

A New Conformation of the Eight-membered Phosphazene Ring: X-Ray Crystallographic Evidence

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Summary The *cis*-isomer of 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazetetrane (m.p. 190°) has been shown by X-ray crystal-structure analysis to contain molecules in which the eight-membered phosphazene ring has a somewhat flattened crown conformation.

THREE isomers of 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazetetrane $N_4P_4Ph_4Cl_4$ are known¹ and have been assigned *cis*- or *trans*-structures on the basis of proton n.m.r. data and dielectric constant measurements.² Last year one of these compounds [designated (A),¹ m.p. 248°] was shown by crystal-structure analysis to be the β -*trans*-isomer containing centrosymmetric molecules in which the eight-membered phosphazene ring has a chair conformation.³ A variety of ring shapes is known for tetrameric phosphazenes and it was suggested by Bullen, Mallinson, and Burr³ that there might be conformational as well as configurational differences between the isomers of $N_4P_4Ph_4Cl_4$. We have examined the crystal structure of a second isomer [designated (B)¹] and have found this to be so. Moreover, the ring shape in compound (B) is quite different from the shapes which have been found in other tetrameric phosphazenes.

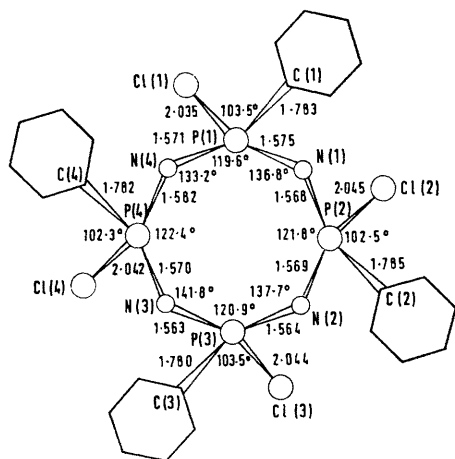


FIGURE 1. Bond lengths (Å) and bond angles. Estimated standard deviations are: for the lengths P-Cl 0.004 Å, P-N 0.008 Å, P-C 0.010 Å, for the angles not more than 0.5°.

Shaw and Stratton¹ reported the m.p. of compound (B) as 202° but Grushkin *et al.*² found that after several slow recrystallisations, melting, and remelting, it was 225.5—226°. We find that material recrystallised at room temperature from a mixture of benzene and light petroleum (b.p. 40—60°) melts at 190° but when the melt is held just above the m.p. it resolidifies and then melts only at 226°. There thus appear to be two modifications of this substance and this may explain the discrepancy in the reported m.p.s.

The structure described below is that of the modification which crystallises from solution and has m.p. 190°.

2,4,6,8-Tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazetetrane (m.p. 190°), $N_4P_4Ph_4Cl_4$, $M = 630.16$, triclinic, $a = 14.07$, $b = 11.67$, $c = 9.00$ Å, $\alpha = 99.7^\circ$, $\beta = 88.5^\circ$, $\gamma = 102.1^\circ$, $U = 1423$ Å³, $Z = 2$, $D_c = 1.47$ g cm⁻³, $D_m = 1.45$ g cm⁻³, space group $P\bar{1}$ (C_i^1 , No. 2). 4519 X-ray reflexions with statistically significant intensities were measured on a Philips PAILRED diffractometer using Mo- K_α radiation. The phosphorus and chlorine atoms were located by the application of direct methods and the nitrogen and carbon atoms by subsequent Fourier syntheses. The structure has been refined to $R = 0.11$ using individual isotropic temperature factors. The phenyl hydrogen atoms were included in the calculations by placing them at positions estimated from the molecular geometry.

Bond lengths and bond angles calculated at the present stage of the refinement are shown in Figure 1 and the ring shape in Figure 2. The four nitrogen atoms are nearly coplanar with deviations from their mean plane of only 0.02 Å. The phosphorus atoms all lie on the same side of this plane at the following distances from it: P(1) 0.55, P(2) 0.12, P(3) 0.41, P(4) 0.09 Å. The ring is thus crown-shaped with the crown somewhat flattened at P(2) and P(4).

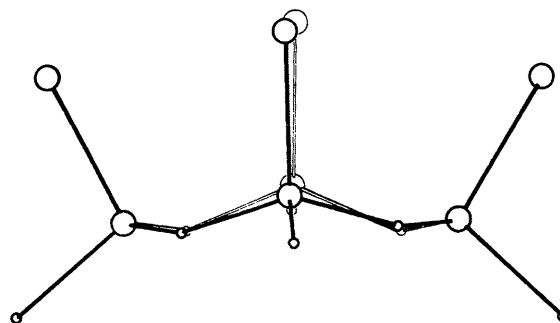


FIGURE 2. Ring shape in *cis*- $N_4P_4Ph_4Cl_4$. The large circles represent P and Cl atoms, small circles the N and C atoms.

Although a crown could theoretically possess symmetry $4mm$ (C_{4v}) the actual symmetry of the ring is only very approximately $mm2$ (C_{2v}). The flattening of the crown leads to large P-N-P angles, particularly at N(3) (142°). The only tetrameric phosphazene to show larger P-N-P angles than this is $N_4P_4F_8$ in which the ring is planar and the angles at nitrogen are 147°. These large angles can be attributed to delocalisation of the lone pair of electrons on the nitrogen atom which is favoured when, as here, the electron release from the exocyclic groups is small.

The four chlorine atoms all lie on the same side of the ring so that compound B is the *cis*-isomer, as suggested by Grushkin *et al.*² In the crystal, therefore, the molecules of compounds (A) and (B) are different in both configuration and conformation. Hitherto it has seemed unlikely that a

phosphazene ring would occur in a crown conformation because this shape involves large steric repulsions between the exocyclic groups,⁴ although the conformation is well known in sulphur systems such as S₈. Since compounds (A) and (B) are isomeric it seems the reason for their different ring shapes is more likely to be steric than electronic. The flattening of the crown in compound (B) avoids too close a contact between non-bonding chlorine atoms (the shortest Cl...Cl contact observed is 3.67 Å).

Paddock has suggested⁵ that the crown shape may be adopted by this *cis*-isomer because it is a conformation which produces different types of environment on opposite sides of the ring. In this respect the crown is the equivalent, for an eight-membered ring, of the chair conformation for a six-membered ring.

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⁴ N. L. Paddock, *Quart. Rev.*, 1964, 18, 168.

⁵ N. L. Paddock, personal communication.