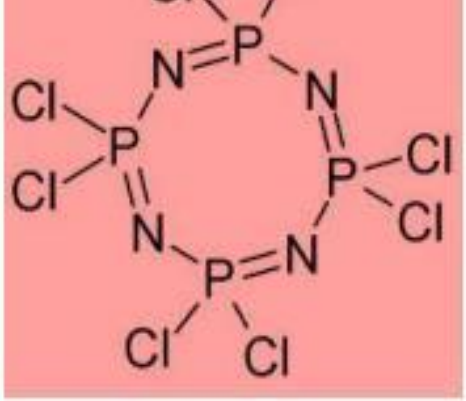
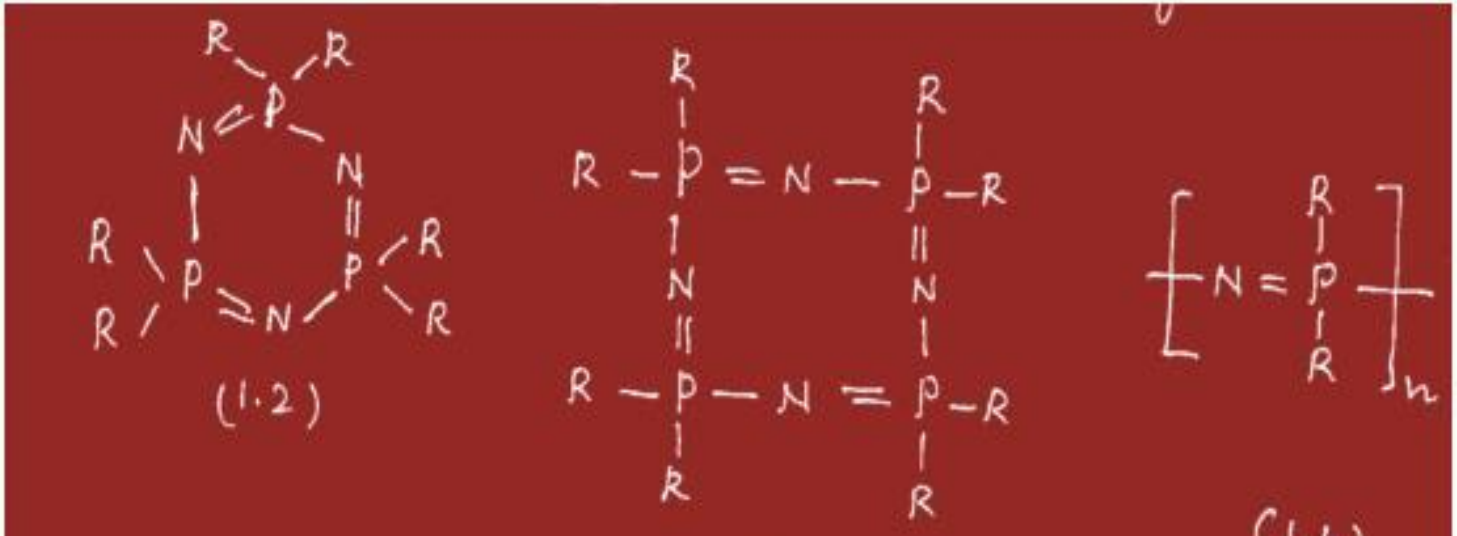


The Phosphazenes are cyclic or chain compounds that contain alternating phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The three main structural types are cyclic trimer (Fig 1.2),cyclic tetramer (Fig 1.3) and the oligomer or high polymer (Fig 1.4). A few cyclic pentamers and hexamers are also known.



(*i*) $(NPCl)_3$ and $(NPCl_2)_4$ can be prepared by the ammonolysis of PCl_5.

$$3PCl_5 + 3NH_3 \longrightarrow (NPCl_2)_3 + 9HCl \; ; 4PCl_5 + 4NH_3 \longrightarrow (NPCl_2)_4 + 12HCl$$

(*ii*) These compounds can be prepared by the reaction between PCl_5 and NH_4Cl in presence of $C_2H_4Cl_2$ or C_6H_5Cl or by heating PCl_5 with solid NH_4Cl at 145-160° C.

$$nPCl_5 + nNH_4Cl \xrightarrow[\text{or } C_6H_5Cl]{C_2H_4Cl_2} (NPCl_2)_n + 4nHCl$$

$$nPCl_5 + nNH_4Cl\,(s) \xrightarrow{145\text{–}160^\circ} (NPCl_2)_n + 4nHCl$$

Both the above reactions produce a mixture of various phosphonitrilic chlorides, but under controlled conditions, high yields of $(NPCl_2)_3$ and $(NPCl_2)_4$ can be obtained. These two compounds can be seperated from each other by using the fact that $(NPCl_2)_3$ sublimes in vacuum at 50°C as a white crystalline solid whereas $(NPCl_2)_4$ does not do so under these conditions.

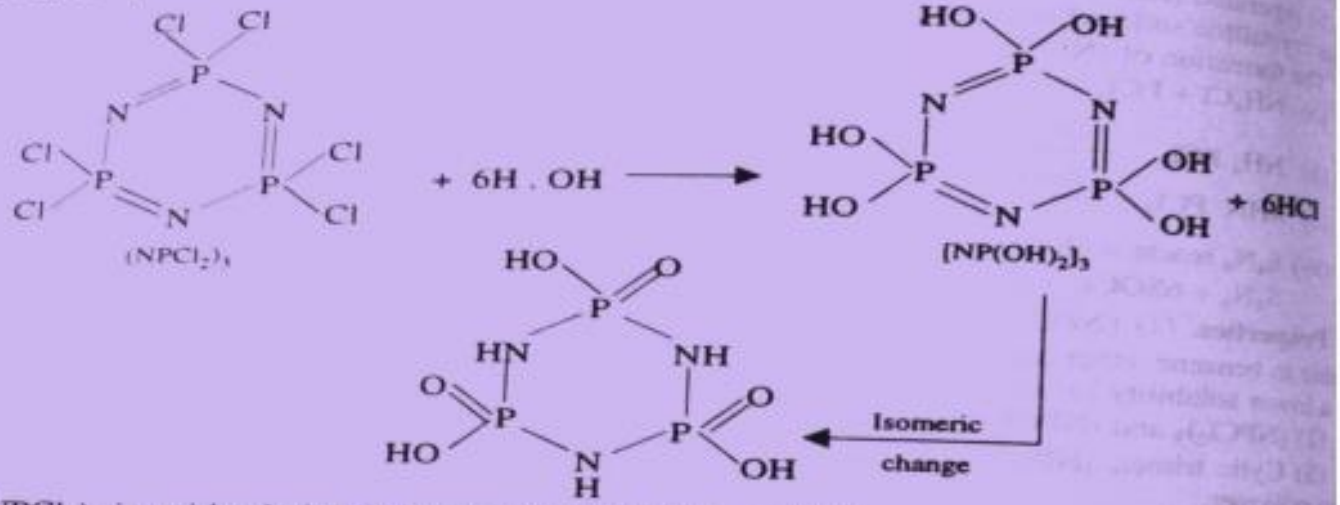
The formation of $(NPCl_2)_n$ takes place through the following steps :

(*a*) $NH_4Cl + PCl_5 \longrightarrow NH_4PCl_6$ (*Ammonium hexachlorophosphate—an unstable compound*)

$$NH_4PCl_6 \xrightarrow{\text{Decomposition}} HN.PCl_3 + 3HCl$$

PROPERTIES

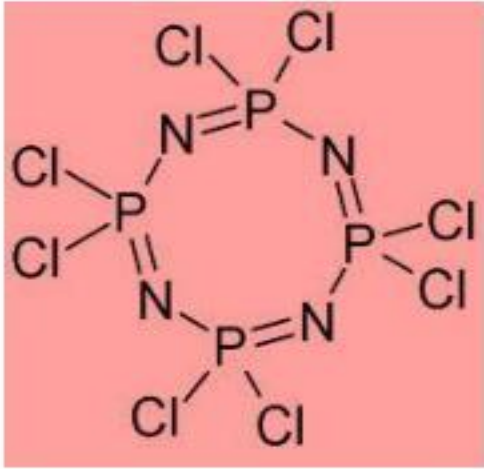
(*v*) *Hydrolysis.* (*a*) When $(NPCl_2)_3$ reacts with H_2O (aqueous ether), all Cl-atoms are replaced by OH groups.



$(NPCl_2)_3$ in acid solution is hydrolysed to H_3PO_4 and NH_3.

(*b*) Hydrolysis of $(NPCl_2)_4$ in boiling water is rapid and a stable product is obtained.

STRUCTURE



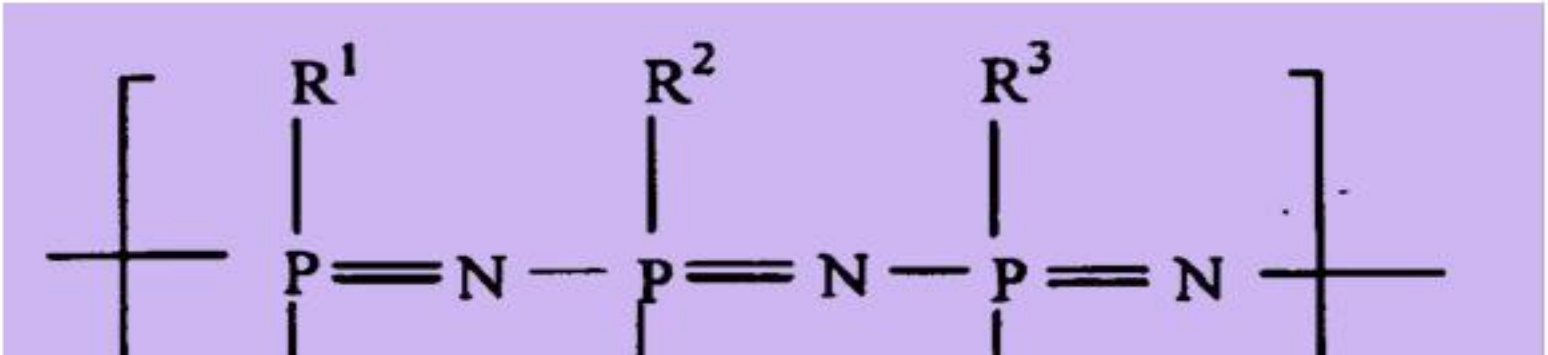
The halide trimers consist of planar six membered rings. The bond angles are consistent with SP ^{2} hybridization of the nitrogen and approximately SP ^{3} hybridization of the phosphorous. Two of the SP2 o r b i t a l of nitrogen, containing one electron each, are used for 's' bonding and the third contains a lone pair of electron. This leaves one electron for the unhybridised PZ orbital.

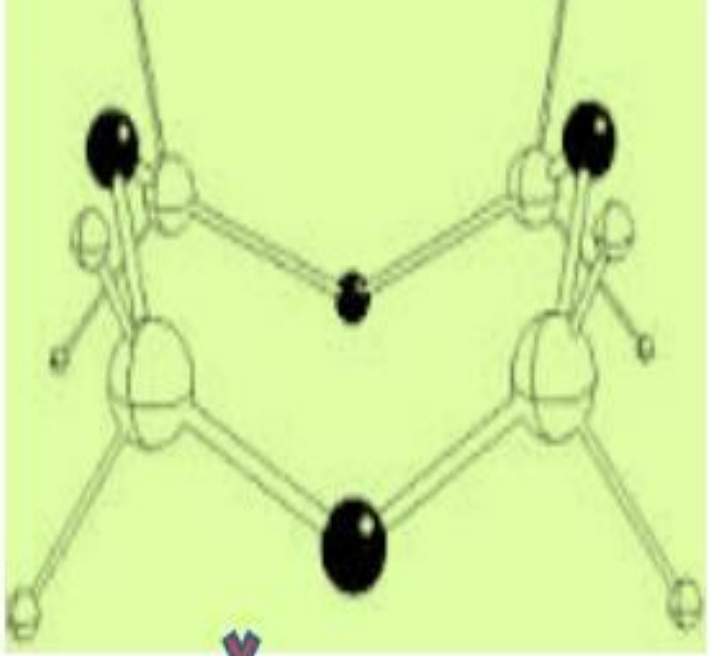
The four SP ^{3} hybrid orbital (containing four electrons) of phosphorous are used for 's' bonding leaving a fifth electron to occupy a 'd' orbital. Resonance structures can be drawn like benzene ring indicating aromaticity

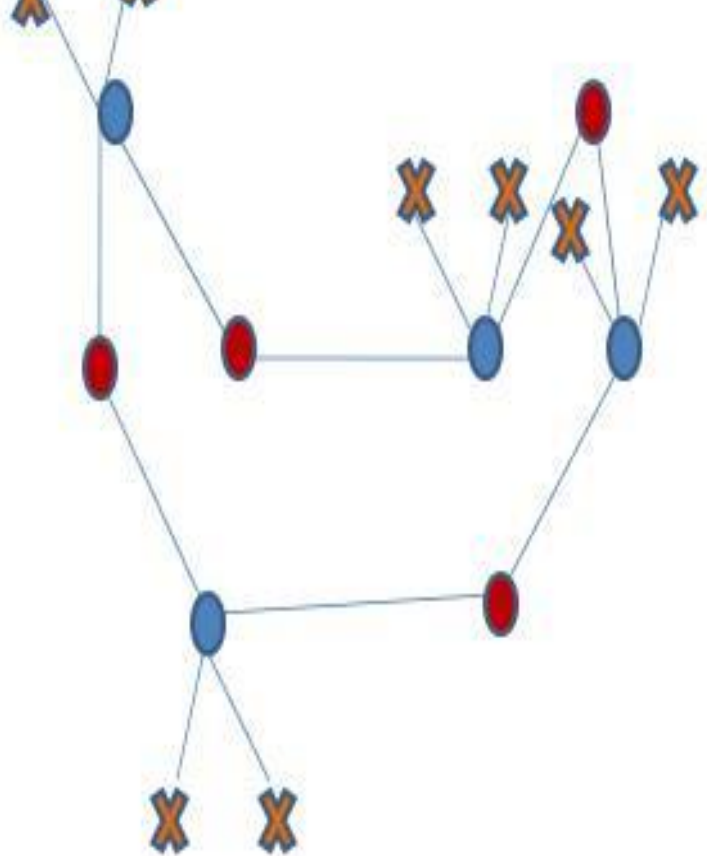
The Planarity of the ring, the equal P-N bond distances and the shortness of the P-N b o n ds, and the stability of the compounds suggest delocalisation. All phosphazenes are not planar.

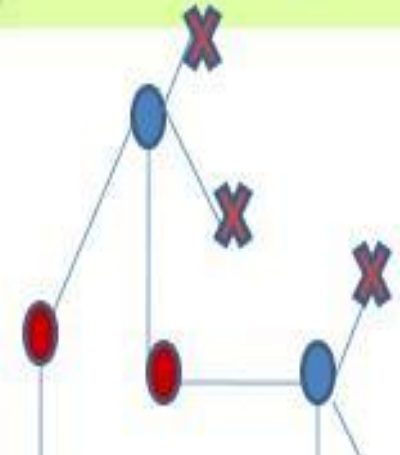
PHOSPHAZENE POLYMERS

Phosphozenes can be polymerized. Their polymers have advantages o v e r c a r b o n -b a s e d p o l y m e rs polyolefin's and polyesters. By varying the nature of the side chain 'R' various elastomers, Plastics, films and fibres have been obtained. They are flexible at low temperatures and water and fire resistant. Some R groups like R=CH2CF3 in OR group in the above reactions are water repellant and do not interact with living and promise to be useful in fabrications of artificial blood vessels and prosthetic devices.









TETRAMER

Nitrogen

(C) Polymerisation of organic or organometallic substituted cyclic phosphazene

In this method organic substituents are introduced at the Cyclic trimerphosphazene followed by ring opening polymerisation of the substituted cyclic trimer to a high Polymer.

PROPERTIES AND STRUCTURES

Cyclic phosphonitrilic halides,($NPCl_2)_3$ and $(NPCl_2)_4$ have been studied

1. *PHYSICAL PROPERTIES : on heating (NPCl2)3 and $(NPCl_2)_4$ polymerise to elastic product of high molecular weight and on heating the product gets depolymerised.*

phosphonitrilic chloride is very reactive and it can be easily replaced by monovalent groups like F, Br, OH, OR, SH, SR, SCN, NH_2, NR_2 et c