	5	3	4	-371	-367	0	2	6	168	179
4	3	3	-171	-154	6	3	4	90	80	1	2	6	52	39
6	3	3	-807	-796	7	3	4	-89	-105	2	2	6	119	120
7	3	3	197	189	8	3	4	-125	-118	4	2	6	-62	-52
8	3	3	54	46	9	3	4	65	76	2	3	6	133	127
9	3	3	164	160	10	3	4	-122	-116	0	4	6	-64	-47

ties was obtained for Hal(3')=F. The value of R_w (5.9%), however, is significantly higher than that of model C ($R_w=3.5\%$), whereas the P-F bond (1.81 Å) appears to be much longer than the expected value of 1.52 Å. This indicates that in space group $Pn2_1a$ also,

Table 7. Bond lengths and valence angles for models of the $N_3P_3Cl_3F$ molecule with different fluorine distributions

	Model A	Model B	Model C
P(1)-N(2)	1.563 (6) Å	1.562 Å	1.561 Å
P(2)-N(2)	1.567 (7)	1.570	1.568
P(2)-N(1)	1.558 (5)	1.564	1.562
P(1)-Hal(1)	1.969 (4)	1.995	1.975
P(1)-Hal(2)	1.949 (5)	1.976	1.964
P(2)-Hal(3)	1.899 (4)	1.939	1.957
P(2)-Hal(4)	1.936 (4)	1.965	1.961
N(2)-P(1)-N(2')	118.5 (5)°	118.7°	118.4°
N(1)-P(2)-N(2)	118.5 (4)	118.8	118.5
P(2)-N(1)-P(2')	122.2 (2)	121.1	121.5
P(1)-N(2)-P(2)	121.5 (4)	121.3	121.5
Hal(1)-P(1)-Hal(2)	100.1 (2)	100.0	100.1
Hal(3)-P(2)-Hal(4)	101.0 (2)	101.0	101.1
N(2)-P(1)-Hal(1)	109.4 (3)	109.5	109.5
N(2)-P(1)-Hal(2)	108.9 (3)	108.8	108.9
N(2)-P(2)-Hal(3)	109.7 (3)	109.7	109.8
N(2)-P(2)-Hal(4)	109.6 (3)	109.3	109.4
N(1)-P(2)-Hal(3)	108.2 (5)	108.0	107.8
N(1)-P(2)-Hal(4)	108.8 (4)	108.5	108.9

a distribution of fluorine over the halogen positions has to be assumed.

Although we think it most probable that $Pnma$ is the correct space group, $Pn2_1a$, with small differences between the occupancy factors for Hal(3) and Hal(3'), or Hal(4) and Hal(4'), cannot strictly be excluded. Further calculations in this space group were not carried out as it was felt that they would not give a better insight into the structure of the molecule. The discussion of the structure given in the next section is based on the models obtained in space group $Pnma$.

Discussion

In spite of the disorder in the molecule the bond lengths in the ring seem to have been determined with fair precision (Table 7). The average P-N bond lengths obtained from the different least-squares refinements do not differ much: they range from 1.562 to 1.565 Å (uncorrected for libration effects). In all models the individual P-N bonds are equal within experimental error.

It is disappointing that the disorder in the molecule made it impossible to observe differences between the individual P-N bonds in the ring. We had hoped to find a shortening of some of the bonds with respect to their lengths in $N_3P_3Cl_6$ as a result of the presence of fluorine. It may be noted that the mean value observed for P-N in $N_3P_3Cl_3F$ is significantly smaller than the value 1.59 Å observed for $N_3P_3Cl_6$ (Wilson & Carroll, 1960), but not considerably larger than the value of 1.56 Å observed for the corresponding hexafluoro compound.

The central ring of the molecule is almost planar, the maximum deviation from the best plane through the six atoms of the ring being 0.011 Å. The valence angles at the phosphorus and nitrogen atoms (see Table 7) have values of about 120°, as in $N_3P_3Cl_6$ and $N_3P_3F_6$.

Also the exocyclic Hal-P-Hal angles have the normal values.

The P-Cl bond lengths could not be determined accurately because of the correlation with the occupancy factors of chlorine and fluorine. The mean value, 1.963 Å, estimated standard deviation 0.005 Å, for both models *B* and *C* is, within experimental error, equal to the values 1.97 and 1.98 Å, which Wilson & Carroll (1960) reported for N₃P₃Cl₈, but in many other phosphazene compounds such as N₄P₄Cl₆, *K* and *T* form (Hazekamp, Migchelsen & Vos, 1962; Wagner & Vos, 1968*a*), larger P-Cl bond lengths of 1.99 Å are observed. The rather short distances in N₃P₃Cl₅F may partly be the result of librational effects. A thermal analysis could not be attempted, however, as the disorder in the atomic positions would increase the thermal parameters of the atoms.

In Fig. 2 the intermolecular distances are shown which are approximately equal to the sum of the van der Waals radii of a nitrogen and a chlorine atom, 3.20 Å, and of two chlorine atoms, 3.60 Å. The values given correspond to model *A*.

We are grateful to Professor N. L. Paddock for sending us crystals of N₃P₃Cl₅F. We wish to thank Professor Aafje Vos for her interest throughout the investigation and for many valuable discussions. Calculations were done at the Groningen University Computing Centre. The work was supported by the Netherlands Organization for the advancement of Pure Research (Z. W. O.).

APPENDIX

The calculated structure factor for a reflexion *hkl* is:

$$F(hkl) = F_{P+N} + a_1 \cdot F_{Cl(1)} + a_2 \cdot F_{Cl(2)} + a_3 \cdot F_{Cl(3)} \\ + a_4 \cdot F_{Cl(4)} + (4 - a_1) \cdot F_{F(1)} + (4 - a_2) \cdot F_{F(2)} \\ + (8 - a_3) \cdot F_{F(3)} + (8 - a_4) \cdot F_{F(4)},$$

where F_{P+N} is the contribution of phosphorus and nitrogen to the structure factor, a_i is the occupancy factor, including the multiplicity, for chlorine at position Hal(*i*).

The occupancy factors for three chlorine atoms can be varied independently, as the total number of chlorine

atoms in the cell is fixed, *viz.* 20. We have chosen $a_4 = 20 - a_1 - a_2 - a_3$. In the program used (a modification of the Busing & Levy least-squares program) the variations of only two parameters can be coupled. To couple the variation of a_4 to those of a_1 to a_3 the atom Cl(4) was formally considered to consist of three parts Cl(4;1), Cl(4;2) and Cl(4;3). The following restraints were applied:

$$da[Cl(4;i)] = -da_i; da[F(i)] = -da_i; da[F(4;i)] = da_i, \\ i = 1, 2, 3$$

$$dp[X(4;2)] = dp[X(4;1)]; dp[X(4;3)] = dp[X(4;1)],$$

with X = Cl or F and *p* a general parameter.

In this way it appeared to be possible to do the refinement by use of the proper restraints without modifying the least-squares program.

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