CST
Inorganic polymer

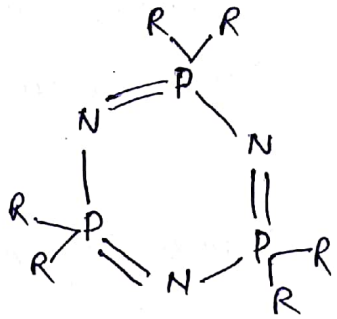
Phosphazenes

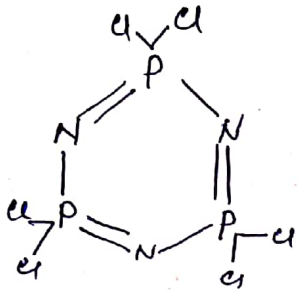
- Phosphazenes are cyclic or acyclic polymers of phosphorus & Nitrogen.
- They possess $\left(N=\overset{R}{\underset{R}{P}}-\right)$ group as repeating unit. (where R = Cl, OMe, OEt etc).
- Usually R=Cl, Such polymers are called polyphosphonitrillic chlorides. Now these are called polychlorophosphazenes.

Classification of phosphazenes:

(i) Cyclic Trimer:

When three units of $-N=\overset{R}{\underset{R}{P}}-$ unit are join together to form a cyclic compound is known as cyclic trimer. Ex-

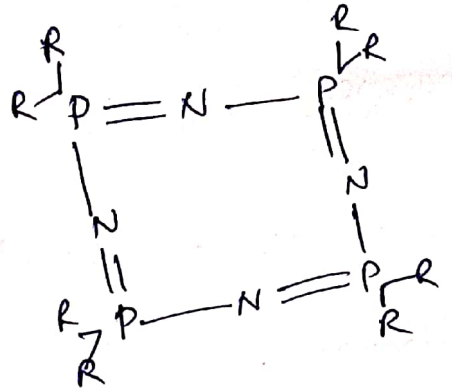




, Hexchlorocyclotriphosphaze.

(ii) Cyclic Tetramer:

When four units of $-N=\overset{R}{\underset{R}{P}}-$ units are join together to form a cyclic compound known as cyclic tetramer. Ex-



R = Cl, NH_2, OMe etc.

(iii) Chain polymer:

When $-(N=\overset{R}{\underset{R}{P}}-)$ units presents repeately but they are not forming Cyclic structure, they are present like a chain.

Preparation of phosphazene:

$$n\,PCl_5 + n\,NH_4Cl \xrightarrow[120-150^\circ C]{C_6H_5Cl \text{ or } C_6H_4Cl_2} (NPCl_2)_n + 4n\,HCl$$

Steps:

(i) $NH_4Cl + PCl_5 \longrightarrow NH_4PCl_6$

(ii) $NH_4PCl_6 \longrightarrow HNPCl_3 + 3HCl$

(iii) $n\,HNPCl_3 \xrightarrow{\text{Condensation}} [NPCl_2]_n + n\,HCl$

N:B: At Controlled Condition the main products are Cyclic trimer and Cyclic tetramer.

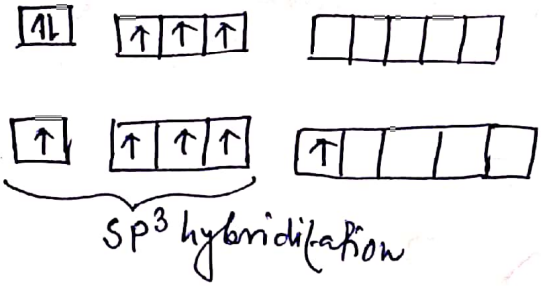
Structure of Hexachloro Cyclotriphosphazene $(NPCl_2)_3$.

It is a planner structure, and this is six member and 'N' & 'P' are present alternatively. The angle of $\angle P-N-P$ and $\angle Cl-P-Cl$ are 118° and 108° respectively.

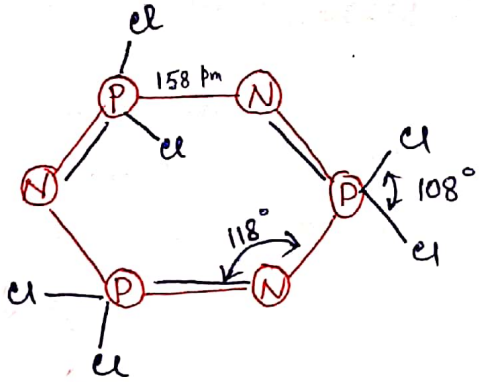
N =

sp^2 hybridization

P =



sp^3 hybridization



This molecule is planner and there have single & double bond in ring alternatively. But actual there have no alternative double-bond, all bonds are same and are partially double bond in nature due to resonance. So, it have a resonating structure as like benzene. But there has some other differences between benzene and phosphazenes due to present of d-orbital in 'P' atom. There have also differente in hybridization of ring atoms.

Delocalization involves P-orbital of Nitrogen and d-orbital of phosphorus.:

Two types of π-bonding involves here—

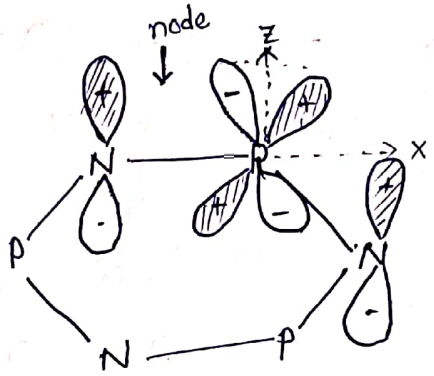
(I) When P_z of N & d-orbital of 'P' are involved in bonding. This type of bonding are two type.

(i) Heteromorphic π-bonding or pseudo aromatic bonding.

(ii) Homomorphic π-bonding.

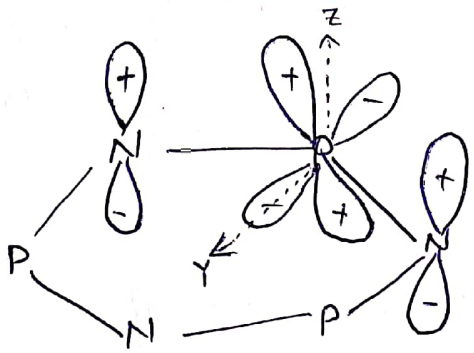
(i) Heteromorphic π- bonding —

When d_{xz} of 'p' and p_z of N forms bond, then this type of bond is formed. There will be a node.



(ii) Homomorphic π- bonding —

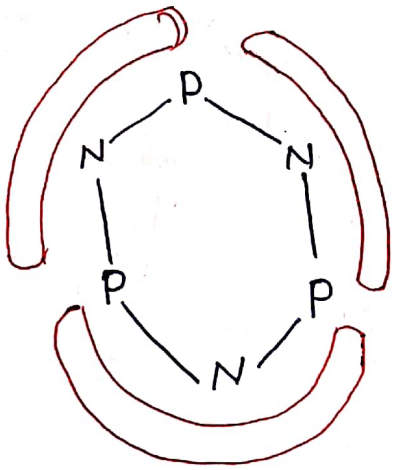
When d_{yz} orbital of P overlaps with p_z of N. This type of bond is formed. There will be no node.



(II) When donation of lone pair of e^- on sp^2 orbital of N to the vacant d_{xy} or $d_{x^2-y^2}$ orbital of P. This is known as π' bonding.

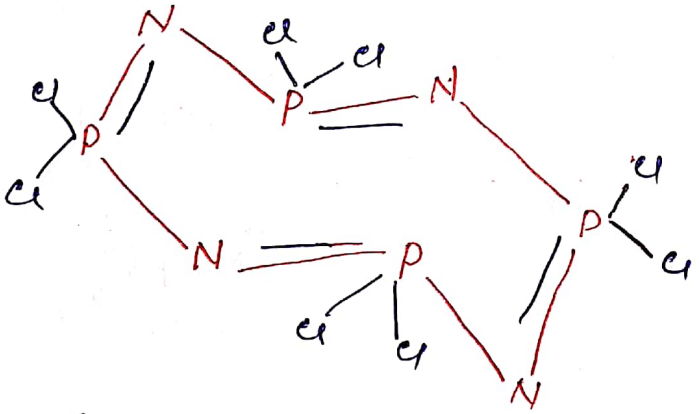
N:B:- This overlapping in phosphazene can be explained by Island Model. According to this model d_{xz} or

d_{yz} orbitals overlap to form two orbitals. There are directed towards the two adjacent nitrogen atom. This allows the formation of 3-Centre bonds covering the N-atom.



There are nodes at phosphorus atoms, because two hybrid orbitals of phosphorus are orthogonal to each other. So, there have three nodes at three 'p'-atom.

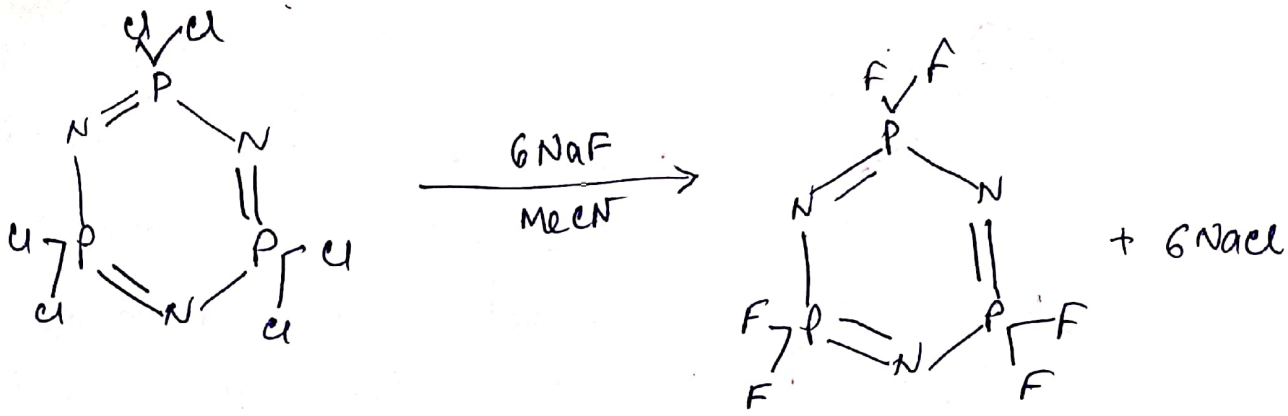
Structure of Octachlo Cyclopolyphosphazene $[NPCl_2]_4$:



Chair form Str. of $[NPCl_2]_4$. Boat form str. is also possible, but this will be least stable due to Steric effect.

Chemical properties

(i) Replacement of 'Cl' group by other nucleophile -

(a) 

(b) $[NPCl_2]_3 \xrightarrow{6\,CH_3MgI} [NP(CH_3)_2]_3 + 3\,MgCl_2 + 3\,MgI_2$

(c) $[NPCl_2]_3 \xrightarrow{6\,NaSCN} [NP(SCN)_2]_3 + 6\,NaCl$

(d) $[NPCl_2]_3 \xrightarrow{6\,(CH_3)_2NH} [NP((CH_3)_2N)_2]_3 + 6\,HCl$

(e) $(NPCl_2)_3 \xrightarrow{6\,NaOR} [NP(OR)_2]_3 + 6\,NaCl$

(f) $[NPCl_2]_3 \xrightarrow{6\,PhLi} [NP(Ph)_2]_3 + LiCl$

Physical properties

⇒ It ranges from fluids, solid to elastomers.

⇒ Insoluble in water, soluble in organic solvent and incase of higher molecular wt. phosphazenes they are insoluble in organic solvent.

⇒ Resembles vulcanised rubber in properties, so are called inorganic rubber.

Uses of phosphazenes :

⇒ phosphazenes forms a large no of polymers.

⇒ Fluorinated phosphazenes appear to be prospective material for fuel hoses, gasket etc. in extreme climate & aircrafts.

⇒ Alkoxy phosphazenes have excellent repelling properties.