

Synthesis and Crystal Structure of the Hydrogen Bonded Complex of Tri-metatoluidylphosphazenyloxy with Bis-metatoluidine Hydrochloride

T. STANLEY CAMERON

Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada

(Z. Naturforsch. **32b**, 1001–1002 [1977]; received June 13, 1977)

X-ray, Crystal Structure, P–N Bond Lengths, $p\pi-d\pi$ Interaction

The title complex was synthesised and its structure determined by x-ray crystallography. The structure contains two hydrogen bonds between the phosphoryl oxygen atom and the two *meta*-toluidinium ions. The P–N bond lengths are significantly different and the differences, attributed to varying $p\pi-d\pi$ interactions along the bonds, confirm earlier observations on tri-*para*-toluidylphosphazenyloxy.

In a continuation¹ of the study of the factors responsible for the variation² in the P–N bond length in phosphazenyloxy groups the structure of tri-*meta*-toluidylphosphazenyloxy (MTPO) has been determined.

Experimental

Phosphoryl chloride (0.05 mole) was added very slowly to excess *m*-toluidine at 5 °C, the resultant oil was washed with dilute hydrochloric acid and separated. Crystals slowly formed from a solution of the oil in 10 ml of ethyl alcohol to which a few drops of 5 N HCl had been added.

The triclinic crystals are unstable unless they are in contact with the syrupy solution and so for the x-ray diffraction study they were sealed in contact with the liquid in Lindermann glass capillaries. The space group is $P\bar{1}$ with $a = 8.035 \pm 0.004$, $b = 15.366 \pm 0.0009$, $c = 16.480 \pm 0.011$ Å, $\alpha = 79.1 \pm 0.1^\circ$, $\beta = 105.8 \pm 0.1^\circ$, $\gamma = 109.7 \pm 0.1^\circ$. $V = 1832.6$ Å³, $C_{21}H_{24}N_3OP \cdot 2(CH_3C_6H_4NH_3^+Cl^-)$, $MW = 652.6$, $D_{calc} = 1.183$ g/cm³ for $Z = 2$; 841 independent reflections significantly above the background using $CuK\alpha$ radiation; $R = 0.08$.

The structure contains a tri-*meta*-toluidylphosphazenyloxy molecule where the phosphoryl oxygen atom is hydrogen bonded to two non-equivalent *m*-toluidinium ions with N...O contacts of 2.73 and 2.79 Å. The arrangement is shown in the figure where it can be seen that the phosphorus, oxygen and the two nitrogen atoms concerned are all practically coplanar with P–O...N angles of 118°

and 143°. The C–N...P angles are 110° (N(4)) and 123° (N(5)). The hydrogen atoms cannot be located in the difference Fourier synthesis, but both N(4) and N(5) also have close contacts to the Cl[–] ions (3.21 and 3.05 Å respectively). If these contacts represent a linear N–H...Cl hydrogen bond then from the geometry of the toluidinium ion the N–H...O bond will also be nearly linear. The P=O bond length is 1.556 ± 0.013 Å. This compares¹ with 1.495 ± 0.008 Å in the corresponding *p*-toluidine derivative (PTPO), 1.492 ± 0.005 Å in a diazaphosphocine oxide³ where there is no hydrogen bonding, and 1.639 ± 0.006 Å in the hydroxytriphenylphosphonium ion⁴ (Ph_3OH^+). It seems likely therefore that the ion $(CH_3C_6H_4NH_3^+)POH^+$ contributes a significant portion to this present structure. The arrangement of the three toluidyl groups is very similar to that observed¹ in PTPO. In that compound the angles between N–P–O and P–N–C planes were 60.4°, 64.6°* and 3.2° and these compare with 66.2° (N(1)), 68.3° (N(2)) and 13.9° (N(3)) in this compound; but where as the interplane angle of 3.2° was associated with a short P–N bond length in PTPO, in this compound the P–N bond lengths are 1.623 ± 0.012 Å (N(1)), 1.689 ± 0.013 Å (N(2)) and 1.661 ± 0.013 Å (N(3)) with the small interplane angle associated with one of the longer lengths. However the plane containing the P–O...H atoms (*i.e.* the plane that defines the orientation of the P=O π bond) has been rotated about 25° with respect to the phosphazenyloxy molecule between PTPO and MTPO; moreover the P–O...H plane is rotated 37.8° with respect to the P–N–C planes with the small interplane angle. This is enough to alter the axis of the p_z orbital on the nitrogen atom from a favourable to an unfavourable orientation for a

Requests for reprints should be sent to Prof. T. S. CAMERON, Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada.

* This angle incorrectly given as 84.6° in ref.¹.

$p\pi-d\pi$ interaction. In this compound as in PTPO, if the orientation of the nitrogen p_z orbital is in a favourable position for a $p\pi-d\pi$ interaction along the short P–N bond then the p_z orbitals on the other two nitrogen atoms are not so favourably placed.

Several more structures of this type must be examined though before any general conclusions on the interaction are possible.

Full details of the crystallographic part of this work may be obtained from the author.

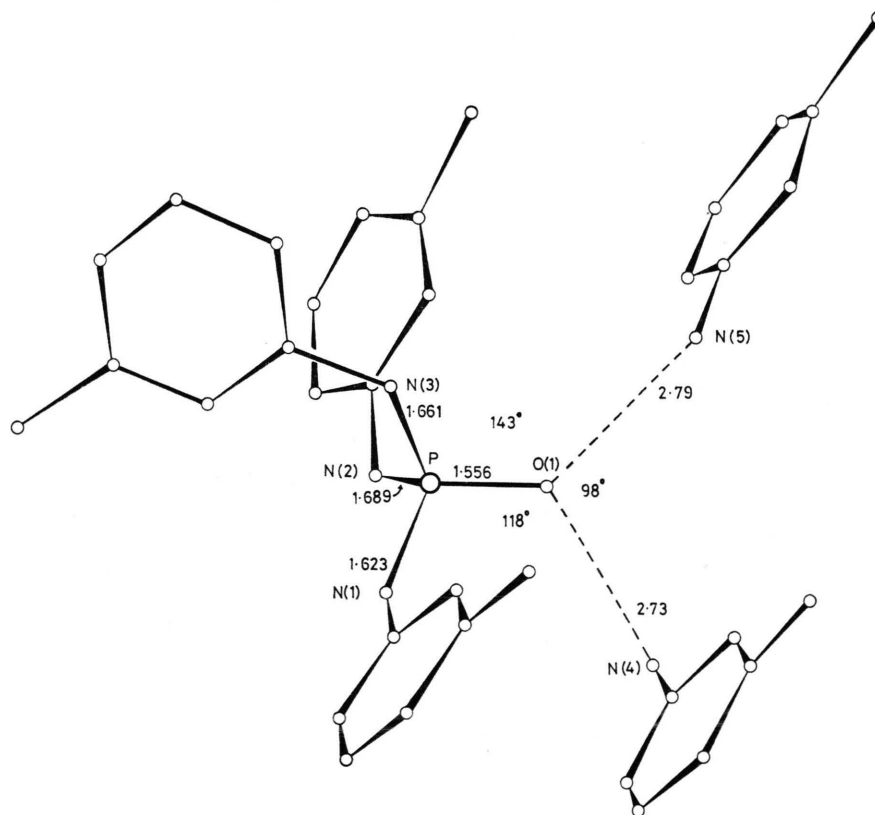


Figure. The complex, with selected distances and angles, viewed perpendicular to the least-squares plane through atoms P, O(1), N(4), N(5).

¹ T. S. CAMERON, M. G. MAGEE, and S. McLEAN, *Z. Naturforsch.* **31b**, 1295 [1976].

² D. E. C. CORBRIDGE, *The Structural Chemistry of Phosphorus*, p. 358, Elsevier, Netherlands 1975.

³ T. S. CAMERON, *J. C. S. Perk. II.* **1972**, 591.

⁴ T. S. CAMERON and C. K. PROUT, *Soc. (C)* **1969**, 2289.