598. *Phosphonitrilic Derivatives. Part X.*[1] *The Crystal Structure of Trimeric Phosphonitrilic Fluoride.*

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An *X*-ray crystal-structure analysis of the trimeric phosphonitrilic fluoride, $(PNF_2)_3$, shows that four discrete molecules with symmetry *m* and planar P–N rings, crystallise in an orthorhombic cell, with the dimensions $a = 6·948$, $b = 12·190$, $c = 8·723$ Å, and space group *Pnma*. The three crystallographically non-equivalent P–N bond lengths are found, by three-dimensional anisotropic refinement, to be 1·546, 1·563, and 1·572 Å. The average P–F bond length is 1·521 Å; the ring angles are 119·6° and 121·1° at nitrogen, and 119·5° and 119·3° at phosphorus.

ACCURATE crystal-structure analyses have been reported for four tetrameric phosphonitrilic derivatives;[2] of these, the fluoride[2c] is unique in having a large angle at the nitrogen atom. The present study, on trimeric phosphonitrilic fluoride, was undertaken to investigate the effect, on the geometry of the six-membered P–N ring, of replacing the chlorine atom in trimeric phosphonitrilic chloride[3] by fluorine. Jagodzinski and Oppermann[4] have reported a preliminary structure analysis which they do not intend to continue.

EXPERIMENTAL

The crystals of trimeric phosphonitrilic fluoride were kindly prepared by Mr. J. Emsley. The very high volatility of the material prevented manipulation of the crystals in the open air, even in a room kept at −13°; a method similar to that used by McGeachin and Tromans[2c] was adopted. Liquid, introduced into a thin-walled glass capillary tube, of internal diameter 0·2 mm., was crystallised by cooling. It was found possible to grow single cylindrical crystals, with the required axis along the length of the tube, by alternately warming and cooling the tube.

Thermal splitting always occurred if the crystals were cooled to 140°K; consequently all the photographs were taken at room temperature. Cell dimensions were obtained from oscillation photographs in the Straumanis position. The intensities were measured on multiple-film, equi-inclination Weissenberg photographs, recorded for the layers *0kl*–*4kl*, *h0l*–*h6l*, and *hk0*–*hk5*. A total of 744 of the possible 880 reflections gave measurable intensities; these were estimated visually by comparison with a calibration strip. Lorentz, polarisation, and absorption corrections were calculated and applied on the Leeds University Pegasus computer[5] by a programme written by Mr. J. G. F. Smith.

The three-dimensional refinement was carried out on the Pegasus computer by the method of least squares,[5] the S.F.L.S. programme being used. The scattering factor used for phosphorus was that of Tomiie and Stam[6] and for nitrogen and fluorine those of Berghuis *et al.*[7] were used; for atoms situated on the mirror plane, halves of these values were used. The weighting factor used for the initial cycles was $1/F_0$; this was changed to $1/(a + F + cF^2)$ for the last three cycles in order to decrease the effect of some strong low-order planes. The calculation of molecular dimensions and the analysis of the thermal motion were carried out on the Pegasus computer.[5]

Crystal Data.—$(PNF_2)_3$. $M = 249·0$. M. p. 27·8°. Orthorhombic. $a = 6·948$, $b = 12·190$, $c = 8·723$, all $\pm 0·006$ Å; $U = 728·8$ Å^3. D_m was not measured. $Z = 4$, $D_c = 2·24$ g./ml., $F(000) = 360$. Space group either *Pnma* (D_{2h}^{16} No. 62), implying molecular symmetry *m*, or $Pn2_1a$ (C_{2v}^{9} No. 33), implying molecular symmetry 1. Cu-K_α radiation. $\mu = 80·2$ cm.$^{-1}$.

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[1] Part IX, Dougill, *J.*, 1961, 5471.

[2] (*a*) Hazekamp, Migchelsen, and Vos, *Acta Cryst.*, 1962, **15**, 539; (*b*) Bullen, *J.*, 1962, 3193; (*c*) McGeachin and Tromans, *J.*, 1961, 4777; (*d*) Dougill, *J.*, 1961, 5471.

[3] Wilson and Carroll, *J.*, 1960, 2548.

[4] Jadgodzinski and Oppermann, *Z. Krist.*, 1960, **113**, 241.

[5] Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter, " Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis," Pergamon Press, Oxford, 1961.

[6] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

[7] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

Structure Determination.—Statistical analysis[8] of the intensity distribution of the $0kl$ reflections provided evidence for choosing the space-group *Pnma*; it was confirmed by the solution of the structure. This implies that the molecule must be situated on the mirror plane perpendicular to the *b*-axis.

Although the co-ordinates of the phosphorus atoms were found from Patterson projections they were not sufficiently accurate to solve the structure in projection. Three-dimensional intensity measurements were used to calculate a three-dimensional Patterson synthesis, from which accurate phosphorus co-ordinates were derived. Fourier methods were used to locate the nitrogen and the fluorine atoms on two projections. Two-dimensional refinement, by alternate structure-factor and difference-Fourier calculations, was discontinued at $R(hk0) = 0{\cdot}25$ and $R(0kl) = 0{\cdot}22$.

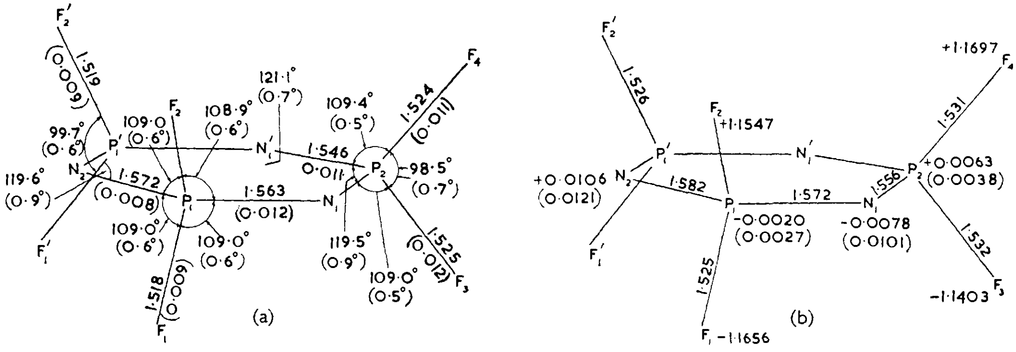

FIG. 1. (a) The bond lengths (Å) and angles in the $(PNF_2)_3$ molecule before correction for the rotational oscillations; the mirror plane is through $N_2P_2F_3F_4$. (The standard deviations are given in parentheses.)

(b) The heights of the atoms above and below the best molecular plane. (The standard deviations perpendicular to the plane are given in parentheses.) The bond lengths (Å) after correction for rotational oscillations.

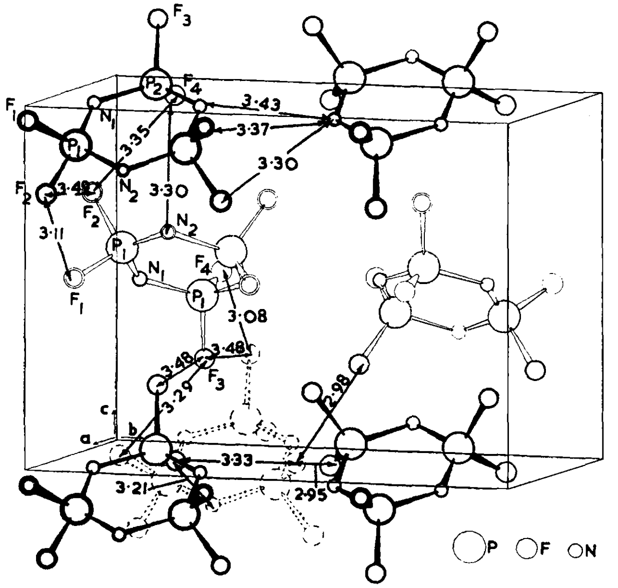

FIG. 2. A clinographic drawing of the structure showing the shortest intermolecular distances in (Å).

Individual isotropic temperature factors were used for the first three cycles of the three-dimensional refinement; thereafter refinement was carried out anisotropically. For the first

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[8] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

TABLE 1.

Observed and calculated structure factors (× 10) (only those structure factors which were used in the least-squares refinement are included).

h	*k*	*l*	$\lvert F_o\rvert$	F_c	*h*	*k*	*l*	$\lvert F_o\rvert$	F_c	*h*	*k*	*l*	$\lvert F_o\rvert$	F_c	*h*	*k*	*l*	$\lvert F_o\rvert$	F_o
0	0	2	1014	1109	1	1	11	44	−42	1	13	1	184	167	2	8	0	44	−37
0	0	4	721	650	1	2	1	502	−498	1	13	2	99	−91	2	8	1	104	101
0	0	6	357	−350	1	2	2	445	−415	1	13	3	21	17	2	8	2	66	66
0	0	8	44	38	1	2	3	239	−221	1	13	4	52	−47	2	8	3	351	386
0	0	10	36	31	1	2	4	209	−195	1	13	5	65	−60	2	8	4	176	186
0	1	1	359	345	1	2	5	78	72	1	14	1	43	38	2	8	5	110	115
0	1	3	271	254	1	2	7	85	85	1	14	2	67	66	2	8	6	68	77
0	1	5	315	−297	1	2	9	39	43	1	14	4	43	44	2	8	7	27	−23
0	1	7	224	−225	1	2	10	30	19	1	15	1	52	−50	2	8	9	44	−46
0	1	9	78	−76	1	3	1	1052	−1136	1	15	2	29	30	2	9	0	107	−108
0	1	11	24	18	1	3	2	399	398	1	15	3	17	−19	2	9	1	138	−148
0	2	0	769	−848	1	3	3	467	−450	2	0	0	688	−760	2	9	2	193	−202
0	2	2	415	−402	1	3	4	113	113	2	0	1	1001	1153	2	9	3	185	−214
0	2	4	177	175	1	3	5	131	−114	2	0	2	133	−96	2	9	4	124	141
0	2	6	140	135	1	3	6	99	90	2	0	3	146	155	2	9	5	37	−41
0	2	8	70	73	1	3	7	170	168	2	0	4	211	192	2	9	7	35	34
0	2	10	45	39	1	3	8	91	−95	2	0	5	441	445	2	10	0	137	140
0	3	1	953	1083	1	3	9	37	−42	2	0	6	115	103	2	10	1	170	−175
0	3	3	140	123	1	4	1	379	−335	2	0	7	213	−222	2	10	3	125	−149
0	3	5	632	661	1	4	2	153	−144	2	0	9	103	−94	2	10	4	65	−76
0	3	7	89	−97	1	4	3	137	−112	2	0	10	35	−31	2	10	5	94	−94
0	3	9	43	−46	1	4	4	202	−184	2	0	11	23	−35	2	10	6	44	−43
0	3	11	26	−24	1	4	5	37	30	2	1	1	435	−395	2	10	7	42	44
0	4	0	243	−217	1	4	6	168	161	2	1	2	55	45	2	11	0	55	−56
0	4	2	406	−353	1	4	7	85	−81	2	1	3	425	−406	2	11	2	110	−121
0	4	4	196	197	1	4	8	141	154	2	1	4	256	244	2	11	3	41	49
0	4	6	121	123	1	4	9	72	−71	2	1	5	68	−62	2	12	3	46	−47
0	4	8	61	−60	1	4	10	45	38	2	1	6	70	75	2	12	4	37	−34
0	4	10	126	−112	1	5	1	384	378	2	1	7	57	53	2	12	5	55	50
0	5	1	146	−145	1	5	2	358	−338	2	1	8	49	−50	2	12	6	48	−52
0	5	3	679	−686	1	5	3	71	53	2	1	9	42	32	2	13	0	182	182
0	5	5	235	−219	1	5	4	321	−304	2	1	10	86	−76	2	13	1	39	36
0	5	7	126	135	1	5	5	377	−371	2	2	1	139	−108	2	13	2	39	30
0	5	9	146	135	1	5	7	183	−193	2	2	2	108	−107	2	13	3	54	59
0	6	0	776	−707	1	5	8	58	61	2	2	3	379	−358	2	13	4	47	−52
0	6	2	99	70	1	5	10	49	42	2	2	4	171	−154	2	13	5	33	33
0	6	4	421	−421	1	6	1	223	191	2	2	5	212	−214	2	14	0	47	−47
0	6	6	40	−23	1	6	2	109	−76	2	2	6	34	25	2	14	1	60	56
0	6	8	30	−19	1	6	3	182	162	2	2	7	36	−28	2	14	2	23	−18
0	6	10	69	65	1	6	4	72	70	2	2	8	31	25	2	14	3	24	30
0	7	1	135	118	1	6	5	40	30	2	2	9	30	25	2	14	4	23	30
0	7	3	34	23	1	6	6	137	−130	2	3	0	725	−753	2	15	0	52	−57
0	7	5	230	237	1	6	7	106	112	2	3	2	631	602	2	15	2	15	−14
0	7	7	70	72	1	6	8	58	−63	2	3	3	91	−88	3	0	1	184	143
0	8	0	461	481	1	6	9	47	40	2	3	4	78	81	3	0	2	29	26
0	8	2	323	340	1	6	10	28	−29	2	3	5	157	−128	3	0	3	677	644
0	8	4	231	−241	1	7	1	142	−131	2	3	6	388	429	3	0	4	107	101
0	8	6	157	−159	1	7	2	94	85	2	3	8	60	66	3	0	5	471	482
0	8	8	63	−49	1	7	3	141	−147	2	3	9	27	22	3	0	6	139	136
0	9	1	37	29	1	7	4	49	43	2	3	10	33	28	3	0	7	300	335
0	9	3	274	291	1	7	5	100	−97	2	4	0	121	−86	3	0	8	31	−27
0	9	5	137	−145	1	7	6	71	71	2	4	1	88	−73	3	0	9	19	−16
0	9	7	101	−106	1	7	7	61	64	2	4	2	99	−77	3	1	1	408	389
0	9	9	74	−68	1	8	1	372	374	2	4	3	300	−286	3	1	2	335	−310
0	10	0	560	−630	1	8	2	320	331	2	4	4	267	−252	3	1	3	23	6
0	10	2	197	−216	1	8	3	153	153	2	4	5	114	109	3	1	4	219	−219
0	10	6	106	113	1	8	4	218	223	2	4	6	257	−271	3	1	5	109	−98
0	10	8	27	23	1	8	5	82	−80	2	4	7	124	137	3	1	6	68	63
0	11	1	81	−71	1	8	6	50	−54	2	4	8	65	−73	3	1	7	78	−82
0	11	3	68	71	1	8	7	40	−41	2	4	9	54	51	3	1	8	85	93
0	11	5	36	35	1	8	8	62	−53	2	4	10	22	22	3	1	9	44	−48
0	11	7	39	32	1	9	1	81	−82	2	5	0	655	663	3	1	10	22	21
0	12	0	56	51	1	9	2	46	40	2	5	2	480	466	3	2	1	164	151
0	12	4	84	83	1	9	3	167	183	2	5	3	215	198	3	2	2	53	−53
0	12	6	25	22	1	9	5	211	241	2	5	4	225	−219	3	2	3	82	75
0	13	1	150	−134	1	9	6	75	−84	2	5	5	82	81	3	2	4	212	−220
0	13	3	151	−150	1	9	7	38	42	2	5	6	225	−236	3	2	5	88	−72
0	13	5	104	−93	1	9	8	51	−41	2	5	7	55	−60	3	2	6	103	−109
0	14	0	159	143	1	9	9	19	−17	2	5	8	75	−73	3	2	7	57	−60
0	14	2	51	45	1	10	1	220	−220	2	5	9	49	−46	3	2	10	25	24
0	15	1	34	31	1	10	2	267	−294	2	6	0	234	201	3	3	1	210	−194
0	15	3	43	46	1	10	3	42	−37	2	6	1	277	−246	3	3	2	354	−350
1	0	1	782	884	1	10	4	133	−152	2	6	2	114	105	3	3	3	105	95
1	0	2	1095	1353	1	10	5	36	33	2	6	3	266	253	3	3	4	53	−62
1	0	4	464	460	1	10	6	34	−33	2	6	4	178	173	3	3	5	45	42
1	0	5	125	−124	1	10	7	66	57	2	6	5	185	−186	3	3	6	34	−28
1	0	6	175	151	1	10	8	47	42	2	6	6	147	172	3	3	7	75	81
1	0	7	218	−226	1	11	1	49	39	2	6	7	33	−15	3	3	8	100	108
1	0	8	153	−154	1	11	2	44	39	2	6	8	59	59	3	3	9	36	37
1	0	10	28	−17	1	11	3	35	−30	2	6	9	31	−27	3	4	1	228	221
1	1	1	379	−352	1	11	4	60	68	2	7	0	183	−173	3	4	2	126	118
1	1	2	37	−24	1	11	5	29	18	2	7	1	70	65	3	4	3	170	−156
1	1	3	362	337	1	11	6	29	25	2	7	2	52	44	3	4	4	207	211
1	1	4	117	−110	1	11	7	31	17	2	7	3	75	76	3	4	5	320	−330
1	1	5	301	287	1	12	1	43	−33	2	7	4	57	−55	3	4	6	100	107
1	1	6	172	−162	1	12	2	38	−32	2	7	5	37	−35	3	4	7	73	−77
1	1	8	74	−77	1	12	4	33	−29	2	7	6	53	55	3	4	8	35	−35
1	1	9	60	−60	1	12	6	23	22	2	7	7	29	−25	3	4	9	35	32
1	1	10	27	−2	1	12	7	34	−23	2	7	8	44	43	3	4	10	25	−29

TABLE 1. (*Continued.*)

h	k	l	$\lvert F_o\rvert$	F_c	h	k	l	$\lvert F_o\rvert$	F_c	h	k		$\lvert F_o\rvert$	F_c	h	k		$\lvert F_o\rvert$	F_c
3	5	1	180	151	4	3	7	29	19	5	2	7	43	−40	6	4	5	67	−75
3	5	2	453	451	4	3	9	21	−14	5	2	9	27	−34	6	4	6	96	97
3	5	4	349	361	4	4	0	128	−131	5	3	1	311	306	6	5	1	69	−65
3	5	5	46	−48	4	4	1	268	252	5	3	2	40	−30	6	5	2	53	−53
3	5	7	32	−26	4	4	2	130	−121	5	3	4	95	−95	6	5	3	82	−87
3	5	8	70	−68	4	4	3	403	423	5	3	5	34	29	6	5	4	43	−49
3	5	9	48	−45	4	4	4	192	−194	5	3	6	91	−112	6	5	5	48	45
3	5	10	16	−23	4	4	5	134	132	5	3	8	37	−36	6	5	6	17	−13
3	6	1	272	−264	4	4	7	75	−70	5	3	9	21	26	6	5	7	63	63
3	6	2	105	−99	4	4	8	39	39	5	4	1	435	−457	6	6	0	99	102
3	6	3	112	−100	4	4	9	50	−55	5	4	2	190	189	6	6	1	97	95
3	6	4	141	−145	4	5	0	296	−313	5	4	3	113	−122	6	6	2	39	31
3	6	5	93	89	4	5	1	136	130	5	4	4	85	89	6	6	3	46	48
3	6	6	86	−95	4	5	2	166	−160	5	4	5	90	87	6	6	4	95	−90
3	6	7	36	−36	4	5	3	255	266	5	4	6	67	−77	6	6	5	72	69
3	6	8	35	32	4	5	4	136	127	5	4	7	72	72	6	6	6	64	−69
3	6	9	26	−20	4	5	5	76	77	5	4	8	47	−47	6	7	0	99	102
3	7	1	136	−123	4	5	6	78	79	5	5	1	198	−192	6	7	2	76	62
3	7	3	40	42	4	5	8	29	−21	5	5	2	71	−71	6	7	3	65	−61
3	7	4	55	56	4	6	0	291	302	5	5	3	35	26	6	7	4	41	47
3	7	5	49	50	4	6	1	119	−116	5	5	5	102	107	6	7	5	37	−34
3	7	6	39	−35	4	6	2	63	60	5	5	6	72	80	6	8	0	53	40
3	7	7	49	53	4	6	3	234	−240	5	5	7	20	20	6	8	2	33	27
3	7	9	27	28	4	6	4	188	205	5	5	8	52	52	6	8	3	33	−28
3	8	1	249	−236	4	6	5	77	−78	5	6	1	288	314	6	8	4	39	−39
3	8	4	86	95	4	6	6	51	−48	5	6	2	70	−67	6	9	0	99	−79
3	8	5	156	169	4	6	7	26	21	5	6	3	94	103	6	9	1	86	61
3	8	6	43	45	4	6	9	22	24	5	6	4	32	−31	6	9	2	25	−19
3	8	7	79	71	4	7	0	151	−151	5	6	5	36	−27	6	9	3	122	117
3	9	1	169	168	4	7	1	116	−109	5	6	6	67	65	6	9	5	37	36
3	9	2	192	−201	4	7	2	136	−134	5	6	7	43	−42	6	10	0	86	−71
3	9	4	134	−156	4	7	3	54	−49	5	6	8	18	15	6	10	1	29	17
3	9	5	35	−33	4	7	5	67	−67	5	7	2	93	−90	6	10	2	37	−32
3	9	6	41	44	4	7	6	36	40	5	7	4	99	−110	6	11	0	28	13
3	9	7	41	−40	4	7	7	27	−26	5	7	5	38	40	6	11	2	26	23
3	9	8	51	55	4	7	8	23	19	5	8	1	57	47	7	0	1	64	65
3	10	1	96	91	4	8	0	50	−37	5	8	2	74	−73	7	0	2	69	71
3	10	3	75	−83	4	8	1	59	−53	5	8	4	85	−80	7	0	4	41	41
3	10	4	36	−38	4	8	2	79	−75	5	9	1	52	46	7	0	6	39	−36
3	10	5	125	−116	4	8	3	122	−127	5	9	2	151	131	7	0	7	12	9
3	10	6	44	−42	4	8	4	68	71	5	9	3	31	−28	7	1	1	130	−145
3	10	7	91	−85	4	8	6	94	84	5	9	4	119	114	7	1	2	40	39
3	11	1	86	−93	4	8	7	48	43	5	9	5	103	−93	7	1	5	113	103
3	11	4	25	−13	4	8	8	41	40	5	10	2	75	66	7	1	6	32	−31
3	11	5	30	23	4	9	0	285	326	5	10	3	26	23	7	2	1	31	−18
3	12	1	76	69	4	9	1	72	66	5	10	4	50	48	7	2	2	55	50
3	12	2	31	27	4	9	2	175	194	5	10	5	33	31	7	2	4	37	44
3	12	3	22	−12	4	9	3	41	−41	5	11	2	38	−34	7	2	6	23	30
3	12	4	55	54	4	9	4	44	−43	5	11	3	25	−19	7	3	1	55	−59
3	12	5	43	−41	4	9	5	59	51	5	11	4	43	−45	7	4	1	34	−29
3	12	6	26	32	4	9	6	90	−87	5	12	1	97	−80	7	4	2	176	−166
3	13	2	124	120	4	9	7	23	19	5	12	2	47	43	7	4	4	110	−116
3	13	3	21	−17	4	10	0	75	75	5	12	3	18	−18	7	4	5	20	24
3	13	4	59	60	4	10	1	59	55	5	13	1	48	−65	7	5	1	29	22
3	14	1	33	−36	4	10	3	48	52	6	0	0	300	335	7	5	3	69	−66
3	14	2	22	−18	4	10	4	25	−17	6	0	1	112	−111	7	5	5	67	−66
3	14	3	39	50	4	10	6	74	−70	6	0	2	164	180	7	6	1	29	22
4	0	0	520	−529	4	10	7	33	−47	6	0	3	33	25	7	6	2	98	95
4	0	1	227	−192	4	11	0	43	−40	6	0	4	35	31	7	6	3	30	24
4	0	2	129	108	4	11	3	60	−53	6	0	5	81	−79	7	6	4	68	68
4	0	3	143	−146	4	11	6	27	33	6	0	6	32	−25	7	6	5	8	−9
4	0	4	109	−97	4	12	0	59	−48	6	0	7	23	−20	7	7	1	47	40
4	0	6	249	244	4	12	1	56	49		0	8	49	36	7	7	2	28	−19
4	0	7	146	145	4	12	2	39	−32		1	0	153	−154	7	8	1	44	33
4	0	8	39	39	4	12	3	74	73	6	1	1	116	106	7	8	2	27	19
4	0	9	86	80	4	12	4	60	−60	6	1	2	90	−93	7	9	1	80	−68
4	0	10	15	11	4	12	5	18	19	6	1	3	173	196	7	9	2	24	23
4	1	0	530	517	4	13	0	70	−70	6	1	5	77	83	8	0	0	53	−42
4	1	1	106	92	4	13	3	46	49	6	1	6	56	64	8	0	1	37	30
4	1	2	274	277	4	14	0	17	−11	6	1	7	58	−55	8	0	2	52	−51
4	1	3	51	39	5	0	1	79	−71	6	1	8	36	38	8	0	4	41	37
4	1	4	97	−86	5	0	2	232	−241	6	2	0	90	88	8	0	5	27	−33
4	1	5	69	68	5	0	3	112	−105	6	2	1	46	44	8	1	0	114	−101
4	1	6	169	−181	5	0	4	139	−141	6	2	2	35	23	8	1	1	45	−39
4	1	7	47	50	5	0	5	114	−112	6	2	3	59	65	8	1	2	40	−36
4	1	8	38	−42	5	0	6	43	−50	6	2	5	38	46	8	1	3	65	−67
4	1	10	21	26	5	0	8	83	79	6	2	6	22	−15	8	1	4	46	46
4	2	0	81	79	5	0	9	48	40	6	2	7	22	18	8	1	5	30	−46
4	2	1	69	−58	5	1	1	144	135	6	2	8	20	−20	8	2	3	25	27
4	2	2	125	125	5	1	2	242	240	6	3	0	162	172	8	3	2	50	48
4	2	3	33	−27	5	1	3	37	22	6	3	1	87	75	8	3	3	37	−36
4	2	6	97	−106	5	1	4	219	237	6	3	2	40	32	8	3	4	20	20
4	2	7	33	−20	5	1	5	103	−102	6	3	3	36	29	8	4	3	68	−77
4	2	8	66	−59	5	1	6	51	56	6	3	4	88	108	8	4	4	38	−46
4	2	10	11	−17	5	1	7	36	−35	6	3	5	27	−28	8	5	1	40	32
4	3	0	115	−113	5	1	8	59	−51	6	3	6	36	−23	8	5	2	21	−12
4	3	1	429	−420	5	1	9	28	28	6	3	7	31	−30	8	5	3	37	41
4	3	2	294	−279	5	2	1	139	137	6	4	0	292	−322	8	6	0	47	−41
4	3	3	75	−67	5	2	3	41	40	6	4	1	88	−89	8	6	1	21	17
4	3	4	216	−227	5	2	4	48	53	6	4	2	132	−148	8	7	0	42	46
4	3	5	198	−197	5	2	5	31	−27	6	4	3	97	−105					
4	3	6	103	−107	5	2	6	27	21	6	4	4	86	93					

cycles of refinement, during which the R value decreased from 0·251 to 0·096, the observed structure factors had not been corrected for absorption. Another five cycles were computed with the corrected observations; R decreased from 0·122 to 0·076 (for observed reflections only). Thirteen badly correlated planes were omitted from the least-squares refinement.

Results.—A list of observed and calculated structure factors is given in Table 1. The final co-ordinates with the standard deviations are given in Table 2; the bond lengths and angles shown in Fig. 1a were calculated from co-ordinates given in Table 2. The correction for rotational oscillation to the bonds P(2)–N(1), P(1)–N(1), and P(1)–N(2) are 0·0098, 0·0086, and 0·0099 Å, respectively, and to each of the four P–F bonds it is 0·0072 Å. The correction to the angles is less than 10′ in each case.

TABLE 2.

Atomic co-ordinates (in Å) before the correction for thermal motion; four places of decimals are given since these were used to calculate the bond lengths (σ is twice the standard deviation of the last least-squares cycle).

	x	σx	y	σy	z	σz
P(1)	1·2091	0·0030	1·6889	0·0028	−0·7903	0·0032
P(2)	−0·7243	0·0042	3·0475	0	0·5325	0·0044
N(1)	−0·0746	0·0112	1·7124	0·0106	0·1018	0·0118
N(2)	1·8534	0·0144	3·0475	0	−1·2499	0·0136
F(1)	2·2691	0·0082	0·8439	0·0088	−0·1078	0·0100
F(2)	0·9444	0·0096	0·8277	0·0074	−2·0128	0·0090
F(3)	−0·9010	0·0132	3·0475	0	2·0471	0·0116
F(4)	−2·1949	0·0102	3·0475	0	0·1334	0·0138

Atomic co-ordinates as fractions of the cell edge.

	x/a	y/b	z/c
P(1)	0·1740	0·1385	−0·0906
P(2)	−0·1042	0·2500	0·0610
N(1)	−0·0107	0·1405	0·0117
N(2)	0·2668	0·2500	−0·1433
F(1)	0·3266	0·0692	−0·1236
F(2)	0·1359	0·0679	−0·2307
F(3)	−0·1297	0·2500	0·2347
F(4)	−0·3159	0·2500	0·0153

To allow for the uncertainty of the thermal-oscillation corrections, the standard deviations in the co-ordinates were taken to be twice those obtained from the last cycle of the least-squares refinement. The bond standard deviations calculated from these values are shown in Fig. 1a. Table 3 gives the parameters of anisotropic thermal motion, from which were calculated the principal axes of the vibration ellipsoids [9] for the individual atoms and their direction cosines which respect to the orthorhombic axes.[9] Analysis has shown that the molecule, which is assumed to behave as a rigid body, is oscillating with torsional amplitudes of 4·2°, 5·4°, and 4·7° about the three molecular axes, defined as the normal to the ring, the line joining atoms P(2) and N(2), and the mutually perpendicular direction, respectively.[10] The corrections [11] for the rotational oscillations given in Table 4 are thought to be reliable since the agreement

TABLE 3.

Thermal parameters (units in 10^{-4}Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{13}	σ	U_{23}	σ
P(1)	586	8	485	7	664	8	43	11	29	11	97	12
P(2)	504	10	678	11	633	10	0	0	0	0	143	17
N(1)	658	28	600	26	843	32	−155	47	125	44	234	48
N(2)	591	36	576	33	659	37	0	0	0	0	175	58
F(1)	745	24	761	24	1058	31	447	40	476	43	85	40
F(2)	1037	30	673	21	845	26	−186	45	−350	39	215	43
F(3)	864	36	1065	42	665	30	0	0	0	0	385	54
F(4)	507	28	991	43	1005	42	0	0	0	0	16	50

TABLE 4.

Co-ordinate corrections (in Å) due to the rotational oscillation.[10]

	x	y	z		x	y	z
P(1)	+0·0037	−0·0088	−0·0023	F(1)	+0·0089	−0·0117	+0·0023
P(2)	+0·0075	0	+0·0045	F(2)	+0·0009	−0·0118	−0·0083
N(1)	−0·0036	−0·0087	+0·0023	F(3)	−0·0062	0	+0·0118
N(2)	+0·0075	0	−0·0047	F(4)	−0·0141	0	+0·0007

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[9] Cruickshank, *Acta Cryst.*, 1956, **9**, 747.

[10] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

[11] Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

between the observed and the calculated U_{ij} values is satisfactory. The atomic numbers were convenient to use as weighting factors when the best plane through the phosphorus and the nitrogen atoms was calculated. The direction cosines of this plane are −0·5676, 0·0000, and −0·8233; the distance of the atoms from the plane are shown in Fig. 1b. The shortest intermolecular distances between fluorine atoms and between fluorine and nitrogen atoms are shown in Fig. 2.

Description of the Structure.—The clinographic projection (Fig. 2) shows the discrete molecules consisting of planar six-membered rings arranged in a herring-bone pattern, similar to trimeric phosphonitrilic chloride[3] and other planar-ring molecules. The dihedral angle between the planes of the molecules related by symmetry is 69°.

The intermolecular distances, shown in Fig. 2, are all greater than the sum of the van der Waals radii for fluorine and nitrogen atoms given by Pauling[12] (2·70 Å for F–F and 2·85 Å for F–N).

The difference of 0·026 Å in the lengths of bonds P(2)–N(1) and P(1)–N(1) is possibly significant,[13] when the standard deviations given in Fig. 1a are used; all other equivalent bond lengths are not significantly different. All non-bonded intramolecular distances between two atoms not bonded to a common atom are greater than 3·1 Å, the value for the contact P(2)–N(2).

DISCUSSION

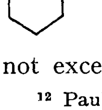
The space group of the trimeric phosphonitrilic fluoride is the same as that of the chloride trimer[3] and the lengths of the *b*-axes are almost equal. Although the type of packing in the two structures is the same, the difference in the van der Waals radius of fluorine and chlorine is thought to cause the dihedral angle between the molecular planes in the chloride to be 20° less than in the fluoride and accounts for the inequality of the *a*- and *c*-axes in the two structures.

The shortest intermolecular F–F distance (2·95 Å) is shorter than any found in the tetrameric fluoride[2c] or in $(PCF_3)_4$. In discussing the van der Waals radius of fluorine in the structures of $(PCF_3)_4$[14] and hydrogen fluoride[15] Atoji and Lipscomb suggest that this length should be 1·50 Å. In view of the results reported here it appears that this distance should not be greater than 1·45 Å.

It was necessary to explain the non-planarity of the trimeric chloride ring by a short intermolecular N–Cl contact. In the fluoride the N–F distances are normal and, within experimental error, the ring is planar (Fig. 1b). The slightly longer P(1)–N(1) bond length in the fluoride molecule cannot be explained by abnormally short distances made by N(2), either within the molecule or between molecules.

The average P–N bond length of 1·560 Å (1·570 Å after correction for thermal motion) is significantly shorter than that found in octamethylcyclotetraphosphonitrile (1·595 Å); it is not significantly shorter than the values observed in trimeric phosphonitrilic chloride[3] (1·59 Å), the tetrameric chloride[2a] (1·570 Å), or the tetrameric phosphonitrile dimethylamide[2b] (1·578 Å).

The short P–N bond length (1·51 Å) observed in the tetrameric fluoride[2c] is associated with the large angle at the nitrogen atom (147·2°). This short bond is thought[16] to be due to in-plane π′-bonding, which occurs when the d_{xy}- or $d_{x^2-y^2}$-orbitals on the phosphorus atom overlap the lone-pair orbital on the nitrogen atom. This type of bonding is considered less important than the π-bonding due to overlap of d_{xz}- and d_{yz}-orbitals on phosphorus with the *p*-orbital on nitrogen. The observed angle at phosphorus in a number of compounds[17] where bonding is thought to occur is 120°. In the present case of a six-membered ring the angle at the nitrogen cannot exceed 120°, so reducing the participation of the lone pair in the π′-bond system.



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[12] Pauling, " Nature of the Chemical Bond," 3rd edn., Cornell University Press, p. 260.

[13] Cruickshank and Robertson, *Acta Cryst.*, 1953, **6**, 698.

[14] Palenik and Donohue, *Acta Cryst.*, 1962, **15**, 564.

[15] Atoji and Lipscomb, *Acta Cryst.*, 1954, **7**, 173.

[16] Craig and Paddock, *J.*, 1962, 4118.

[17] Romers, Ketelaar, and MacGillavry, *Acta Cryst.*, 1951, **4**, 114; Ondik, Block, and MacGillavry, *ibid.*, 1961, **14**, 555.

The P–N bond length is, therefore, longer than that in the tetrameric fluoride (by 0·05 Å), whereas the analogous difference for the chlorides is only 0·02 Å. It is to be expected, therefore, that the difference in the P–N bond energies will also show a parallel greater difference in the fluorides.

Within experimental error, the average length of the P–F bond (1·521 Å) agrees with the length reported for the tetrameric fluoride (1·514 Å) and the oxyfluorides of phosphorus.[18] The angles FPF are slightly smaller than those reported for the tetramer, but the difference is not significant.

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[18] Williams, Sheridan, and Gordy, *J. Chem. Phys.*, 1952, **20**, 164; cf. Sutton *et al.*, " Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, 1958, M55.