# Synthesis and Crystal Structure of the Hydrogen Bonded Complex of Tri-paratoluidylphosphazenyl Oxide with Ethyl Alcohol

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

The title compound was synthesised and its structure determined by X-ray crystallography. The structure contains a hydrogen bond between the OH group of the alcohol and the phosphoryl oxygen atom. The P–N bond lengths are significantly different and the differences can be attributed to varying p$\pi$–d$\pi$ interactions along the bonds.

In an attempt to identify the factors responsible for the variation[1] of the P–N bond lengths in phosphazenyl groups the structures of tri-*ortho*-, tri-*meta*-, and tri-*para*-toluidylphosphazenyl oxide and the corresponding N-methytoluidine derivatives
$((CH_3C_6H_4NR)_3\,P{:}\,O,\ R = H,\ Me))$
are being determined.

## Experimental

Phosphoryl chloride (0.05 mole) was added very slowly to excess *p*-toluidine at 5 °C, the resultant solid was washed with dilute hydrochloric acid and recrystallised from ethanol, to give the title compound, m.p. 198 °C (60% yield).

The compound crystallised in the triclinic space group P $\bar{1}$ with $a = 9.343 \pm 0.002$, $b = 12.857 \pm 0.002$, $c = 11.859 \pm 0.002$ Å, $\alpha = 86.0 \pm 0.1°$, $\beta = 107.1 \pm 0.1°$, $\gamma = 119.5 \pm 0.1°$. $V = 1179.8$ Å$^3$, $C_{21}H_{24}N_3OP \cdot C_2H_6O$, MW = 411.5, $D_{calc}$ 1.158 g/cm$^3$ for $Z = 2$, $D_{exp}$ 1.137; 1212 independent reflections significantly above the background using $CuK_\alpha$ radiation; $R = 0.06$.

The structure contains a hydrogen bonded complex of tri-*para*-toluidylphosphazenyl oxide with ethanol. The hydrogen bond is formed between the phosphoryl oxygen and the alcohol hydroxyl group with an O···O interatomicseparation of $2.765 \pm 0{,}009$ Å, a C–O···O angle of $114.9 \pm 0.1°$ and a P–O···O angle of $122.2 \pm 0.1°$. From the difference Fourier synthesis it appears that the hydrogen atom is more closely associated with the ethanol than the phosphazenyl molecule and so the form $(p\text{-tol})_3\,POH^+\,{}^-OEt$ has only a very small contribution in the full structure. The phosphoryl P=O bond length of $1.495 \pm 0.008$ Å compares[2] with $1.492 \pm 0.005$ Å in a chloro-diazaphosphocine oxide where there is no hydrogen bond to the phosphoryl oxygen atom and this is much shorter[3] than the P=O bond length of $1.639 \pm 0.006$ Å in the hydroxytriphenylphosphonium salt of 4-imino-8-*aci*-nitrobenzo(1,2-*c*:4,4-*c*[1]) difurazan where the major contribution comes from the form $Ph_3POH^+$ $(C_6 \cdot NO_2 \cdot NH \cdot (N_2O)_2)^-$. The bond lengths and angles in the *p*-toluidyl groups are as expected but there is a significant variation in the P–N bond lengths which are $1.620 \pm 0.007$, $1.635 \pm 0.007$ and $1.669 \pm 0.009$ Å at nitrogen atoms N(1), N(2) and N(3) respectively. The differences may be the result of a $p\pi$–$d\pi$ interaction along the P–N bonds, with the nitrogen atom N(1) in a more favourable conformation than N(2) or N(3). The torsional angles between the planes though the O–P–N and P–N–C atoms are 60.4°, 3.2° and 84.6° for nitrogen atoms N(1), N(2) and N(3). If the non-bonding $p_z$ orbital of an $sp^2$ nitrogen atom at N(1) is in a favourable position for a $\pi$ interaction with an unoccupied *d* orbital on the phosphorus atom then from the geometry of the molecule the $p_z$ orbital of N(2) is in a somewhat less favourable position, and the orbital at N(3) is most unfavourably placed. In thiophosphoryl-tri-cyclohexylamine $(C_6H_{11}NH)_3$ P:S, the P–N bond lengths are[4] $1.636 \pm 0.008$, $1.658 \pm 0.006$ and $1.658 \pm 0.006$ Å. In this compound also if the $p_z$ orbital on the nitrogen atom with the short P–N bond length is in

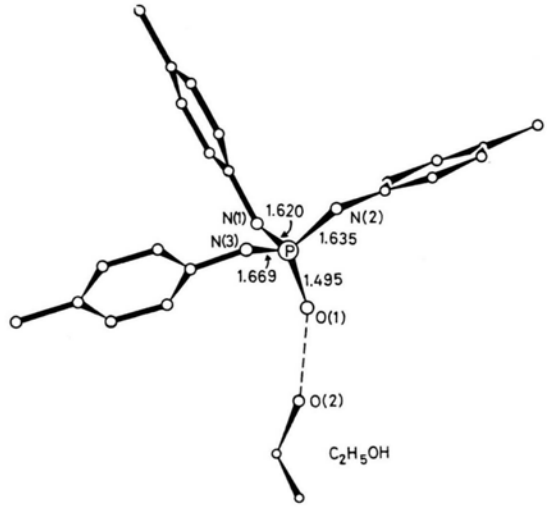


Figure. The complex viewed perpendicular to axis *a* with selected interatomic distances.

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a favourable position for a $p\pi$–$d\pi$ interaction, then the $p_z$ orbitals on the other two nitrogen atoms are not. Confirmation of the interaction may come from the structures of the other compounds in this series.

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

[1] D. E. C. Corbridge, The Structural Chemistry of phosphorus, p. 358, Elzevier, Netherlands 1975.
[2] T. S. Cameron, J. C. S. Perk II, **1972**, 591.
[3] T. S. Cameron and C. K. Prout, J. Chem. Soc. (C) **1969**, 2289.
[4] T. S. Cameron, K. D. Howlett, and C. K. Prout, unpublished work.