Formation and Crystal Structure of an Unusual Bicyclic Phosphazene $N_4P_4(NMe_2)_5(NHEt)(NEt)$

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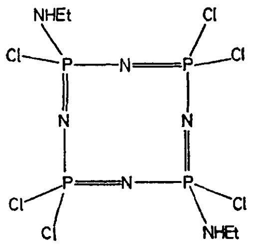
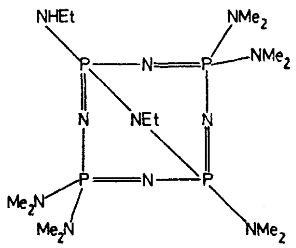
Summary The formation, 220 MHz ^1H n.m.r. spectrum, and the X-ray crystal structure of the first bicyclic phosphazene are described; the P–N bond lengths are typically those of a phosphazene except at the bridgehead where they are significantly longer.

One of the products of the reaction of hexachlorobisethylaminocyclotetraphosphazatetraene[1] (I) with an excess of Me_2NH in $CHCl_3$ is a compound having molecular formula $C_{14}H_{41}N_{11}P_4$. The 220 MHz ^1H n.m.r. spectrum of this compound shows signals at τ 8·89 and 8·83 [2 × t (1 : 1), $NCH_2\mathit{Me}$], 7·44, 7·37, and 7·12 [3 × d (2 : 2 : 1), $N\mathit{Me}_2$] and *ca.* 6·9 and 7·1 (2 × m, $NC\mathit{H}_2$). Many ethylamino-derivatives of the cyclic phosphazenes, $N_3P_3Cl_6$[2] and $N_4P_4Cl_8$,[1,3] have now been synthesised but it has not been possible to distinguish Me protons of ethylamino-groups in different



(I)



(II)

chemical environments,[2] *e.g.*, in 2,2-Cl_2-4,4,6-$(NHEt)_3$-6-$(OEt)N_3P_3$, even by 220 MHz n.m.r. spectroscopy. The two distinct ethylamino-signals in this spectrum suggest that the molecule contains some unusual structural features and the compound has been examined by *X*-ray crystallography.

Crystal data: $C_{14}H_{41}N_{11}P_4$, monoclinic, space group $C2/c$; $a = 10{\cdot}81(1)$, $b = 17{\cdot}52(1)$, $c = 28{\cdot}48(2)$ Å, $\beta = 94{\cdot}8(2)$ Å; $U = 5374.9$ Å^3; $D_m = 1{\cdot}21$, $D_c = 1{\cdot}205$ g cm^{-3} for $Z = 8$. 921 non-zero reflections were estimated from equi-inclination Weissenberg photographs by the Harwell film scanning service.

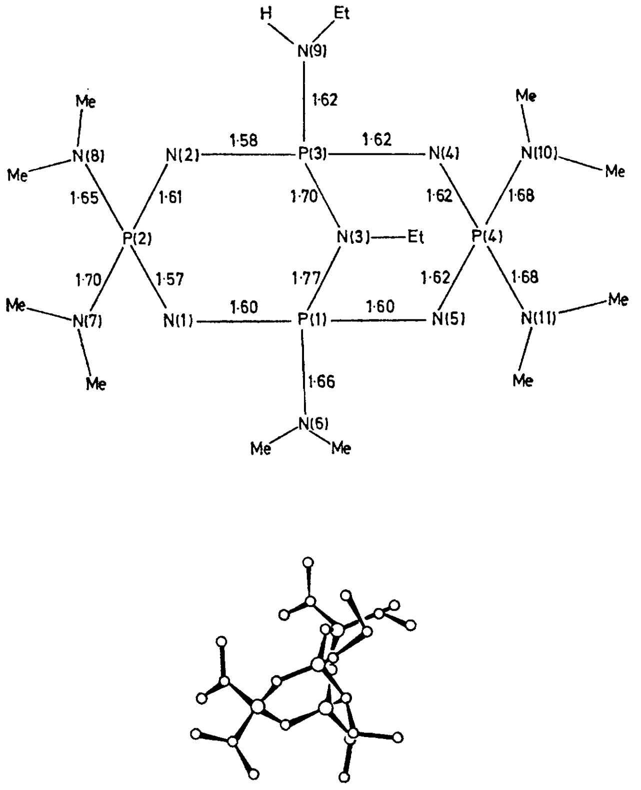


FIGURE. Interatomic distances (±0·015 Å) and a projection along *c*.

The structure was solved by the heavy atom method and refined by block-diagonal least-squares with anisotropic temperature factors to $R = 0{\cdot}09$. The hydrogen atoms have not yet been located.

The phosphazene ring was found to be intact, but the compound is bicyclic with an NEt group bridging the 2,6 positions (II) so that the molecular skeleton looks somewhat like adamantane.

The original heterocycle retains its phosphazene character. The mean deviations from the least-squares best planes through atoms P(1)–N(1)–P(2)–N(2)–P(3) (plane 1) and P(3)–N(4)–P(4)–N(5)–P(1) (plane 2) are 0·03 and 0·07 Å respectively, and the mean cyclic and exocyclic ($P{-}NMe_2$) bond lengths of 1·602(8) and 1·674(9) Å are within the range of expected values.[4] The P–N bond lengths at the bridgehead however appear to be non-equivalent and longer [P(1)–N(3) 1·772 and P(3)–N(3) 1·693 Å] with one of them close to 1·769 Å, the length normally[5] associated with a P–N single bond. The sum of the interbond angles at nitrogen atom N(3) is 337·6° which suggests that this atom has considerable sp^3 character. The reason for the non-equivalence of the two bonds is not yet clear. The angles between the plane through atoms P(1)–N(3)–P(3) and plane 1 and plane 2 are 114·8° and 126·7°, which compares[6] with the interplane angles (125°) at the bridge-head in adamantane. The angle between plane 1 and plane 2 is 118·4°.

It would appear that this is the first example in phosphazene chemistry of a compound which must be formed by an intramolecular trans-annular reaction.

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