Crystal Structure and Chemistry of Nitrilohexaphosphonitrilic Chloride

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Summary Nitrilohexaphosphonitrilic chloride $P_6N_7Cl_9$ has a condensed ring structure with comparatively weak central bonds, one of which is broken on reaction with dimethylamine.

NITRILOHEXAPHOSPHONITRILIC chloride was discovered in 1897 with the series $(NPCl_2)_n$.[1] There have been many structural and chemical studies of the monocyclic derivatives, but apart from mass-spectroscopic evidence,[2] there has been only one brief report[3] of $P_6N_7Cl_9$. We have therefore determined its structure and some of its chemistry; both show unexpected features. Its ^{31}P n.m.r. spectrum (two equal signals at $-20{\cdot}2$ and $+3{\cdot}5$ p.p.m. relative to H_3PO_4) requires the molecule to have threefold symmetry which in view of Raman and i.r. coincidences, is no higher than C_{3v}. The crystal structure determination extends this conclusion. Nitrilohexaphosphonitrilic chloride forms monoclinic crystals, $a = 19{\cdot}817$, $b = 6{\cdot}357$, $c = 29{\cdot}897$ Å, $\beta = 99{\cdot}38°$, $Z = 8$, space group $C2/c$. The structure was determined with Mo-K_α diffractometer data by direct methods, and was refined by electron-density and full-matrix least-squares procedures, to $R = 0{\cdot}048$ for 1935 observed reflexions. Figure 1 shows details of the molecular structure averaged on the assumption of C_{3v} symmetry, from which the actual structure shows small but crystallographically significant deviations.

The central nitrogen atom is nearly coplanar with its neighbours [the deviation of N(7) from the P(2)P(4)P(6) plane is 0·04 Å]. The three 5-atom segments, typically

P(6)N(6)P(1)N(1)P(2), are also almost planar (mean deviation from the plane 0·06 Å), but the molecule as a whole deviates strongly from planarity, the NPN planes at the bridgehead, typically N(1)P(2)N(2), making a mean

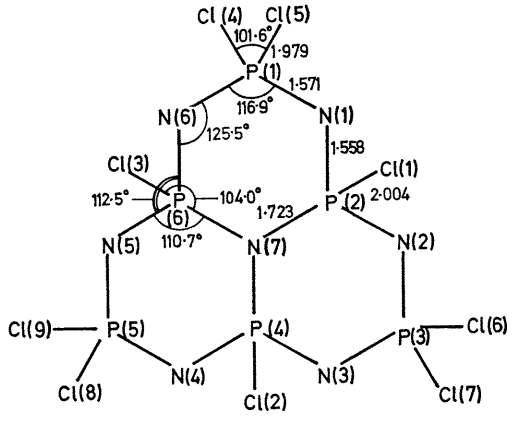

FIGURE 1. *The averaged structure of* $P_6N_7Cl_9$ (*bond lengths in* Å)

angle of 49·0° with the central P(2)P(4)P(6) plane. This non-planarity is unexpected, by comparison with carbocyclic aromatic compounds, as is the length of the central P–N bonds [1·723(6)Å], which is greater than for any other phosphonitrilic derivative hitherto reported. As a direct comparison, they are longer than the exocyclic P–N bonds (1·67—1·68 Å) in $[NP(NMe_2)_2]_{4,6}$ even though the environments of the nitrogen atoms in these latter molecules[4,5] deviate more from planarity. The delocalisation of the lone pair on the central nitrogen atom, suggested by its planar configuration, is nevertheless real, since the base strength of the compound in aqueous sulphuric acid is less, *by 0·1 unit of* H_0, than that of the monocyclic $N_6P_6Cl_{12}$, and it therefore seems probable that the π-bonding from the central atom is normal.

We attribute the non-planarity and the length of the central bonds to the σ-bonding requirements. In a general sense, such pairs of bonds as N(7)P(2)Cl(1) are equivalent to an exocyclic pair such as Cl(4)P(1)Cl(5), and the relation between the angles N(7)P(2)Cl(1) and N(1)P(2)N(2) is close to that expected for two pairs of equivalent orbitals based on an $(s + 3p)$ set, as it is in monocyclic phosphonitrilic derivatives. Detailed geometrical calculation shows this requirement to be incompatible with a planar configuration of the P–N bonds at P(2); shorter central bonds would be achieved if the configuration were planar, but the bridgehead P–Cl bond would then be formed from a pure p-orbital at phosphorus. Some compromise between the σ- and π-requirements is indicated by the small ring angles at nitrogen (125·5°) and phosphorus (116·9°); in $N_5P_5Cl_{10}$ their mean values are 148·6 and 118·4°, respectively.[6]

The interpretation of the structure of $P_6N_7Cl_9$ as containing a set of three weakened σ-bonds supplemented by π-bonds is supported by a study of other properties. Its mass spectrum shows not only ions derived from condensed rings, but also the cyclic and linear fragments characteristic of the monocyclic chlorides, fragmentation being extensive (linear fragments 43·9%, *cf.* $N_6P_6Cl_{12}$, 21·4%[2]). In attempted substitution of the chlorine atoms by more electronegative substituents, such as OMe and F, which would tend to increase the ring angle at nitrogen and thereby weaken the central bonds, quantitative reaction of the halogen is accompanied by molecular breakdown. Substitution by the electron-releasing dimethylamino-group, on the other hand, proceeds more normally, with the formation of the compound $N_6P_6(NH)(NMe_2)_8Cl_2$, for which ^1H and ^{31}P n.m.r. spectroscopy indicate the structure shown in Figure 2. It is interesting that (i) the molecule is

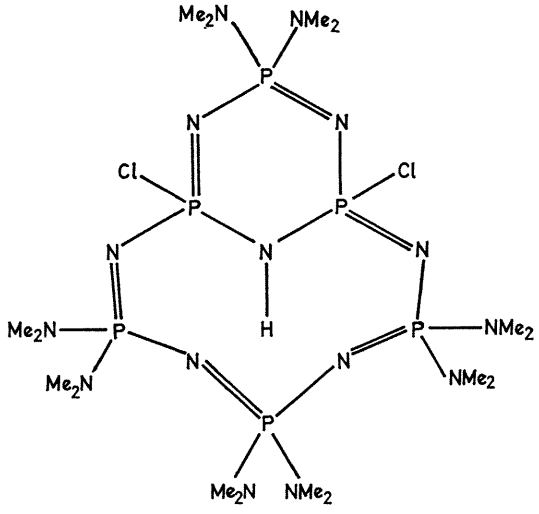

FIGURE 2. *The qualitative structure of* $N_6P_6(NH)(NMe_2)_8Cl_2$.

sufficiently stabilised by the breakage of one central bond; (ii) two bridgehead chlorine atoms remain (possibly because inversion cannot easily take place); (iii) the structure is sufficiently rigid for axial and equatorial dimethylamino-groups to be distinguished; and (iv) the N–H proton resonance is found at low field (τ 3·85) suggestive of a low base strength and hence extensive lone-pair delocalisation from the imino-group into the phosphonitrilic ring system.

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