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## The Crystal Structure of Compounds with (N–P)<sub>n</sub> Rings. V.\* Dodecadimethylaminocyclohexaphosphazahexaene (Hexameric Phosphonitrilic Dimethylamide), N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub>

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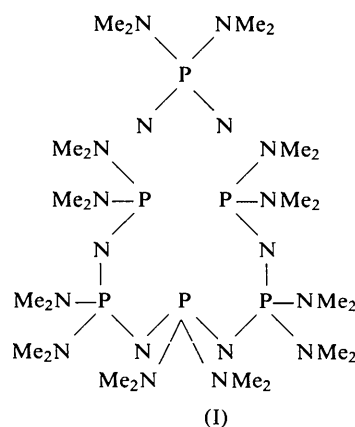
The crystal and molecular structure of the cyclic phosphazene N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub> has been determined by X-ray diffraction at –170°C. The intensities of 777 independent reflexions were measured on integrated equi-inclination Weissenberg photographs. The structure was derived from a three-dimensional Patterson synthesis and refined by anisotropic least-squares analysis ( $R=0.07$ ). The cubic unit cell ( $a=16.198 \pm 0.005$  Å, space group  $Pa\bar{3}$ ) contains four molecules at special positions of symmetry  $\bar{3}$ . The molecules have a twelve-membered ring of alternating phosphorus and nitrogen atoms with two NMe<sub>2</sub> groups attached to each phosphorus atom. The distances from the ring atoms to the mean plane of a molecule are  $\Delta P=0.56$ ,  $\Delta N=0.39$  Å ( $\Delta P/\Delta N=1.49$ ). There are two independent P–N ring bonds, which are equal within experimental error. The average value (with individual standard deviation) is 1.563 (10) Å. The dihedral angles belonging to the ring bonds are 17 and 97°. The two exocyclic P–N bonds are equal (average value 1.669 (10) Å) as well as the four N–C bonds (average value 1.457 (16) Å). The ring angle at nitrogen is 147.5 (7)°. The endocyclic and exocyclic angle at phosphorus are 120.0 (5) and 102.9 (5)° respectively. The large ring angle at nitrogen and the difference between the ring conformations of the present molecule and the corresponding tetrameric molecule N<sub>4</sub>P<sub>4</sub>(NMe<sub>2</sub>)<sub>8</sub> are discussed in terms of steric interactions between the methyl groups.

### Introduction

Investigations in the field of cyclic phosphazenes have been restricted mainly to the monocyclic trimeric and tetrameric compounds N<sub>n</sub>P<sub>n</sub>X<sub>2n</sub>,  $n=3, 4$  (for a review see Paddock, 1964), and to the polycyclic polymers of high molecular weight (see Allcock & Best, 1964, and references therein). Only a few papers have dealt with the monocyclic compounds of medium ring size ( $n=5$  to 20 approximately). Stokes, as early as 1897, described the preparation and properties of the chlorides N<sub>n</sub>P<sub>n</sub>Cl<sub>2n</sub>,  $n=5, 6$ . In 1960 Lund, Paddock, Proctor & Searle obtained some of the higher members of this series. Chapman, Paddock, Paine, Searle & Smith (1960) isolated the fluorides N<sub>n</sub>P<sub>n</sub>F<sub>2n</sub> with  $n=3$  up to 17 in a pure state. Several members ( $n=3$  to 8) were obtained of the four series N<sub>n</sub>P<sub>n</sub>X<sub>2n</sub> with X=NMe<sub>2</sub>, OMe, OCH<sub>2</sub>CF<sub>3</sub> or OPh (Allen, Oldfield, Paddock, Rallo, Serregi & Todd, 1965). Recently the pentameric bromide N<sub>5</sub>P<sub>5</sub>Br<sub>10</sub> has been synthesized (Coxon, Sowerby & Trauter, 1965) and complex formation between hexamethylbenzene and various cyclophosphazenes, including pentameric and hexameric compounds, has been studied (Das, Shaw, Smith & Thakur, 1966).

Accurate determinations of the molecular structures of some lower phosphazenes ( $n=3, 4$ ) by X-ray diffraction have been of great help in discussions on the chemical bonding in these compounds. Since such

studies are not available for molecules with larger rings, we undertook the crystal structure analysis of a hexameric cyclic phosphazene, N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub> (I). Some



results of this work have been published in a short communication (Wagner & Vos, 1965). Recently a preliminary note on the structure of a second medium-sized ring compound, N<sub>5</sub>P<sub>5</sub>Cl<sub>10</sub>, has appeared (Schlueter & Jacobson, 1966).

### Experimental

Crystals of N<sub>6</sub>P<sub>6</sub>(NMe<sub>2</sub>)<sub>12</sub> suitable for the X-ray work were obtained by slow evaporation of a solution in benzene. The crystals were colourless and transparent and had the shape of octahedra with edges of 0.1 to 0.3 mm. The compound crystallizes in the cubic space group No. 205,  $Pa\bar{3}$  ( $hk0$  systematically absent for  $h$

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odd) with a unit-cell edge of 16.4 Å. The measured density of the crystals is 1.20 g.cm<sup>-3</sup>; the density calculated for  $Z=4$  is 1.22 g.cm<sup>-3</sup>.

Since at room temperature only reflexions with  $(\sin \theta)/\lambda < 0.30 \text{ \AA}^{-1}$  were observed, the structure determination was carried out at low temperature ( $-170^\circ\text{C}$ ). Reflexions could be measured then up to  $(\sin \theta)/\lambda = 0.63 \text{ \AA}^{-1}$ , the space group is the same as at room temperature and the unit cell edge is  $16.198 \pm 0.005 \text{ \AA}$ . This value was determined from a Weissenberg photograph taken at  $-170^\circ\text{C}$ , on which a pattern of NaCl spots was superposed at room temperature for calibration purposes [ $\lambda(\text{Cu } K\alpha_1) = 1.54051$ ,  $\lambda(\text{Cu } K\alpha_2) = 1.54433$  and  $a(\text{NaCl}) = 5.6396 \text{ \AA}$ ]. The intensity data were recorded on photographic films with Ni-filtered Cu-radiation. Integrated equi-inclination Weissenberg-films were made of 13 layers about the cubic axis. The multiple-film technique was applied. The integration area of the spots was chosen in such a way that the intensities of all reflexions could be measured with a densitometer, either as  $\alpha_1 + \alpha_2$  or as  $\alpha_1$  (Wagner, 1966). The intensities were corrected in the usual way for the Lorentz and polarization effect. No correction for absorption [ $\mu(\text{Cu}) = 25 \text{ cm}^{-1}$ ] was applied.  $|F|^2$  values obtained from different levels were put on the same relative scale by using the relations  $|F(hkl)|^2 = |F(hk\bar{l})|^2 = |F(klh)|^2$ . The average of the  $|F|^2$  values of equivalent reflexions was used in the analysis of the structure. Comparison of the individual structure factor magnitudes  $|F(\text{ind})|$  with their average value  $|F(\text{av})|$  gave  $\Sigma |F(\text{ind})| - |F(\text{av})| / \Sigma |F(\text{av})| = 0.06$ .

### Determination of the structure

In space group  $Pa\bar{3}$ , depicted in Fig. 1, there is one special position with multiplicity four, which consists of the centres of symmetry on the threefold inversion axes. We started the structure determination with the assumption that the centres of the four molecules  $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}$  are at these sites and that each molecule exhibits threefold inversion symmetry. This implies that only one of the twenty-four units  $\text{NP}(\text{NMe}_2)_2$  is crystallographically independent.

The structure was derived from a three-dimensional Patterson synthesis, the sections of which were calculated perpendicular to the  $\bar{3}$  axis in the  $[111]$  direction. To this end a system of orthogonal axes  $A, B, C$  was chosen, which was related to the cubic system  $a, b, c$  by  $A = a - c$ ,  $B = -a + 2b - c$ ,  $C = a + b + c \equiv [111]$ .

As the maxima corresponding to P-P vectors predominated in the Patterson map, the coordinates of the one independent phosphorus atom could easily be determined. Thereafter the positions of the three nitrogen atoms and of two of the four carbon atoms were found, use being made of the P-N and P-C maxima in the Patterson map and of reasonable values for the bond lengths and angles. The remaining two carbon atoms were found from a three-dimensional Fourier synthesis.

After initial least-squares refinement the positions of all twelve hydrogen atoms could be found from a difference Fourier map of low order reflexions ( $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$ ). In the further least-squares refinement the positions obtained for the hydrogen atoms were kept fixed; the temperature factor of the hydrogen atoms was assumed to be  $\exp[-2.5 \sin^2 \theta/\lambda^2]$ . For the remaining atoms the coordinates were refined as well as the parameters of the anisotropic temperature factor  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ . The least-squares program used worked according to the block-diagonal approximation (Cruickshank, 1961a). The refinement was based on 775 observed independent reflexions. The atomic scattering factors were taken from Moore (1963) and the weighting scheme used was  $w^{-1} = 1 + \{(|F(\text{obs})| - 41)/21\}^2$ . At the end of the refinement  $R$  had dropped to 0.07. In the last cycle the biggest shift in a coordinate was less than 0.1 times its standard deviation.

Final atomic coordinates and temperature factor parameters are listed in Tables 1 and 2. The standard deviations calculated by the least-squares program are given in parentheses. The observed and calculated structure factors are compared in Table 3.

Inspection of Table 2 shows that the molecule cannot be regarded as a rigid body. The relatively small thermal motion of the phosphorus atom in comparison to the vibration of the nitrogen atoms indicates that librations may take place of the  $\text{PN}_4$  tetrahedron about the phosphorus atom. The molecule thus appears to be very flexible. No libration corrections were applied to the coordinates (Cruickshank, 1956).

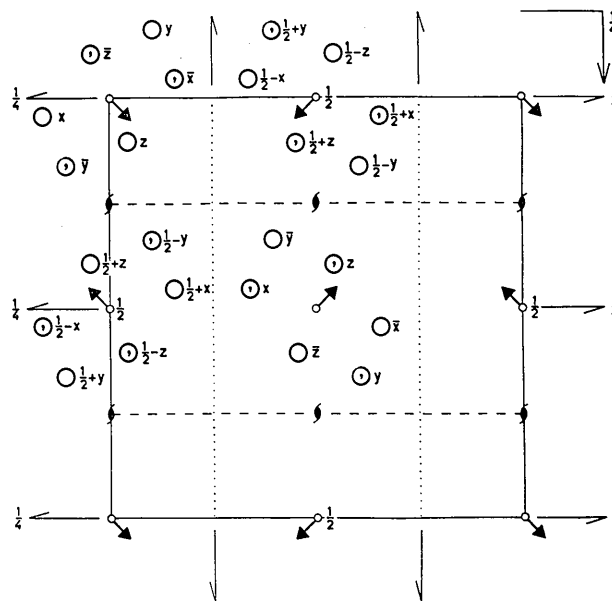


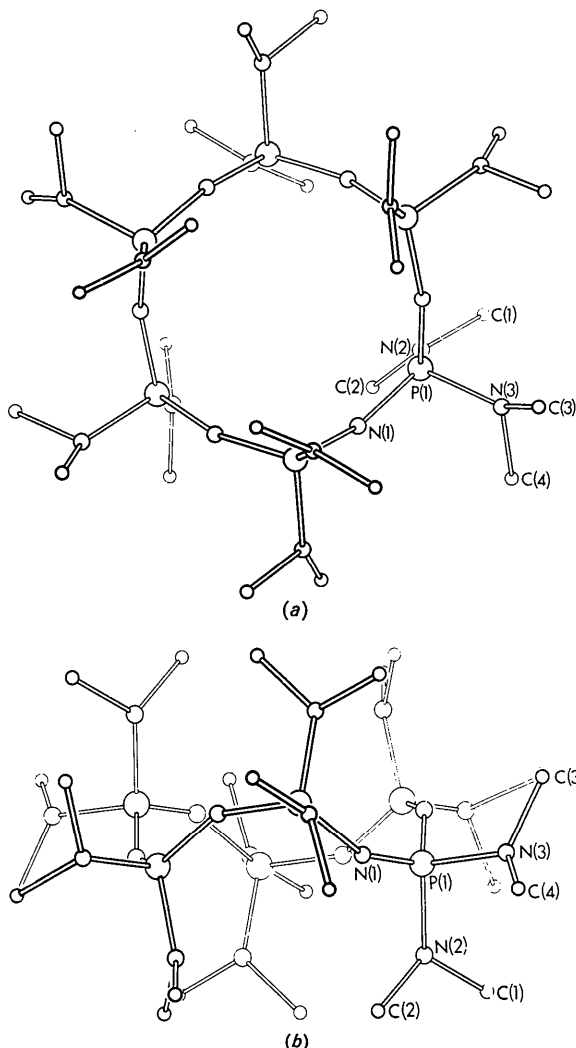
Fig. 1. Symmetry elements and equivalent positions of space group  $Pa\bar{3}$ . The arrows with heavy heads indicate threefold axes in the  $\langle 111 \rangle$  directions. Solid lines indicate the unit cell.

Table 1. Fractional atomic coordinates and standard deviations

	x	y	z
P(1)	0.0352 (1)	0.0648 (1)	-0.1593 (1)
N(1)	0.0960 (3)	-0.0044 (3)	-0.1310 (3)
N(2)	-0.0410 (3)	0.0146 (3)	-0.2064 (3)
N(3)	0.0755 (3)	0.1222 (3)	-0.2353 (3)
C(1)	-0.0981 (4)	0.0600 (4)	-0.2588 (4)
C(2)	-0.0410 (4)	-0.0739 (4)	-0.2195 (4)
C(3)	0.1198 (4)	0.1988 (4)	-0.2179 (4)

Table 1 (cont.)

	x	y	z
C(4)	0.1140 (5)	0.0769 (5)	-0.3032 (4)
H(1)	-0.09	0.05	-0.32
H(2)	-0.09	0.11	-0.26
H(3)	-0.15	0.03	-0.23
H(4)	-0.11	-0.10	-0.21
H(5)	-0.02	-0.10	-0.17
H(6)	-0.02	-0.08	-0.27
H(7)	0.17	0.18	-0.21
H(8)	0.08	0.23	-0.19
H(9)	0.10	0.24	-0.26
H(10)	0.12	0.10	-0.37
H(11)	0.15	0.05	-0.29
H(12)	0.07	0.04	-0.32

Fig. 2. Molecule  $N_6P_6(NMe_2)_{12}$  viewed (a) along and (b) normal to the threefold inversion axis.

## Description of the structure

The crystal structure is composed of molecules  $N_6P_6(NMe_2)_{12}$ , which are placed at the corners and centres of the faces of a cubic unit cell. The molecular symmetry is  $\bar{3}$ . The molecules have the overall shape of a spheroid as is illustrated by Fig. 2 and by the distances from the center ( $M$ ) of the molecule to the independent carbon atoms (methyl groups):  $M \cdots C(1) = 4.59$ ,  $M \cdots C(2) = 3.81$ ,  $M \cdots C(3) = 5.16$  and  $M \cdots C(4) = 5.40$  Å.

The shortest intermolecular contacts are found between the carbon atoms (methyl groups). Four of these distances are shorter than 4.0 Å, the shortest one being 3.79 Å. This is just equal to the value 3.8 Å, expected from the van der Waals radius of a methyl group (1.9 Å; Pauling, 1960).

The most interesting part of the molecule is its twelve-membered ring of alternating phosphorus and nitrogen atoms. The ring is heavily puckered. The ring bonds have dihedral angles of 17 and 97° alternately. The distances from the phosphorus and nitrogen ring atoms to the mean molecular plane are 0.56 and 0.39 Å respectively. This implies that one of the two independent ring bonds is nearly parallel to the mean plane of the molecule, whereas the other one intersects this plane [Fig. 2(b)]. The shape of the twelve-membered ring is thus comparable to the boat form of an eight-membered ring. It may be noted, however, that in the present molecule the nitrogen atoms are closer to the average molecular plane than the phosphorus atoms, whereas in the known tetrameric cyclophosphazenes (Table 5) the opposite is true. To each phosphorus atom there are attached two dimethylamino groups. One of the two P-N(*exo*) bonds is lying approximately

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

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{31}$	$U_{12}$
P(1)	134 (7)	129 (6)	124 (6)	0 (6)	8 (6)	6 (6)
N(1)	228 (29)	237 (27)	260 (29)	-18 (23)	-132 (23)	43 (24)
N(2)	262 (28)	162 (24)	216 (25)	13 (20)	-59 (22)	33 (23)
N(3)	277 (30)	202 (25)	225 (27)	-30 (22)	84 (24)	-72 (24)
C(1)	272 (34)	271 (32)	314 (34)	49 (32)	-86 (29)	35 (31)
C(2)	293 (35)	246 (34)	406 (38)	-4 (31)	-80 (31)	10 (31)
C(3)	293 (36)	208 (34)	319 (37)	88 (30)	10 (31)	-38 (30)
C(4)	510 (47)	426 (45)	202 (32)	-15 (32)	119 (34)	-25 (39)

parallel to the mean plane of the ring, the other one is nearly normal to it.

The intramolecular atomic distances and the valence angles are given in Table 4. In estimating their standard deviations the standard deviations obtained from the least-squares residuals have been multiplied by two.

The two crystallographically non-equivalent ring bonds, P-N(*endo*), are equal within experimental error. The same is true for the exocyclic bonds P-N(*exo*). The average length of the P-N(*endo*) bonds, 1.56 Å, is 0.2 Å smaller than the length of a P-N single bond (1.77 Å, Hobbs, Corbridge & Raistrick, 1953; Cruickshank, 1964). Such a shortening, indicating a strong double bond character, is generally observed in phosphazene rings (Table 5). The average length of the P-N(*exo*) bonds, 1.67 Å, indicates that

there is also some double bonding to the nitrogen atoms outside the ring. The length of the P-N(*exo*) bonds is comparable to the length of the ring bonds in phosphazane structures (Migchelsen, Olthof & Vos, 1965; Mani & Wagner, 1968).

The differences between the four independent N-C bonds are not significant. The average value of 1.46 Å is equal to the N-C bond length found in several aliphatic amines (Sutton, 1958). For the C-H distances approximate values, ranging from 0.9 to 1.2 Å, have been calculated from the hydrogen positions observed in the difference Fourier map.

As to the valence angles the ring angle at nitrogen, 147.5°, is considerably larger than the corresponding angles in other cyclic non-planar phosphazenes (Table 5). The environment of phosphorus is approximately

Table 3. Observed and calculated structure factors

The columns are *k*, 10*F*<sub>o</sub> and 10*F*<sub>c</sub>. Reflexions indicated by an asterisk are not taken into account in the refinement.

0, k, 0	7 1286	-1334	20 254	250	9, k, 1	12 281	-287	6 689	-693	14 259	217	14 505	-815
	8 458	478						7 852	-828			15 473	432
2 1444	1571	9 101	-184	3, k, 1	2 206	-194	18, k, 1	8 533	-542	15, k, 2		16 354	345
6 1324	-1462	10 669	630		6 686	684		10 718	-695			18 545	847
8 561	-575	11 708	736	2 606	606	7 468	-473	4 342	-336	12 409	-351	9 244	-272
10 422	-420	12 510	-494	1392	-1472	9 821	788	9 83	163	17 365	354	5 322	325
16 193	-165	14 281	238	4 440	424	10 505	478			11 367	354	7, k, 3	
		16 375	363	5 751	-773	12 329	351	19, k, 1		8, k, 2		13 262	229
				6 327	-315	15 488	474					4 831	839
				7 277	328	18 176	-186	2 434	409	3 836	907	5 951	-920
1 1098	1085	12, k, 0		8 1106	1046			3 299	236	5 1045	1016	6 374	331
2 1327	-1410	1 766	-715	11 434	374			5 221	203	6 698	-692	4 498	-472
3 630	-694	3 869	-881	13 656	634	10, k, 1		7 648	651	5 375	-348	9 741	771
4 274	249	6 686	725	14 784	773			2, k, 2				10 681	-667
5 390	361	7 282	-261	15 842	826	3 301	-244	10 605	591	17, k, 2		12 590	-596
6 527	516	8 405	390	16 412	-334	5 286	-239	282625	-2850	13 360	-356	18 271	236
7 666	651	11 568	568	17 329	322	6 267	227	3 611	597	15 259	-242	3 394	-280
8 282	-263	12 419	-391	18 591	-573	7 548	-518	4 390	-407	16 344	341	4 274	-265
9 1037	982	13 355	-343	19 322	276	9 392	-387	6 882	897	17 110	-282	5 425	-431
10 334	-340	14 405	-381			13 385	331	8 302	254	18 186	-175	9 341	353
12 671	636	16 442	-403	4, k, 1		15 377	341	11 307	-243			10 224	260
13 847	623	17 121	181			17 83	147	12 189	248	9, k, 2		11 166	179
14 1095	1085			2 718	-770			13 377	349			12 572	323
15 319	287	14, k, 0		3 510	-491	11, k, 1		15 209	159	3 610	-572	18, k, 2	
16 623	603			7 369	-392			19 164	-243	5 267	259	10 703	693
17 560	-928	2 791	-785	8 666	629	2 928	-517	6 417	-385	5 360	-367	11 532	-952
18 304	292	3 741	-705	4 678	-666	4 238	-666	6 115	-182	6 115	-182	12 372	367
19 365	-348	4 447	-399	15 527	519	5 434	406	9 684	688	10 395	-377	13 490	-490
		5 603	606	17 241	256	6 380	-388	382085	2301	10 236	-263	14 279	-246
		6 771	755			7 955	325	4 1311	1392	11 404	430	15 357	-387
		7 530	539	5, k, 1		8 1510	-1560	5 1927	196	14 321	-322	17 402	-285
1 179	153	8 575	570			9 455	434	7 887	912	15 133	-204	18 229	214
2 503	449	11 585	543	2 764	-782	10 188	260	9 449	436				
3 1085	-1077	12 399	-373	3 439	424	16 236	213	10 307	-277	10, k, 2		9, k, 3	
4 1184	-1270	14 528	-467	4 149	-1574			11 279	-227				
5 1191	-1282			5 233	213	12, k, 1		12 302	-244			20, k, 2	
6 282	-300	16, k, 0		6 1023	-1031			16 425	406	3 329	-261		4 691
7 782	826			7 625	-677	4 229	-239	4 307	254	3 214	-166	5 350	-352
8 419	-390	2 1337	-1347	8 500	464	6 925	-973	5 714	736	4 110	-89	6 776	750
9 558	545	3 218	-245	9 372	-328	9 106	-184	6 159	-189	7 653	-665	8 413	-413
11 344	-317	4 591	-608	10 709	-699	13 306	295	7 108	84	3, k, 3		12 307	-301
13 671	707	8 465	477	11 633	-613	16 163	-196	3 950	959	9 995	-1047	13 322	-326
14 547	866	9 500	-472	12 312	-250			4 228	-180	10 218	234	3 1392	-1493
15 304	385	11 189	-213	13 588	-626	14 208	176	5 854	-854	13 321	-271	4 284	289
17 359	-319	12 404	470	14 193	304	13, k, 1		6 246	250	6 347	350	8 904	896
19 264	-204			15 331	325	2 493	-481	8 350	-308	16 444	398	6 349	287
		18, k, 0		16 296	266	4 432	367	10 281	237	17 302	292	7 387	400
				17 161	-160	6 733	743	11 786	-787	11, k, 2		9 666	811
				18 161	-160	6 733	743	12 372	-310			10 576	-507
				19 208	-203	7 542	557	13 302	-244			11 238	206
1 430	458	4 111	103	20 503	517	10 430	379	19 243	211	4 586	-544	12 503	-467
2 774	812	6 440	424			11 259	-284	20 199	165	5 359	-346	19 269	201
3 1792	-1846	8 189	-157	6, k, 1		13 334	-290	6 347	350	20 281	259	13 503	840
4 440	475	9 410	-383			14 395	-336	7 430	-387				
5 1517	-1607	10 304	-321	2 314	-323	15 473	-422	8 164	-272	4, k, 3		11, k, 3	
8 294	-228			4 279	-306			3 385	317	11 301	263		
9 113	-195	20, k, 0		5 821	-790	14, k, 1		4 467	-452	14 502	477	4 573	598
11 359	366			6 1527	-1569	16 370	366	6 1527	-1569	16 370	366	5 261	-295
12 945	-967	1 432	429	8 272	-206	2 319	-253	7 324	-291	7 510	-514	8 834	-809
13 508	486	2 350	325	9 457	-454	4 429	-442	12 500	490	8 311	268	9 397	-349
14 452	-395	3 239	219	11 372	-371	6 543	-511	13 289	-286	9 508	482	14 404	-366
15 547	586			12 343	-323	14 208	176	14 343	-323	3 473	-458	14 558	16
16 407	-398			13 581	323			16 744	746	4 223	222	14 365	-368
		1, k, 1		14 291	241	15, k, 1		17 183	191	5 427	398	15 714	732
				15 452	420			18 168	217	7 334	-283	17 317	268
		8, k, 0		16 105	181			19 331	344	8 370	-321		
3 540	-553	3 551	-530			3 930	-911			9 457	-449	5, k, 3	
4 159	-184	6 259	-146	7, k, 1		7 333	296			11 309	287		4 364
5 209	169	9 334	-301	2 164	139	13 387	344	6, k, 2		13 360	-334	4 350	-317
6 889	-932	10 307	191	4 631	-592			5 636	-619	14 189	192	5 862	875
7 668	827	11 418	-473	5 317	-251			6 185	-194	17 169	345	7 432	452
9 1098	1135	13 500	448	7 462	-423	16, k, 1		7 229	211	7 169	345	9 294	280
10 748	756	14 482	419	8 533	489	7 211	222	9 385	-359	13, k, 2		10 897	-904
11 1226	1255	19 376	312	9 681	702	9 131	199	10 135	201	12 947	-929	13 375	317
13 583	558			10 606	604	10 387	385	11 985	-956	3 555	-545	13 517	-501
16 286	247	2, k, 1		12 581	554	12 201	232	12 882	-877	5 1061	-1118	20 419	495
17 583	-569			13 723	-720			13 184	-282	7 199	-234		
18 404	-372	2 1583	1741	18 571	-546	17, k, 1		14 214	-280			6, k, 3	
19 616	-656	4 1329	1465	19 424	-433			15 184	177			7 341	-326
		6 243	-214			2 284	244	16 166	231	14, k, 2		5 231	231
		8 591	604	8, k, 1		3 620	-594	18 276	-262	5 377	374	6 444	-409
		12 342	-345			4 211	-261	19 299	302	7 257	240	7 654	-628
1 161	-184	13 417	-424	7 754	-770	6 191	-204	8 463	-462	8 728	-718		



Table 5. Geometry of cyclophosphazenes

Molecular symmetry	Ring shape	$\Delta P^*$	$\Delta N$	$\Delta P/\Delta N$	Dihedral angles	P-N	PNP	NPN	XPX	Literature
$N_3P_3F_6$	planar				1, 1, 2°	1.56 Å	120°	119°	99°	Dougill (1963)
$N_3P_3Cl_6$	nearly planar				2, 5, 9	1.59	120	120	102	Wilson & Carroll (1960)
$N_3P_3Br_6$	slight chair				11, 18, 26	1.58	123	117	103	Giglio & Puliti (1967)
$N_3P_3Cl_4Ph_2$	slight chair				5, 7, 12	1.58	119	115	104	Mani, Ahmed & Barnes (1965)
					16, 15, 9	1.56	122	119	100	
$N_3P_3Cl_2Ph_4$	slight boat				3, 9, 4	1.58	121	116	104	Mani, Ahmed & Barnes (1966)
					6, 11, 6	1.56	125	121	99	
$N_4P_4F_8$	nearly planar				3, 4, 6, 6	1.51	147	123	100	McGeachin & Tromans (1961)
$N_4P_4Cl_8(K)$	boat	0.35 Å	0.47 Å	0.75	16, 57	1.57	131	121	103	Hazekamp, Mighelsen & Vos (1962)
$N_4P_4Cl_8(T)$	chair				20, 45, 76, 59	1.56	134	121	103	Wagner & Vos (1968)
$N_4P_4Me_8$	boat/saddle	0.21	0.54	0.39	31, 55	1.60	132	120	104	Dougill (1961)
$N_4P_4(NMe_2)_8$	boat/saddle	0.18	0.52	0.35	32, 52	1.58	133	120	104	Bullen (1962)
$N_4P_4(OMe)_8$	saddle	0.10	0.53	0.19	†	1.57	132	122	105	Ansell & Bullen (1967)
$N_6P_6(NMe_2)_{12}$	analogous to boat	0.56	0.39	1.49	17, 97	1.56	148	120	103	This work

\*  $\Delta P$  ( $\Delta N$ ) is the distance from the phosphorus (nitrogen) ring atoms to the mean plane of the molecule.

† No data available.

displacement parameter and which is defined as the ratio  $\Delta P/\Delta N$  of the displacements  $\Delta P$  and  $\Delta N$  of the phosphorus and nitrogen atoms from the mean plane of the ring. It should be noted that the displacement parameter can be defined only for molecules, in which all phosphorus (nitrogen) atoms have the same distance  $\Delta P$  ( $\Delta N$ ) to the mean molecular plane. This is *e.g.* the case for molecules with rotation-inversion symmetry. The values of  $\Delta P$ ,  $\Delta N$  and  $\Delta P/\Delta N$  for the cyclophosphazenes, which satisfy the condition just stated, have been added to Table 5.

The displacement parameter gives a picture of the conformation of a ring, which is very easily imaginable. For example, for an eight-membered ring  $\Delta P/\Delta N = 1$ , if the conformation is boat-shaped with equal displacements of both P and N. The parameter has values between 1 and 0, if the conformation passes on to a saddle form with the P atoms more coplanar than the N, whereas values  $> 1$  are found for a second type of saddle form, in which the N atoms are more coplanar than the P.

#### Steric effects

An outstanding feature of the structure of  $N_6P_6(NMe_2)_{12}$  is the large endocyclic angle PNP (147.5°). It is more than 10° larger than the corresponding angle in the non-planar tetrameric phosphazenes (133° on the average). The equally large angle in the planar tetramer  $N_4P_4F_8$  may be ascribed to the strongly electronegative character of the fluorine atoms. Electronegativity of the ligands cannot, however, be the reason of the widening of the angle PNP in  $N_6P_6(NMe_2)_{12}$ , since in  $N_4P_4(NMe_2)_8$  this angle has the normal value. We suspected that in the hexamer the large angle is due to steric effects. To evaluate this idea more quantitatively, we measured the distances between the carbon atoms in a model of the molecule in which the angle PNP had been reduced from 148 to 133°. The remaining valence angles, the bond lengths and the ring conformation as measured by  $\Delta P/\Delta N$  were kept unchanged. Since in combination with the reduced angle PNP a conformation with some other  $\Delta P/\Delta N$  value (*e.g.* as observed in the tetramers) might be more favourable, similar measurements were made on models with  $\Delta P/\Delta N$  equal to 0.75 and 0.35. The results are presented in Table 6. In each of the models tried at least one carbon...carbon distance is inacceptably short. For the model with  $\Delta P/\Delta N > 1$  the short distance is of the type  $C \cdots C''$ , whereas for the models with  $\Delta P/\Delta N < 1$ , it is of type  $C \cdots C'$ . These results were taken as evidence that in  $N_6P_6(NMe_2)_{12}$ , due to the bulky  $NMe_2$  groups, no conformation can accommodate a ring angle at nitrogen smaller than 148°.

It should be mentioned that we have observed a similar, though smaller, effect in the structure of  $N_4P_4Cl_8(T)$  (Wagner & Vos, 1968). In this molecule the two independent angles PNP are 138 and 134°.

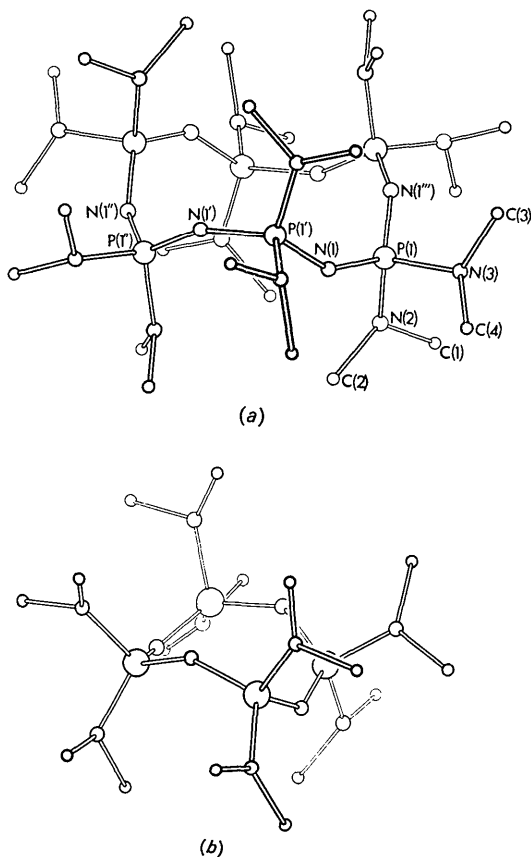


Fig. 3. Comparison of (a) hexameric and (b) tetrameric dimethylaminocyclophosphazene.

The difference is significant. It was shown that, as a consequence of the chair form of the molecule, for a smaller value than  $138^\circ$  some of the chlorine atoms at neighbouring phosphorus atoms would come too close together.

There is a second point which may be discussed in terms of steric effects, *viz.* the difference between the ring conformations of  $N_6P_6(NMe_2)_{12}$  and  $N_4P_4(NMe_2)_8$ . This difference is shown clearly by the mutual orientation of  $NMe_2$  groups on adjacent phosphorus atoms in the two molecules (Fig. 3). Non-bonded distances between carbon atoms, calculated for the two molecules and measured in various models derived from the molecules by changing the ring conformation, are collected in Table 7. In the two molecules the  $C \cdots C$  distances of each type are, surprisingly, the same, suggesting that the ring conformations of  $N_6P_6(NMe_2)_{12}$  and  $N_4P_4(NMe_2)_8$  are equally favourable from the point of view of methyl...methyl interactions. On the other hand some of the  $C \cdots C$  distances in the models are always shorter than in the molecules themselves, indicating that changes in the ring conformation lead to less favourable steric conditions for both  $N_6P_6(NMe_2)_{12}$  and  $N_4P_4(NMe_2)_8$ . One is thus led to the tentative conclusion that in phosphazene rings with bulky ligands steric factors are of preponderant importance in determining the shape of the central ring.

#### Chemical bonding

It is generally accepted that in cyclic phosphazenes a double system of  $\pi$  molecular orbitals exists, extending

Table 6.  $C \cdots C$  distances in  $N_6P_6(NMe_2)_{12}$  and in models of the molecule with angle PNP equal to  $133^\circ$

	$\Delta P/\Delta N$	Angle PNP	$C \cdots C^*$		$C \cdots C''^*$	
			<i>s</i>	<i>a</i>	<i>s</i>	<i>a</i>
			$\text{\AA}$	$\text{\AA}$	$\text{\AA}$	$\text{\AA}$
$N_6P_6(NMe_2)_{12}$	1.49	$148^\circ$	3.78	5.79	3.77	7.32
Model	1.49	133	4.2	5.8	1.8	6.2
Model	0.75	133	2.8	5.4	3.0	7.0
Model	0.35	133	2.4	5.2	5.0	7.8

\*  $C \cdots C$  distances are characterized according to the labeling of the atoms in Fig. 3.

*s*: shortest distance.

*a*: average distance.

Table 7.  $C \cdots C$  distances in hexameric and tetrameric dimethylaminocyclophosphazene and in models with different ring conformations

	$\Delta P/\Delta N$	Angle PNP	$C \cdots C^*$		$C \cdots C^*$		$C \cdots C''^*$	
			<i>s</i>	<i>a</i>	<i>s</i>	<i>a</i>	<i>s</i>	<i>a</i>
			$\text{\AA}$	$\text{\AA}$	$\text{\AA}$	$\text{\AA}$	$\text{\AA}$	$\text{\AA}$
$N_6P_6(NMe_2)_{12}$	1.49	$148^\circ$	3.52	4.16	3.78	5.79	3.77	7.32
Model	0.35	148			2.6	5.2	6.4	8.2
Model	0.75	148			3.0	5.3	5.6	8.0
$N_4P_4(NMe_2)_8$	0.35	133	3.54	4.15	3.81	5.81	3.99	7.49
Model	1.49	133			3.8	6.0	2.8	6.4
Model	0.75	133			3.0	5.8	4.4	7.2

\* See footnote to Table 6.

around the ring and sometimes, depending on the nature of the ligands, also to the ligands (Cruickshank, 1961*b*; Craig & Paddock, 1962). The  $\pi$  molecular orbitals originate from overlap of  $d$  orbitals on phosphorus with  $p$  orbitals (and  $sp^2$  hybrids) on nitrogen ( $d\pi-p\pi$  overlap). Cruickshank (1961*b*) assumes that because of the approximately tetrahedral environment of phosphorus two equi-energetic  $d$  orbitals,  $d(x^2-y^2)$  and  $d(z^2)$ , are of much more importance for  $\pi$  bonding than the remaining three. He states that in non-planar rings linear combination of these two  $d$  orbitals may give two hybrids at phosphorus, which are strongly bonding and which overlap equally well with the orbitals of the neighbouring nitrogen atoms, even when the dihedral angles of the two neighbouring P-N bonds are not equal. It is thus expected that also in non-planar phosphazene rings, provided the ring is substituted uniformly, short and equal lengths are found for crystallographically non-equivalent neighbouring P-N bonds. This has been observed indeed in all cases investigated so far and the present molecule  $N_6P_6(NMe_2)_{12}$  is no exception. It may be noted, however, that in this case the dihedral angles of the ring bonds show a larger difference than in other cyclophosphazenes. Their values, close to 0 and 90°, mean that the two hybrids at phosphorus are rather pure  $d(x^2-y^2)$  and  $d(z^2)$  orbitals.

The P-N ring bond in  $N_6P_6(NMe_2)_{12}$  is 0.02 Å shorter than in  $N_4P_4(NMe_2)_8$ . The widening of the ring angle PNP in  $N_6P_6(NMe_2)_{12}$ , caused by steric factors as discussed above, may be related to the shortening of the P-N bond. It is expected that in  $N_6P_6(NMe_2)_{12}$  owing to the larger angle PNP, the lone pair orbital at nitrogen has more  $p$  character (and the  $\sigma$  orbitals to the neighbouring phosphorus atoms less) than in  $N_4P_4(NMe_2)_8$ . It is further expected that in  $N_6P_6(NMe_2)_{12}$  the nitrogen lone pair orbital gives a better overlap with the  $d$  orbitals at phosphorus than in  $N_4P_4(NMe_2)_8$ . These differences result in greater strength of the  $\pi$  bonds in  $N_6P_6(NMe_2)_{12}$ .

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