

The Structure of 2,4,6-Trimethoxy-1,3,5-trimethyl-2,4,6-trioxocyclotriphosphazane, $N_3Me_3P_3O_3(OMe)_3$

By G. B. ANSELL and G. J. BULLEN

(Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex)

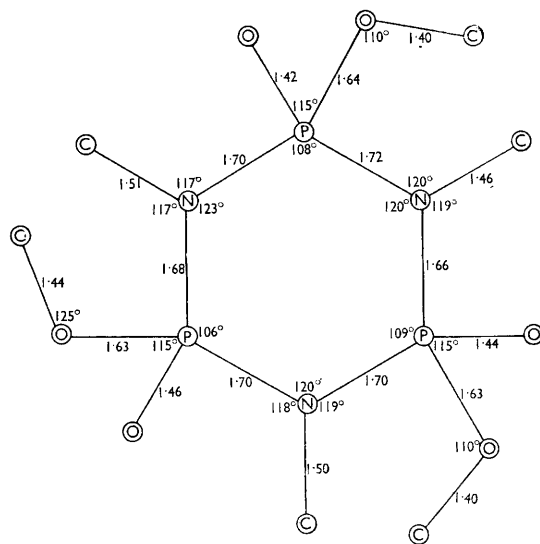
VARIOUS alkoxyoxophosphazanes have been prepared, many by thermal rearrangement of alkoxyphosphazenes.¹ Detailed structure analysis of these compounds is of interest in connection with the question of π -bonding in phosphazene and phosphazane rings. The only comparable compound of which the structure has been reported is sodium trimetaphosphimate tetrahydrate $N_3H_3P_3O_6Na_3 \cdot 4H_2O$.² We now give the results of an analysis of the crystal structure of 2,4,6-trimethyl-2,4,6-trioxocyclotriphosphazane.

Samples of this compound prepared by thermal rearrangement from hexamethoxycyclotriphosphazatriene $N_3P_3(OMe)_6$ were obtained from Dr. R. A. Shaw and Dr. C. Hewlett. Small crystals suitable for *X*-ray study were grown from a solution in toluene. They are monoclinic with $a = 11.32 \text{ \AA}$, $b = 8.29 \text{ \AA}$, $c = 7.63 \text{ \AA}$, $\beta = 98.33^\circ$, $Z = 2$, $D_m = 1.45 \text{ g.cm.}^{-3}$, $D_c = 1.49 \text{ g.cm.}^{-3}$. The density was measured by flotation (in potassium iodide solution), but as the crystals are soluble in water and many organic solvents it was necessary to coat them with a polymer to prevent dissolution. Systematic absences of *X*-ray reflections are $Ok0$ when $k = 2n + 1$, indicating space group $P2_1$ or $P2_1/m$. The latter would require the molecules to occupy special positions and the subsequent analysis of the structure favoured an arrangement of molecules in general positions in space group $P2_1$.

The positions of the phosphorus atoms and some indication of other atomic positions were obtained from a Patterson synthesis, directly and by a superposition technique. Fourier and least-squares methods were used to locate all atoms, except hydrogen, and to refine the structure. These calculations were carried out using 581 reflections for which $|F| \geq 4|F|_{\min}$, $|F|_{\min}$ being the minimum observable value, on the I.B.M. 7090 computer³ at Imperial College, London. At the present stage of the refinement $R = 0.126$ for these

581 reflections. When the same atomic parameters are used to calculate R for the full 977 observed reflections a value of 0.173 is obtained. Isotropic temperature factors of 2.1 \AA^2 for phosphorus, 2.6 \AA^2 for nitrogen, and 3.4 \AA^2 for oxygen and carbon were used.

The six-membered ring of alternate phosphorus and nitrogen atoms is non-planar, having a slightly twisted "boat" form. Bond lengths (in \AA) and bond angles are shown in the Figure. The P-N lengths are intermediate between the accepted single-bond length⁴ and those found in cyclophosphazene structures,^{5,6,7} being similar to those in the ring of sodium trimetaphosphimate tetrahydrate.² This, coupled with the essentially planar arrangement of the three bonds at each nitrogen atom, suggests that the lone-pair electrons on the nitrogen atoms are participating in π -bonding with vacant



¹ B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J. Chem. Soc.*, 1964, 4459.

² R. Hazekamp and A. Vos, *Acta Cryst.*, 1963, 16, Supplement A38, Section 4, 61.

³ Programmes used were (a) A Fortran Crystallographic Least Squares Program, by W. R. Busing, K. O. Martin, and H. A. Levy, I.U.Cr. World List of Crystallographic Computer Programs, No. 360; (b) Crystallographic Fourier Summation Program, by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende.

⁴ E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Cryst.*, 1953, 6, 621.

⁵ G. J. Bullen, *J. Chem. Soc.*, 1962, 3193.

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

⁷ M. Dougill, *J. Chem. Soc.*, 1961, 5471.

d-orbitals of the phosphorus atoms. The cyclo-triphosphazane ring is thus not a simple saturated system. The same effect was observed, for the exocyclic nitrogens, in the structure of octakisdimethylaminocyclotetraphosphazetetrane.⁵ The N-C bonds, with normal lengths, are unaffected by this tendency to double bonding. The lengths of the P=O and P-O bonds clearly differ and are individually comparable with the corresponding

lengths found in the molecule of P₄O₁₀ (respectively 1.39 Å and 1.62 Å).⁸ The P-N-P, N-P-N, and O-P-O angles are similar to those found by Hazekamp and Vos², the O-P-O angle being larger than the exocyclic angles usually found at phosphorus in cyclophosphazene structures.^{5,6,7}

The refinement of the structure is being continued using full three-dimensional data.

(Received, September 6th, 1965; Com. 561.)

⁸ "Interatomic Distances", Special Publication No. 11, Chemical Society, 1958, p. M58.