Molecular Structures of Non-geminally Substituted Phosphazenes. Part III.[1] Crystal Structure of 2,*cis*-4,*trans*-6,*trans*-8-Tetrachloro-2,4,6,8-tetrakis(dimethylamino)cyclotetraphosphazatetraene

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Crystals of the title compound are triclinic, a = 12·67, b = 10·96, c = 8·68 Å, α = 92·6, β = 106·0, γ = 106·6°, space group $P\bar{1}$, Z = 2. The structure was determined from diffractometer X-ray data by Patterson and Fourier methods and refined by full-matrix least squares to R 0·098 for 2666 reflections. The eight-membered phosphazene ring has a hybrid crown–saddle conformation with P–N–P angles in the range 133·3—140·6°. Mean bond lengths are: P–N(endocyclic) 1·556, P–N(exocyclic) 1·626, P–Cl 2·043, and N–C 1·47 Å. Bond lengths are discussed in terms of the electronegativities of the exocyclic groups and the ring conformation compared with that in other phosphazene and cyclo-octane derivatives.

THE reaction of dimethylamine with octachlorocyclotetraphosphazatetraene gives a number of chloro(dimethylamino)cyclotetraphosphazatetraenes,[2-4] among which three isomers of composition $N_4P_4Cl_4(NMe_2)_4$ have been isolated.[3] According to ^1H and ^{31}P n.m.r. studies only one of these (m.p. 200 °C) is entirely non-geminally substituted and this was assigned[5] the configuration 2,*cis*-4,*trans*-6,*trans*-8-tetrachloro-2,4,6,8-tetrakis(dimethylamino)cyclotetraphosphazatetraene (I) (the β-*trans*-configuration). As the β-*trans*-isomers of

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[2] K. John, T. Moeller, and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 5616.

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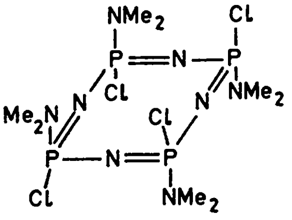
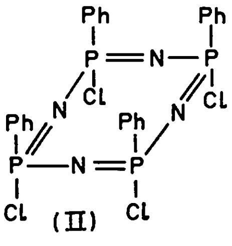
$N_4P_4(NHMe)_4Ph_4$ [6] and $N_4P_4Cl_4Ph_4$ [7] are known to have phosphazene rings with a chair conformation, we decided to examine the crystal structure of $N_4P_4Cl_4(NMe_2)_4$ (m.p. 200 °C) in order to verify the geometric configuration and to find whether the chair conformation again occurs. Our analysis shows that it does not.


(I)


(II)

The difference in electronegativity between the chloro- and dimethylamino-groups provides a further test for the suggestions made in Part II of this series [1] concerning the lengths of the bonds between phosphorus and the exocyclic groups and the orientation of those groups.

EXPERIMENTAL

Crystal Data.—$C_8H_{24}Cl_4N_8P_4$, M = 498·04, Triclinic, a = 12·67 ± 0·03, b = 10·96 ± 0·03, c = 8·68 ± 0·02 Å, α = 92·6, β = 106·0, γ = 106·6° (all angles ±0·3°), U = 1114 Å^3, D_m = 1·49 (by flotation), Z = 2, D_c = 1·48, $F(000)$ = 512. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 8·1 cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

Crystals were grown from benzene–light petroleum (b.p. 40—60 °C) solutions at room temperature, as tablets with {010} most well developed. *X*-Ray intensities were measured at 22—25 °C on a Philips PAILRED diffractometer by use of monochromatised Mo-K_α radiation. It was necessary to use three crystals to make the measurements because the intensities were found to have decreased after long exposure of the crystal to the *X*-ray beam. A similar deterioration of the crystal on exposure to *X*-rays occurs for $N_3P_3Cl_3(NMe_2)_3$.[8] The three crystals of $N_4P_4Cl_4(NMe_2)_4$ (all with dimensions *ca.* 0·5 × 0·2 × 0·1 mm) were used to collect the layers *hkL* where *L* is (i) 0—4, (ii) 5, 6, 8, and 9, and (iii) 7 and 10. All reflections with $\sin\theta < 0\cdot5$ were measured and of these 2666 reflections gave statistically significant intensities, with $I > 2\sigma(I)$. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

The least-squares refinement was carried out at the Atlas Computer Laboratory, Chilton, by use of the '*X*-Ray '63' programme package. Atomic scattering factors were taken from ref. 9.

Structure Determination.—Standard *hk*0 reflections were measured at the beginning, middle, and end of data collection for each layer so that all the data could be placed on the same (relative) scale. Intensity statistics suggested the space group to be $P\bar{1}$ and this was confirmed by the subsequent analysis. The data were adjusted to an absolute scale by Wilson's method [10] and the three-dimensional Patterson function calculated. The molecule was expected to contain an eight-membered phosphazene ring and, initially, the four phosphorus atoms in the ring were assumed to be coplanar with equal distances between them. The two peaks, of a height corresponding to four phosphorus–phosphorus vectors, expected in the Patterson function *ca.* 3 Å from the origin, were located and the orientation of the ring therefore determined. The Patterson function also contained an extended strong peak centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, which suggested two roughly centrosymmetric molecules centred at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. This information yielded the positions of the four phosphorus atoms in the asymmetric unit. Peaks corresponding to phosphorus–chlorine vectors were located *ca.* 2 Å from the origin and, from these, the positions of two of the chlorine atoms were deduced. The remaining non-hydrogen atoms were located by successive Fourier syntheses.

Three cycles of full-matrix least-squares refinement in which atomic co-ordinates, isotropic temperature factors, and individual layer scale factors were varied reduced R to 0·155. Two more cycles with atomic co-ordinates and anisotropic temperature factors as variables brought R to 0·103. The methyl hydrogen atoms could not be located from difference-Fourier syntheses calculated either at this stage or before the anisotropic refinement, and they were therefore considered to be disordered. A fixed contribution to the structure factors from the hydrogen atoms was included in subsequent cycles by placing twelve hydrogen 'atoms', each with an occupancy of 0·25, symmetrically about each carbon atom. C–H was taken as 1·08 Å, N–C–H assumed to have the tetrahedral value, and B_H was taken as 5·0 Å^2. The weighting scheme $w = (A + B|F_o| + C|F_o|^2)^{-1}$ [for $0 < |F_o| < 20$, $A = 10\cdot42$, $B = -1\cdot25$, and $C = 0\cdot04$; for $20 < |F_o| < 75$, $A = 4\cdot0$, and $B = C = 0$; for $75 < |F_o| < 200$, $A = 10\cdot0$ and $B = C = 0$] was introduced to give similar average values of $w\Delta^2$ for ranges of increasing $|F_o|$ and $\sin\theta/\lambda$. Two further cycles of least-squares refinement reduced R to its final value of 0·098 for 2666 reflections. The weighted factor R' was 0·103 $[R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. In the final cycle most parameter shifts were $<0\cdot3\sigma$ though a few fell in the range $(0\cdot3$—$0\cdot6)\sigma$. A difference-Fourier synthesis based on the final parameters contained no residual peaks higher than 0·7 eÅ^{-3}.

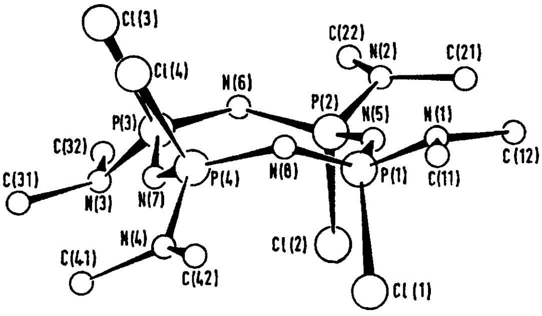


FIGURE 1 Molecular shape and labelling of the atoms

RESULTS

The final atomic co-ordinates and thermal parameters with estimated standard deviations are listed in Tables 1 and 2 (see Figure 1 for the numbering of the atoms).

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[6] Part I, G. J. Bullen and P. R. Mallinson, *J.C.S. Dalton*, 1972, 1412.

[7] G. J. Bullen, P. R. Mallinson, and A. H. Burr, *Chem. Comm.*, 1969, 691.

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[10] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x/a	y/b	z/c
Cl(1)	3162(3)	1133(3)	−86(4)
Cl(2)	2593(3)	4350(3)	−102(4)
Cl(3)	1471(3)	3511(3)	5642(4)
Cl(4)	1945(3)	432(3)	5554(3)
P(1)	3896(2)	1930(2)	2295(3)
P(2)	3415(2)	4373(2)	2287(3)
P(3)	1397(2)	3202(2)	3280(3)
P(4)	1878(2)	772(2)	3247(3)
N(1)	5152(8)	1725(10)	2799(13)
N(2)	4344(9)	5787(9)	2869(14)
N(3)	207(9)	3483(10)	2271(13)
N(4)	1093(8)	−575(8)	2081(13)
N(5)	4092(8)	3402(9)	2400(13)
N(6)	2490(9)	4247(10)	3178(14)
N(7)	1182(7)	1756(8)	2785(12)
N(8)	3177(8)	1103(8)	3282(11)
C(11) *	5215(13)	412(15)	2922(21)
C(12)	6118(14)	2603(18)	2413(24)
C(21)	5389(13)	6100(15)	2474(24)
C(22)	3911(15)	6892(13)	2989(21)
C(31)	−900(12)	2624(19)	2330(24)
C(32)	261(16)	4848(17)	2348(23)
C(41)	−203(11)	−973(12)	1687(17)
C(42)	1576(15)	−1648(15)	2186(24)

* The first number of the C atom label is that of the nitrogen atom to which it is attached.

TABLE 2

Anisotropic thermal parameters (× 10^4) with estimated standard deviations in parentheses *

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl(1)	114(4)	145(5)	161(6)	47(3)	48(4)	5(4)
Cl(2)	117(3)	154(4)	148(6)	60(3)	6(4)	28(4)
Cl(3)	128(4)	141(4)	166(6)	71(3)	74(4)	22(4)
Cl(4)	115(3)	130(4)	156(5)	63(3)	70(3)	69(4)
P(1)	49(2)	75(3)	144(5)	33(2)	41(3)	25(3)
P(2)	53(2)	58(3)	146(5)	20(2)	40(3)	18(3)
P(3)	62(2)	76(3)	158(6)	44(2)	57(3)	36(3)
P(4)	57(2)	55(3)	134(5)	27(2)	41(3)	27(3)
N(1)	59(8)	118(12)	217(21)	49(8)	50(11)	25(13)
N(2)	83(10)	63(10)	269(25)	16(8)	47(13)	34(12)
N(3)	81(9)	127(13)	228(22)	76(9)	47(12)	62(13)
N(4)	91(10)	61(9)	230(21)	39(8)	78(12)	44(11)
N(5)	60(8)	74(10)	251(22)	31(7)	59(11)	34(12)
N(6)	108(11)	95(11)	282(26)	54(9)	118(14)	40(13)
N(7)	67(8)	66(9)	180(17)	39(7)	55(9)	36(10)
N(8)	77(8)	60(9)	165(17)	28(7)	59(10)	19(10)
C(11)	133(16)	166(20)	346(39)	122(16)	119(21)	92(22)
C(12)	101(15)	22(26)	394(46)	74(16)	136(22)	108(27)
C(21)	86(13)	111(17)	438(49)	0(12)	103(21)	26(22)
C(22)	163(18)	62(13)	316(37)	35(12)	90(21)	−3(17)
C(31)	62(12)	241(27)	365(44)	52(15)	50(19)	108(28)
C(32)	183(21)	175(22)	362(43)	153(18)	101(24)	107(24)
C(41)	80(12)	99(14)	198(26)	−6(10)	40(14)	−3(15)
C(42)	149(19)	92(16)	420(47)	64(14)	79(24)	48(21)

* The temperature factor is in the form: $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl)$.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20535 (16 pp., 1 microfiche).* Bond lengths are listed in Table 3 and bond angles in Table 4. Their estimated standard deviations were calculated from the formulae of ref. 11, the maximum of $\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ being taken as the standard deviation $\sigma(r)$ of the atomic position. In view of the large standard deviations of the anisotropic thermal parameters a vibrational analysis was not considered worthwhile. The parameters b_{33} may also be subject to error because individual layer scale factors had been refined before anisotropic parameters were introduced. The amplitudes of vibration corresponding to the thermal parameters listed in Table 2 are given in Table 5.

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

Endocyclic			
P(1)–N(5)	1·554(10)	P(1)–Cl(1)	2·052(5)
P(2)–N(5)	1·538(11)	P(2)–Cl(2)	2·044(5)
P(2)–N(6)	1·552(12)	P(3)–Cl(3)	2·035(5)
P(3)–N(6)	1·550(12)	P(4)–Cl(4)	2·039(5)
P(3)–N(7)	1·549(10)	Mean	2·043(3)
P(4)–N(7)	1·576(10)		
P(4)–N(8)	1·572(10)		
P(1)–N(8)	1·554(10)	N(1)–C(11)	1·47(2)
Mean	1·556(4)	N(1)–C(12)	1·46(2)
		N(2)–C(21)	1·41(2)
Exocyclic		N(2)–C(22)	1·48(2)
P(1)–N(1)	1·614(11)	N(3)–C(31)	1·46(2)
P(2)–N(2)	1·613(12)	N(3)–C(32)	1·48(2)
P(3)–N(3)	1·644(12)	N(4)–C(41)	1·51(2)
P(4)–N(4)	1·633(11)	N(4)–C(42)	1·47(2)
Mean	1·626(6)	Mean	1·47(1)

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

N(8)–P(1)–N(5)	120·4(6)	N(1)–P(1)–N(5)	107·3(6)
N(5)–P(2)–N(6)	120·8(6)	N(1)–P(1)–N(8)	107·6(5)
N(6)–P(3)–N(7)	121·8(6)	N(2)–P(2)–N(6)	108·1(6)
N(7)–P(4)–N(8)	121·5(5)	N(2)–P(2)–N(5)	107·5(6)
		N(3)–P(3)–N(7)	105·0(6)
P(1)–N(5)–P(2)	140·6(8)	N(3)–P(3)–N(6)	111·6(6)
P(2)–N(6)–P(3)	137·5(8)	N(4)–P(4)–N(8)	111·0(5)
P(3)–N(7)–P(4)	135·8(7)	N(4)–P(4)–N(7)	106·0(5)
P(4)–N(8)–P(1)	133·3(6)		
		P(1)–N(1)–C(11)	118·4(10)
Cl(1)–P(1)–N(1)	104·7(4)	P(1)–N(1)–C(12)	120·8(10)
Cl(2)–P(2)–N(2)	105·4(5)	P(2)–N(2)–C(21)	120·6(11)
Cl(3)–P(3)–N(3)	104·4(4)	P(2)–N(2)–C(22)	118·3(10)
Cl(4)–P(4)–N(4)	106·2(4)	P(3)–N(3)–C(31)	118·4(10)
		P(3)–N(3)–C(32)	115·4(10)
Cl(1)–P(1)–N(5)	108·6(4)	P(4)–N(4)–C(41)	119·5(9)
Cl(1)–P(1)–N(8)	107·3(4)	P(4)–N(4)–C(42)	117·5(10)
Cl(2)–P(2)–N(6)	106·2(5)		
Cl(2)–P(2)–N(5)	107·8(4)	C(11)–N(1)–C(12)	114·8(12)
Cl(3)–P(3)–N(7)	109·6(5)	C(21)–N(2)–C(22)	113·3(13)
Cl(3)–P(3)–N(6)	103·1(4)	C(31)–N(3)–C(32)	113·4(13)
Cl(4)–P(4)–N(8)	102·8(4)	C(41)–N(4)–C(42)	114·5(12)
Cl(4)–P(4)–N(7)	108·6(4)		

TABLE 5

Ranges of root-mean-square amplitudes of thermal vibration (in Å) along the principal axes of the vibration ellipsoids

	Minor	Medium	Major
Cl	0·19—0·22	0·23—0·28	0·29—0·31
P	0·14—0·17	0·18—0·20	0·22—0·25
N	0·16—0·18	0·19—0·26	0·25—0·33
C	0·15—0·20	0·26—0·33	0·30—0·41

DISCUSSION

The molecule has a β-*trans*-configuration as suggested by Desai *et al.*[5] but the phosphazene ring has a conformation previously unknown in this series of compounds.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[11] G. A. Jeffrey and D. W. J. Cruickshank, *Quart. Rev.*, 1953, **7**, 335.

The four phosphorus atoms are coplanar and three of the nitrogen atoms lie on one side of this plane while the fourth, N(7), lies on the other (see Figure 1 and Table 6). The ring has approximate mirror symmetry as indicated by the torsion angles of the ring bonds shown in Figure 2(a) (a mirror operation reverses the sign of a torsion angle). The conformation is discussed further on p. 2441.

TABLE 6

Equations of mean planes through sets of atoms and distances (Å) of these and other atoms from the plane (in square brackets). Co-ordinates in Å are referred to orthogonal axes *a′*, *b′*, and *c*, where *b′* lies in the *bc* plane

Plane (i):
P(1)—(4) $0{\cdot}551X + 0{\cdot}091Y + 0{\cdot}830Z = 2{\cdot}980$
[P(1) 0·007, P(2) −0·007, P(3) 0·007, P(4) −0·007, N(5) 0·230, N(6) 0·336, N(7) −0·501, N(8) 0·445]

Plane (ii):
P(1), N(1), C(11), C(12) $0{\cdot}264X + 0{\cdot}256Y + 0{\cdot}930Z = 1{\cdot}906$
[P(1) −0·052, N(1) 0·162, C(11) −0·054, C(12) −0·056]

Plane (iii):
P(2), N(2), C(21), C(22) $0{\cdot}339X - 0{\cdot}187Y + 0{\cdot}922Z = 1{\cdot}275$
[P(2) −0·059, N(2) 0·183, C(21) −0·064, C(22) −0·060]

Plane (iv):
P(3), N(3), C(31), C(32) $0{\cdot}019X + 0{\cdot}229Y + 0{\cdot}973Z = 2{\cdot}780$
[P(3) 0·075, N(3) −0·240, C(31) 0·084, C(32) 0·080]

Plane (v):
P(4), N(4), C(41), C(42) $-0{\cdot}100X - 0{\cdot}252Y + 0{\cdot}963Z = 1{\cdot}731$
[P(4) 0·063, N(4) −0·196, C(41) 0·066, C(42) 0·067]

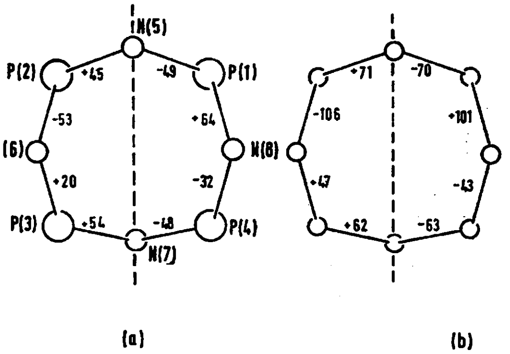

FIGURE 2 Torsion angles (°) in eight-membered rings with approximate symmetry *m* (the mirror plane is shown by a broken line): (a) β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ (this work), and (b) *trans*-cyclo-octane-1,2-dicarboxylic acid (from ref. 18)

The P–N bond lengths in the ring are equal, mean 1·556 Å (Table 3). In related compounds the bond lengths are: $N_4P_4(NMe_2)_8$ 1·58[12] and $N_4P_4Cl_8$ 1·56—1·57 Å.[13] The cyclic P–N bond length in tetrameric phosphazenes varies with the electronegativity of the exocyclic groups,[1,14] and the result for β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ was included in the graphical correlation given in Part II.[1] The P–N bonds in this compound are 0·01 Å shorter than in derivatives with similar exocyclic group electronegativity [$N_4P_4(OMe)_8$ and $N_4P_4Cl_4Ph_4$] and this emphasises the imprecise nature of the correlation.

In discussing the structure of *cis*-$N_4P_4Cl_4Ph_4$ (II) we suggested[1] that in a non-geminal phosphazene $N_4P_4R^1{}_4R^2{}_4$, if the group R^1 is capable of electron donation and the group R^2 of electron withdrawal, the $P\text{–}R^1$ bond will be shortened and the $P\text{–}R^2$ bond lengthened with respect to such bonds in the parent $N_4P_4R^1{}_8$ or $N_4P_4R^2{}_8$. The bond lengths in β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ support this suggestion, the mean P–Cl bond length (2·043 Å) being long, as in *cis*-$N_4P_4Cl_4Ph_4$, and the mean exocyclic P–N bond length (1·626 Å) being much shorter than the exocyclic bonds in $N_4P_4(NMe_2)_8$ (1·679 Å)[12] or $N_4P_4(NHMe)_4Ph_4$ (1·677 Å),[6] and almost as short as the endocyclic P–N bonds in some phosphazenes. Electron donation by the exocyclic nitrogen atoms is also indicated by the approach to planarity of the $PNMe_2$ groups, the sum of the three bond angles at nitrogen being 354, 352, 347, and 352° for N(1)—(4) (see also the deviations from the mean planes of the $PNMe_2$ groups, Table 6). A similar pair of exocyclic bond lengths has been found at the non-geminally substituted phosphorus atom in 2,2,4-trichloro-4,6,6-tris(dimethylamino)cyclotriphosphazatriene (P–Cl 2·051, P–N 1·628 Å).[8] Short exocyclic P–N bonds also occur in gem-$N_3P_3Cl_2(NHPr^i)_4$,HCl (mean 1·609 Å),[15] the reason in this case being that protonation of a ring nitrogen atom reduces π-bonding in the ring and so facilitates acceptance of electrons by phosphorus from the exocyclic nitrogen atoms.

The four NMe_2 groups are all orientated so that the C–N–P–Cl torsion angles are near 90° (the angles between the $PNMe_2$ mean plane and the adjacent NPCl plane lie in the range 93—96°). A similar symmetrical orientation of phenyl groups was found in *cis*-$N_4P_4Cl_4Ph_4$ and was attributed[1] mainly to equalisation of non-bonded contacts between chlorine and carbon atoms, although it was noted that this orientation is favourable for π-overlap with the phosphorus $3d_{z^2}$ orbital (Craig and Paddock axial system[16]) which is not already involved in the π-system of the ring. These considerations apply equally well to β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ and to $N_3P_3Cl_3(NMe_2)_3$ where a C–N–P–Cl torsion angle close to 90° for the non-geminal $\gtrdot PCl(NMe_2)$ group contrasts with torsion angles of *ca.* 40° for the geminal $\gtrdot P(NMe_2)_2$ group.[8]

The P–N–P angles in the ring range from 133·3—140·6°. A similar spread of P–N–P angles was found in the molecule of *cis*-$N_4P_4Cl_4Ph_4$ and it was noted that such large angles appear characteristic of molecules containing chlorine or fluorine.[1] The other types of

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[15] N. V. Mani and A. J. Wagner, *Acta Cryst.*, 1971, **B27**, 51.

[16] D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118.

bond angle shown in Table 4 are similar to those found in general in phosphazenes. There is some distortion at P(3) and P(4) in that the Cl–P–N(exo) plane is not perpendicular to the N(endo)–P–N(endo) plane so that pairs of Cl–P–N(endo) angles [or N(exo)–P–N(endo) angles] are not equal. This distortion, which does not occur at P(1) and P(2), avoids too close a contact between atoms Cl(3) and Cl(4) (their distance apart is 3·61 Å, the accepted van der Waals diameter of a chlorine atom). At the other end of the molecule atoms Cl(1) and Cl(2) are further apart (3·80 Å) so that there is no need for the angles around P(1) and P(2) to be distorted. The greater Cl(1) · · · Cl(2) distance is connected with the flattening of the ring in this area, N(5) being the closest of all the ring nitrogen atoms to the mean plane of the phosphorus atoms, but whether the flattening is the cause of the greater Cl · · · Cl distance or *vice versa* is not clear. The mean C–N–C angle is only 114·0° whereas the P–N–C angles are nearer to 120°. Other phosphazenes containing dimethylamino-groups also show C–N–C angles smaller than the P–N–C angles, *e.g.* $N_6P_6(NMe_2)_{12}$ with mean C–N–C 112·9°,[17] or $N_4P_4(NMe_2)_8$ with mean C–N–C 116°.[12]

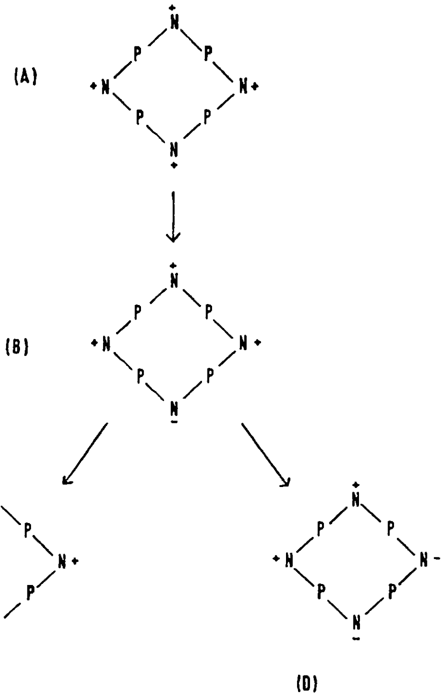

FIGURE 3 Relations between conformations of the ring in tetrameric phosphazenes: A crown, B crown–saddle, C saddle, and D chair

The relation of the observed phosphazene ring conformation to other known conformations is shown in Figure 3. In each case the four phosphorus atoms are coplanar and the nitrogen atoms are placed above (+) or below (−) their plane, ideally by equal amounts. The present conformation (B) can thus be regarded as intermediate between crown and saddle or crown and chair and we shall arbitrarily choose to call it a crown–saddle. Phosphazene examples of all the conformations in Figure 3 are known, though often with departures from ideality, *e.g.* in *cis*-$N_4P_4Cl_4Ph_4$ the crown conformation is deformed because steric interference between the chlorine atoms prevents the phosphorus atoms being coplanar.[1] In β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ the displacements of the nitrogen atoms from the plane of the phosphorus atoms are unequal (Table 6).

Conformation (B) has been found in several cyclo-octane derivatives.* [18,19] In these the ring is more highly puckered than in the cyclophosphazene as can be seen from a comparison of the torsion angles in Figures 2(a) and (b). Strain-energy minimisation calculations on cyclo-octane conformations [20,21] suggest that, although no one form of the ring is clearly favoured energetically, the conformation (B) has the lowest energy of the ten forms considered by a margin of *ca.* 1 kcal mol^{-1}. Clearly there are substantial differences between cyclo-octane and cyclotetraphosphazene rings (principally that the nitrogen atoms carry no substituents and the bond angles in the phosphazene ring are larger) which will alter the relative energies of

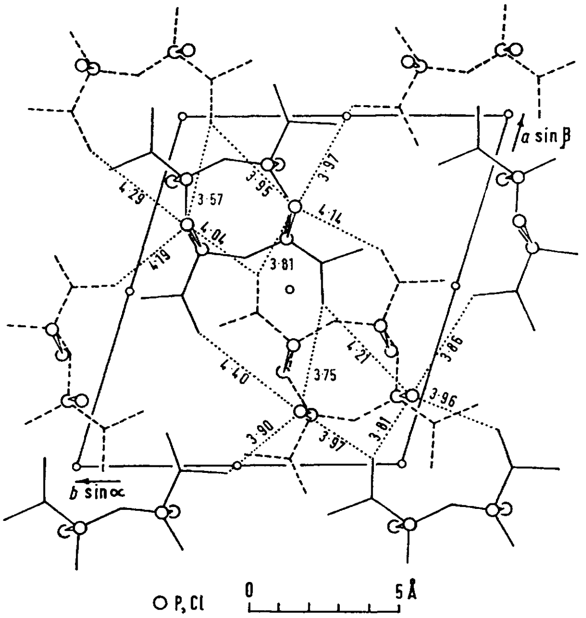

FIGURE 4 Projection of the structure down the *c* axis. Broken lines are used to represent molecules at an approximate height ¼*c* and full lines those at ¾*c* or −¼*c*. Intermolecular C · · · Cl distances (Å) are marked by dotted lines

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* In discussions of cyclo-octanes this conformation has been called the ' boat–chair,' by an extension of cyclohexane terminology, which is not really appropriate and can be applied only to rings possessing at least mirror symmetry.[20] We suggest the term ' crown–saddle ' is preferable.

[17] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1423.

[18] M. Dobler, J. D. Dunitz, and A. Mugnoli, *Helv. Chim. Acta*, 1966, **49**, 2492.

[19] H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1968, **51**, 1514; P. Groth, *Acta Chem. Scand.*, 1967, **21**, 2695; J. v. Egmond and C. Romers, *Tetrahedron*, 1969, **25**, 2693.

[20] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1964, **86**, 4854; 1967, **89**, 7036.

[21] M. Bixon and S. Lifson, *Tetrahedron*, 1967, **23**, 769.

the various conformations and explain why the crown–saddle form (B) has not appeared more often in phosphazene systems.

It seems likely that, where the eight substituent groups in a cyclotetraphosphazene are not identical, the conformation found will be that which minimises repulsions between neighbouring substituents and hence that different geometrical isomers will choose different conformations.[1] As a corollary one might have expected (say) all β-*trans*-isomers of $N_4P_4R^1_4R^2_4$, irrespective of R^1 and R^2, to show a preference for one conformation, provided that the various R^1 and R^2 groups are similar in size. It is therefore curious that β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ possesses the crown–saddle conformation (B) while β-*trans*-$N_4P_4Cl_4Ph_4$ and β-*trans*-$N_4P_4(NHMe)_4Ph_4$ both have the chair conformation (D).[6,7] A molecular model of β-*trans*-$N_4P_4Cl_4(NMe_2)_4$ based on a chair conformation involves no undue steric interactions whereas, as mentioned above, the observed conformation involves a close approach of Cl(3) and Cl(4) which must be relieved by distortion. We can only suggest that the apparently less favourable crown–saddle conformation occurs because it facilitates packing of the molecules in the crystal lattice. The major part of the molecule, comprising the phosphazene ring and the dimethylamino-groups, is approximately planar (Figure 1) which would not be the case for a chair conformation (or for a pure crown or a pure saddle). This planar grouping occurs in layers roughly parallel to the (001) plane of the lattice, at z/c *ca.* $\frac{1}{4}$ and $\frac{3}{4}$, with the chlorine atoms of one molecule fitting into holes in the layers above and below (Figure 4). The packing within a layer is therefore controlled both by intermolecular $C \cdots C$ contacts (ranging from 3·67 Å upwards) and $C \cdots Cl$ contacts (from 3·57 Å upwards). The closest intermolecular $Cl \cdots Cl$ contacts occur between molecules separated by the c lattice translation: $Cl(1') \cdots Cl(4)$ 3·62 and $Cl(2') \cdots Cl(3)$ 3·54 Å (primed atoms at $x, y, 1 + z$). If we are correct in attributing the choice of conformation to crystal lattice forces, we might expect a different (or more than one) conformation to be found in solution.

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