The Crystal Structure of $N_3P_3Cl_2(NHPr^i)_4,HCl$

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THE ability of cyclophosphazenes to give addition compounds with Lewis acids is well known. Among the examples reported are $N_3P_3Cl_6,HClO_4$ and $N_4P_4Cl_8,2HClO_4$,[1] $N_3P_3Cl_6,3SO_3$,[2] $N_4P_4Me_8,Mo(CO)_4$,[3] $N_3P_3Me_6,MCl_4$ (M = Sn, Ti),[4] and $N_3P_3Me_6$,RI and $N_4P_4Me_8$,RI (R = Me, Et).[5] For some of these compounds i.r. or ^1H n.m.r. spectra indicated that the Lewis acid is linked to a nitrogen atom of the phosphazene ring. The aminocyclophosphazenes $N_3P_3R_6$ and $N_4P_4R_8$ (R = NH_2, NHMe, NHEt, NHPr, NHBu, NMe_2 *etc.*)[6] are strong Lewis bases towards HCl. Here the ring nitrogen atoms, as well as the exocyclic nitrogen atoms, are potential basic centres. Measurement of the basicities[6] and analysis of i.r. and ^1H n.m.r. spectra[7] indicated that protonation is most likely to occur at one of the ring nitrogen atoms.

Although there is strong evidence that the ring nitrogens are the basic centres this has not yet been directly demonstrated. We determined the crystal structure of the adduct $N_3P_3Cl_2(NHPr^i)_4$,HCl by *X*-ray diffraction and established that the hydrogen atom of HCl is attached to an endocyclic nitogen atom.

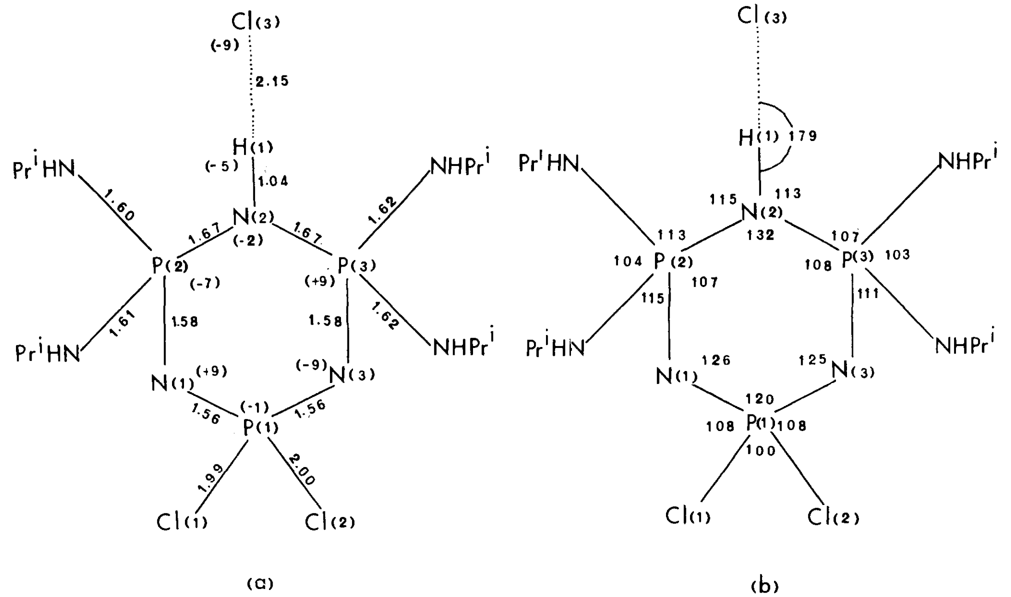

FIGURE 1. (a) *Bond lengths* (Å) *and deviations* (10^{-2} Å, *in parentheses*) *of the ring atoms from the best plane through the ring*; (b) *Valence angles* (°). *The e.s.d.'s are* P–N 0·005, N–C 0·010, C–C 0·014, P–Cl 0·002, *and* N–H 0·025 Å, PNP *and* NPN 0·4, ClPCl *and* ClPN 0·3, PNC 0·6, NCC *and* CCC 0·9, PNH 1·0°.

Crystals of the above compound (m.p. 195°) were grown as acicular prisms from light petroleum and chloroform (3 : 1). The crystallographic characteristics are: triclinic, space group $P\bar{1}$, $a = 10{\cdot}45$, $b = 14{\cdot}12$, $c = 9{\cdot}66$ Å, $\alpha = 104{\cdot}8$, $\beta = 100{\cdot}1$, $\gamma = 70{\cdot}1°$, $U = 1289$ Å^3, $D_m = 1{\cdot}20$ g.ml.$^{-1}$, $Z = 2$, $D_c = 1{\cdot}22$ g.ml.$^{-1}$.

The intensities of 2785 non-zero independent reflections up to $(\sin\theta)/\lambda = 0{\cdot}57$ Å^{-1} were measured on a Nonius automatic single crystal diffractometer by the θ—2θ scan technique using Mo-K_α radiation. The intensities were corrected for Lorentz and polarization factors and for absorption [μ(Mo) = 5·5 cm.$^{-1}$].

The structure was derived from a three-dimensional Patterson synthesis and refined by Fourier methods and anisotropic block-diagonal least-squares analysis. All 33 hydrogen atoms were located from a three-dimensional difference synthesis and included in the refinement cycles at an appropriate stage. The *R*-index for the observed reflections is 0·07.

The principal bond lengths and valence angles are shown in Figure 1. The shortest distance of the chloride ion Cl(3) to an atom of the phosphazene molecule is 3·19 Å from Cl(3) to N(2). Figure 2 shows the residual electron-density distribution, with the contribution of H(1) omitted from the F_c values, in the best plane through the atoms P(2), N(2), P(3), and Cl(3). It is seen that these four atoms lie almost exactly in the same plane and that H(1) is off this plane by only 0·01 Å. H(1) lies nearly on the line joining N(2) and Cl(3) at 1·04 Å from N(2).

The protonation of N(2) has affected the geometry of the phosphazene molecule in two respects: the bonds P(2)–N(2) and P(3)–N(2) (1·67 Å) are much longer than the ring bonds

(1·56—1·60 Å) in ordinary six-membered phosphazene rings and the exocyclic P–N bonds (1·62 Å) are short compared to the corresponding bonds (1·67 Å) in the dimethylaminocyclophosphazenes $N_4P_4(NMe_2)_8$[8] and en $N_6P_6(NMe_2)_{12}$.[9] The lengths of the bonds P(2)–N(2) and P(3)–N(2) are the same as those found in cyclophosphazane structures.[10] Both in the segment P(2)–N(2)–P(3) of $N_3P_3Cl_2$-$(NHPr^1)$,HCl and in cyclophosphazanes only a single system of π-bonds is effective, as distinct from the double π-system occurring in cyclophosphazenes.[11] However, unlike a cyclophosphazane molecule, the present structure carries a positive charge, formally on the atom N(2). It is to be expected that this charge is spread partly over the exocyclic nitrogen atoms, thus accounting for partial double bonding in the exocyclic P–N bonds and for the relatively short lengths of these bonds.

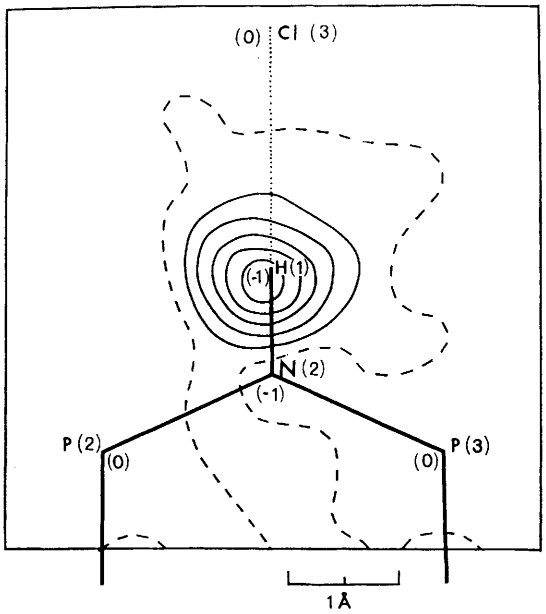

FIGURE 2. *Residual electron density distribution in the best plane through* P(2), N(2), P(3), *and* Cl(3). *The contribution of* H(1) *was omitted from the* F_c *values. Contours are at* 0·1 e.Å^{-3} *beginning with* 0·15 e.Å^{-3} *(dotted). Numbers in parentheses denote deviations of the atoms from the best plane.*

The P–N bonds just considered are of four types. On the basis of our analysis [σ(P–N) = 0·005 Å] their mean values, 1·67, 1·62, 1·58, and 1·56 Å, are shown to be significantly different. The difference between the bonds meeting at N(1) or (N)3 may be related to the different side groups attached to P(1), P(2), and P(3). A relationship between the lengths of the ring bonds and the electronegativity of the ligands has been observed in the chlorophenylcyclotriphosphazenes.[12]

The central ring of the molecule is nonplanar and has a distorted boat form. Distances from the ring atoms to the best plane of the ring are shown in parentheses in Figure 1(a). The ring angle at N(2) (132°) is large compared to the angle at nitrogen in six-membered phosphazene or phosphazane rings (120—123°). This large angle may result from steric hindrance arising from the $NHPr^1$ groups. A similar effect has been observed in the case of $N_6P_6(NMe_2)_{12}$.[9]

The P–Cl bonds (mean 2·00 Å) and the valence angles at P(1) have normal values. The $NHPr^1$ groups also have the expected tetrahedral geometry, the mean values for the bond lengths being C–N = 1·47 and C–C = 1·51 Å and for the angles PNC = 125, NCC = 110, and CCC = 112°.

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