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The Crystal Structure of Compounds with (N-P)_n Rings IV*. The Stable Modification (*T* Form) of Tetrameric Phosphonitrilic Chloride, N₄P₄Cl₈

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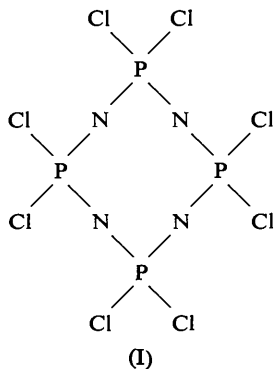
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The *T* form of tetrameric phosphonitrilic chloride, N₄P₄Cl₈, crystallizes in the tetragonal space group *P*4₂/*n* with cell dimensions *a* = 15.324 and *c* = 5.988 Å. There are four molecules in the unit cell on special positions of symmetry $\bar{1}$. The intensities of 1080 reflexions, measured on Weissenberg films, were used in the structure analysis. Anisotropic least-squares refinement reduced the *R* value to 0.07. The molecules have an eight-membered (N-P)₄ ring and are chair-shaped with approximate symmetry 2/*m*. The two independent valence angles PNP are significantly different: 133.6 and 137.6°, s.d. 0.8°. This difference is explained in terms of steric interactions between chlorine atoms. No further significant differences are observed between chemically equivalent bonds or angles. Average values with individual standard deviations are: P-N 1.559 Å, s.d. 0.012 Å; P-Cl 1.992 Å, s.d. 0.004 Å; NPN 120.5°, s.d. 0.7°; ClPCL 103.1°, s.d. 0.2°.

Introduction

Tetrameric phosphonitrilic chloride (I) was first prepared by Stokes (1897).



Two crystal modifications of the compound, generally called the *K* and the *T* form, are known. The crystal structure of the *K* form was determined by Ketelaar & De Vries (1939). This structure has recently been refined in our department as part of a program of structure analyses of compounds having (N-P)_n rings (Hazekamp, Migchelsen & Vos, 1962).

The first evidence for the existence of the *T* form was obtained by Chapman & Wilson (Paddock, 1964,

ref. 141) in 1960 from measurements of the pure ³⁵Cl nuclear quadrupole resonance spectrum. Preliminary X-ray work on this modification has been done by Wilson (Paddock, 1964, ref. 138).

At room temperature the *T* form is the stable modification. Crystallization of N₄P₄Cl₈ from solutions at room temperature, however, yields the metastable *K* form. The *T* form can be obtained by heating crystals of the *K* form to about 70°C and during the transition the crystals remain single. The *T* form can also be obtained directly by crystallizing N₄P₄Cl₈ from solutions above 70°C or from the melt.

In this paper the structure determination of the *T* form by X-ray diffraction is described.

Experimental

Crystals of N₄P₄Cl₈, *K* form, were available in the laboratory [melting point 123.4°C; literature value 122.8°C (Lund, Paddock, Proctor & Searle, 1960)]. They were transformed into crystals of the *T* form by keeping them at 70°C for a few hours. The density of the crystals obtained was measured by flotation [2.17 g.cm⁻³; literature value for the *K* form 2.18 g.cm⁻³ (Lund *et al.*, 1960)]. The crystallographic data of the two modifications are compared in Table 1. The cell dimensions of the *T* form were measured from a powder diffractogram, on which silicon powder lines were superposed for calibration purposes [$\lambda(\text{Cu } K\alpha_1) = 1.54051$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å].

* Part III: Migchelsen, T., Olthof, R. Vos, A. *Acta Cryst.* (1965). **19**, 603.

For the intensity measurements a cylindrical crystal along the *c* axis was used. The intensities of the reflexions *hkl* with *l* from 0 to 5 were recorded with Ni-filtered Cu radiation on equi-inclination Weissenberg photographs. Both integrated and non-integrated films were made. For the integrated photographs a special layer line screen was used, which allowed simultaneous recording of the *l*th level in equi-inclination setting and the zero level in anti-equi-inclination setting on the lower and upper half of the film respectively (Wagner, 1966).

The intensities of the reflexions with $\theta \leq 60^\circ$ were measured with a densitometer on the integrated photographs. Reflexions with $\theta \geq 60^\circ$ were estimated visually from the non-integrated films. For the latter reflexions a correction for spot deformation was applied (Phillips, 1956). After correction for the Lorentz-polarization effect, and for absorption ($\mu = 182 \text{ cm}^{-1}$) according to Bond's (1959) method, the $|F|^2$ values of the different layers were scaled using the *hk0* reflexions recorded on the upper half of the integrated photographs. Of the 1370 independent reflexions which could be recorded on the films, 1092 were observed to be non-zero.

Determination of the structure

As may be seen from Table 1 the unit cell of the *T* form is twice as large as that of the *K* form and contains twice as many molecules. Both modifications belong to the space group $P4_2/n$ with eightfold general positions. The two molecules in the *K* form occupy a twofold special position (*a*) with symmetry $\bar{4}$ and are boat-shaped (Hazekamp *et al.*, 1962). For the four molecules in the *T* form two fourfold special positions [(*c*) and (*e*)] with symmetry $\bar{4}$ and 2 respectively are available. Of these positions (*e*) can be ruled out, since it requires that in the direction of the *c* axis the molecules are placed at distances of only $c/2 = 3 \text{ \AA}$. We therefore assumed that the molecules lie at the inversion centres and are chair-shaped.

Comparison of the Weissenberg photograph of the *hk0* layer with the corresponding photograph of the *K* form facilitated a direct solution of the structure. The reflexions common to both forms appear to have about the same intensity, whereas the additional reflexions of the *T* form are relatively weak. It could therefore be assumed that the positions of the atoms in [001] projection are approximately the same for the two modifications. The *z* coordinates of the atoms in

the *T* form were found by transforming the boat-shaped molecules of the *K* form into molecules which are chair-shaped. This was accomplished, as shown in Fig. 1, by reflecting the half NPN'P'' of each molecule against a plane normal to the fourfold inversion axis and passing through N and N''. The structure model so derived yielded indices *R* of 0.18 and 0.35 for the reflexions *hk0* and *h0l* respectively.

For the three-dimensional refinement use was made of the least-squares method. In the first few cycles with isotropic temperature factors (Schoone, 1961) 532 reflexions, chosen at random, were taken into account. The anisotropic refinement (Rollett, 1961), based on all observed reflexions of reliable intensity (1080), was kindly carried out by Dr Rollett on the Mercury computer at Oxford, England. The atomic scattering factors were taken from *International Tables* (1962), and the weighting scheme used was $w^{-1} = 1 + \{(F_{\text{obs}} - 59)/35\}^2$. At the end of the refinement *R* was 0.07. In the last cycle the maximum shift in a coordinate was 0.1 times its estimated standard deviation.

Final values for the atomic parameters are given in Tables 2 and 3 with their standard deviations as calculated by the least-squares program. In Table 4 observed and calculated structure factors are compared. The *F_c* values in this Table were obtained on the TR4 computer in Groningen with a program requiring analytical functions (Moore, 1963) for the atomic scattering factors.

Table 2. Fractional atomic coordinates and standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	-0.0646 (1)	0.1118 (1)	-0.0138 (3)
P(2)	0.1085 (1)	0.0621 (1)	-0.1429 (3)
N(1)	0.0202 (4)	0.1128 (4)	-0.1567 (11)
N(2)	0.1170 (4)	-0.0250 (3)	-0.0113 (10)
Cl(1)	-0.0432 (1)	0.1651 (1)	0.2840 (3)
Cl(2)	-0.1447 (1)	0.1963 (1)	-0.1602 (4)
Cl(3)	0.1482 (1)	0.0478 (1)	-0.4571 (3)
Cl(4)	0.1997 (1)	0.1406 (1)	-0.0122 (4)

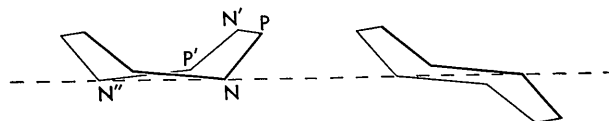


Fig. 1. Central ring of a molecule in the *K* form (left) and in the *T* form (right).

Table 1. Crystallographic data of $\text{N}_4\text{P}_4\text{Cl}_8$

	<i>T</i> form	<i>K</i> form
Crystal system	Tetragonal	Tetragonal
Cell dimensions	$a = b = 15.324 \pm 0.001 \text{ \AA}$ ($= 1/2 \times 10.836$) $c = 5.988 \pm 0.002 \text{ \AA}$	$a = b = 10.844 \pm 0.002 \text{ \AA}$ $c = 5.961 \pm 0.005 \text{ \AA}$
Space group	$P4_2/n$	$P4_2/n$
<i>Z</i>	4	2
Systematic absences	<i>hk0</i> for <i>h</i> + <i>k</i> odd <i>00l</i> for <i>l</i> odd	<i>hk0</i> for <i>h</i> + <i>k</i> odd <i>00l</i> for <i>l</i> odd

An attempt was made to interpret the anisotropic thermal movement of the individual atoms in terms of rigid body translations and rotations (Cruickshank,

1956). The least-squares fit, however, was very poor and therefore no corrections for librations were applied to the atomic coordinates.

Table 3. *Thermal parameters and standard deviations* ($\text{\AA}^2 \times 10^{-4}$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
P(1)	187 (5)	208 (5)	242 (7)	12 (5)	2 (5)	26 (4)
P(2)	207 (5)	228 (5)	270 (7)	30 (5)	35 (5)	9 (4)
N(1)	270 (20)	417 (23)	500 (29)	91 (21)	60 (19)	122 (18)
N(2)	388 (21)	270 (20)	331 (27)	65 (18)	-11 (19)	-40 (16)
Cl(1)	591 (8)	481 (8)	313 (8)	-106 (6)	-43 (6)	-33 (6)
Cl(2)	325 (6)	327 (6)	543 (9)	123 (6)	-67 (6)	92 (5)
Cl(3)	473 (8)	562 (8)	275 (8)	55 (6)	148 (6)	136 (6)
Cl(4)	395 (6)	378 (6)	563 (10)	71 (6)	-88 (6)	-177 (5)

Table 4. *Observed and calculated structure factors*

The columns are h , $10F_o$ and $10F_c$.
 Reflexions indicated by an asterisk are not taken into account in the refinement.

h, k, l	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	$10F_o$	$10F_c$	
H, C, 0	2 430	-420	9 46	-51	15 360	-365	2 253	258	10 166	147	H, 1, 2	9 270	242								
2 766	843	4 2151	2418	16 157	148	3 253	-236	11 745	-225	12 199	-201	1 954	-1036	11 1079	1084						
4*1443	-1957	8 1093	-1064	H, 18, 0	18 237	250	5 92	-86	13 263	-272	2 525	570	12 435	399							
6 612	611	10 696	668	2 286	285	6 122	-102	14 53	52	3 1014	-1071	13 381	-358								
8 405	-420	12 211	223	4 293	-304	7 89	50	5 736	780	15 816	-799										
10 577	-850	14 474	425	6 190	-213	H, 4, 1	8 234	215	H, 14, 1	4 142	-96	11 168	138								
12 804	-767	16 88	90	8 136	109	9 136	109	9 136	109	9 136	109	10 138	129								
14 142	113	H, 9, 0	H, 19, 0	1 520	-526	12 348	-336	1 97	-101	8 568	-510	H, 6, 2	9 824	-798							
16 280	252	3 127	174	2 687	628	13 213	-187	3 97	-96	9 824	-798	9 824	-798								
18 140	133	5 723	-747	3 787	711	15 386	382	4 149	139	10 138	129	10 138	129								
H, 1, 0	1 277	-252	H, 0, 1	5 723	-747	7 148	161	5 162	143	12 166	155	2 330	-334								
3 66	-32	7 124	-113	6 490	-467	H, 9, 1	7 90	7 90	-91	13 656	630	3 419	-389								
5 227	-213	9 157	-129	7 927	-941	1 200	175	8 211	-221	14 249	-228	4 529	-488								
7 358	349	13 172	172	8 446	-431	15 157	-159	6 98	-72	15 216	234	5 190	183								
9 208	184	17 123	162	9 316	993	9 438	429	2 523	-515	11 309	328	16 221	-216								
11 165	-172	5 1215	1288	10 346	379	3 555	540	13 159	179	12 221	-216	7 265	285								
13 320	275	6 446	-401	12 59	58	4 237	-257	10 451	-387	8 84	56	8 593	-42								
15 61	97	H, 10, 0	7 130	104	14 207	-222	7 858	-826	H, 15, 1	1 765	787	10 104	82								
17 161	-174	2 832	827	8 745	-728	15 130	-134	8 128	-101	1 59	-68	2 315	303	11 374	-344						
H, 2, 0	4 621	583	9 304	-287	19 82	103	9 716	-709	3 590	-607	3 443	472	12 270	213							
2 65	33	6 862	-838	10 140	121	11 398	-396	4 259	259	4 135	133	13 428	-410								
4 1182	1413	10 621	-588	13 150	-151	13 773	737	6 174	-166	6 221	-166	6 221	-166								
6 65	36	14 413	401	16 105	85	2 523	-491	16 114	114	8 61	-62	8 370	368								
8 1096	1141	16 196	-226	18 89	101	3 116	-1102	17 157	-175	9 520	483	5 84	56								
10 100	97	H, 11, 0	19 21	31	5 98	-63	H, 10, 1	11 227	233	12 568	-522	1 467	-477								
12 1164	-1167	H, 1, 1	7 1852	1890	8 238	-206	1 420	-417	H, 16, 1	13 76	91	2 195	185								
14 662	-631	1 131	123	3 130	127	1 1289	1322	8 238	-206	2 123	-99	3 1443	-1468								
18 609	606	5 138	133	2 407	423	10 201	-182	3 231	223	1 224	198	17 165	170	4 805	-786						
H, 3, 0	9 234	-253	3 45	94	11 192	-153	4 82	51	2 172	-147	3 68	32	5 297	-279							
1 78	-57	11 195	-214	4 863	-899	12 205	-195	5 490	474	3 103	-111	H, 3, 2	7 740	-725							
3 165	-160	5 1300	-1356	13 115	-140	6 134	149	4 188	207	4 188	207	8 239	-213								
5 393	-389	6 1217	-127	14 465	-427	7 143	-110	5 63	64	1 1063	1078	9 303	260								
7 51	57	H, 12, 0	7 852	-851	15 89	62	8 312	307	7 315	-313	2 316	394	10 327	-345							
11 74	-92	2 1505	1587	8 709	691	16 147	-139	9 140	-136	8 30	-57	3 964	998	11 787	758						
17 55	64	4 205	198	9 1113	1097	17 134	-126	11 373	-366	9 232	-240	4 517	500	12 142	-111						
19 81	94	6 605	-573	10 232	-225	18 111	113	14 118	114	5 138	117	15 130	123								
H, 4, 0	10 149	152	12 389	391	H, 6, 1	5 98	-63	H, 17, 1	10 27	-39	10 451	-387	6 138	-116							
2*2175	-3343	14 669	-699	14 574	559	1 299	299	2 217	176	1 111	105	8 446	447								
4 1386	-1497	15 584	532	2 217	176	1 1058	1065	3 212	195	10 715	715	H, 8, 2	9 332	-478							
6 1378	1541	16 259	-249	3 162	123	3 162	123	4 165	-191	11 500	-460	8 466	-158								
8 507	473	17 439	410	4 634	-613	3 1058	1059	5 425	-424	12 238	-216	2 123	114								
10 701	-647	3 192	187	5 284	-292	4 135	102	7 122	-128	13 61	65	3 114	69								
12 635	590	5 174	177	6 320	-293	5 232	-210	8 123	133	14 267	-241	4 500	460								
14 416	-359	7 126	115	7 482	482	6 432	436	9 111	120	15 447	-408	5 515	-508								
18 293	310	9 65	65	8 155	-154	7 165	151	9 257	-290	6 138	-116	7 257	267	17 22	-58						
H, 5, 0	11 119	125	H, 2, 1	9 90	-69	8 400	-382	H, 18, 1	17 88	-72	7 359	361									
1 211	181	H, 14, 0	2 520	528	11 195	-170	10 213	-192	1 188	182	H, 4, 2	9 732	739								
3 65	65	3 424	-452	12 74	-74	11 239	-242	2 70	70	3 271	282	10 220	-205								
5 61	76	4 111	122	5 105	-114	15 57	-60	6 159	-152	2 465	-422	12 132	141								
7 163	140	6 132	105	7 347	-376	16 32	69	3 469	401	14 185	162	4 185	162								
9 300	-278	10 821	818	8 323	294	17 78	71	4 335	-283	16 178	-187										
11 223	-226	12 39	-27	9 798	809	H, 12, 1	H, 19, 1	5 180	184												
15 165	-164	10 116	95	H, 7, 1	1 73	-60	1 73	-60	1 21	41	5 180	184									
17 82	-97	H, 15, 0	11 473	457	2 168	-167	3 309	307	3 59	-56	7 470	-467	H, 9, 2	8 566	-528						
H, 6, 0	7 192	-119	13 220	-200	2 998	-994	4 249	-240	H, 0, 2	9 88	-112	2 66	-67								
2 66C	-666	7 126	-150	16 66	-61	4 478	-472	6 220	209	1* 863	-1098	11 362	-309	3 569	524						
4 662	-796	9 105	-90	5 61	-58	7 500	498	2 189	183	13 592	-										

Table 4 (cont.)

5	168	-165	5	136	-129	14	454	-439	4	144	-114	11	288	-253	6	215	-218	H, 16, 4	7	228	229				
6	59	1	6	130	-132	15	103	-88	5	70	-64	12	119	104	7	219	-209		8	157	158				
7	136	131	7	127	-119	16	242	-235	7	135	-132	13	335	323	8	89	105	3	169	-214	10	539	521		
9	219	-222				17	80	68	12	77	78	14	55	-59	9	346	320		11	81	-98				
10	153	-125							13	110	-113	15	245	250	10	269	276	H, 0, 5	12	148	138				
11	107	119	H, 18, 2						14	131	172	16	111	100	11	447	437		13	148	-185				
12	189	176		1	178	166									12	55	-58	2*	150	-159					
13	245	259		2	132	-129	1	136	74										4	148	144	H, 7, 5			
15	139	164		3	149	-154	2	478	-453										5	270	-264				
16	119	-192		4	106	-112	3	287	201										6	104	89				
				5	161	-192	4	120	-121	1	258	-278	1	750	-755					7	122	-156	2	148	107
				6	57	56	3	155	138	3	517	-520	4	425	427					8	457	-445	3	197	-208
				7	81	-72	4	120	-121	4	213	-248	4	188	180	5	176	183	10	72	-87	7	126	-125	
				8	50	58	5	148	151	5	313	298	6	88	89	11	68	-94	8	80	75	8	203	-566	
				9	55	65	6	96	1007	6	323	340	7	89	-104	12	266	228	9	112	113	9	112	113	
				10	146	-150	7	161	-175	7	162	-155	8	86	-111	13	144	-151	11	151	111	10	575	194	
				11	110	98	8	63	64	8	85	80	10	193	177	14	225	214	12	319	413				
				12	63	53	15	63	53	9	243	-259	11	246	278	11	440	455							
				13	52	-54	10	542	-554	12	82	53	14	66	-65										
				14	55	-28				13	112	118													
				15	105	135	H, 6, 3			14	55	-28													
				16	159	-1609	H, 13, 3			15	142	112													
				17	128	103		1	304	312	2	155	146	16	20	-35									
				18	250	-248		2	135	135	3	257	257												
				19	280	298		3	444	-452	6	163	-165												
				20	289	298		4	925	-932	7	195	211												
				21	289	295		5	369	-378	8	142	-156	1	378	343									
				22	146	-150		6	479	-472	9	97	114	3	902	888									
				23	110	98		7	280	218	9	97	114	3	902	888									
				24	63	53		8	344	-364	10	151	-179	4	316	342									
				25	159	-1609		9	479	-472	10	151	-179	4	316	342									
				26	159	-1609		10	686	672															
				27	159	-1609		11	112	139															
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				63	159	-1609		47	112	139															
				64	159	-1609		48	112	139															
				65	159	-1609		49	112	139															
				66	159	-1609		50	112	139															
				67	159	-1609		51	112	139															
				68	159	-1609		52	112	139															
				69	159	-1609		53	112	139															
				70	159	-1609		54	112	139															
				71	159	-1609		55	112	139															
				72	159	-1609		56	112	139															
				73	159	-1609		57	112	139															
				74	159	-1609		58	112	139															
				75	159	-1609		59	112	139															
				76	159	-1609		60	112	139															
				77	159	-1609		61	112	139															
				78	159	-1609		62	112	139															
				79	159	-1609		63	112	139															
				80	159	-1609		64	112	139															
				81	159	-1609		65	112	139															
				82	159	-1609		66	112	139															
				83	159	-1609		67	112	139															
				84	159	-1609		68	112	139															

which is boat-shaped in the *K* form and chair-shaped in the *T* form (Fig. 3).

The intramolecular distances and angles in the *T* form are given in Table 6. The standard deviations listed in the Table are twice those obtained from the standard deviations in the coordinates (Table 2).

Table 6. *Intramolecular distances and angles*

Atoms related by a centre of symmetry are distinguished by primed numbers.

P(1)–N(1)	1.557 (12) Å	N(2')P(1) N(1)	119.3 (7)°
P(2)–N(1)	1.563 (12)	N(1) P(2) N(2)	121.7 (7)
P(2)–N(2)	1.555 (12)	P(1) N(1)P(2)	133.6 (8)
P(1')–N(2)	1.561 (12)	P(2) N(2)P(1')	137.6 (8)
P(1)–Cl(1)	1.989 (4)	Cl(1)P(1) Cl(2)	103.3 (2)
P(1)–Cl(2)	1.988 (4)	Cl(3)P(2) Cl(4)	102.9 (2)
P(2)–Cl(3)	1.990 (4)	Cl(1)P(1) N(1)	110.6 (5)
P(2)–Cl(4)	2.002 (4)	Cl(1)P(1) N(2')	110.4 (5)

Table 6 (cont.)

P(1)⋯P(2)	2.867 (4)	Cl(2)P(1) N(1)	105.5 (5)
P(1)⋯P(2')	2.905 (4)	Cl(2)P(1) N(2')	106.3 (5)
P(1)⋯P(1')	3.961 (4)	Cl(3)P(2) N(1)	105.7 (5)
P(2)⋯P(2')	4.198 (4)	Cl(3)P(2) N(2)	111.0 (5)
N(1)⋯N(2)	2.722 (17)	Cl(4)P(2) N(1)	109.0 (5)
N(1)⋯N(2')	2.691 (17)	Cl(4)P(2) N(2)	105.0 (5)
N(1)⋯N(1')	3.981 (17)		
N(2)⋯N(2')	3.668 (17)		

The molecules have four independent P–N bonds of equal length. The observed value, 1.56 Å, is considerably smaller than the length of a P–N single bond (1.77 Å; Hobbs, Corbridge & Raistrick, 1953; Cruickshank, 1964). The occurrence of short P–N bonds is a general phenomenon for phosphonitrilic molecules, as may be seen from Table 7. The small bond lengths indicate that the ring bonds have appreciable double

Table 7. *Geometry of phosphonitrilic molecules*

A B X	Symmetry	A–B	BAB	ABA	XBX	Literature
N ₃ P ₃ F ₆	<i>m</i>	1.56 Å	120°	119°	99°	Dougill (1963)
N ₃ P ₃ Cl ₆	<i>m</i>	1.59	120	120	102	Wilson & Carroll (1960)
N ₄ P ₄ F ₈	$\bar{1}$	1.51	147	123	100	McGeachin & Tromans (1961)
N ₄ P ₄ Cl ₈ (<i>K</i>)	$\bar{4}$	1.57	131	121	103	Hazekamp <i>et al.</i> (1962)
N ₄ P ₄ Cl ₈ (<i>T</i>)	$\bar{1}$	1.56	134, 138	121	103	
N ₄ P ₄ Me ₈	$\bar{4}$	1.60	132	120	104	Dougill (1961)
N ₄ P ₄ (NMe ₂) ₈	$\bar{4}$	1.58	133	120	104	Bullen (1962)
N ₆ P ₆ (NMe ₂) ₁₂	3	1.56	148	120	103	Wagner & Vos (1965)

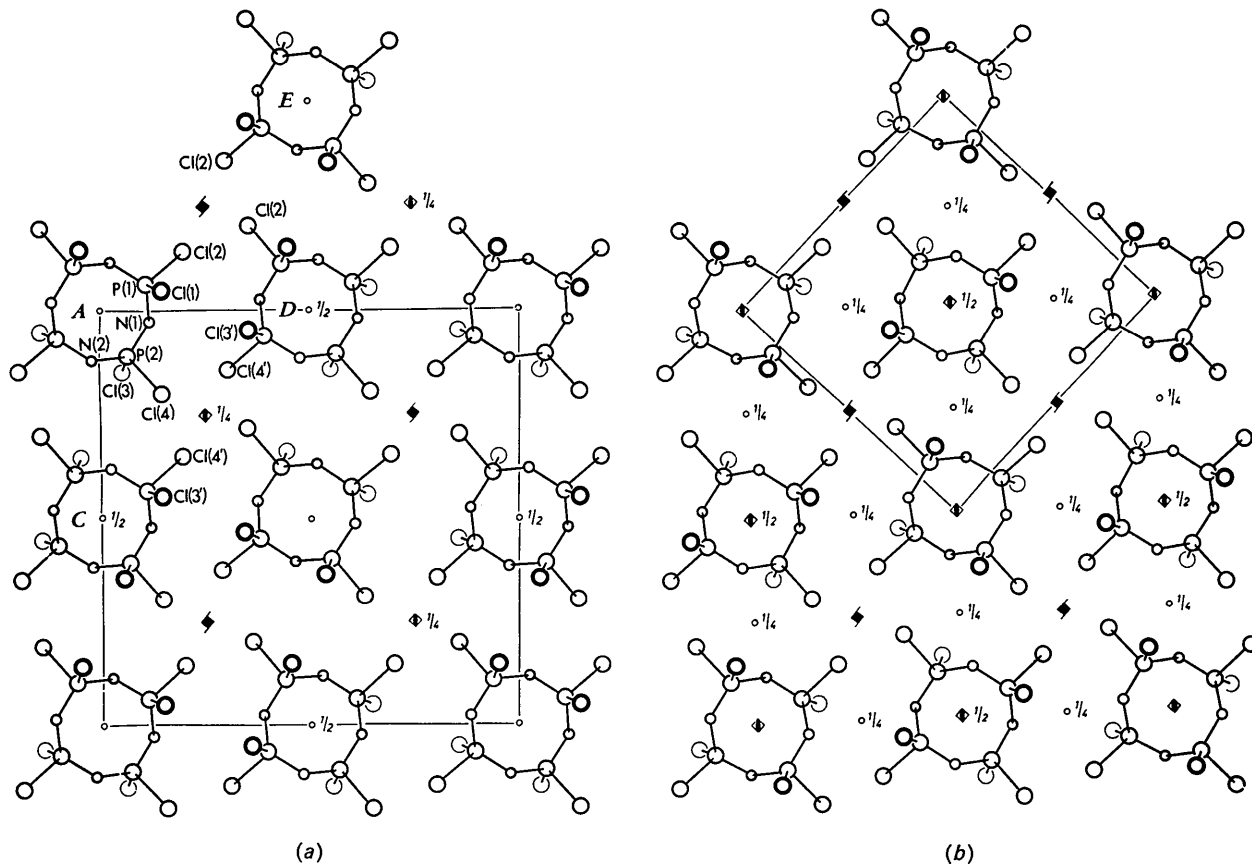


Fig. 2. [001] projection: (a) *T* form and (b) *K* form. Solid lines outline the unit cell.

bond character. The formation of double bonds by $d\pi(P)-p\pi(N)$ overlap and their delocalization in the ring has been discussed in a great many papers; see e.g. Cruickshank (1961) and Craig & Paddock (1962).

Equal lengths have also been found for the four independent P-Cl bonds. The observed P-Cl distance is equal to that in $N_4P_4Cl_8$, *K* form, and in $OPCl_3$ (Sutton, 1958).

The two independent valence angles NPN are equal within experimental error. As seen in Table 7 the average value of 120.5° agrees well with the endocyclic angles at phosphorus observed in other phosphonitrilic molecules. The same is true for the exocyclic angles ClP-Cl.

There is, on the other hand, a significant difference of 4.0° between the two independent ring angles PNP. Reference to Table 7 makes it clear that the larger angle of 137.6° is indeed significantly greater than any of the angles PNP in other non-planar phosphonitrilic molecules. (The hexameric dimethylamide is an exception which will be discussed in the next paper of this series.) The relatively large value of the angle $P(2)N(2)P(1')$ is a consequence of the chair-conformation of the (N-P)₄ ring, which makes four of the eight Cl...Cl distances between chlorine atoms of neighbouring phosphorus atoms different from those in the boat-conformation (see Table 8 and Fig. 3). In particular, the distance between Cl(1') and Cl(3) is short. From a model of the molecule it became clear that a normal value for the angle $P(2)N(2)P(1')$ would result in a still shorter Cl(1')...Cl(3) distance.

Table 8. Intramolecular Cl...Cl distances

	<i>T</i>	<i>K</i>
Cl(1)...Cl(3)	5.62 Å	5.62 Å
Cl(1)...Cl(4)	4.14	4.23
Cl(2)...Cl(3)	5.34	5.38
Cl(2)...Cl(4)	5.42	5.41
Cl(1')...Cl(3)	3.78	
Cl(1')...Cl(4)	5.51	
Cl(2')...Cl(3)	5.26	
Cl(2')...Cl(4)	5.33	

The molecular symmetry, which is strictly $\bar{1}$, approximates to $2/m$. This is illustrated in Fig. 4 and in Table 9. As pseudo-mirror plane is taken the best plane through P(1)Cl(1)Cl(2) and the centrosymmetrically related PCl_2 group. The deviations from $2/m$ symmetry are reflected best in the values of the dihedral angles of the ring bonds (Fig. 4). These angles should be equal in pairs, if the symmetry were indeed $2/m$. In point of fact the difference between the dihedral angles belonging to P(1)-N(1) and P(1')-N(2) is as much as 17° and that between the angles belonging to P(2)-N(1) and P(2)-N(2) is 25° .

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Table 9. Distances of the atoms from the pseudo-mirror plane $0.8011x + 0.4615y - 0.3810z = 0$ (x, y, z in Å)

P(1)	0.029 Å	P(2)	2.098 Å
Cl(1)	-0.011	N(1)	1.403
Cl(2)	-0.023	N(2)	1.285
		Cl(3)	3.201
		Cl(4)	3.473

work. We are grateful to Dr J.S. Rollett of the University of Oxford, England and to the staff of the Computing Centre of the University of Groningen for performing the calculations.

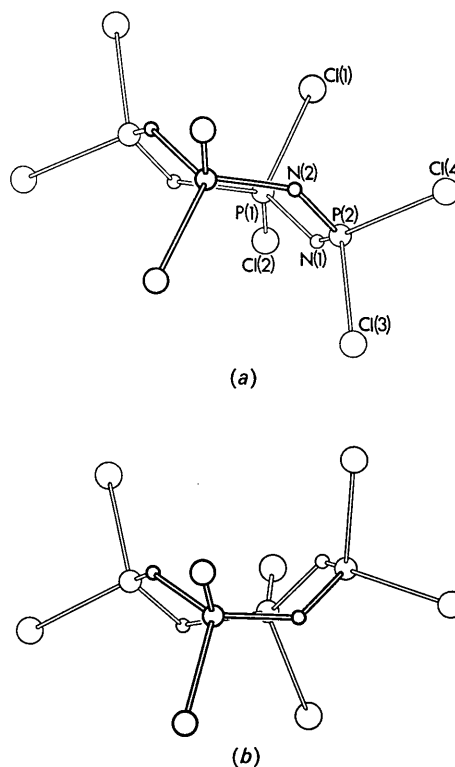


Fig. 3. Molecule $N_4P_4Cl_8$: (a) in the *T* form and (b) in the *K* form.

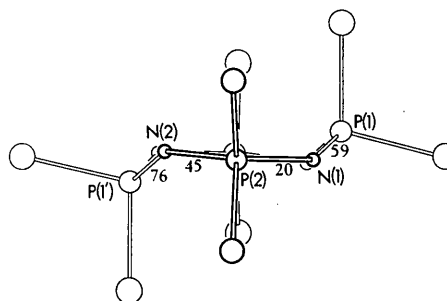


Fig. 4. Molecule $N_4P_4Cl_8$ (*T* form) projected on the pseudo-mirror plane (see text). The numbers are the dihedral angles of the ring bonds.

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The Crystal Structure of the Molecular Complex Formed by Acetonitrile and Bromine in the Mole Ratio 2:1

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The crystal structure of the molecular complex formed by two molecules of acetonitrile and one molecule of bromine (melting point -41.5°C) has been determined from three-dimensional X-ray data obtained at -70°C . The monoclinic unit cell of dimensions: $a=13.94$, $b=6.19$, $c=5.14$ Å and $\beta=114.9^{\circ}$ contains two molecules of bromine and four molecules of acetonitrile. The space group is $C2/m$. The structure exhibits linear, centrosymmetric groups of nitrogen-halogen-halogen-nitrogen atoms. The interhalogen bond length is 2.328 Å, and the nitrogen-halogen distance is 2.84 Å. The complex is apparently weakly bonded, and in this respect it differs from the complexes formed by halogen and aliphatic amines or other nitrogen containing compounds. Bond properties are discussed. Nuclear magnetic resonance spectra taken at 77°K agree with a model wherein the methyl group rotates about its threefold axis. The X-ray data requires this rotation to be associated with preferential orientations of the methyl group and is thus restricted.

Introduction

The crystal structures of molecular 1:1 complexes formed by amines and halogen molecules so far reported in the literature exhibit a common feature in that the nitrogen atom of the organic molecule forms, with the attached halogen molecule, an approximately linear grouping in the solid (Hassel & Rømming, 1962).

In these compounds the nitrogen atom is believed to acquire a formal positive charge, whose counterpart, to the extent of say roughly half a unit, is transferred by delocalization of the σ electrons of the group in the bond formation to the outer halogen atom. The latter is always the more electronegative in cases of

hetero-halogen molecular acceptors. The central halogen atom is further believed to become only slightly charged.

These complexes are all 'strong' charge transfer complexes. This is indicated by the short nitrogen-halogen bond distances compared with the accepted van der Waals distances; the elongated halogen-halogen bond distances compared with the corresponding gas phase values; the high values of the heats of formation and melting points; *etc.* Many complexes involving sulphur compounds show similar relationships (Hassel & Rømming, 1962; Briegleb, 1961).

Weaker complexes containing ethers, ketones, alcohols or benzene as donors, and homo-halogen mol-