942. *Phosphonitrilic Derivatives. Part VII.*[1] *The Crystal Structure of Tetrameric Phosphonitrilic Fluoride.*

By H. McD. McGeachin and F. R. Tromans.

The *X*-ray analysis of crystalline $(PNF_2)_4$ shows that the P–N ring is planar and that the molecule has only slight deviations from $4/mmm$ (D_{4h}) symmetry. These deviations are ascribed to close approaches of neighbouring molecules. The P–N bond lengths are equal and short (1·51 ± 0·02 Å). The P–F bond lengths are also 1·51 ± 0·02 Å and values of 147·2° ± 1·4°, 122·7° ± 1·0° and 99·9° ± 1·0° are found for the angles $\widehat{PNP}$, $\widehat{NPN}$, and $\widehat{FPF}$, respectively.

This study was undertaken to investigate the structural effects of substituting fluorine for chlorine in the phosphonitrilic halides. Ketelaar and de Vries[2] showed that the symmetry of the tetrameric chloride was $\bar{4}$ while space-group considerations indicated that that of the fluoride was $\bar{1}$. The shape of the eight-membered P–N ring thus depends on the substituents; this work reports how the bond lengths and angles are modified by the substitution of the more electronegative fluorine for chlorine.

Shortly before our work was completed, Jagodzinski and Oppermann[3] published an account of some preliminary structural work on $(PNF_2)_4$; they do not intend to continue the investigation. A brief note on our results has appeared.[4]

Crystal Data.—$(PNF_2)_4$, $M = 331{\cdot}96$, m. p. 30·4°, monoclinic, $a = 7{\cdot}40$, $b = 13{\cdot}83$, $c = 5{\cdot}16$ Å, $\beta = 109{\cdot}5°$, $U = 500$ Å^3, $D_m = 2{\cdot}22$, $Z = 2$, $D_c = 2{\cdot}20$, $F(000) = 320$, $\mu = 8{\cdot}8$ cm.$^{-1}$ Mo for radiation. Space group $P2_1/a$ $(C^5_{2h}$, No. 14), implied molecular symmetry $\bar{1}$, optically biaxial negative, refractive indices $\alpha = 1{\cdot}379 \pm 0{\cdot}002$, $\beta = 1{\cdot}428 \pm 0{\cdot}005$, $\gamma = 1{\cdot}463 \pm 0{\cdot}002$ (optical results from J. K. Leary). Because of the low melting point, the thermal vibrations are large and no high-order reflections are observed. The dimensions of the unit cell, determined from rotation photographs, are therefore probably less accurate than we would wish; they can be compared with Jagodzinski and Oppermann's values $a = 7{\cdot}53$, $b = 14{\cdot}0$, $c = 5{\cdot}15$ Å, $\beta = 111{\cdot}1°$.

EXPERIMENTAL

Tetrameric phosphonitrilic fluoride sublimes rapidly in air and crystal specimens must be grown in sealed capsules. Two different sets of three-dimensional intensity measurements were made. In the first (*A*), one of several single crystals grown from the melt in a Lindemann glass tube was used with copper radiation. It was impossible to control the shape of the specimen, and during exposure both size and shape changed as the crystal sublimed inside the tube. Since we had no precise knowledge of the crystal dimensions, we could not apply the anisotropic absorption corrections which were clearly desirable. At a later stage another set (*B*) of intensity measurements were made with molybdenum radiation and a spherical crystal. This was grown in a Lindemann glass sphere (0·8 mm. diam.) completely filled with the melt; cycles of partial melting and recrystallisation (controlled either by varying the

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[1] Part VI, Chapman, Holmes, Paddock, and Searle, *J.*, 1961, 1825.

[2] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

[3] Jagodzinski and Oppermann, *Z. Krist.*, 1960, **113**, 241.

[4] McGeachin and Tromans, *Chem. and Ind.*, 1960, 1131.

TABLE 1.

Observed and calculated structure factors.

h k	*l*	10|F_o|	10F_c
0 0	1	351	295
	2	382	−384
	3	353	377
	5	79	−82
2 0	0	1248	−1210
	1	139	−167
	3	239	−277
	4	93	−107
	−1	442	357
	−2	522	487
	−3	248	−224
	−4	176	165
	−5	63	87
4 0	0	103	106
	1	199	207
	2	64	−43
	4	85	83
	−1	353	−387
	−2	276	−256
	−3	120	−134
	−4	257	−227
6 0	0	211	218
	1	56	−53
	−1	234	259
	−3	86	89
	−4	88	107
0 1	1	57	−56
	2	89	76
	3	111	110
1 1	0	397	343
	1	709	−624
	2	101	−97
	3	117	113
	4	161	−172
	−1	823	779
	−3	136	−151
	−4	137	151
2 1	0	131	136
	1	167	−152
	2	180	−177
	3	89	−102
	−1	247	217
	−3	85	67
3 1	0	213	−260
	1	221	234
	2	85	71
	3	141	−149
	−1	111	−121
	3	86	−61
	0	63	−59
	1	58	−76
	2	97	−85
	−1	158	−201
	−2	65	70
	−3	57	53
5 1	0	317	350
	1	78	67
	2	69	−61
	3	62	70
	−3	100	117
	−4	75	−80
6 1	2	73	60
	−1	126	163
	−3	132	−86
7 1	0	62	−90
0 2	0	687	430
	1	177	−145
	2	103	−105
	3	90	107
1 2	0	83	65
	1	910	815
	2	334	330
	−1	998	862
	−2	405	413
	−3	253	−258
2 2	0	308	307
	2	113	114
	−1	204	194
	−2	65	40
	−3	129	−110
2 2	−4	90	90
3 2	0	51	28
	1	335	−335
	2	236	−254
	3	72	−82
	−1	163	163
	−2	290	281
	−3	342	303
4 2	0	119	140
	1	72	77
	2	79	−83
	−1	118	−135
	−3	65	63
	−4	72	−72
5 2	1	140	−155
	3	88	70
	−1	93	−106
	−2	334	−337
	−3	130	−136
6 2	1	55	−57
	−1	45	48
7 2	−2	129	160
0 3	1	450	−349
	2	144	172
	3	294	278
	4	60	−62
1 3	1	116	112
	3	105	83
	−1	369	−301
2 3	0	200	−181
	1	149	146
	3	229	−233
	−1	267	232
	−2	380	337
	−3	121	99
3 3	0	191	−157
	1	60	54
	3	60	−46
	−1	54	−51
	−2	102	109
	−3	73	−37
4 3	0	100	116
	1	162	−203
	2	172	−181
	3	74	93
	−1	306	−320
	−2	156	−162
	−3	108	108
5 3	0	78	−71
	1	122	−130
	3	55	26
	−3	60	−12
6 3	2	112	109
	−1	226	231
	−3	122	−143
0 4	0	1248	−1095
	1	452	−383
	2	192	−183
	3	112	−135
	4	53	58
1 4	0	536	−518
	1	76	82
	2	253	251
	3	116	−123
	−1	503	495
	−2	104	101
	−3	294	−310
	−4	71	67
2 4	0	244	190
	1	78	76
	2	320	300
	3	137	175
	−1	81	55
	−2	65	−66
	−4	117	−126
3 4	0	200	187
	1	95	89
	2	197	−196
	−1	434	−427
	−2	73	83
3 4	−3	235	265
	−4	159	−131
4 4	0	110	100
	1	94	−77
	2	105	−95
	−1	112	130
	−2	156	154
	−3	192	199
	−4	147	146
5 4	1	89	−100
	2	83	69
	−1	166	174
	−2	113	−113
	−3	95	−94
	−4	89	88
6 4	0	187	−185
	−1	178	−160
	−3	53	−68
7 4	−2	100	76
0 5	1	153	155
	2	78	42
	4	103	−67
1 5	0	268	−232
	1	99	−86
	2	124	137
	3	117	82
	4	129	136
	−2	136	−135
	−3	101	−104
	−4	121	−117
2 5	0	290	−266
	1	147	164
	2	135	133
	−1	140	120
	−2	117	162
	−3	143	−150
3 5	0	243	235
	1	67	63
	−2	160	164
	−3	159	176
4 5	0	220	224
	1	42	−36
	−1	63	−58
	−2	179	−179
	−3	92	100
5 5	0	306	−289
	1	126	−129
	−3	116	−97
	−4	48	55
	−5	74	45
6 5	0	87	− 85
	2	77	30
7 5	0	78	59
0 6	0	288	−255
	1	98	102
	3	120	−114
1 6	0	67	−95
	1	298	−278
	2	226	−212
	3	137	−110
	4	149	14
	−1	296	−287
	−2	310	−319
2 6	0	175	179
	1	119	135
	−1	325	−289
	−2	89	82
	−3	146	154
	−4	165	−164
3 6	1	192	182
	2	127	121
	3	110	115
	−1	219	−218
	−2	84	−91
	−3	129	−108
	−4	132	−139
4 6	0	71	−75
	1	156	−157
	−1	234	221
	−2	61	−58
4 6	−3	74	−89
	−4	123	134
5 6	0	62	66
	1	46	41
	−1	149	150
	−2	120	112
	−3	84	77
	−4	71	60
6 6	1	81	77
	−1	88	−71
7 6	0	79	−65
	1	154	155
	2	110	−111
	3	199	−223
1 7	0	192	−181
	1	159	170
	3	132	−141
	−2	136	134
2 7	1	126	−120
	3	132	135
	−1	178	−162
	−2	277	−249
	−3	140	−152
3 7	0	396	367
	1	142	−122
	2	87	−93
	3	111	97
	−2	204	−208
	−3	125	123
4 7	0	74	72
	1	172	184
	2	102	107
	−1	140	142
	−2	128	127
5 7	0	106	−121
	1	68	59
	2	94	82
	−1	76	82
	−2	99	88
	−3	108	−94
6 7	0	60	−46
	1	63	−55
	−1	75	−69
0 8	0	88	93
	1	374	357
	2	219	217
	3	120	−124
1 8	0	59	58
	1	73	−81
	2	139	−132
	−1	230	−219
	−3	137	132
2 8	0	131	145
	1	72	−51
	2	276	−289
	−1	258	−260
	−3	191	204
3 8	0	63	−59
	2	158	147
	−1	169	166
	−2	68	−48
	−3	114	−138
4 8	0	70	−74
	2	119	108
	−1	82	81
	−2	161	−177
	−3	189	−188
5 8	2	55	−57
	−1	46	−58
	−2	65	45
	−3	84	75
6 8	0	51	52
	1	76	86
	−1	52	43
	−2	110	108
1 9	0	119	124
	1	60	63
	2	189	−168
	3	140	−94
	−1	99	113
1 9	−2	204	203
2 9	0	154	143
	1	153	−143
	3	106	94
	−2	95	−101
3 9	0	111	−96
	1	116	−113
	−1	147	−139
	−2	181	−181
4 9	0	135	−128
	1	65	68
	3	71	−84
	−2	117	118
5 9	0	93	90
	1	91	98
	2	58	48
	−1	108	117
	−2	48	39
	−3	50	−45
6 9	0	54	42
	−1	61	−42
0 10	0	145	177
	1	88	83
1 10	0	375	358
	1	96	96
	2	70	−83
	3	119	95
2 10	0	115	−110
	1	132	−162
3 10	0	154	−136
	1	146	−139
	−1	206	219
	−2	114	95
4 10	1	73	77
	−1	63	−63
	−2	43	−55
5 10	−1	135	−125
	−4	90	−55
0 11	1	235	252
2 11	0	175	180
	1	132	−150
	−1	271	281
3 11	0	116	−133
	1	59	50
4 11	0	168	−187
	−1	83	−82
	−3	47	−53
5 11	0	46	45
6 11	0	80	87
0 12	1	112	−141
	2	98	−76
1 12	0	187	260
	1	58	37
	−2	68	−75
2 12	0	104	−60
	2	124	114
	−1	58	73
3 12	0	102	−113
	−2	70	46
4 12	−2	82	82
	−3	70	69
0 13	1	84	57
1 13	2	74	78
	−2	123	−118
3 13	1	85	80
	−1	104	90
	−2	104	107
5 13	1	64	−46
	−1	83	−86
	−3	69	53
1 14	0	89	− 87
0 14	1	67	−95
2 14	2	107	96
4 14	−2	70	69
0 15	1	62	−67
4 15	1	87	80
2 15	−1	89	−89
1 16	0	67	−90

aperture of the lamp of the polarising microscope by which it was viewed, or by warming with the fingers) eventually produced single crystals. Bond's [5] corrections for absorption were applied to this set, which consisted of 398 independent non-zero values, compared with 560

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[5] Bond, *Acta Cryst.*, 1959, **12**, 381; "International Tables for *X*-ray Crystallography," Kynoch Press, Birmingham, 1959, Vol. II.

in set (*A*); the smaller number is due to the heavier background associated with molybdenum radiation. Weissenberg photographs about four axes were used for (*A*) and about three for (*B*). The four films (Ilford Industrial G) simultaneously exposed were interleaved with 0·001 in. copper foil when molybdenum radiation was used, to give an effective film factor of about 3.

The *R* factor between sets (*A*) and (*B*) of F_{obs} was 17·7%.

Solution of the Structure.—The structure was determined from Patterson projections with the help of trial-and-error methods, and refined initially by (F_o-F_c) syntheses on four projections and later by three-dimensional least-squares analysis on a Pegasus computer, the Leeds programme being used which refines atomic co-ordinates, anisotropic vibrations, and scale factor. Five cycles reduced the *R* factor from 40% to 17% (calculated on the non-zero F_{obs} only). The bond lengths of this structure (*A*) were scarcely credible: the P–N bonds, for example, ranged from 1·38—1·65 Å in an unsystematic way. This refinement used F_{obs} values derived from intensities (*A*), and the disappointing results were the reason for measuring the new set (*B*). The new F_{obs} were scaled layer-line by layer-line with the calculated values of structure (*A*) and, by using them, five cycles of refinement reduced the *R* factor to 10·2% and gave the satisfactory structure (*B*) described below.

This situation seems surprising. It is not unexpected that the values of U_{ij}, the components of the tensor which defines the anisotropic thermal vibrations, would be spurious when based on F_{hkl} whose errors are distributed anisotropically, but it was hoped that this error distribution would not have any very serious effect on the atomic co-ordinates, and also that if such an effect were in fact present it would be revealed by large values of the co-ordinate standard deviations σ. Both these hopes were disappointed. If the values of the co-ordinates in the satisfactory structure (*B*) are taken for this purpose as correct, so that the differences between (*A*) and (*B*) are considered as errors in (*A*), 6 out of the 24 independent co-ordinates in (*A*) have errors greater than 3·2 σ and the largest is 8·1 σ. If σ is a true measure of the standard deviation, these errors, which are associated with the light nitrogen and fluorine atoms, are most unlikely; hence in this case σ has been grossly underestimated. It is no criticism of Cruickshank's[6] method of calculating standard deviations to point out that if used with systematically unreliable data it gives unreliable results, but it seems worth emphasising that when systematic errors are present the calculated values of σ may be worthless.

Values of F_{obs} of set (*B*) and F_{calc} are listed in Table 1.

TABLE 2.

Co-ordinates of atoms (Å).

	Monoclinic axes			Orthogonal axes		
	x	*y*	*z*	*x′*	*y′*	*z′*
P(1)	1·4282	1·0489	1·6185	1·3462	1·0489	1·1418
(2)	1·3890	−1·5562	0·3949	1·3093	−1·5562	−0·0687
N(1)	0·0022	1·6822	0·8061	0·0021	1·6822	0·8054
(2)	1·8320	−0·3079	1·2794	1·7268	−0·3079	0·6679
F(1)	2·5673	−1·9050	−0·1983	2·4199	−1·9050	−1·0553
(2)	1·5083	−2·7107	1·3840	1·4217	−2·7107	0·8805
(3)	1·6340	1·1411	3·2048	1·5402	1·1411	2·6594
(4)	2·5556	2·0103	1·5514	2·4089	2·0103	0·6983

TABLE 3.

Standard deviations of co-ordinates (Å).

	Monoclinic axes			Orthogonal axes			
	σ(*x*)	σ(*y*)	σ(*z*)	σ(*x′*)	σ(*y′*)	σ(*z′*)	σ(ζ)
P(1)	0·0044	0·0043	0·0052	0·0041	0·0043	0·0054	0·0051
(2)	0·0049	0·0046	0·0063	0·0046	0·0046	0·0065	0·0060
N(1)	0·0149	0·0166	0·0229	0·0140	0·0166	0·0234	0·0212
(2)	0·0186	0·0147	0·0192	0·0175	0·0147	0·0202	0·0191
F(1)	0·0124	0·0151	0·0151	0·0117	0·0151	0·0156	0·0149
(2)	0·0188	0·0122	0·0163	0·0177	0·0122	0·0175	0·0168
(3)	0·0163	0·0138	0·0146	0·0154	0·0138	0·0156	0·0153
(4)	0·0116	0·0118	0·0149	0·0109	0·0118	0·0154	0·0143

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[6] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

THE STRUCTURE

The co-ordinates of the atoms are given in Table 2, where x, y, z are referred to the monoclinic crystal axes, and x', y', z' to orthogonal axes given by the transformation $x' = x \sin \beta$, $y' = y$, $z' = z + x \cos \beta$. Table 3 shows the estimated standard deviations of the atoms with respect to both co-ordinate systems. Table 4 shows the components of the vibration tensor U_{ij} with respect to x, y, z, for each atom, and Table 5 their standard deviations. Bond lengths and angles are given in Tables 6 and 7 with their estimated standard deviations σ. σ (ϕ) was calculated from the equation (due to D. F. Carroll):

$$\begin{aligned}(r_1r_2 \sin \phi)^2\sigma^2(\phi) = {} & [(x_3 - x_2) - (x_1 - x_2)r_2 \cos \phi/r_1]^2\sigma^2(x_1) \\ & + [(x_1 - 2x_2 + x_3) - (x_1 - x_2)r_2 \cos \phi/r_1 - (x_3 - x_2)r_1 \cos \phi/r_2]^2\sigma^2(x_2) \\ & + [(x_1 - x_2) - (x_3 - x_2)r_1 \cos \phi/r_2]^2\sigma^2(x_3) \\ & + \text{corresponding terms in } y \text{ and } z.\end{aligned}$$

TABLE 4.

Components U_{ij} of vibration tensors (Å^2).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
P(1)	0·0544	0·0565	0·0667	−0·0181	−0·0256	0·0284
(2)	0·0650	0·0509	0·0906	0·0292	0·0116	0·0425
N(1)	0·0728	0·0703	0·1283	0·0025	−0·0846	−0·0294
(2)	0·1016	0·0553	0·0767	0·0120	−0·0164	−0·0044
F(1)	0·0872	0·1413	0·1383	0·0797	−0·0282	0·0916
(2)	0·1988	0·0615	0·1235	0·0300	0·0540	0·0511
(3)	0·1314	0·1284	0·0790	−0·0459	−0·0728	0·0739
(4)	0·0931	0·0837	0·1218	−0·0542	−0·0171	0·1022

TABLE 5.

Standard deviations in U_{ij}.

	$\sigma(U_{11})$	$\sigma(U_{22})$	$\sigma(U_{33})$	$\sigma(U_{12})$	$\sigma(U_{23})$	$\sigma(U_{13})$
P(1)	0·0024	0·0026	0·0030	0·0038	0·0049	0·0039
(2)	0·0028	0·0023	0·0038	0·0041	0·0055	0·0049
N(1)	0·0100	0·0103	0·0173	0·0153	0·0227	0·0211
(2)	0·0112	0·0089	0·0113	0·0164	0·0183	0·0156
F(1)	0·0084	0·0121	0·0136	0·0161	0·0186	0·0166
(2)	0·0144	0·0077	0·0123	0·0166	0·0151	0·0213
(3)	0·0107	0·0113	0·0090	0·0167	0·0169	0·0153
(4)	0·0082	0·0081	0·0108	0·0120	0·0144	0·0140

TABLE 6.

Bond lengths (Å).

	r	$\sigma(r)$		r	$\sigma(r)$
P(1)–N(1)	1·523	0·016	P(1)–F(3)	1·533	0·016
P(1)–N(2)	1·487	0·016	P(1)–F(4)	1·500	0·013
P(2)–N(1)′	1·510	0·017	P(2)–F(1)	1·526	0·015
P(2)–N(2)	1·508	0·017	P(2)–F(2)	1·499	0·016

TABLE 7.

Bond angles.

	ϕ	$\sigma(\phi)$		ϕ	$\sigma(\phi)$
N(1) $\widehat{\text{P(1)}}$ N(2)	122·3	1·04	N(1) $\widehat{\text{P(1)}}$ F(3)	107·8	0·99
N(1)′ $\widehat{\text{P(2)}}$ N(2)	123·2	0·96	N(1) $\widehat{\text{P(1)}}$ F(4)	107·1	0·83
			N(2) $\widehat{\text{P(1)}}$ F(3)	109·8	0·98
P(1) $\widehat{\text{N(1)}}$ P(2)′	147·1	1·36	N(2) $\widehat{\text{P(1)}}$ F(4)	108·0	0·83
P(1) $\widehat{\text{N(2)}}$ P(2)	147·2	1·43	N(2) $\widehat{\text{P(2)}}$ F(2)	107·9	1·00
			N(1)′ $\widehat{\text{P(2)}}$ F(2)	108·0	1·00
F(3) $\widehat{\text{P(1)}}$ F(4)	99·5	0·86	N(2) $\widehat{\text{P(2)}}$ F(1)	107·7	0·92
F(1) $\widehat{\text{P(2)}}$ F(2)	100·3	0·90	N(1)′ $\widehat{\text{P(2)}}$ F(1)	107·3	1·03

ϕ is the angle at atom (2), r_1 and r_2 the distances (1)—(2) and (2)—(3) respectively. This is a more exact form of Ahmed and Cruickshank's [7] expression.

There are no significant differences in bond lengths and angles of a given type, and the mean values are P–N = 1·507 ± 0·017 Å, P–F = 1·514 ± 0·015 Å, $\widehat{\mathrm{NPN}}$ = 122·7° ± 1·0°, $\widehat{\mathrm{PNP}}$ = 147·2° ± 1·4°, $\widehat{\mathrm{FPF}}$ = 99·9° ± 0·9° and $\widehat{\mathrm{NPF}}$ = 108·0° ± 1·0°. The striking features are the short length P–N and the large angle PNP. The sum of the two independent angles is 269·9° and this close approximation to 270° suggests that the ring may be planar. The deviations ζ of the nitrogen atoms from the plane of the phosphorus atoms are not significant and the standard deviations $\sigma(\zeta)$ of all the ring atoms in a direction normal to this plane were used to obtain weighting factors $1/\sigma^2(\zeta)$ for a least-squares calculation of the mean plane of the ring, the equation of which is

$$0{\cdot}4069x' + 0{\cdot}3811y' - 0{\cdot}8302z' = 0. \qquad (1)$$

The pairs of fluorine atoms are distributed not quite symmetrically about the plane, and this was still true even when the mid-points of F(1)–F(2) and F(3)–F(4) were included in another weighted least-squares calculation. It was concluded that the plane of the ring was not quite a mirror for the fluorine atoms and that the best plane was therefore plane (1). Fig. 1 shows the projection of a molecule down the normal to this plane. The distances ζ of the atoms from the plane are shown in Fig. 1 and the standard deviations of these distances appear as $\sigma(\zeta)$ in Table 3. The molecule obviously has symmetry close to $4/mmm$ (D_{4h}). Exact symmetry would impose conditions on the molecular geometry in addition to the planarity of the ring and the equality of chemically similar bonds and angles already noted. These conditions are examined in turn and the experimental values of the parameters, with their standard deviations in parentheses, are listed in brackets. The last column gives the ratio of the discrepancy to its standard deviation, calculated before the figures had been rounded off. F(1) $\cdots\cdot$ F(2)^r is the distance between F(1) and the reflection of F(2) in the plane of the ring; cf. 0 is the origin at the centre of the molecule.

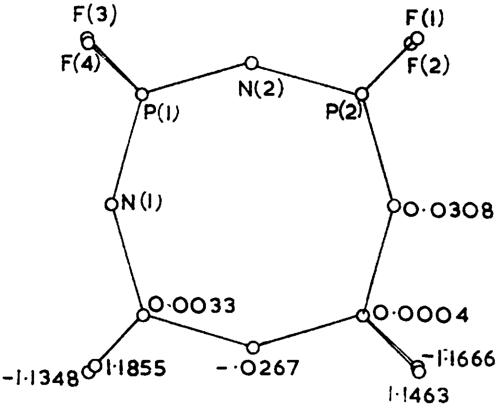

FIG. 1. Projection of the molecule in a direction perpendicular to the mean plane of the ring. Distances in Å from the plane are shown.

(*a*)	P(1) ··· 0 = P(2) ··· O	[2·053 (0·005); 2·035 (0·005)]	2·83
(*b*)	N(1) ··· 0 = N(2) ··· O	[1·865 (0·018); 1·877 (0·021)]	0·42
(*c*)	$\mathrm{P(1)}\,\widehat{0}\,\mathrm{P(2)} = 90°$	[89·28° (0·19)]	3·79
(*d*)	$\mathrm{N(1)}\,\widehat{0}\,\mathrm{N(2)} = 90°$	[89·61° (0·68)]	0·57
(*e*)	$\mathrm{P(1)}\,\widehat{0}\,\mathrm{N(1)} = 45°$	[45·45° (0·48)]	0·94
(*f*)	F(1) ··· F(2)^r = 0	[0·108 (0·021)]	5·16
(*g*)	F(3) ··· F(4)^r = 0	[0·086 (0·019)]	4·48

The significant discrepancies are in (*a*), (*c*), (*f*), and (*g*), notably the last two.

The intermolecular contacts are:

Contact	F(1) ··· F(4)′	F(2) ··· F(3)‴	F(2) ··· F(4)‴	F(1) ··· F(3)′
Distance (Å)	3·01	3·13	3·23	3·29
Contact	N(2) ··· F(3)‴	N(2) ··· F(4)′	N(1) ··· F(4)″	
Distance (Å)	3·49	3·57	3·58	

All other intermolecular F ··· F distances are greater than 3·4 Å. The values listed are all very large compared with those predicted from Pauling's values of van der Waals radii (2·70 Å for F ··· F and 2·85 Å for N ··· F). This suggests that the fluorine atoms may be charged. The three shortest separations are shown by broken lines (two curved to prevent confusion) in Fig. 2, which is the projection of the structure down the *b* axis. The non-zero values of $F \cdots F^r$ can be explained qualitatively if it is assumed that F(1) and F(4)′, the atoms of the shortest contact, experience a mutual repulsion. From Fig. 1 it is seen that the major distortions (*f*) and (*g*) can be described approximately as (*f*) a small rotation about P(2) of the triangle P(2) F(1) F(2) in its plane in the direction F(1) ⟶ F(2) and (*g*) a small rotation of the triangle P(1) F(3) F(4) about an axis through P(1) and in its plane, thereby twisting its plane and bringing F(4) closer to N(1). With the help of models it can be seen that these effects would be predictable from a postulated mutual repulsion of F(1) and F(4), if the triangles are considered rigid and anchored at the phosphorus atom. The reason for the differences in the two cases is that F(1) ··· F(4)′ makes only a small angle with the plane through P(2), F(1), and F(2), but a much larger one with that through P(1), F(3), and F(4). It is suggested that this distortion might push the phosphorus atoms out of their natural positions and that this might account for the small but significant discrepancies in the values of P(1) ··· 0, P(2) ··· 0, and $P(1)\widehat{0}P(2)$.

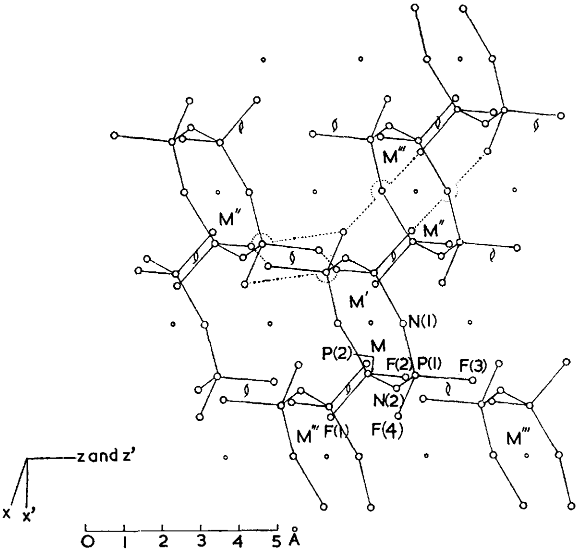

FIG. 2. The structure projected down the b axis. The three shortest intermolecular contacts are shown by broken lines.

If this is accepted, the molecule in its free state can be considered to have full 4/*mmm* symmetry and could be represented by Fig. 3.

The mean P–F bond length (1·51 Å) agrees well with the mean values in the phosphorus oxyhalides studied by Brockway and Beach.[9]

The P–N bond lengths are equal and short (1·51 Å). The purest P–N single bond

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[7] Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385.

[8] Pauling, "The Nature of the Chemical Bond," 2nd edn., Oxford, 1950.

[9] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

reported is that in $NaHPO_3(NH_2)$ (1·78 Å) although this is a zwitterion structure;[10] Nordman's value[11] (1·635 Å) in $(H_2N)_3,PBH_3$ will be modified by the charge which the phosphorus atom carries, at least formally. A more proper comparison is with the analogous values obtained by Wilson and Carroll[12] (1·59 Å) in $(PNCl_2)_3$ and Ketelaar and de Vries[2] (1·67 Å) in $(PNCl_2)_4$. The completely planar ring, which is quite unexpected, is made possibly by the unusually large angle (147°) at the nitrogen atoms, which therefore appear to be partially deficient in their lone-pair electrons.

The effect on the PN skeleton of substituting fluorine for chlorine is shown in the following Table.

Compound	Ring	P–N	$\widehat{PNP}$	$\widehat{NPN}$	$\widehat{RPR}$
$(PNCl_2)_4$	puckered	1·67 Å	123°	117°	105·5°
$(PNF_2)_4$	planar	1·51	147·2°	122·7°	99·9°

Another crystalline form is obtained at low temperature with the same space group $P2_1/a$ and the same unit-cell dimensions except that *c* is doubled. The reflections appearing on the extra layer-lines are very weak and the reflections common to both forms have very similar intensities. In the low-temperature form molecular symmetry $\bar{1}$ is no longer mplied, but the crystal structure is obviously very similar to that described above. One explanation is that the molecules in the high-temperature form are distorted in a " chair-like " way while those in the low-temperature form have " boat-like " distortions; another is that the high-temperature form is composed of molecules with " boat-like " distortion distributed in a statistically disordered way. If the boat form has in itself 2 or *m* symmetry, which would seem likely, a superposition of two molecules to give a mean structure with a planar ring would not give mean positions of fluorine atoms asymmetrically disposed on either side of the ring and thus the hypothesis of disorder seems less likely, on admittedly speculative grounds. In any case the distortions must be small and would be unlikely to affect the conclusion that in its free state the molecule would have 4/*mmm* symmetry.

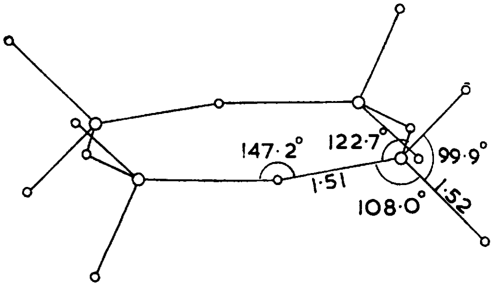

FIG. 3. The idealised molecule with mean values of bond lengths and angles.

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[10] Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621.
[11] Nordman, *Acta Cryst.*, 1960, **13**, 535.
[12] Wilson and Carroll, *J.*, 1960, 2548.