Chair Forms of Non-geminally Substituted Phosphazene Molecules

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TETRAMERIC cyclic phosphazenes exhibit an interesting variety of ring shapes, *viz.* planar, saddle, boat, and chair. Several examples of rings which approximate to the saddle or boat shapes are known[1] but hitherto the chair form has seemed rare, having been found only in the T form of $N_4P_4Cl_8$.[2] This compound exhibits conformational isomerism since the ring is boat-shaped in the second (K) form. We now report that 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene and the corresponding 2,4,6,8-tetrakismethylamino-2,4,6,8-tetraphenyl derivative provide two further examples of chair-shaped rings. These two compounds are also the first non-geminally substituted phosphazenes (of any ring size) whose crystal structures have been elucidated.

TABLE 1. *Geometrical parameters of some tetrameric phosphazene molecules* $N_4P_4X_4Y_4$ *in their crystal structures* (*data taken from refs.* 2 *and* 6 *and present work*)

X	Y	Molecular symmetry	Average P–N length	P–N–P	Angles N–P–N	X–P–Y
Cl	Cl (K form)	$\bar{4}$	1·57 Å	131°	121°	103°
Cl	Cl (T form)	$\bar{1}$	1·56	134, 138	121	103
Ph	Cl	$\bar{1}$	1·57	132, 139	120	104
Ph	NHMe	$\bar{1}$	1·59	125, 131	120	106

The reaction of $PhPCl_4$ with ammonium chloride produced three isomeric non-geminal phosphazenes with the composition $N_4P_4Ph_4Cl_4$, distinguished by their melting points (A) 248°, (B) 202°, (C) 148°,[3] later revised to (A) 260—263°, (B) 225·5—226°, (C) 155—156°.[4] These were regarded by Shaw and Stratton as three of the four possible geometrical isomers resulting from different mutual arrangements of the chloro- and phenyl groups. Grushkin *et al.* assigned *cis-* or *trans*-structures to the three compounds on the basis of proton n.m.r. data and dielectric constant measurements[4] but reached no conclusions as to the ring shape in these compounds or the possibility that they might be conformational isomers. The isomer whose structure is reported below is compound (A) to which Grushkin *et al.* assigned the β-*trans*-structure in which the chlorine atoms in positions 2 and 4 are on one side of the ring and the chlorines in positions 6 and 8 on the other.

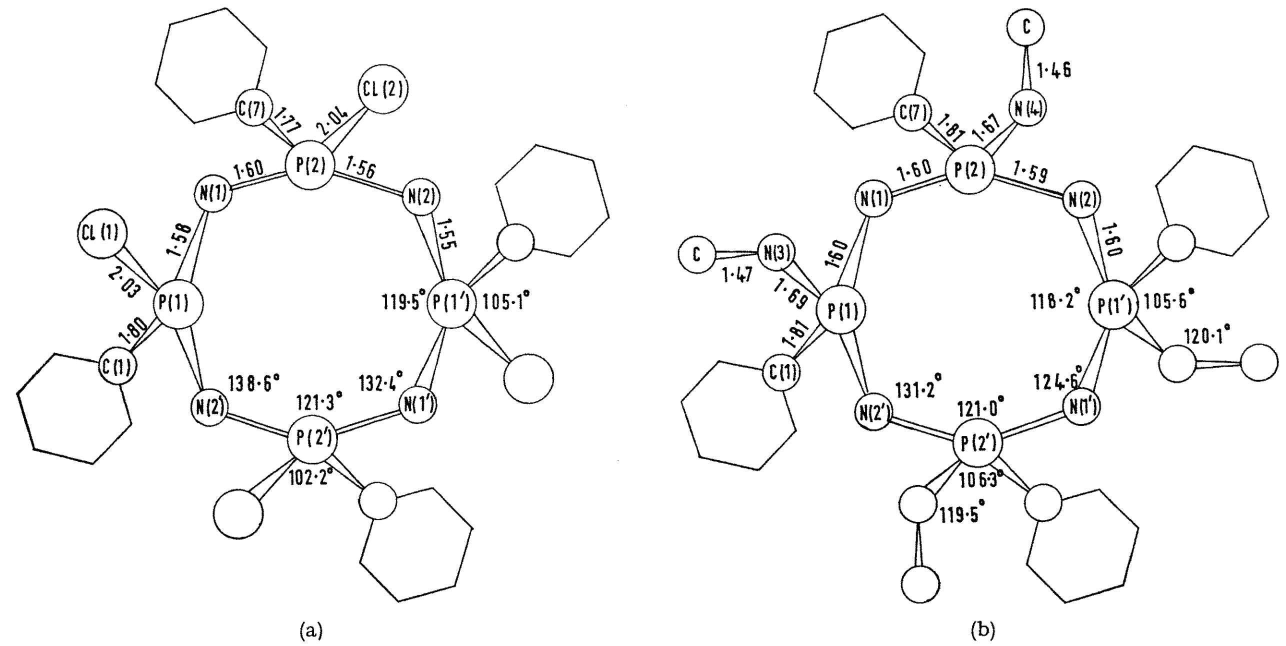
The substitution of the chlorine atoms in compound (A) by methylamino-groups produces a non-geminal $N_4P_4Ph_4(NHMe)_4$ (A′) which crystallises in four polymorphic modifications with the melting points: α 126°, β 129·5°, γ 130·5°, δ 151—154°.[3-5] The crystal structure reported below is that of the γ-modification which is produced by crystallisation from a benzene–petroleum (b.p. 60—80°) solution at room temperature.

2,4,6,8-Tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (m.p. 248°), $N_4P_4Ph_4Cl_4$, $M = 630{\cdot}16$, triclinic, $a = 11{\cdot}44$, $b = 9{\cdot}24$, $c = 8{\cdot}10$ Å, $\alpha = 113{\cdot}9°$, $\beta = 115{\cdot}1°$, $\gamma = 90{\cdot}2°$, $U = 693$ Å^3, $Z = 1$, $D_c = 1{\cdot}51$ g.cm.$^{-3}$, $D_m = 1{\cdot}50$ g.cm.$^{-3}$, space group $P\bar{1}(C_i^1$, No. 2). The intensities of 1867 X-ray reflections were measured photographically using the equi-inclination Weissenberg technique with Cu-K_α radiation. The structure was solved from the sharpened Patterson function with the help of a superposition method and was refined by Fourier and least-squares techniques. At the present stage of the refinement, with the use of anisotropic temperature factors and inclusion in the calculations of the hydrogen atoms at positions estimated from the molecular geometry, R is 0·101.

2,4,6,8-Tetrakismethylamino-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (m.p. 130·5°), $N_4P_4Ph_4(NHMe)_4$, $M = 608{\cdot}55$, triclinic, $a = 10{\cdot}88$, $b = 11{\cdot}37$, $c = 6{\cdot}30$ Å, $\alpha = 95{\cdot}7°$, $\beta = 100{\cdot}2°$, $\gamma = 85{\cdot}4°$, $U = 762$ Å^3, $Z = 1$, $D_c = 1{\cdot}33$ g.cm.$^{-3}$, $D_m = 1{\cdot}33$ g.cm.$^{-3}$, space group $P\bar{1}(C_i^1$, No. 2). 2913 X-ray reflections with statistically significant intensities were measured on a Philips PAILRED automatic diffractometer using Mo-K_α radiation. The structure was first solved in projection along [001] using the heavy-atom method. The positions of all atoms were then obtained from the three-dimensional Patterson function. Refinement by Fourier and least-squares using isotropic temperature factors has proceeded to $R = 0{\cdot}096$. The phenyl hydrogen atoms were included in the calculations by placing them at positions estimated from the molecular geometry.

In both of these compounds the molecule occupies a crystallographic centre of symmetry and the eight-membered phosphorus–nitrogen ring has the chair conformation. Both are β-*trans*-isomers, the only one of the four geometrical isomers which can be centrosymmetric, so that the assignment of structure by Grushkin *et al.*[4] is confirmed. Bond lengths and bond angles calculated at the present stage of refinement are shown in the Figure. In both compounds the six atoms N(1), P(2), N(2), N(1′), P(2′), and N(2′) are almost coplanar. Some geometrical parameters of the molecules are compared in Table 1 with those of the two forms of the parent compound $N_4P_4Cl_8$. The three molecules with symmetry $\bar{1}$ all show two significantly different P–N–P angles in the ring. The angles are smaller in $N_4P_4Ph_4(NHMe)_4$ than in the other two compounds and 125° is the smallest P–N–P angle yet found in a tetrameric derivative (the usual range is 131—134°).

As in T-$N_4P_4Cl_8$ the symmetry of the ring is approximately $2/m$ in both compounds, the plane containing P(1), P(1′), and their four exocyclic ligand atoms being the pseudo-mirror plane. The diad axis passes through P(2) and P(2′). The deviations from symmetry 2/*m* are demonstrated by the dihedral angles of the ring bonds (Table 2). If the symmetry were perfect the dihedral angle of bond P(1′)–N(2) would be equal to that of P(1)–N(1); similarly those of bonds P(2)–N(2) and P(2)–N(1) would be equal.



(a) (b)

FIGURE. *Bond lengths* (Å) *and bond angles in* (a)$N_4P_4Ph_4Cl_4$ *and* (b) $N_4P_4Ph_4(NHMe)_4$. *E.s.ds are not more than* 0·01 Å *for the lengths and* 0·6° ($N_4P_4Ph_4Cl_4$) *or* 0·5° [$N_4P_4Ph_4(NHMe)_4$] *for the angles.*

TABLE 2. *Dihedral angles of ring bonds* (*data taken from ref.* 2 *and present work*)

Compound	P(1′)–N(2)	P(1)–N(1)	P(2)–N(2)	P(2)–N(1)
$N_4P_4Cl_8$ (*T* form)	76°	59°	45°	20°
$N_4P_4Ph_4Cl_4$	76	62	42	24
$N_4P_4Ph_4(NHMe)_4$	95	73	53	21

The molecular structures of $N_4P_4Ph_4Cl_4$ and $N_4P_4Ph_4(NHMe)_4$ show that the preparation of the latter compound from the former by a substitution reaction involves retention of configuration. The molecules are closely similar in shape with just the P–Cl bonds replaced by P–NHMe. For example, in both molecules the bonds P(1)–C(1), which lie in the pseudo-mirror plane, are almost coplanar with the planar part of the central ring N(1)–P(2)–N(2) ··· N(1′)–P(2′)–N(2′) while the bonds P(1)–Cl(1) and P(1)–N(3) lie at a large angle (70—80°) to this plane. This means that inversion of configuration has not occurred unless the ring shape has altered drastically.

As the two known forms of $N_4P_4Cl_8$ have been shown to be conformational isomers[2,6] the question arises as to whether compounds (B) and (C) ($N_4P_4Ph_4Cl_4$) or the other three polymorphic modifications of $N_4P_4Ph_4(NHMe)_4$ have ring shapes different from the two structures reported here. There is evidence that compounds (A), (B), and (C) are geometrical isomers[4] but this does not preclude their being conformational isomers as well. Further work is in progress with a view to resolving this question.

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