Molecular Structures of Non-geminally Substituted Phosphazenes. Part IV.[1] Crystal Structure of 2,4,4,*trans*-6,8,8-Hexachloro-2,6-bis(dimethylamino)cyclotetraphosphazatetraene

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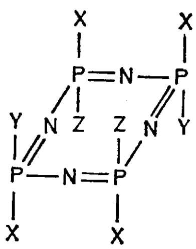
Crystals of the title compound (Ib) are triclinic, $a = 8{\cdot}55$, $b = 8{\cdot}68$, $c = 7{\cdot}51$ Å (all $\pm0{\cdot}02$ Å), $\alpha = 105{\cdot}3$, $\beta = 102{\cdot}0$, $\gamma = 114{\cdot}8°$ (all $\pm0{\cdot}3°$), space group $P\bar{1}$, $Z = 1$. The structure was determined from diffractometer *X*-ray intensity data by the heavy-atom method and refined by full-matrix least squares to *R* 0·053 for 2801 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, 1·580 and 1·558 Å. The P–Cl bonds in the non-geminal groups are considerably longer (2·062 Å) than those in the geminal groups (2·009 Å). The exocyclic P–N bond length is 1·618 Å. P–N–P angles in the ring are 130·9 and 137·6°. The dimethylamino-groups occupy equatorial positions, in which their intramolecular contact with the chlorine atoms is minimised.

IN the description[1] of the molecular structure of 2,*cis*-4,*trans*-6,*trans*-8:2,4,6,8-$N_4P_4Cl_4(NMe_2)_4$ (Ia) it was noted



(I) a; X = Cl, Y = Z = NMe_2
b; X = Y = Cl, Z = NMe_2
c; X = Cl, Y = Z = Ph
d; X = NHMe; Y = Z = Ph

that in the non-geminal $\geqslant PCl(NMe_2)$ group the P–Cl bond is markedly longer than in $N_4P_4Cl_8$ [2,3] which contains geminal $\geqslant PCl_2$ and the P–N bond is shorter than in $N_4P_4(NMe_2)_8$ [4] which contains geminal $\geqslant P(NMe_2)_2$. The cause of this was considered to be a co-operative electron withdrawal by chlorine and electron-donation by nitrogen.[1] In order to examine this effect further we decided to study the molecular structures of non-geminal isomers of $N_4P_4Cl_6(NMe_2)_2$ and $N_4P_4Cl_2(NMe_2)_6$, because the $\geqslant PCl(NMe_2)$ group may then be compared directly with geminal groups in the same molecule and we would expect to find in the former molecule an even shorter exocyclic P–N bond and in the latter an even longer P–Cl bond than hitherto.

The present paper describes the results for 2,2,4,*trans*-6,8,8-hexachloro-2,6-bis(dimethylamino)cyclotetraphosphazatetraene (Ib). These results are also of interest in respect of the factors affecting phosphazene ring conformation, which varies with the nature and configuration of the substituents.[1,5] The reaction of dimethylamine with $N_4P_4Cl_8$ produces five isomers of composition $N_4P_4Cl_6(NMe_2)_2$.[6-9] The compound whose structure is described in this paper is the isomer with m.p. 171 °C to which the 2,*trans*-6-configuration has already been assigned.[8,9]

EXPERIMENTAL

Crystal Data.—$C_4H_{12}Cl_6N_6P_4$, $M = 480{\cdot}75$, Triclinic, $a = 8{\cdot}55$, $b = 8{\cdot}68$, $c = 7{\cdot}51$ Å (all $\pm0{\cdot}02$ Å), $\alpha = 105{\cdot}3$, $\beta = 102{\cdot}0$, $\gamma = 114{\cdot}8°$ (all $\pm0{\cdot}3°$), $U = 454$ Å^3, $D_m = 1{\cdot}72$ g cm^{-3} (by flotation), $Z = 1$, $D_c = 1{\cdot}76$, $F(000) = 240$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 13·1 cm^{-1}. Space group $P\bar{1}$ (No. 2).

Suitable crystals were grown from a solution in n-pentane at room temperature. The forms best developed are the pinacoids {100}, {010}, and {001}. The crystals are roughly equidimensional in cross-section, but slightly elongated along *c*. *X*-Ray intensities of the thirteen layers of reflexions, *hk*0—12 were measured on a Philips PAILRED diffractometer by use of monochromated Mo-K_α radiation. These comprised all possible reflexions with $\sin\theta/\lambda \leqslant 0{\cdot}85$ Å^{-1}, 2801 of which gave statistically significant intensities $[I > 2\sigma(I)]$. Intensities were corrected for Lorentz and polarisation effects, but not for absorption.

Least-squares refinement was carried out on the University of Essex PDP 10 computer with a program written by G. M.

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Sheldrick. Atomic scattering factors were calculated by the analytic function $f = C + \sum_{i=1}^{4} A_i \exp(-B_i \sin^2 \theta/\lambda^2)$, the parameters A, B, and C being taken from ref. 10 for chlorine, phosphorus, nitrogen, and carbon, and from ref. 11 for hydrogen.

Structure Determination.—The positions of the phosphorus and chlorine atoms were deduced from the Patterson function. A centrosymmetric arrangement of the four phosphorus atoms in the unit cell was indicated by the occurrence of two double- and two single-weight phosphorus–phosphorus peaks in the asymmetric unit. All the chlorine atoms in the molecule were also located from peaks assigned to phosphorus–chlorine and chlorine–chlorine vectors. As a centrosymmetric molecule accounted satisfactorily for all the large Patterson peaks, it was concluded that the space group was $P\bar{1}$.

The carbon and nitrogen atoms were located by use of the heavy-atom technique and the atomic positions were refined

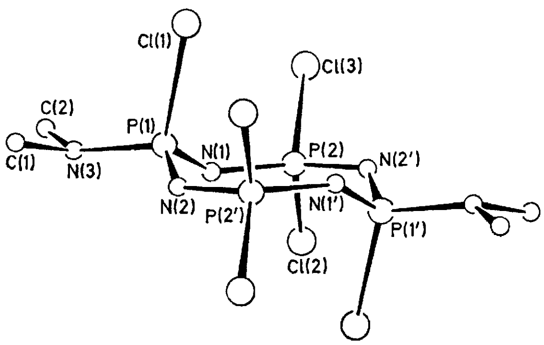

FIGURE 1 Molecular shape and numbering of the atoms. A primed atom is related to the corresponding unprimed atom by inversion through the molecular centre, at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

by least squares using isotropic temperature factors until R had dropped to 0·16. During the refinement individual layer scale factors were allowed to vary relative to each other by up to 3%. A difference-Fourier synthesis calculated at this stage showed the hydrogen atoms of one of the methyl groups clearly but failed to locate those in the other. With the three hydrogens inserted and assigned isotropic temperature factors 1Å^2 greater than those of the carbon atom to which they are attached, the temperature factors of all other atoms except carbon were allowed to become anisotropic. Further refinement reduced R to 0·063, and a difference-Fourier synthesis calculated at this stage gave the positions of the hydrogen atoms in the second methyl group. The carbon atom temperature factors were now allowed to become anisotropic. The weighting scheme $w = (A/|F_o|)^2$ if $|F_o| > A$ and $w = (|F_o|/A)^2$ if $|F_o| \leqslant A$ was also introduced, the value of A being adjusted (final value 6·5 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 $|F_o|$. Nine cycles of refinement were carried out with the hydrogen atom parameters fixed. The final R is 0·053 for 2801 reflexions and $R'[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ is 0·057. In the last cycle of refinement all parameter shifts were $<0{\cdot}069\sigma$.

RESULTS

The shape of the molecule and the numbering of the atoms are shown in Figure 1. The final atomic co-ordinates and temperature factor parameters are given in Tables 1—3. Observed and calculated structure factors are listed in

TABLE 1

Fractional atomic co-ordinates with estimated standard deviations in parentheses

	$10^5x/a$	$10^5y/b$	$10^5z/c$
Cl(1)	72039(12)	32181(12)	44819(13)
Cl(2)	168(10)	17355(14)	21338(14)
Cl(3)	21648(15)	−371(9)	37448(14)
P(1)	58509(8)	41758(8)	28890(9)
P(2)	25784(8)	23882(8)	36733(9)
	$10^4x/a$	$10^4y/b$	$10^4z/c$
N(1)	3714(3)	2886(3)	2340(4)
N(2)	6766(4)	6306(3)	4131(4)
N(3)	6221(3)	3896(3)	837(3)
C(1)	8024(5)	5165(6)	869(5)
C(2)	5254(6)	2073(5)	−773(5)

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) *	841	643	170	826
H(12)	796	517	−39	826
H(13)	894	481	131	826
H(21)	568	123	−49	842
H(22)	390	151	−107	842
H(23)	556	230	−188	842

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

TABLE 3

Components U_{ij} of thermal vibration tensors (Å^2, $\times 10^4$) with estimated standard deviations, at 19 ± 2 °C

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	662(5)	723(5)	719(5)	374(4)	222(4)	469(4)
Cl(2)	335(3)	825(6)	751(5)	120(5)	136(3)	211(4)
Cl(3)	983(7)	312(3)	781(6)	190(3)	316(5)	227(4)
P(1)	354(3)	341(3)	380(3)	122(2)	169(2)	179(2)
P(2)	348(3)	289(3)	453(3)	86(2)	161(3)	111(2)
N(1)	425(12)	557(13)	542(13)	176(11)	211(11)	195(10)
N(2)	648(15)	392(11)	519(13)	127(10)	240(12)	218(11)
N(3)	505(12)	498(12)	479(12)	152(10)	254(10)	245(10)
C(1)	705(22)	902(26)	705(22)	382(20)	458(19)	323(20)
C(2)	936(27)	625(19)	523(18)	60(15)	351(18)	318(19)

TABLE 4

Bond lengths (Å) with estimated standard deviations

(a) Derived from the least-squares refinement

(i) Endocyclic			
P(1)–N(1)	1·577	P(1)–Cl(1)	2·054
P(1)–N(2)	1·572	P(2)–Cl(2)	2·003
P(2)–N(1)	1·553	P(2)–Cl(3)	2·001
P(2)–N(2′)	1·554	σ	0·001
σ	0·002		
		N(3)–C(1)	1·461
(ii) Exocyclic		N(3)–C(2)	1·457
P(1)–N(3)	1·614	σ	0·004
σ	0·002		

(b) Corrected for molecular oscillations

(i) Endocyclic			
P(1)–N(1)	1·582	P(1)–Cl(1)	2·062
P(1)–N(2)	1·577	P(2)–Cl(2)	2·010
P(2)–N(1)	1·557	P(2)–Cl(3)	2·008
P(2)–N(2′)	1·558	σ	0·003
σ	0·004 *		
		N(3)–C(1)	1·466
(ii) Exocyclic		N(3)–C(2)	1·462
P(1)–N(3)	1·618	σ	0·004
σ	0·004		

* The σ values have been enlarged to allow for error in the unit-cell parameters.

Supplementary Publication No. SUP 20701 (13 pp., 1 microfiche).* Bond lengths are given in Table 4 and bond angles in Table 5.

TABLE 5

Bond angles (°). Estimated standard deviations are 0·1° for all angles at P atoms and 0·2° for angles at N atoms

N(1)–P(1)–N(2)	118·9	Cl(1)–P(1)–N(1)	107·1
N(1)–P(2)–N(2′)	122·2	Cl(1)–P(1)–N(2)	106·9
		Cl(2)–P(2)–N(1)	105·4
P(1)–N(1)–P(2)	130·9	Cl(2)–P(2)–N(2′)	111·2
P(1)–N(2)–P(2′)	137·6	Cl(3)–P(2)–N(1)	109·4
		Cl(3)–P(2)–N(2′)	105·2
Cl(2)–P(2)–Cl(3)	101·7		
		P(1)–N(3)–C(1)	118·8
Cl(1)–P(1)–N(3)	107·9	P(1)–N(3)–C(2)	120·8
N(1)–P(1)–N(3)	107·1	C(1)–N(3)–C(2)	114·6
N(2)–P(1)–N(3)	108·4		

TABLE 6

Translational (**T**/Å²) and librational (**ω**/deg.²) tensors for the molecule (see text for definition of the molecular axial system)

$$\boldsymbol{T} \quad \begin{pmatrix} 0{\cdot}031(3) & -0{\cdot}007(2) & 0{\cdot}002(3) \\ & 0{\cdot}058(2) & 0{\cdot}008(3) \\ & & 0{\cdot}056(4) \end{pmatrix}$$

$$\boldsymbol{\omega} \quad \begin{pmatrix} 11{\cdot}1(10) & 2{\cdot}2(12) & -0{\cdot}6(8) \\ & 15{\cdot}2(15) & 1{\cdot}4(12) \\ & & 5{\cdot}7(9) \end{pmatrix}$$

An analysis of the anisotropic thermal parameters in terms of a rigid-body motion of the whole molecule gave the translational and librational tensors shown in Table 6. These tensors are referred to orthogonal molecular axes chosen with the origin at the molecular centre, X along the P(2) · · · P(2′) line, and Z perpendicular to the mean plane (i) listed in Table 7. Since the off-diagonal elements of **ω** are not significantly different from zero, the librations can be described satisfactorily in terms of the molecular axes chosen. The libration with the largest amplitude (3·9°) is about the axis approximately parallel to the length of the molecule. Bond lengths corrected for the effect of these molecular oscillations [12] are given in Table 4(*b*).

TABLE 7

Equations of mean planes through sets of atoms and distances (Å) of the 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): N(1), P(2), N(2′), N(1′), P(2′), N(2)

$$0{\cdot}535X - 0{\cdot}774Y + 0{\cdot}339Z = 0{\cdot}907$$

[P(2) −0·022, N(1) 0·017, N(2) −0·018]

Plane (ii): P(1), N(3), C(1), C(2)

$$0{\cdot}523X - 0{\cdot}745Y + 0{\cdot}414Z = 1{\cdot}459$$

[P(1) 0·051, N(3) −0·158, C(1) 0·053, C(2) 0·054]

DISCUSSION

Ring Shape.—As the single molecule in the unit cell occupies a crystallographic centre of symmetry (at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$), the compound must be the 2,*trans*-6-isomer and the previous assignment of structure [8] is confirmed. The phosphazene ring has a chair conformation (Figure 1) and, like the ring in the T form of $N_4P_4Cl_8$,[3] has the approximate symmetry C_{2h} (2/*m*). The diad axis passes through P(2) and P(2′) and the mirror plane is that containing P(1), P(1′), and their four exocyclic ligand atoms. The approximate C_{2h} symmetry extends also to the exocyclic chlorine atoms and dimethylamino-groups. Six of the eight atoms in the ring [N(1), P(2), N(2′), N(1′), P(2′), and N(2)] are almost coplanar [Table 7, plane (i)], the deviations from their mean plane being only 0·02 Å. The other two atoms, P(1) and P(1′), lie 0·61 Å from this plane. The departure from exact C_{2h} symmetry is shown by the inequality of the P–N–P angles at N(1) and N(2) (Table 5) and by the differences between the torsion angles in the ring (Figure 2). True C_{2h} symmetry would require the torsion angles of the two bonds meeting in a given phosphorus atom to be equal in magnitude. The ring shape is almost identical to that of β-*trans*-$N_4P_4Cl_4Ph_4$ (Ic) and T-$N_4P_4Cl_8$,[3,13] and is much less distorted than that of β-*trans*-$N_4P_4(NHMe)_4Ph_4$ (Id).[14]

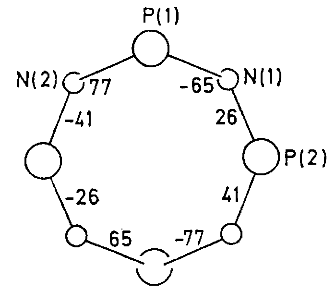

FIGURE 2 Torsion angles (°) in the phosphazene ring

Bond Lengths and Angles.—There are two different lengths for the P–N bonds in the ring, those adjacent to P(1) being *ca.* 0·02 Å longer than those adjacent to P(2) (Figure 3). The same effect was found [15] in 2,2,6,6-tetrafluoro-4,4,8,8-tetramethylcyclotetraphosphazatetraene ($N_4P_4F_4Me_4$), where the bonds adjacent to methyl-substituted phosphorus are longer than those adjacent to fluoro-substituted phosphorus. As with $N_4P_4F_4Me_4$ the variation in length results from the differing abilities of the exocyclic groups to withdraw electrons. At P(2) the two chlorine atoms are strongly electron-withdrawing, so promoting the transfer of electrons from adjacent nitrogen atoms into the P–N π-bonding system. At P(1) donation of electrons from the exocyclic nitrogen atom has the opposite effect, so reducing the π-character of the adjacent ring bonds. The P(2)–N bond lengths are almost exactly the same as in T-$N_4P_4Cl_8$ (1·559 Å) [3] and the P(1)–N lengths the same as in $N_4P_4(NMe_2)_8$ (1·58 Å).[4] Surprisingly, the mean cyclic P–N length in (Ia) is shorter, 1·556 Å.[1]

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

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

[15] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 569.

(Ib) Also exhibits two different P–Cl bond lengths (Figure **3** and Table **4**). The lengths of the bonds at the geminally substituted P(2) are again much the same as in $N_4P_4Cl_8$ but the P(1)–Cl(1) bond is **0·05** Å longer. When the exocyclic bond lengths are compared (Table 8) with those in other cyclotetraphosphazenes containing chloro- and dimethylamino-groups, it is seen that replacement of geminal by non-geminal groups produces longer P–Cl and shorter P–N bonds owing to co-operative electron-donation by nitrogen and electron withdrawal by chlorine at a non-geminal centre.[1,5] (Ib) Shows this effect most clearly in having two different P–Cl bond lengths. The shortening of the exocyclic P–N bond is further enhanced by inductive effects from the adjacent geminal $\geqslant PCl_2$ groups, so making it the shortest in the series, as expected.

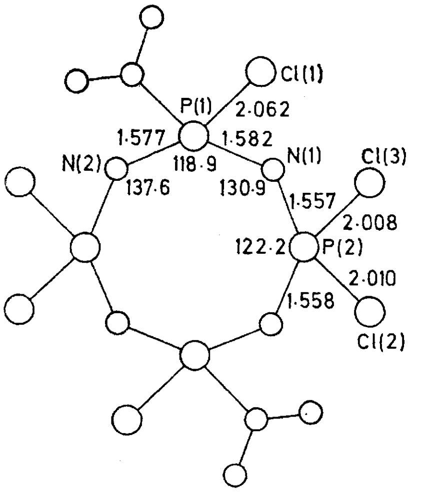

FIGURE 3 Variation of bond lengths (Å) and angles (°) in the phosphazene ring and of the P–Cl bond lengths

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), 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)
$N_4P_4(NMe_2)_8$ [d]			1·679(7)	

[a] *T*-form, ref. 3; *K*-form, ref. 2. [b] (Ib), This work. [c] (Ia), ref. 1. [d] Ref. 4.

The significant difference between the angles N(1)–P(1)–N(2) and N(1)–P(2)–N(2′) is compatible with the greater π-character of the cyclic bonds adjacent to P(2). The larger endocyclic angle is accompanied by a small exocyclic angle (Cl–P–Cl **101·7°**) and *vice versa*. The occurrence of two entirely different P–N–P angles is a usual feature of eight-membered phosphazene rings having the chair conformation.[3,13,14] Clearly the size of the P–N–P angle is not closely controlled by the electronic structure of the molecule.

The $PNMe_2$ group is almost planar, the deviations of the atoms from their mean plane [Table 7, plane (ii)] being comparable to those for the most planar of the four $PNMe_2$ groups in (Ia). The NMe_2 group is orientated symmetrically, the two Cl–P–N–C torsion angles being 76° (+ and −). This symmetrical orientation, which is also found in (Ia), probably results from equalisation of non-bonded contacts between chlorine and carbon atoms [Cl(1) ··· C(1) **3·60**, Cl(1) ··· C(2) **3·63** Å]. The choice of the axial position for the chlorine atom attached to P(1) and the equatorial position for the NMe_2 group (Figure 1) follows the pattern found in previous studies in this series whereby the more bulky groups go to the equatorial positions, *e.g.* in (Ia) or 2,*cis*-4,*cis*-6,*cis*-8:2,4,6,8-$N_4P_4Cl_4Ph_4$. The intramolecular Cl ··· Cl distances [Cl(1) ··· Cl(2′) **3·76**, and Cl(1) ··· Cl(3) **3·85** Å] are comparable to the corresponding contacts in these other two chlorophosphazenes.

Intermolecular Distances.—The closest Cl ··· Cl, Cl ··· CH_3, N ··· CH_3, and N ··· N distances between molecules are shown in Figure 4, and there is in addition Cl(1) ··· Cl(2) (at $1 + x, y, z$) **3·70** Å which is not marked. All other intermolecular contacts are $\geqslant$**3·9** Å, and the closest $CH_3 \cdots CH_3$ contact (not marked) is **3·95** Å.

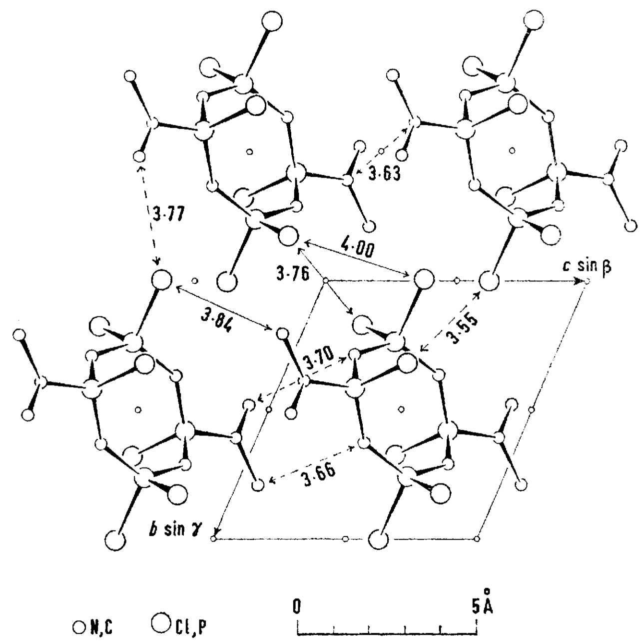

FIGURE 4 Projection of the structure down the *a* axis. Distances (Å) marked by full arrows are between molecules at the same *x* height and those marked by broken arrows are between molecules differing in height by one *a* lattice translation

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