The Crystal Structure of $N_3P_3Cl_5(NPPh_3)$ — a Novel Conformation in Phosphazenylcyclophosphazene Chemistry

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Pentachloro(triphenylphosphazenyl)-cyclotriphosphazatriene, X-ray, Crystal Structure, Triphenylphosphazenyl Group Conformation

An X-ray crystallographic structure investigation of pentachloro(triphenylphosphazenyl)cyclotriphosphazatriene, $N_3P_3Cl_5(NPPh_3)$, reveals a novel conformation (type I) of the triphenylphosphazenyl group with respect to the adjacent ring segment. This is contrasted with the structure of gem. $-N_3P_3Cl_4Ph(NPPh_3)$, where a type II conformation is observed.

Phosphazenylcyclophosphazenes have aroused a good deal of attention lately. Basicity studies[1] revealed two types of behaviour, which were suggested to relate to endocyclic and exocyclic protonation. It was deduced that these were functions of the relative conformation of the triphenylphosphazenyl-substituent with respect to the local ring NPN segment, to which they were attached. These were called type I and type II conformations, and have been discussed in detail[2, 3]. Briefly, type I would be associated with the N–P bond of the substituent being approximately perpendicular to the axis of the adjacent P–X bond (where X is the first atom of the other substituent on the same phosphorus atom), whilst in type II it is coplanar with this. The latter has recently been reported for 2,2,4,4-tetrachloro-6-phenyl-6-triphenylphosphazenylcyclotriphosphazatriene, $N_3P_3Cl_4Ph(NPPh_3)$ (**1**)[4].

We now report the structure of pentachloro-(triphenylphosphazenyl)cyclotriphosphazatriene, $N_3P_3Cl_5(NPPh_3)$ (**2**) as an example of type I conformation.

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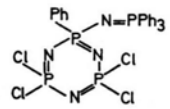
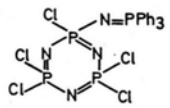


1



2

The structure analysis of compound **1** was done by diffractometric, that of **2** by photographic methods; hence the former is of greater accuracy.

$N_3P_3Cl_5(NPPh_3)$ (**2**)[6], (m.p. 215 °C), crystallizes monoclinic with $a = 20.14\,(2)$, $b = 8.69\,(1)$, $c = 14.92\,(2)$ Å, $\beta = 98.8\,(3)°$, $V = 2580$ Å^3, $Z = 4$, $D_c = 1.51$, $D_m = 1.54$ g/cm^3, MW = 591.5 space group $P2_1/n$, μ(for CuKα) = 75.8 cm^{-1}.

Intensity data were collected by the Weissenberg method for hkl reflections, $k = 0$ to 7, using CuKα radiation. Intensities of 1450 reflections were estimated visually. The structure was solved by direct methods using the weighted multisolution tangent refinement procedure and refined by least squares with anisotropic temperature factors for all non-hydrogen atoms. R at the present stage is 0.068. Hydrogen atoms were included in the calculation by

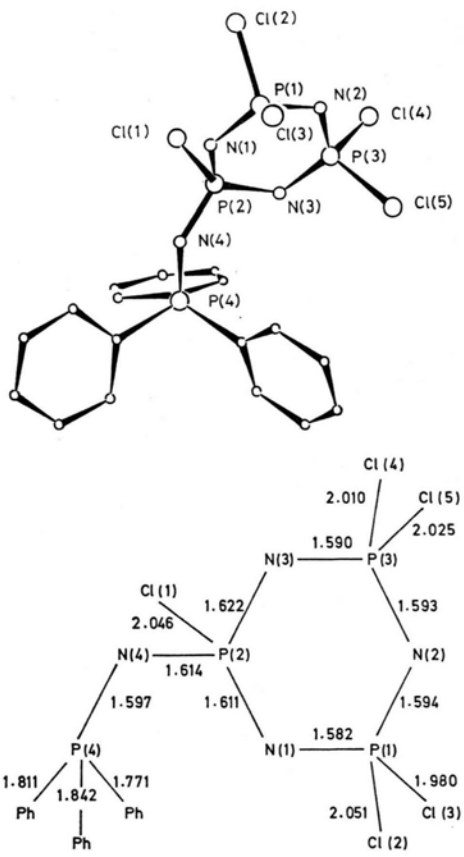


Figure. The e.s.d.'s for the bond lengths (Å) in $N_3P_3Cl_5(NPPh_3)$ are P–Cl ~0.005, P–N ~0.008, P–C ~0.01 Å.

placing them at positions deduced from molecular geometry. The bond lengths for compound **2** are shown in the Figure.

The outstanding feature to emerge from the present work is the difference in conformation of the triphenylphosphazenyl substituent in the two compounds **1** and **2**. In compound **1**[4], the N–P bond of the substituent is approximately perpendicular to the local ring NPN segment (type II conformation) and coplanar with the adjacent P–C bond. In compound **2**, where the values for the torsion angles P(4)–N(4)–P(2)–N(3), P(4)–N(4)–P(2)–N(1) and P(4)–N(4)–P(2)–Cl(1) are 34°, 164° and —83° respectively, the N–P bond is approximately perpendicular (type I conformation) to the P–Cl bond (*cf.* Fig.). The conformation of the $NPPh_3$ group relative to the ring is remarkably similar to that of a triazine derivative, $N_3C_3Cl(NMe_2)(NPPh_3)$ [5].

In both compounds **1** and **2**, the phosphorus atom carrying the $NPPh_3$ group is somewhat below the mean plane of the other five ring atoms. Again in both compounds extensive delocalisation in the exocyclic P–N–P segment makes both of these P–N bonds of equal length within the accuracy obtained.

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