A Novel Phosphorus-containing Eight-membered Heterocycle

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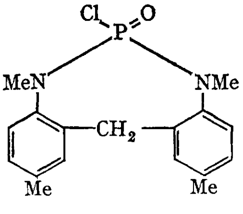
IN our studies on neutral ambident nucleophiles,[1] we have investigated the reactions of *NN*-dialkylanilines and related compounds with phosphorus halides. We report an unusual reaction leading to a novel phosphorus-containing eight-membered heterocycle.

When phosphorus oxychloride reacts at 130° with *NN*-dimethyl-4-toluidine, the major product, m.p. 170—171°, has a composition (elemental analysis) and molecular weight (mass spectrometry) corresponding to $C_{17}H_{20}ClN_2OP$. Its ^1H n.m.r. spectrum, measured on a Varian HA 100 spectrometer (at 35°), has four features: (i) a broad signal centred at τ 2·94; (ii) an AB quartet at τ 5·99; (iii) two very broad featureless humps of approximately equal intensity, at about τ 6·97 and 7·69, the latter being partially obscured by (iv) a slightly broadened singlet at τ 7·74. Integration showed these signals to be in the ratio 6 : 2 : 6 : 6. The whole spectrum is somewhat temperature dependent, and this is most marked for the two signals at τ 6·97 and 7·69. At temperatures of 0° and below, each of these has become a sharp doublet of separation 10·6 Hz compatible with the assignment $J_{P\text{-}N\text{-}C\text{-}H}$. At 50—55° the two signals have coalesced and at higher temperatures this broad hump at about τ 7·26, resolves into one doublet of separation 10·6 Hz. At low temperature, the singlet (iv) at τ 7·74 ($C\text{-}CH_3$) has resolved into two slightly broadened singlets [overlapping in part, the high-field signals from (iii)] and the absorption (i) at τ 2·94 (aromatic protons) has become more complex. The AB quartet (ii) (CH_2) changed little over the temperature range −60 to 140° (−60 to 55° in $CDCl_3$, 20 to 140° in $PhNO_2$). Hydrolytic degradation yielded the diamine, $CH_2(C_6H_3Me\cdot NHMe)_2$, m.p. 84—85°.

The structure most compatible with the above findings is shown below:



An *X*-ray crystallographic investigation gave the following results: crystal data: triclinic, $a = 9{\cdot}151$, $b = 9{\cdot}610$, $c = 13{\cdot}801$ Å; $\alpha = 96{\cdot}10°$, $\beta = 126{\cdot}12°$, $\gamma = 106{\cdot}25°$; $D_m = 1{\cdot}294$, D_c for 2 ($C_{17}H_{20}ClN_2OP$), 1·304 g. cm.$^{-3}$. Space group $P\bar{1}$, Cu-K_α-radiation, $\mu = 22{\cdot}14$ cm.$^{-1}$; 2696 independent reflections were visually estimated from equi-inclination Weissenburg photographs.

The 20 light-atom positions were located from an F_0 synthesis phased on the phosphorus and chlorine atom positions established from a Patterson function sharpened to "point atoms at rest." The trial structure, with individual isotropic temperature factors, was refined by least squares. The *R* factor is now 12·9% and the refinement is continuing.

The structure suggested by the physico-chemical measurements is confirmed. Some interesting features emerge from the *X*-ray determination. The P–N bond lengths (*cf.* Figure) of 1·64 and 1·65 Å are longer than those in some cyclophosphazenes, *e.g.*, 1·58 Å for $N_3P_3Cl_6$,[2] and for $N_4P_4(NMe_2)_8$,[3] but the same length as that in 1-(2′,2′,2′-triphenylphosphazen-1′-yl)-2-nitrosobenzdifurazan.[4]

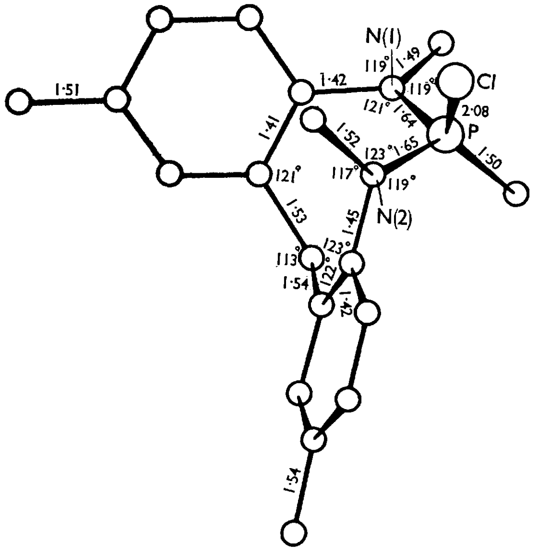


FIGURE. *Structure projected onto the least-squares best plane through the benzene ring bonded to N*(1). *The interatomic distances are in* Å *units.*

The nitrogen atoms deviate by only 0·01 [N(1)] and 0·08 [N(2)] Å from the plane of the three atoms bonded to them, indicating a contribution from a π-bond involving the lone-pair of electrons on the nitrogen atoms. The C–N bond lengths and the orientation of the trigonal planes containing the nitrogen atoms are inconsistent with strong delocalisation to the benzene rings, whilst the sp^2-hybridisation of the nitrogen atoms and the P–N bond lengths are in keeping with some p_π–d_π bonding involving the phosphorus atom.

The eight-membered ring containing the phosphorus atom has a distorted chair configuration (*cf.* Figure), and the two *N*-methyl groups can be seen to be non-equivalent due to differences in the local environment of the ring.

The temperature-dependence of the ^{1}H n.m.r. spectrum and, in particular, the appearance below 50°, of two signals arising from the *N*-methyl groups, show that the non-equivalence of these groups persists in solution. It is not yet clear whether this is due to the same causes as in the crystal or to the synchronous inversion at two non-planar nitrogen atoms.[5]

We thank the Henry Lester Trust (C.Y.C.) and the U.S. National Institutes of Health (T.S.C.), for financial support.

(*Received, March* 14*th*, 1968; *Com.* 319.)

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