The Structure of Octamethoxycyclotetraphosphazatetraene $N_4P_4(OMe)_8$

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THE shapes of the eight-membered rings in phosphazene (phosphonitrilic) derivatives $(NPX_2)_4$ vary considerably as the substituent X changes (see data in Table). This variation has been discussed by Paddock[1] who showed in particular that, depending on the competition between π- and π'-bonding, one could expect shapes ranging from an ideal saddle shape, in which the four phosphorus atoms are coplanar and the nitrogen atoms are at some distance alternately above and below their plane, to an ideal boat shape, in which P and N atoms are all equally displaced from the mean plane of the ring. An approach to the boat shape is shown[2] by $(NPCl_2)_4$ while $(NPMe_2)_4$ and $[NP(NMe_2)_2]_4$ are intermediate between boat and saddle.[3,4] We are now able to announce that the structure of $[NP(OMe)_2]_4$ is even closer to the ideal saddle shape.

The structure was determined by *X*-ray analysis of crystals grown from a solution in petroleum. These are orthorhombic with $a = 17·85$, $b = 16·55$, $c = 13·06$ Å, $Z = 8$, $D_m = 1·481$ g. cm.$^{-3}$, $D_c = 1·474$ g. cm.$^{-3}$ The space group is determined unequivocally as *Pbca* from the systematic absences of *X*-ray reflections: $0kl$ when k is odd, $h0l$ when l is odd, and $hk0$ when h is odd.

The positions of the four phosphorus atoms in the molecule were found from the sharpened Patterson synthesis. The nitrogen, oxygen, and carbon atoms were located using Fourier syntheses including generalised projections, and the structure was refined by the least-squares method. The refinement was carried out with 1180 observed intensities on the Mercury computer at London University and the I.B.M. 7090 computer at Imperial College, London.[5] At present the *R*-factor is 0·11. This has been achieved using individual isotropic temperature-factors in the calculations and neglecting hydrogen atoms.

The bond lengths and bond angles calculated at this stage of the refinement are indicated in Figure 1 and the actual shape of the molecule is shown in Figure 2. The eight-membered ring of phosphorus and nitrogen atoms closely approaches the saddle shape, the phosphorus atoms being more nearly coplanar than in any other eight-membered phosphazene ring so far examined except the fluoride.[6] The plane giving the closest fit to the four P atoms was found by a least-squares calculation. The deviations of the phosphorus atoms from this plane are +0·11, −0·10, +0·10, and −0·11 Å (positive and negative deviations represent displacements on opposite sides of the plane). The four nitrogen atoms are displaced from the same plane by +0·53, −0·54, +0·49, and −0·54 Å.

TABLE. *Shapes of ring in tetrameric phosphazene derivatives* $(NPX_2)_4$ *and average displacements of phosphorus* (Δ_P) *and nitrogen* (Δ_N) *atoms from the average plane of the phosphorus atoms* (*data taken from Ref.* 1 *and present work*).

X	Shape	Δ_P	Δ_N	Ratio Δ_P/Δ_N
Cl	boat	0·35 Å	0·47 Å	0·75
Me	between boat and saddle	0·21	0·54	0·39
NMe_2		0·18	0·52	0·35
OMe	close to saddle	0·10	0·53	0·19
F	planar	0·00	0·03	0

Whereas, for the various compounds studied, the value of the phosphorus displacement varies from compound to compound (Table), the nitrogen displacement remains remarkably constant [except in $(NPF_2)_4$]. The symmetry of the ring in $[NP(OMe)_2]_4$ is approximately $S_4(\bar{4})$ and approaches D_{2d} ($\bar{4}2m$). This suggests that π-bonding plays a greater part in the electron delocalisation than does π'-bonding.[1] Paddock has correlated a decrease of π'-bonding and hence a decrease in Δ_P/Δ_N (see Table) with the increase in electron release of the substituent X, in the order Cl < Me < NMe_2. Octamethoxycyclotetraphosphazatetraene, although having a similar Δ_N-value to the other three derivatives, does not appear to obey this correlation since the electron release from OMe should be less than that from NMe_2. This could indicate that factors other than electron release, such as steric requirements for the more bulky NMe_2 groups, are playing a part in determining the ring shape.

The P–N bond lengths and the angles N–P–N and P–N–P are similar to those found in other phosphazene molecules.[2–4] The differences between their individual values are probably not significant at this stage of the refinement. The same applies to the P–O lengths which are similar to the lengths found for such bonds in our recent work[7] on a cyclotriphosphazane derivative.

The refinement of the structure is being continued using anisotropic temperature factors and taking account of hydrogen atoms.

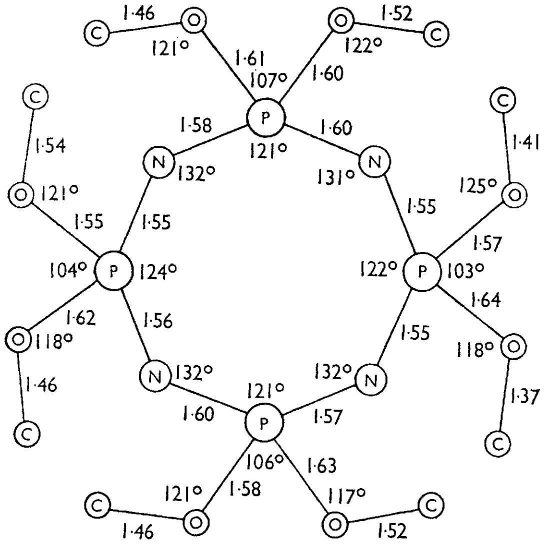

FIGURE 1. *Bond lengths* (Å) *and bond angles.*

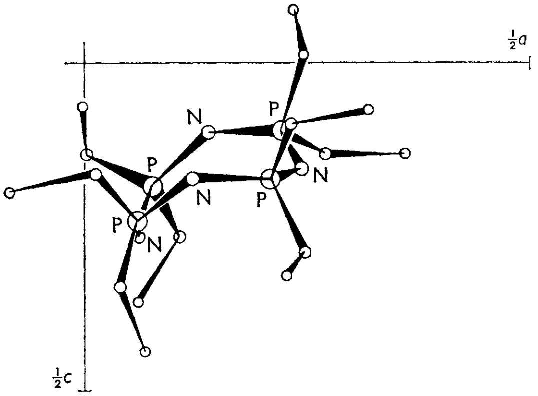

FIGURE 2. *Structure of the molecule as viewed in projection along the crystallographic* b*-axis.*

(*Received, May* 27*th,* 1966; *Com.* 361.)

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