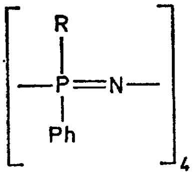
Molecular Structures of Non-geminally Substituted Phosphazenes. Part I. Crystal Structure of 2,*cis*-4,*trans*-6,*trans*-8-Tetrakismethylamino-2,4,6,8-tetraphenylcyclotetraphosphazene

By **G. J. Bullen** * and **P. R. Mallinson,** Department of Chemistry, University of Essex, Colchester, Essex

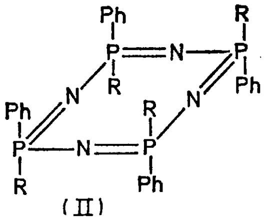
The crystal structure of the title compound has been determined from *X*-ray diffractometer intensity data and refined by least-squares methods to *R* 0·068 for 2913 reflexions. The crystals (γ-modification, m.p. 130·5°) are triclinic with a = 10·88 ± 0·03, b = 11·37 ± 0·03, c = 6·30 ± 0·02 Å; α = 95·7°, β = 100·2°, γ = 85·4° (all ±0·2°); Z = 1, space group $P\bar{1}$. The molecule occupies a crystallographic centre of symmetry and the phosphazene ring has the chair conformation, with approximate symmetry $2/m$ (C_{2h}). Mean bond lengths (Å) are: P–N(cyclic) 1·593, P–N(exocyclic) 1·672, and P–C 1·808. There are two different P–N–P angles in the ring: 124·6 and 131·3°. The molecule is very similar in shape to that of its parent compound $N_4P_4Cl_4Ph_4$.

PHOSPHONITRILIC chlorides $[NPCl_2]_n$ undergo substitution reactions to give both geminal and non-geminal series of derivatives which display positional, geometrical, and conformational isomerism.[1] The molecular structures of several geminally substituted trimeric and tetrameric cyclic phosphazenes have been determined.[2-5] We now report the crystal structure of 2,*cis*-4,*trans*-6,*trans*-8-tetrakismethylamino-2,4,6,8-tetraphenylcyclotetraphosphazene, the first of a series of determinations for non-geminal derivatives, which show differences in both configuration and conformation of the phosphazene ring. The only phosphazene for which conformational isomerism has been demonstrated is $(NPCl_2)_4$.[6,7]



$$\left[-\overset{R}{\underset{Ph}{P}}=N- \right]_4$$

(I)



(II)

$N_4P_4(NHMe)_4Ph_4$ (I; R = NHMe) is formed by the reaction of 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazene (I; R = Cl) with methylamine.[8] $N_4P_4Cl_4Ph_4$ itself exists as three isomers, *A*, *B*, and *C*,[8] of which *A* (m.p. 260—263 °C) has been shown to possess the centrosymmetric 2,*cis*-4,*trans*-6,*trans*-8-structure (II; R = Cl) † by ^1H n.m.r. spectra of derivatives[9] and by its crystal structure.[10] All three isomers give methylamino-derivatives. Isomer *A* gives a derivative (II; R = NHMe) which crystallises as four polymorphic modifications,[8,10,11] and this paper describes the structure of the γ-form (m.p. 130·5 °C). The crystal structure of (II; R = Cl) will be described fully in a later paper. Preliminary results for both compounds have already been reported.[10]

EXPERIMENTAL

Crystal Data.—$C_{28}H_{36}N_8P_4$, M = 608·55, Triclinic, a = 10·88 ± 0·03, b = 11·37 ± 0·03, c = 6·30 ± 0·02 Å, α = 95·7°, β = 100·2°, γ = 85·4° (all angles ±0·2°), U = 762 Å^3, D_m = 1·33 (by flotation), Z = 1, D_c = 1·33, $F(000)$ = 320. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 2·85 cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

---

† Hereafter 2,*cis*-4,*trans*-6,*trans*-8- will be abbreviated to β-*trans*.

[1] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

[2] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1965, **19**, 693; 1966, **21**, 375.

[3] C. W. Allen, J. B. Faught, T. Moeller, and I. C. Paul, *Inorg. Chem.*, 1969, **8**, 1719.

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

[5] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 569, 573.

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

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

[8] R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 1962, 5004.

[9] B. Grushkin, A. J. Berlin, J. L. McClanahan, and R. G. Rice, *Inorg. Chem.*, 1966, **5**, 172.

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

[11] G. J. Bullen and R. L. Valente, *Acta Cryst.*, 1963, **A16**, 72

The γ-modification of $N_4P_4(NHMe)_4Ph_4$, m.p. 130·5 °C, is obtained from benzene–light petroleum (b.p. 60—80 °C) solution at room temperature,[10] as transparent, acicular crystals (elongated along *c*) with an octagonal cross-section, displaying the forms {100}, {010}, {110}, $\{\bar{1}10\}$, and {001}. Crystallisation from toluene gives transparent crystals with a slightly different habit which become opaque and white when left in the air. Their *X*-ray diffraction patterns and density are different from those of the γ-form and it seems most probable that they contain solvent of crystallisation which escapes from the lattice when in the air. A single crystal of the γ-form of dimensions 0·08 × 0·08 × 1 mm was used for the measurement of 5112 independent reflexions at room temperature (*ca.* 24 °C) in nine layers (*hk*0—8) on a Philips PAILRED diffractometer with monochromatised Mo-K_α radiation. These comprised all possible reflexions with $\sin\theta/\lambda \leqslant 0·75$ Å^{-1}, 2913 of which had $I > 2\sigma(I)$, the remaining 2199 being considered unobserved. The intensities were measured by the ω-scan method; Lorentz and polarisation corrections, but no absorption corrections, were applied. The unit-cell parameters are those reported by Bullen and Valente.[11] Although γ is an acute angle, this unit cell was used in preference to the reduced cell because the parameters of the latter include a longer axis (15·09 Å) and an angle of 134°. Our *a, b,* and *c* are the three shortest lattice translations.

The least-squares refinement was carried out at the Atlas Computer Laboratory, Chilton, Didcot, Berkshire. Atomic scattering factors were taken from ref. 12. The principal computer programmes used are listed in ref. 13.

Structure Determination.—A notable feature of the *X*-ray pattern is that, although the crystal is triclinic, the *hk*0 reciprocal lattice section shows pseudo-four-fold symmetry, both in the positions and intensities of the reflexions. This suggested that the phosphazene ring is orientated approximately perpendicular to the *c* axis, and this deduction enabled the structure to be solved first in projection along *c* by the heavy-atom technique. A complete solution was then obtained from the three-dimensional Patterson function, the structure factors having been placed on an approximate absolute scale by Wilson's method.[14] A centrosymmetric arrangement of the four phosphorus atoms in the unit cell was indicated by the occurrence of two double-weight and two single-weight phosphorus–phosphorus peaks. All the carbon and nitrogen atoms in the molecule were also located from peaks assigned to phosphorus–carbon and phosphorus–nitrogen vectors. As a centrosymmetric molecule accounted satisfactorily for all the Patterson peaks, it was concluded that the space group was $P\bar{1}$.

The first structure-factor calculation gave *R* 0·37 (excluding unobserved reflexions) which was reduced to 0·29 after two cycles of Fourier refinement using reflexions for which $|F_c| > 0·5\,|F_o|$. Three cycles of least-squares refinement of scale, positional, and individual isotropic thermal parameters brought *R* to 0·096. For the third cycle the positions of the hydrogen atoms in the phenyl groups were estimated from the molecular geometry assuming C–H bond length 1·08 Å, and then included in the calculation but not refined. A difference Fourier synthesis calculated at this stage showed clearly the positions of the hydrogen atoms in the NH groups and one hydrogen atom in each methyl group, giving sufficient information for co-ordinates to be calculated for the remaining hydrogen atoms assuming a tetrahedral disposition.

For the anisotropic refinement the nine layers of reflexions were all placed on the same scale as the measurement of standard reflexions had shown that the diffractometer data were all measured under constant conditions. The weighting scheme used [$w = x\,.\,y$, where $x = 30/|F_o|$ if $|F_o| > 30$ (on absolute scale) but otherwise $x = 1$, and $y = \sin\theta/0·3$ if $\sin\theta < 0·3$ but otherwise $y = 1$] gave similar average values of $w\Delta^2$ for various ranges of $|F_o|$ or $\sin\theta$. *w* Was also put equal to zero if $|F_o| > 3|F_c|$. The overall scale-factor, positional, and anisotropic thermal parameters of all atoms except hydrogen were refined in eight cycles. Because of a limitation on computer store all parameters could not be varied simultaneously and so various sets were kept fixed in successive cycles (equivalent to using a normal matrix with large diagonal blocks). In the later cycles oscillations of atomic positions were damped by halving the parameter shifts.

The final *R* is 0·068 for 2913 reflexions. In the last cycle of least squares all shifts were $<0·24\sigma$ and $0·8\sigma$ for the positional and thermal parameters respectively. A difference Fourier synthesis calculated from the final structure factors weighted according to the least-squares weights showed no fluctuations $> \pm 0·4$ eÅ^{-3}.

RESULTS

The atomic co-ordinates and thermal vibration parameters with their estimated standard deviations are listed in Tables 1—3. The hydrogen atoms were given an isotropic temperature factor with *B* 5 Å^2, equivalent to $(\overline{u^2})^{\frac{1}{2}}$ 0·25 Å. The root-mean-square amplitudes of vibration along the principal axes of the vibration ellipsoids lie in the range 0·14—0·18 Å for the phosphorus atoms, 0·15—0·22 Å for nitrogen, and 0·15—0·39 Å for carbon.

TABLE 1

Atomic co-ordinates (as fractions of unit-cell edges) with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
P(1)	−0·06756(8)	0·15925(8)	0·01896(16)
P(2)	0·15286(8)	0·05088(8)	0·24672(16)
N(1)	0·0319(3)	0·1408(3)	0·2336(6)
N(2)	0·1607(3)	−0·0576(3)	0·0694(5)
N(3)	0·0010(3)	0·1896(3)	−0·1863(6)
N(4)	0·1727(3)	0·0045(3)	0·4938(6)
C(1)	−0·1617(3)	0·2919(3)	0·0854(7)
C(2)	−0·2490(5)	0·3388(4)	−0·0792(8)
C(3)	−0·3164(5)	0·4460(5)	−0·0386(10)
C(4)	−0·2970(5)	0·5052(4)	0·1645(10)
C(5)	−0·2126(5)	0·4588(4)	0·3283(9)
C(6)	−0·1431(5)	0·3532(4)	0·2900(8)
C(7)	0·2878(3)	0·1320(3)	0·2393(6)
C(8)	0·3279(5)	0·2148(5)	0·4062(10)
C(9)	0·4293(6)	0·2809(5)	0·3983(12)
C(10)	0·4915(4)	0·2646(4)	0·2248(10)
C(11)	0·4536(5)	0·1826(6)	0·0593(10)
C(12)	0·3528(5)	0·1152(5)	0·0664(8)
C(13)	0·0723(4)	0·2949(4)	−0·1671(9)
C(14)	0·2811(5)	−0·0730(4)	0·5678(8)

---

[12] 'International Tables for *X*-Ray Crystallography,' Vol. 3, Kynoch Press, Birmingham, 1962, pp. 202, 203.

[13] Computer programmes used: '*X*-Ray '63 System,' compiled by J. M. Stewart and D. F. High, University of Maryland Technical Report TR 64 6: programmes FOURR for Fourier synthesis, ORFLS for least-squares refinement, and BONDLA for bond lengths and angles; a PAILRED Data Reduction Programme, by P. R. Mallinson.

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

Observed and calculated structure factors are listed in Supplementary Publication No. 20359 (7 pp., 1 microfiche).† Of the 2199 unobserved reflexions, 10 gave $|F_o|$ values greater than twice the $|F_o|$ corresponding to the minimum significant intensity.

TABLE 2

Co-ordinates of hydrogen atoms used for the final structure-factor calculations.

	x/a	y/b	z/c
H(1,2) *	−0·2646	0·2910	−0·2386
H(2,3)	−0·3845	0·4838	−0·1661
H(3,4)	−0·3501	0·5885	0·1927
H(4,5)	−0·2006	0·5064	0·4883
H(5,6)	−0·0742	0·3182	0·4181
H(6,8)	0·2800	0·2265	0·5461
H(7,9)	0·4461	0·3377	0·5455
H(8,10)	0·5656	0·3194	0·2080
H(9,11)	0·5043	0·1710	−0·0756
H(10,12)	0·3224	0·0499	−0·0657
H(11,13)	0·0843	0·3002	−0·3333
H(12,13)	0·1648	0·2782	−0·0676
H(13,13)	0·0160	0·3734	−0·1156
H(14,14)	0·2795	−0·1445	0·5000
H(15,14)	0·3670	−0·0335	0·5521
H(16,14)	0·2888	−0·0816	0·7431
H(17,N3)	−0·0500	0·1833	−0·3000
H(18,N4)	0·1392	0·0463	0·6000

* The second digit gives the number of the carbon (or nitrogen) to which the atom is attached.

TABLE 3

Components U_{ij} ($\times 10^3$) of thermal vibration tensors and their estimated standard deviations (in Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	21·2(4)	19·6(4)	32·1(5)	−0·7(3)	5·6(4)	1·8(3)
P(2)	20·2(4)	23·3(5)	30·4(5)	−1·5(3)	3·5(4)	2·3(3)
N(1)	25(1)	27(2)	38(2)	3(1)	3(1)	−2(1)
N(2)	25(1)	25(1)	38(2)	−3(1)	7(1)	−2(1)
N(3)	35(2)	30(2)	43(2)	−4(1)	13(2)	6(1)
N(4)	34(2)	39(2)	35(2)	5(1)	7(1)	10(2)
C(1)	26(2)	21(2)	42(2)	−2(1)	9(2)	2(1)
C(2)	45(2)	42(2)	48(3)	17(2)	2(2)	1(2)
C(3)	44(3)	44(3)	72(4)	19(2)	5(2)	7(2)
C(4)	48(3)	24(2)	85(4)	2(2)	24(3)	−1(2)
C(5)	67(3)	33(2)	62(3)	6(2)	17(3)	−9(2)
C(6)	51(3)	32(2)	47(3)	5(2)	4(2)	−4(2)
C(7)	23(2)	23(2)	37(2)	−2(1)	4(1)	0(2)
C(8)	49(3)	62(3)	73(4)	−27(3)	30(3)	−31(3)
C(9)	58(3)	60(4)	110(5)	−31(3)	34(4)	−42(4)
C(10)	33(2)	35(2)	91(4)	−11(2)	10(2)	11(2)
C(11)	50(3)	76(4)	67(4)	−26(3)	23(3)	7(3)
C(12)	56(3)	72(4)	43(3)	−34(3)	19(2)	−14(2)
C(13)	42(2)	45(3)	58(3)	−16(2)	12(2)	14(2)
C(14)	45(3)	45(3)	42(3)	12(2)	2(2)	7(2)

Bond lengths are listed in Table 4 and bond angles in Table 5, together with their estimated standard deviations calculated from the co-ordinate estimated standard deviations in Table 1 (assumed uncorrelated). The molecular shape is shown in Figure 1 and a view of the structure in projection along the *c* axis in Figure 2.

DISCUSSION

Molecular Configuration and Conformation.—The single molecule in the unit cell occupies a crystallographic centre of symmetry. The compound is therefore the β-*trans*-isomer since this is the only one of the four possible geometric isomers which can be centrosymmetric.[9]

TABLE 4

Bond lengths (Å) with estimated standard deviations in parentheses. A primed atom is related to the corresponding unprimed atom by the centre of symmetry at the origin

Endocyclic	
P(1)–N(1)	1·596(3)
P(2)–N(1)	1·596(3)
P(2)–N(2)	1·587(3)
P(1′)–N(2)	1·591(3)
Mean	1·593(2)
Exocyclic	
P(1)–N(3)	1·679(4)
P(2)–N(4)	1·665(4)
Mean	1·672(3)
N(3)–C(13)	1·461(6)
N(4)–C(14)	1·451(6)
Mean	1·456(4)
P(1)–C(1)	1·810(4)
P(2)–C(7)	1·806(4)
Mean	1·808(3)

C(1)–C(2)	1·393(6)
C(2)–C(3)	1·396(7)
C(3)–C(4)	1·375(8)
C(4)–C(5)	1·371(7)
C(5)–C(6)	1·390(7)
C(6)–C(1)	1·393(6)
C(7)–C(8)	1·374(7)
C(8)–C(9)	1·395(9)
C(9)–C(10)	1·374(10)
C(10)–C(11)	1·357(8)
C(11)–C(12)	1·397(9)
C(12)–C(7)	1·390(7)

TABLE 5

Bond angles (°) with estimated standard deviations in parentheses

N(1)–P(1)–N(2′)	118·1(2)	P(1)–N(3)–C(13)	120·4(3)
N(1)–P(2)–N(2)	120·9(2)	P(2)–N(4)–C(14)	119·7(3)
P(1)–N(1)–P(2)	124·6(2)	P(1)–C(1)–C(2)	118·4(3)
P(1′)–N(2)–P(2)	131·3(2)	P(1)–C(1)–C(6)	122·3(3)
		P(2)–C(7)–C(8)	120·0(4)
N(3)–P(1)–C(1)	105·9(2)	P(2)–C(7)–C(12)	122·0(3)
N(4)–P(2)–C(7)	106·2(2)		
		C(1)–C(2)–C(3)	120·2(4)
N(1)–P(1)–N(3)	111·9(2)	C(2)–C(3)–C(4)	119·9(5)
N(2′)–P(1)–N(3)	107·9(2)	C(3)–C(4)–C(5)	120·3(4)
N(1)–P(2)–N(4)	104·7(2)	C(4)–C(5)–C(6)	120·6(5)
N(2)–P(2)–N(4)	110·9(2)	C(5)–C(6)–C(1)	119·9(4)
		C(7)–C(8)–C(9)	120·4(6)
N(1)–P(1)–C(1)	104·8(2)	C(8)–C(9)–C(10)	121·0(6)
N(2′)–P(1)–C(1)	107·4(2)	C(9)–C(10)–C(11)	119·3(5)
N(1)–P(2)–C(7)	109·0(2)	C(10)–C(11)–C(12)	120·2(6)
N(2)–P(2)–C(7)	104·4(2)	C(11)–C(12)–C(7)	121·1(5)
		C(6)–C(1)–C(2)	119·1(4)
		C(12)–C(7)–C(8)	118·0(4)

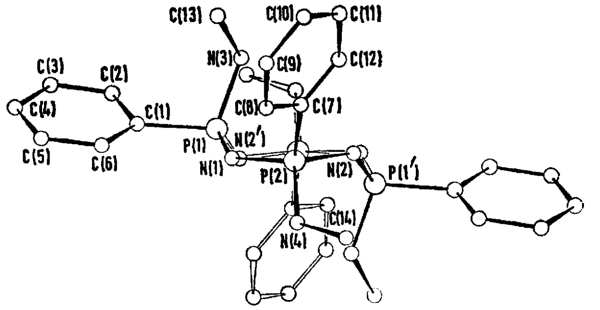


FIGURE 1 Molecular shape and numbering of the atoms

The phosphazene ring has a chair conformation (Figure 1) and, like the ring in the *T* form of $N_4P_4Cl_8$,[7]

---

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, issue No. 20 (items less than 10 pp. are supplied as full page copies).

has the approximate symmetry $2/m$. The diad axis passes through P(2) and P(2′), and the mirror plane is the plane containing P(1), P(1′), and their four exocyclic ligand atoms. Clearly the symmetry $2/m$ does not apply to the phenyl and methylamino-groups. Six of the eight atoms in the ring, *viz.* N(1), P(2), N(2), N(1′), P(2′), and N(2′), are almost coplanar (Table 6), the deviations from their mean plane being 0·05—0·06 Å. The other two atoms, P(1) and P(1′), lie 0·72 Å from this plane. The departure from exact $2/m$ symmetry is shown by the inequality of the P–N–P angles at N(1) and N(2) (Table 5) and more sensitively by the differences between the dihedral angles of the ring bonds (Table 7). True $2/m$ symmetry would require the dihedral angles of the two bonds meeting in a given phosphorus atom to be equal. The ring is clearly more distorted in β-*trans*-$N_4P_4(NHMe)_4Ph_4$ than in *T*-$N_4P_4Cl_8$ or β-*trans*-$N_4P_4Cl_4Ph_4$.

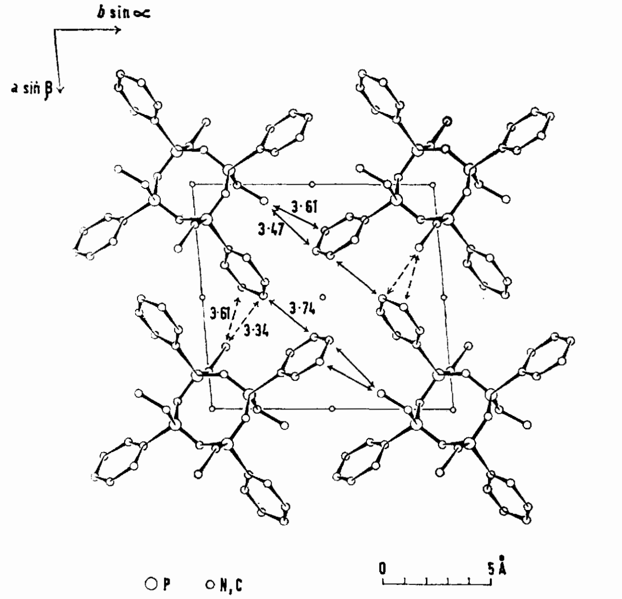


FIGURE 2 Projection of the structure down the *c* axis. Distances (in Å) marked by full arrows are between molecules at the same *z* height and those by broken arrows between molecules differing in height by one *c* lattice translation

TABLE 6

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

Plane (i): $-0{\cdot}2946X - 0{\cdot}5642Y + 0{\cdot}7713Z = 0$
[P(2) 0·062, P(2′) −0·062, N(1) −0·047, N(1′) 0·047, N(2) −0·052, N(2′) 0·052]

Plane (ii): $0{\cdot}7138X + 0{\cdot}5453Y - 0{\cdot}4395Z = 0{\cdot}2782$
[C(1) 0·000, C(2) −0·004, C(3) 0·002, C(4) 0·005, C(5) −0·010, C(6) 0·007]

Plane (iii): $0{\cdot}6216X - 0{\cdot}6563Y + 0{\cdot}4278Z = 1{\cdot}1539$
[C(7) −0·008, C(8) 0·002, C(9) 0·003, C(10) −0·002, C(11) −0·003, C(12) 0·008]

The directions of the bonds P(1)–N(3) and P(1)–C(1) can be described as respectively axial and equatorial with reference to the plane passing through the four phosphorus atoms. The corresponding bonds at P(2) cannot be differentiated in this way because they are almost equally inclined to the phosphazene ring. The choice of an equatorial, rather than axial, direction for the P–C bonds at P(1) and P(1′) is sterically more favourable as it avoids too close a contact between phenyl groups in the molecule. Exactly the same conformation is found in β-*trans*-$N_4P_4Cl_4Ph_4$,[10] the axial positions now being taken by the chlorine atoms. The formation of β-*trans*-$N_4P_4(NHMe)_4Ph_4$ by substitution of the chlorine atoms in β-*trans*-$N_4P_4Cl_4Ph_4$ has therefore occurred with retention of configuration (unless the phosphazene ring has itself undergone inversion).

TABLE 7

Dihedral angles (°) of ring bonds (angles between adjacent P–N–P and N–P–N planes)

Molecule	P(1)–N(2′)	P(1)–N(1)	P(2)–N(1)	P(2)–N(2)
T-$N_4P_4Cl_8$	76	59	20	45
β-*trans*-$N_4P_4Cl_4Ph_4$	76	62	24	42
β-*trans*-$N_4P_4(NHMe)_4Ph_4$	95·0	72·9	20·9	52·5

Bond Lengths and Angles.—With the exception of the C–C bonds, the agreement between the lengths of chemically equivalent bonds is good. There are no significant differences between the four endocyclic P–N bonds or between the pairs of P–C or C–N bonds. The difference between the exocyclic bonds P(1)–N(3) and P(2)–N(4) is possibly significant. Eleven of the twelve C–C bonds lie within the range 1·371—1·397 Å (mean 1·386 Å, σ 0·010 Å) but C(10)–C(11) is markedly shorter. On the whole the bond angles are more variable but there are two pairs for which the difference is within experimental error: the P–N–C angles (mean 120·1°) and the exocyclic angles N(3)–P(1)–C(1) and N(4)–P(2)–C(7) (mean 106·1°).

The mean endocyclic P–N bond length (1·593 Å) lies near the upper end of the range of lengths found in tetrameric phosphazene rings. This is in accord with the comparatively low electronegativities of the exocyclic groups[15] (*cf.* $N_4P_4Me_8$, mean P–N 1·596 Å[16]). The exocyclic P–N bonds are longer (mean 1·672 Å) though still 0·1 Å shorter than a single P–N bond.[17] Comparable lengths, found for the exocyclic bonds in $N_4P_4(NMe_2)_8$ (1·68 Å)[18] and $N_6P_6(NMe_2)_{12}$ (1·67 Å),[19] have been taken to indicate partial π-character. The 120° angles at N(3) and N(4) support this but unfortunately the hydrogen-atom positions are not known with sufficient certainty to say whether the co-ordination of these exocyclic nitrogen atoms is trigonal planar.

The molecule shows two significantly different P–N–P

---

[15] G. B. Ansell and G. J. Bullen, *J. Chem. Soc. (A)*, 1971, **2498**.
[16] M. W. Dougill, *J. Chem. Soc.*, 1961, 5471.
[17] D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 671.
[18] G. J. Bullen, *J. Chem. Soc.*, 1962, 3193.
[19] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1423.

angles in the ring. This is the case also for the two other tetrameric phosphazenes in which the ring has a chair conformation: *T*-$N_4P_4Cl_8$ (133·6 and 137·6°)[7] and β-*trans*-$N_4P_4Cl_4Ph_4$ (132 and 139°).[10] The angles in β-*trans*-$N_4P_4(NHMe)_4Ph_4$ are smaller than these and 124·6° is the smallest cyclic P–N–P angle so far found in a tetrameric phosphazene.

The phenyl groups in β-*trans*-$N_4P_4(NHMe)_4Ph_4$ are planar (see Table 6), the distances of the carbon atoms from their mean plane being comparable to the estimated standard deviations of their positions. The phosphorus atoms lie slightly out of the planes of the phenyl groups to which they are attached, P(1) by 0·13 Å and P(2) by 0·07 Å.

Intra- and Inter-molecular Distances.—Contacts between a phenyl group and the three nitrogen atoms bonded to the same phosphorus atom will necessarily be short. However, the orientation of the phenyl groups is such that for each of them one side of the ring is actually eclipsed with a nitrogen atom: C(6) · · · N(1) 2·99, C(12) · · · N(2) 2·98 Å. The remaining C · · · N contacts range from 3·18—3·36 Å. The carbon atoms of the methylamino-groups are able to adopt a staggered conformation, C(13) being almost equidistant from C(1) and N(1) (3·29 and 3·32 Å respectively), and C(14) from C(7) and N(2) (3·28 and 3·20 Å).

The shortest intermolecular contacts $<3·9$ Å are: CH · · · CH_3 3·34, NH · · · NH 3·44, N(ring) · · · CH_3 3·61, N(ring) · · · NH 3·63, and CH · · · CH 3·74 Å. Two of these contacts are shown in Figure 2; the other three shortest contacts are between molecules mutually related by a *c*-lattice translation. All of them are consistent with van der Waals forces. There seem to be no hydrogen-bond linkages, the shortest nitrogen to nitrogen distance of 3·44 Å, between atom N(3) in one molecule and atom N(4) in another, being beyond the accepted range of N–H · · · N lengths.[20]

Since the three polymorphic modifications (α, β, and γ) of $N_4P_4(NHMe)_4Ph_4$ can be interconverted easily through crystallisation and melting processes

e.g. $\gamma \longrightarrow \text{liquid} \longrightarrow \alpha \longrightarrow \gamma,$

or

$\beta \longrightarrow \text{solution in benzene} \longrightarrow \gamma \longrightarrow \text{liquid} \longrightarrow \alpha \longrightarrow \beta,$

there cannot be gross changes in molecular structure. There may however be differences in molecular conformation or merely in the arrangement of the molecules.

We thank Professor R. A. Shaw and Dr. C. Stratton 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, and the Department of Physical Chemistry, University of Cambridge for its hospitality (to G. J. B.) while this paper was being prepared.

[1/2381 *Received, 13th December,* 1971]

---

[20] G. C. Pimentel and A. L. McClellan, ' The Hydrogen Bond,' Freeman, San Francisco, 1960, pp. 288—293.