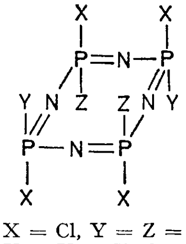
# Molecular Structures of Non-geminally Substituted Phosphazenes. Part V.[1] Crystal Structure of 2,*trans*-6-dichloro-2,4,4,6,8,8-hexakis(dimethylamino)cyclotetraphosphazatetraene

By **Graham J. Bullen** * and **Peter E. Dann**, Department of Chemistry, University of Essex, Colchester CO4 3SQ

Crystals of the title compound are triclinic, $a = 9{\cdot}93$, $b = 9{\cdot}39$, $c = 8{\cdot}78$ (all $\pm 0{\cdot}02$) Å, $\alpha = 114{\cdot}2$, $\beta = 114{\cdot}7$, $\gamma = 93{\cdot}4$ (all $\pm 0{\cdot}3$)°, space group $P\bar{1}$, $Z = 1$. The structure was determined from diffractometer *X*-ray intensity data and refined by full-matrix least squares to *R* 0·062 for 2359 reflexions. The molecule occupies a crystallographic centre of symmetry and the eight-membered phosphazene ring has the chair conformation with approximate symmetry $C_{2h}$ (2/*m*). There are two significantly different P–N bond lengths in the ring, 1·586 and 1·555 Å. The P–Cl bonds (2·100 Å) are considerably longer than those in $N_4P_4Cl_8$. Exocyclic P–N bond lengths range from 1·640 to 1·669 Å. P–N–P angles in the ring are 135·3 and 135·5°. The non-geminal dimethylamino-groups occupy equatorial positions, where they avoid close contact with the other dimethylamino-groups in the molecule.

IN cyclophosphazenes which contain non-geminal $\geqslant PCl(NMe_2)$ groups, co-operative electron withdrawal by chlorine and electron donation by nitrogen leads to longer P–Cl and shorter P–N exocyclic bonds than are found in geminal $\geqslant PCl_2$ and $\geqslant P(NMe_2)_2$ groups.[1-3] Thus the P–Cl bond length of 1·99 Å in $N_4P_4Cl_8$ [4,5] is increased in non-geminal isomers of $N_4P_4Cl_4(NMe_2)_4$ (Ia) and $N_4P_4Cl_6(NMe_2)_2$ (Ib) to 2·04 and 2·06 Å respectively. We have examined the molecular structure of $N_4P_4Cl_2(NMe_2)_6$ (Ic) because we expected the electron-donating effects of the six $NMe_2$ groups in the molecule to so enhance the ionic character of the P–Cl bonds that they would be even longer than in the examples cited. We find indeed that in (Ic) the bond length is 2·10 Å. This work also completes our program of determining the molecular structures of the series of compounds $N_4P_4Cl_{8-n}(NMe_2)_n$ ($n$ = 0, 2, 4, 6, and 8).



(I) a; X = Cl, Y = Z = NMe$_2$
b; X = Y = Cl, Z = NMe$_2$
c; X = Y = NMe$_2$, Z = Cl

Two isomers of composition $N_4P_4Cl_2(NMe_2)_6$ have been obtained by the reaction of dimethylamine with $N_4P_4Cl_8$.[6] The subject of this paper is the isomer with m.p. 168 °C to which the 2,*trans*-6-configuration had already been assigned on the basis of n.m.r. and basicity measurements.[7]

## EXPERIMENTAL

*Crystal Data*.—$C_{12}H_{36}Cl_2N_{10}P_4$, $M = 515{\cdot}29$, Triclinic, $a = 9{\cdot}93$, $b = 9{\cdot}39$, $c = 8{\cdot}78$ Å (all $\pm 0{\cdot}02$ Å), $\alpha = 114{\cdot}2$, $\beta = 114{\cdot}7$, $\gamma = 93{\cdot}4°$ (all $\pm 0{\cdot}3°$), $U = 651$ Å$^3$, $D_m = 1{\cdot}31$ g cm$^{-3}$ (by flotation), $Z = 1$, $D_c = 1{\cdot}32$, $F(000) = 272$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å; $\mu$(Mo-$K_\alpha$) = 5·7 cm$^{-1}$. Space group $P\bar{1}$ (No. 2).

Suitable crystals were grown from a solution in n-hexane at room temperature. The forms developed are the pinacoids {100}, {010}, {001}, and {0$\bar{1}$1}. The crystals are tabular on {100} with a roughly hexagonal cross-section when viewed along *a*. *X*-Ray intensities of the thirteen layers of reflexions *hk*0—12 were measured on a Philips PAILRED diffractometer using monochromated Mo-$K_\alpha$ radiation. These comprised all possible reflexions with $\sin\theta/\lambda \leqslant 0{\cdot}71$ Å, 2359 of which gave significant intensities [$I > 2\sigma(I)$]. The intensities were corrected for Lorentz and polarisation effects. As the crystal was of tabular

---

[1] Part IV, Graham J. Bullen and Peter E. Dann, *J.C.S. Dalton*, 1973, 1453.

[2] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, **B28**, 513, 3530.

[3] Part III, G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 2437.

[4] R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, 1962, **15**, 539.

[5] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 707.

[6] S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1963, 3236.

[7] V. B. Desai, R. A. Shaw, B. C. Smith, and D. Taylor, *Chem. and Ind.*, 1969, 1177.

shape, absorption corrections were also applied, the calculation being performed at the Atlas Computer Laboratory, Chilton, by use of the program 'Abscor.'

Least-squares refinement was carried out on the University of Essex PDP 10 computer with a program written by Dr. G. M. Sheldrick. Atomic scattering factors were calculated by the analytic function $f = C + \sum_{i=1}^{n} A_i \exp(-B_i \sin^2\theta/\lambda^2)$, the values of the parameters $A$, $B$, and $C$ being taken from ref. 8 for chlorine, phosphorus, nitrogen, and carbon ($n = 4$) and from ref. 9 for hydrogen ($n = 2$).

*Structure Determination.*—The positions of the phosphorus and chlorine atoms were deduced from the Patterson function. A centrosymmetric arrangement of the atoms in the unit cell was indicated by the occurrence of six large peaks in the asymmetric unit, which were attributed to double-weight vectors (two P ⋯ P and four P ⋯ Cl). The single-weight P ⋯ P and Cl ⋯ Cl vectors were also located. Thus, as a centrosymmetric molecule accounted satisfactorily for all the large Patterson peaks, it was concluded that the space group was $P\bar{1}$. The point $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ was chosen as the centre of the molecule.

The carbon and nitrogen atoms were located by use of the heavy-atom technique and the atomic positions were refined by full-matrix least squares with isotropic temperature factors until $R$ had dropped to 0·13. A difference-Fourier synthesis calculated at this stage failed to show clearly the positions of the hydrogen atoms in the methyl groups. Further refinement was therefore carried out, with the temperature factors of all the atoms except carbon allowed to become anisotropic. This reduced $R$ to 0·09 and a difference-Fourier synthesis now succeeded in giving the positions of the 18 hydrogen atoms. With these atoms inserted, and assigned isotropic thermal vibration parameters $(\overline{u^2})$ 0·013 Å$^2$ greater than those of the carbon atom to which they are bonded, the temperature factors of the carbon atoms were allowed to become anisotropic. Six cycles of refinement were carried out with the hydrogen atom parameters fixed. The weighting scheme used was $w = (A/|F_o|)^2$ for $|F_o| > A$, and $w = (|F_o|/A)^2$ for $|F_o| \leqslant A$, the value of $A$ being adjusted (final value 7·5 on an absolute scale) until the average $w\Delta^2$ for groups of reflexions $(\Delta = |F_o| - |F_c|)$ was almost constant over the whole range of $|F_o|$. The final $R$ is 0·062 for 2359 reflexions and $R'$ $[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ is 0·075. In the last cycle of refinement all parameter shifts were $< 0{\cdot}06\sigma$.

## RESULTS

The shape of the molecule and the numbering of the atoms are shown in Figure 1. The final atomic co-ordinates and thermal vibration parameters are given in Tables 1—3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20907 (11 pp., 1 microfiche).* Bond lengths are given in Table 4 and bond angles in Table 5. An attempt to analyse the anisotropic thermal parameters in terms of a rigid-body motion of the molecule was unsuccessful because the components of the librational tensor so produced had standard deviations too large for the results to be reliable. It is likely that a phosphazene ring with six dimethylamino-groups attached does not possess the rigidity for this treatment to be valid. Nor was it possible to confine the treatment to the phosphazene ring because the small number (4) of symmetry-independent atoms involved again leads to large standard deviations for the tensor components. The bond lengths could not therefore be corrected for librational error. The

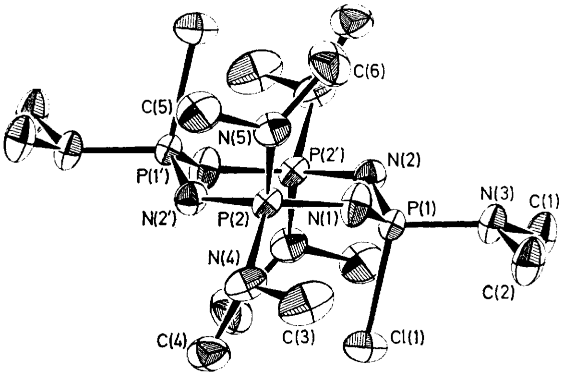


FIGURE 1 Molecular shape and numbering of the atoms. Primed and unprimed atoms are related by inversion through the molecular centre (at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$); thermal ellipsoids are scaled to include 30% probability

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Cl(1) | 6573(2) | 3262(2) | 2814(2) |
| P(1) | 5489(1) | 2926(1) | 4295(1) |
| P(2) | 2768(1) | 3854(1) | 2463(1) |
| N(1) | 3748(4) | 2732(4) | 3106(5) |
| N(2) | 6477(4) | 4244(4) | 6430(4) |
| N(3) | 5648(4) | 1144(4) | 4153(5) |
| N(4) | 2199(4) | 3392(4) | 199(5) |
| N(5) | 1154(4) | 3314(4) | 2439(5) |
| C(1) | 7172(6) | 1029(6) | 5263(8) |
| C(2) | 4727(7) | −322(5) | 2293(8) |
| C(3) | 1405(7) | 1669(7) | −1218(8) |
| C(4) | 3147(6) | 4177(7) | −263(7) |
| C(5) | −39(6) | 4115(8) | 1870(9) |
| C(6) | 1008(7) | 2580(8) | 3551(10) |

TABLE 2

Fractional co-ordinates ($\times 10^3$) and mean-square amplitudes of thermal vibration (Å$^2$, $\times 10^4$) assigned to hydrogen atoms

| | $x/a$ | $y/b$ | $z/c$ | $\overline{u^2}$ |
|---|---|---|---|---|
| H(11) * | 791 | 108 | 481 | 892 |
| H(12) | 757 | 189 | 644 | 892 |
| H(13) | 707 | −3 | 535 | 892 |
| H(21) | 365 | −27 | 179 | 879 |
| H(22) | 477 | −136 | 237 | 879 |
| H(23) | 519 | −27 | 154 | 879 |
| H(31) | 75 | 111 | −93 | 1028 |
| H(32) | 218 | 107 | −138 | 1028 |
| H(33) | 78 | 172 | −232 | 1028 |
| H(41) | 363 | 532 | 60 | 841 |
| H(42) | 255 | 419 | −138 | 841 |
| H(43) | 397 | 363 | −35 | 841 |
| H(51) | 3 | 509 | 288 | 943 |
| H(52) | 9 | 450 | 107 | 943 |
| H(53) | −106 | 341 | 133 | 943 |
| H(61) | 106 | 343 | 464 | 1028 |
| H(62) | 187 | 206 | 391 | 1028 |
| H(63) | 4 | 177 | 301 | 1028 |

* Atom H(*ij*) is attached to atom C(*i*).

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[9] J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

amplitudes of vibration corresponding to the thermal parameters listed in Table 3 are given in Table 6.

TABLE 3

Components $U_{ij}$ of thermal vibration tensors (Å², ×10⁴) at 19 ± 2 °C, with estimated standard deviations in parentheses

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Cl(1) | 764(8) | 824(8) | 651(7) | 308(6) | 445(7) | 138(6) |
| P(1) | 372(5) | 323(4) | 430(5) | 149(4) | 177(4) | 121(3) |
| P(2) | 299(4) | 386(5) | 386(5) | 109(4) | 125(4) | 86(3) |
| N(1) | 389(16) | 455(17) | 801(25) | 245(17) | 167(17) | 119(13) |
| N(2) | 541(19) | 415(15) | 415(16) | 126(13) | 184(15) | 87(14) |
| N(3) | 600(20) | 375(15) | 566(20) | 169(14) | 212(17) | 198(14) |
| N(4) | 481(18) | 676(22) | 427(18) | 98(16) | 169(15) | 89(16) |
| N(5) | 431(17) | 706(22) | 717(24) | 350(19) | 299(17) | 179(16) |
| C(1) | 789(33) | 685(29) | 953(40) | 434(29) | 355(30) | 435(27) |
| C(2) | 955(39) | 378(21) | 751(33) | 93(21) | 272(29) | 164(22) |
| C(3) | 791(38) | 930(41) | 583(31) | −83(28) | 197(28) | −64(31) |
| C(4) | 769(34) | 1006(38) | 558(28) | 417(27) | 338(26) | 351(30) |
| C(5) | 527(27) | 1165(45) | 1197(49) | 678(39) | 512(31) | 389(29) |
| C(6) | 843(41) | 961(41) | 1472(62) | 772(44) | 673(43) | 202(32) |

TABLE 4

Bond lengths (Å), with estimated standard deviations

| | | | |
|---|---|---|---|
| Endocyclic | | | |
| P(1)–N(1) | 1·552 | P(1)–Cl(1) | 2·100 |
| P(1)–N(2) | 1·557 | σ | 0·002 * |
| P(2)–N(1) | 1·589 | | |
| P(2)–N(2′) | 1·583 | N(3)–C(1) | 1·458 |
| σ | 0·003 * | N(3)–C(2) | 1·469 |
| | | N(4)–C(3) | 1·471 |
| Exocyclic | | N(4)–C(4) | 1·440 |
| P(1)–N(3) | 1·647 | N(5)–C(5) | 1·462 |
| P(2)–N(4) | 1·669 | N(5)–C(6) | 1·451 |
| P(2)–N(5) | 1·640 | σ | 0·006 |
| σ | 0·003 * | | |

* When comparing bond lengths with those in other structures σ(P–N) and σ(P–Cl) should be increased to 0·004 Å to allow for error in the unit-cell parameters. σ(N–C) will not be altered significantly.

TABLE 5

Bond angles (°). Estimated standard deviations are 0·2° for all angles at P atoms and 0·3° for angles at N atoms

| | | | |
|---|---|---|---|
| N(1)–P(1)–N(2) | 122·3 | Cl(1)–P(1)–N(1) | 106·9 |
| N(1)–P(2)–N(2′) | 119·1 | Cl(1)–P(1)–N(2) | 107·4 |
| P(1)–N(1)–P(2) | 135·3 | P(1)–N(3)–C(1) | 118·0 |
| P(1)–N(2)–P(2′) | 135·5 | P(1)–N(3)–C(2) | 118·5 |
| | | P(2)–N(4)–C(3) | 115·5 |
| Cl(1)–P(1)–N(3) | 103·8 | P(2)–N(4)–C(4) | 120·4 |
| | | P(2)–N(5)–C(5) | 117·9 |
| N(4)–P(2)–N(5) | 103·6 | P(2)–N(5)–C(6) | 124·2 |
| N(1)–P(1)–N(3) | 107·2 | C(1)–N(3)–C(2) | 112·7 |
| N(2)–P(1)–N(3) | 107·9 | C(3)–N(4)–C(4) | 113·4 |
| N(1)–P(2)–N(4) | 113·2 | C(5)–N(5)–C(6) | 114·1 |
| N(2′)–P(2)–N(4) | 102·5 | | |
| N(1)–P(2)–N(5) | 103·6 | | |
| N(2′)–P(2)–N(5) | 114·1 | | |

TABLE 6

Ranges of root-mean-square amplitudes (Å) of thermal vibration (at 19 °C) along the principal axes of the vibration ellipsoids

| | Minor | Medium | Major |
|---|---|---|---|
| Cl | 0·22 | 0·27 | 0·31 |
| P | 0·17 | 0·19 | 0·22—0·24 |
| N | 0·18—0·20 | 0·21—0·26 | 0·25—0·32 |
| C | 0·19—0·22 | 0·27—0·31 | 0·33—0·41 |

DISCUSSION

The molecular shape of 2,*trans*-6:2,4,4,6,8,8-$N_4P_4Cl_2(NMe_2)_6$ (Ic) is similar in many respects to that of 2,4,4,*trans*-6,8,8:2,6-$N_4P_4Cl_6(NMe_2)_2$ (Ib),[1] with the geminal $\geqslant PCl_2$ groups in the latter merely replaced by $\geqslant P(NMe_2)_2$ groups. Thus both have phosphazene rings in the chair conformation with strict crystallographic symmetry $C_i$ ($\bar{1}$) and approximate symmetry $C_{2h}$ ($2/m$). The torsion angles in the two rings (Figure 2) are also similar and in both cases six of the eight atoms in the ring are almost coplanar [see Table 7, plane (i)]. In $N_4P_4Cl_2(NMe_2)_6$ the remaining two atoms, P(1) and P(1′), lie 0·56 Å from this plane.

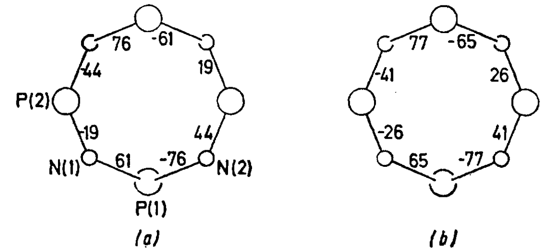


FIGURE 2 Torsion angles (°) in the phosphazene rings of (*a*) $N_4P_4Cl_2(NMe_2)_6$ and (*b*) $N_4P_4Cl_6(NMe_2)_2$

TABLE 7

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

Plane (i):
N(1), P(2), N(2), N(1′), P(2′), N(2′) $0·456X - 0·184Y - 0·871Z = 1·074$
[P(2) −0·053, N(1) 0·041, N(2) −0·043]
Plane (ii):
P(1), N(3), C(1), C(2) $0·463X - 0·054Y - 0·885Z = 1·742$
[P(1) 0·070, N(3) −0·220, C(1) 0·075, C(2) 0·075]
Plane (iii):
P(2), N(4), C(3), C(4) $0·762X - 0·646Y + 0·046Z = 0·055$
[P(2) 0·068, N(4) −0·217, C(3) 0·072, C(4) 0·078]
Plane (iv):
P(2), N(5), C(5), C(6) $0·403X + 0·759Y + 0·511Z = 2·664$
[P(2) 0·041, N(5) −0·129, C(5) 0·042, C(6) 0·045]

There is also a variation of *ca.* 0·03 Å in P–N bond length around the phosphazene ring (Figure 3) attributable to the differing abilities of the exocyclic groups to withdraw electrons, but of course the situation is the reverse of that in $N_4P_4Cl_6(NMe_2)_2$, the P–N bonds adjacent to the non-geminal $\geqslant PCl(NMe_2)$ group now being the shorter. The lengths of the exocyclic bonds provide further evidence that in the compounds $N_4P_4Cl_{8-n}(NMe_2)_n$ replacement of geminal by non-geminal groups leads to lengthening of P–Cl and shortening of P–N bonds (Table 8). As expected, the P–Cl bond in $N_4P_4Cl_2(NMe_2)_6$ is the longest (2·100 Å) in the series. Keat *et al.*[10] found an approximately linear relationship between the $^{35}Cl$ n.q.r. frequency (*x*) in

---

[10] R. Keat, A. L. Porte, D. A. Tong, and R. A. Shaw, *J.C.S. Dalton*, 1972, 1648.

TABLE 8

Lengths (Å) of exocyclic P–Cl and P–N bonds in cyclotetraphosphazenes

| | P–Cl | | P–N | |
|---|---|---|---|---|
| | gem | non-gem | gem | non-gem |
| $N_4P_4Cl_8$ [a] | 1·989(4),<br>1·992(4) | | | |
| $N_4P_4Cl_6(NMe_2)_2$ [b] | 2·009(3) | 2·062(3) | | 1·618(4) |
| $N_4P_4Cl_4(NMe_2)_4$ [c] | | 2·043(3) | | 1·626(6) |
| $N_4P_4Cl_2(NMe_2)_6$ [d] | | 2·100(4) | 1·654(4) | 1·647(4) |
| $N_4P_4(NMe_2)_8$ [e] | | | 1·679(7) | |

[a] *T*-form: ref. 5; *K*-form: ref. 4. [b] Ref. 1. [c] Ref. 3. [d] This work. [e] Ref. 13.

chlorocyclophosphazenes and the P–Cl bond length ($y$), *viz.* $x = (2{\cdot}355 - y)/0{\cdot}0128$.† An increase in the ionic character of the bond, causing bond lengthening, is accompanied by a decrease in the $^{35}$Cl n.q.r. frequency. Among the chlorophosphazenes studied[10] the lowest n.q.r. frequency was 23·30 MHz [for *cis*-non-geminal $N_3P_3Cl_3(NMe_2)_3$ at 293 K]. Application of this linear relationship to $N_4P_4Cl_2(NMe_2)_6$ suggests that the n.q.r. frequency for this compound will be lower still, probably near 21 MHz. Although the non-geminal exocyclic P–N bond length fits well the general pattern in Table 8, the geminal P–N bond lengths are not so satisfactory, the mean being derived from two rather disparate values.

TABLE 9

Endocyclic P–N bond lengths ($l$, Å) and bond angles (°) in the compounds $N_4P_4Cl_{8-n}(NMe_2)_n$

| | | | Endocyclic | Exocyclic | | |
|---|---|---|---|---|---|---|
| $n$ | at | $l$ | N–P–N | Cl–P–Cl | Cl–P–N | N–P–N |
| 2 (Ib) | $\geqslant PCl_2$ | 1·558 | 122·2 | 101·7 | | |
| | $\geqslant PCl(NMe_2)$ | 1·580 | 118·9 | | 107·9 | |
| 4 (Ia) | $\geqslant PCl(NMe_2)$ | 1·556 | 121·1 | | 105·2 | |
| 6 (Ic) | $\geqslant PCl(NMe_2)$ | 1·555 | 122·3 | | 103·8 | |
| | $\geqslant P(NMe_2)_2$ | 1·586 | 119·1 | | | 103·6 |

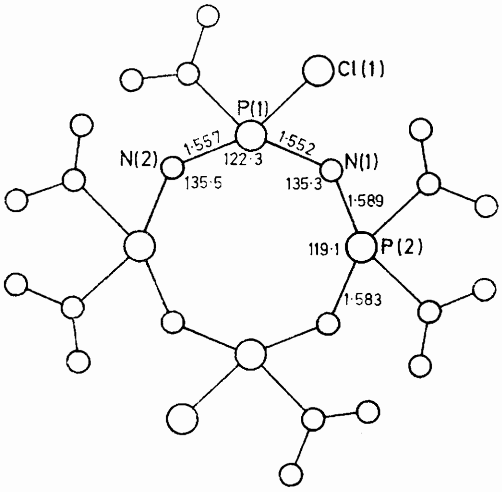


FIGURE 3 Variation of bond lengths (Å) and bond angles (°) in the phosphazene ring

Comparison of bond angles in $N_4P_4Cl_2(NMe_2)_6$ with those of related compounds (Table 9) shows a consistent pattern whereby (i) the larger endocyclic N–P–N angles lie between those endocyclic P–N bonds which are shorter and therefore of higher bond order, and (ii) the (exocyclic) Cl–P–N angle decreases as the endocyclic N–P–N angle at the same phosphorus atom increases. The P–N–P angles in $N_4P_4Cl_2(NMe_2)_6$ are equal (Table 5), in contrast to other eight-membered phosphazene rings with the chair conformation, which all contain P–N–P angles differing by several degrees.[1,5,11,12]

The $PNMe_2$ groups show small departures from planarity [Table 7, planes (ii)—(iv)] similar to those in $N_4P_4Cl_6(NMe_2)_2$ and $N_4P_4Cl_4(NMe_2)_4$. The non-geminal $NMe_2$ group is again oriented symmetrically, with its plane perpendicular to the Cl(1)–P(1)–N(3) plane, so equalising non-bonded contacts between chlorine and carbon atoms. In contrast, the $NMe_2$ planes in the geminal $\geqslant P(NMe_2)_2$ group are twisted relative to the

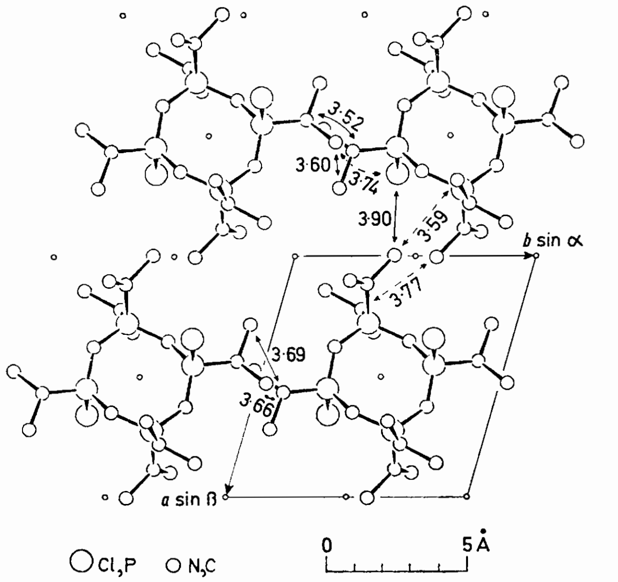


FIGURE 4 Projection of the structure down the $c$ axis with intermolecular distances (Å). Full arrows denote distances between molecules at the same $z$ height and broken arrows those between molecules differing in height by one $c$ lattice translation

---

† The denominator of this expression is given incorrectly in ref. 10 as $0{\cdot}12_8$. Professor Shaw informs us that it should be $0{\cdot}012_8$.

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

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

N(exo)–P–N(exo) plane (Figure 1), as in $N_4P_4(NMe_2)_8$[13] and $N_3P_3(NMe_2)_6$.[14]

Progressive replacement of chlorine by dimethylamino-groups in the series of compounds $N_4P_4Cl_{8-n}(NMe_2)_n$ leads to changes in the ring conformation (Table 10). In the chair and crown-saddle conformations there are exocyclic groups which may be described as equatorial and axial, and, as in cyclohexane derivatives, the latter positions are the more sterically crowded. In all three partially substituted derivatives [(I); a—c] the non-geminal $\geqslant$PCl($NMe_2$) groups are placed so that their chlorine atoms occupy axial positions and their $NMe_2$ groups equatorial positions. This lends support to the view that the phosphazene ring adopts a conformation which permits the more bulky groups to be placed equatorially where they cause less steric interference.[15] The contact between the chlorine atom and the $NMe_2$ groups attached to P(2) and P(2′) is not crowded, the shortest intramolecular distances [Cl(1) ··· N(5′) 3·62, Cl(1) ··· C(6′) 3·67, and Cl(1) ··· C(4) 3·77 Å] being similar to the shortest intermolecular Cl ··· C distances in this structure (3·74 Å, Figure 4) and in $N_4P_4Cl_6(NMe_2)_2$ (3·77 Å).

TABLE 10

Ring conformations in the compounds $N_4P_4Cl_{8-n}(NMe_2)_n$

| $n$ | Conformation |
|---|---|
| 0 | Saddle-boat or chair |
| 2 (Ib) | Chair |
| 4 (Ia) | Crown-saddle |
| 6 (Ic) | Chair |
| 8 | Saddle-boat |

The closest Cl ··· Me, Me ··· Me, N ··· Me, and N ··· N distances between molecules are shown in Figure 4; Me ··· Me contacts >3·60 Å are not shown, and nor are other intermolecular contacts >3·9 Å. These intermolecular distances are normal for van der Waals interaction.

We thank Professor R. A. Shaw (Birkbeck College, London) for supplying a sample of the phosphazene, the University of Essex Computing Centre and the Atlas Computer Laboratory, Chilton, for the use of their facilities, Dr. G. M. Sheldrick for making his computer program available, N. Lewis for the preparation of diagrams, and the S.R.C. for the award of a research studentship (to P. E. D.).

[3/2048 *Received, 4th October,* 1973]

---

[13] G. J. Bullen, *J. Chem. Soc.*, 1962, 3193.

[14] S. J. Rettig and J. Trotter, *Canad. J. Chem.*, 1973, **51**, 1295.

[15] Part II, G. J. Bullen and P. A. Tucker, *J.C.S. Dalton*, 1972, 1651.