

Greenwood & Earnshaw

2nd Edition

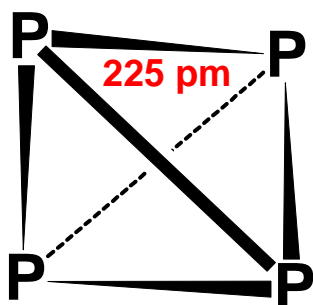
Chapter 12

Phosphorus

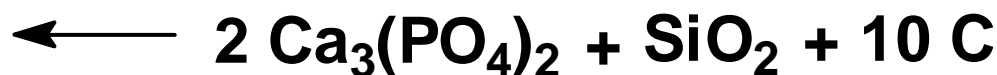
Elemental Phosphorus

^{31}P (100% abundance), $I = 1/2$, eleventh most abundant element in Earth's crust.
 $A = 30.973762(4)$ amu Most important mineral is apatite: $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaX}_2$

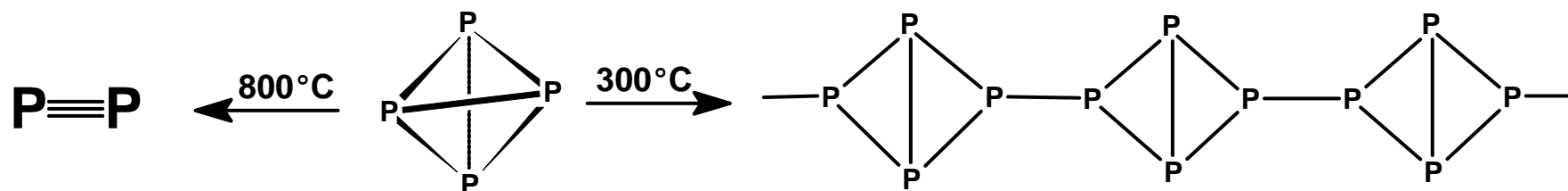
Teeth and bones are mostly hydroxy apatite. $X = \text{OH}, \text{Cl}, \text{F}$
 Vast deposits of fluoroapatite (Phosphate rock)



White Phosphorus



$mp = 44.1^\circ\text{C}$
 $\rho = 1.8232 \text{ g/cm}^3$



Red Phosphorus

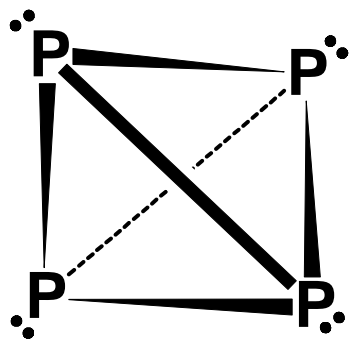
$\rho = 2.16 \text{ g/cm}^3$

Black Phosphorus

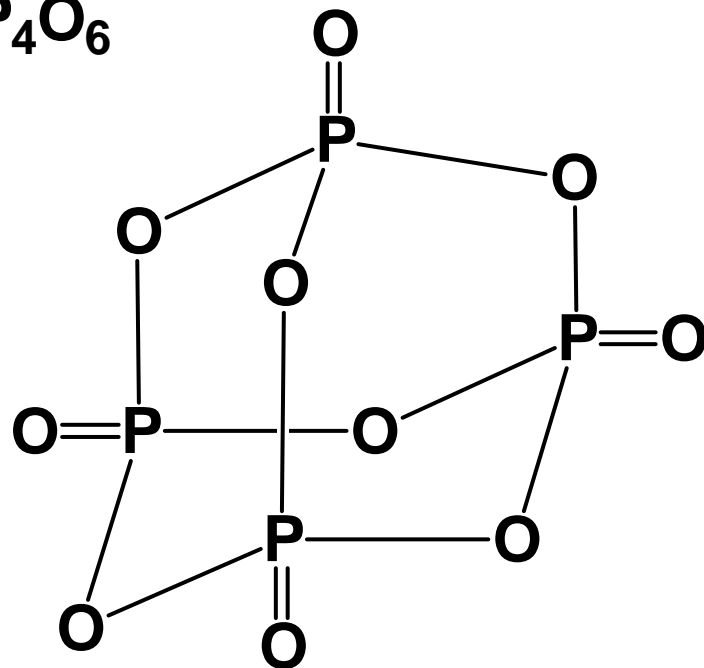
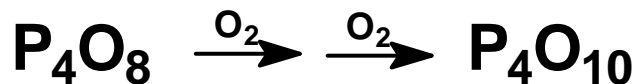
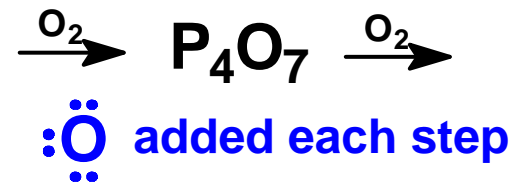
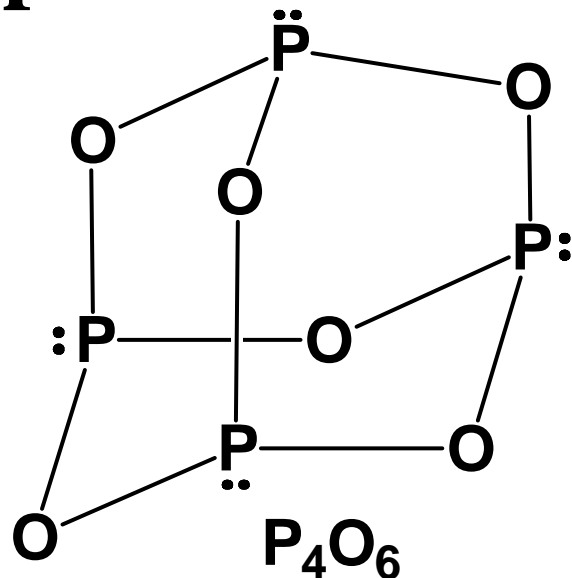
Three forms: orthorhombic; rhombohedral; cubic;

$\rho = 2.69 \text{ g/cm}^3$ $\rho = 3.56 \text{ g/cm}^3$ $\rho = 3.88 \text{ g/cm}^3$

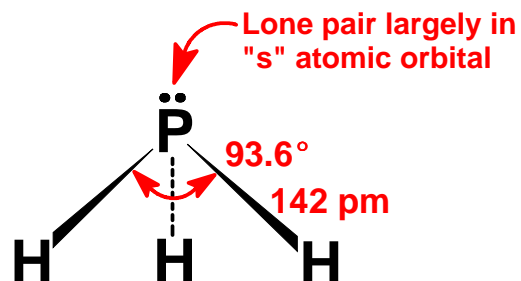
Phosphorus Oxides



limited oxygen



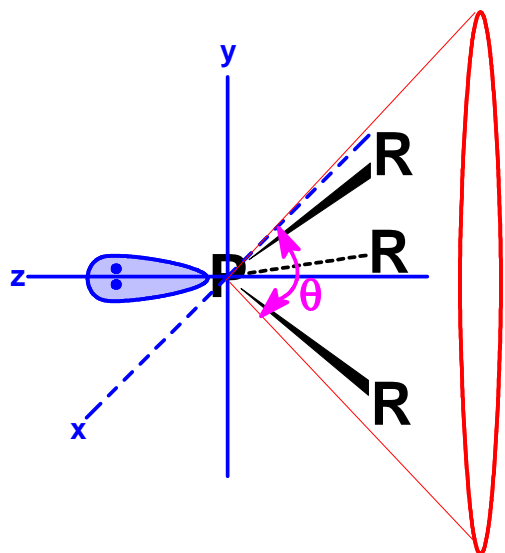
Phosphines & Organophosphines



mp -133.5°C
 bp -87.7°C
 $K_b = 4 \times 10^{-28}$

Insoluble in water, acidic in liquid ammonia, high barrier to inversion (6x that of ammonia). faint garlic odor, easily made by hydrolysis of calcium or aluminum phosphide, pyrolysis of phosphorous acid, reduction of PCl_3 and industrially by alkaline hydrolysis of P_4 . Naturally formed by anaerobic degradation of phosphates along with some P_2H_4 . PH_3 is the only stable phosphine, but P_2H_4 and P_3H_5 have been obtained pure and are pyrophoric.

Organophosphines:



σ donors:



π acceptors:



steric interference: (θ = cone angle)



$\theta = 182^\circ, 145^\circ, 121^\circ, 118^\circ, 107^\circ-109^\circ, 104^\circ, 87^\circ$

Organophosphines are important ligands in organometallic chemistry & catalysis.

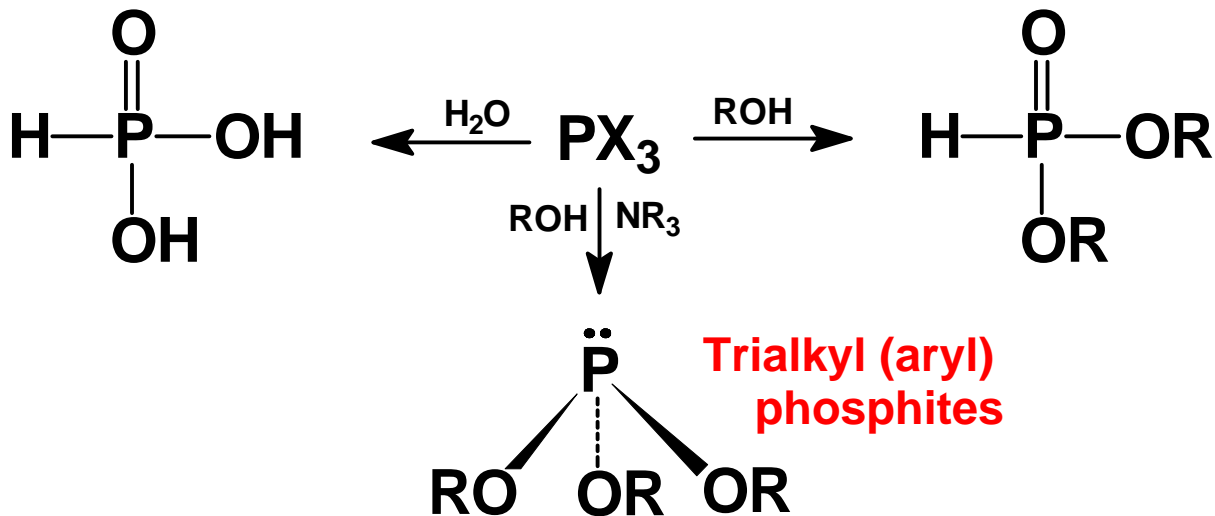
Organophosphines & Phosphorus Halides

- $\text{P}(\text{CH}_3)_3$ – volatile liquid, bp = 37.8°C , strong garlic odor, pyrophoric, very toxic.
- $\text{P}(\text{Bu})_3$ – less volatile liquid, bp = $\sim 240^\circ\text{C}$, faint odor, fumes in air, more air stable, toxic if injected, flammable.
- $\text{P}(\text{Ph})_3$ – not very volatile solid, mp = 80°C , faint “nutty” odor, relatively air stable, toxic if injected.
- PF_3 – gas, bp = -101.8°C , odorless, relatively water stable, unreactive, *very toxic*, ligand properties $\cong \text{CO}$.
- PCl_3 PBr_3 PI_3 – Hydrolyze rapidly, react with oxygen to form $\text{O}=\text{PX}_3$, PX_3 , $\text{X} = \text{Cl}, \text{Br}$ act as ligands .

Phosphorus (III & V) Halides

P(III) Halides:

	Boiling point	\angle XPX
PF ₃	-101.8°C	96.3°
PCl ₃	76.1°C	100°
PBr ₃	173.2°C	101°
PI ₃	>200°C	102°

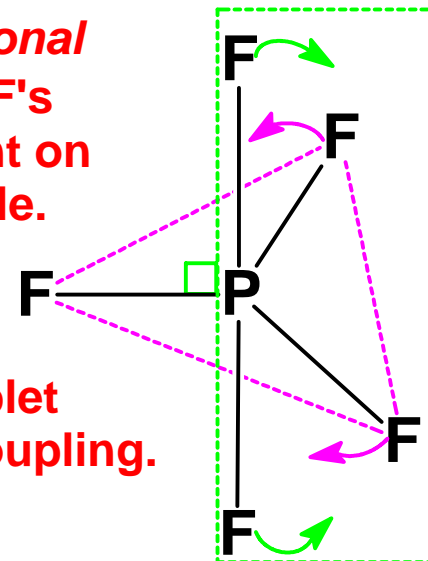


P(V) Halides:

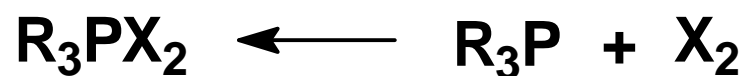
PF ₅	gas, bp = -84.5°C, trigonal bipyramidal molecule, fluoride ion acceptor.
PCl ₅	solid is: PCl ₄ ⁺ PCl ₆ ⁻ T _{subl} = 162°C gas is trigonal bipyramidal molecule.
PBr ₅	solid is: PBr ₄ ⁺ Br ⁻ T _{dec} = 106°C
PI ₅	solid is: PI ₄ ⁺ I ⁻

PF₅ is a fluxional molecule all F's are equivalent on nmr time scale.

¹⁹F nmr is a doublet due to ³¹P-¹⁹F coupling.

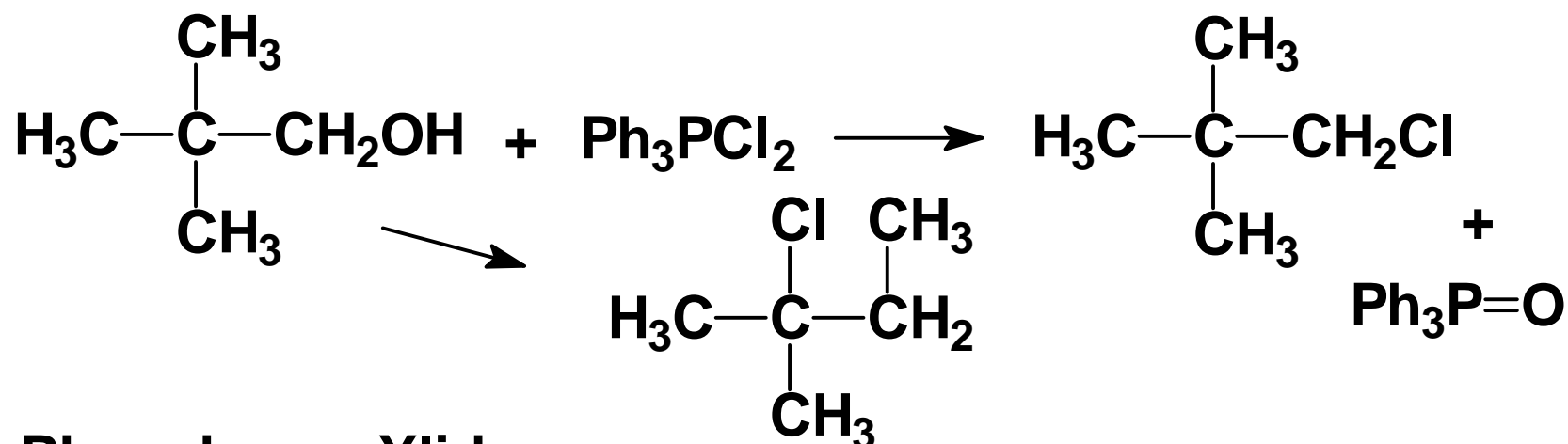


Phosphoranes & Phosphorus Ylids



X = F, Cl species are molecular.
X = Br, I species are ionic.

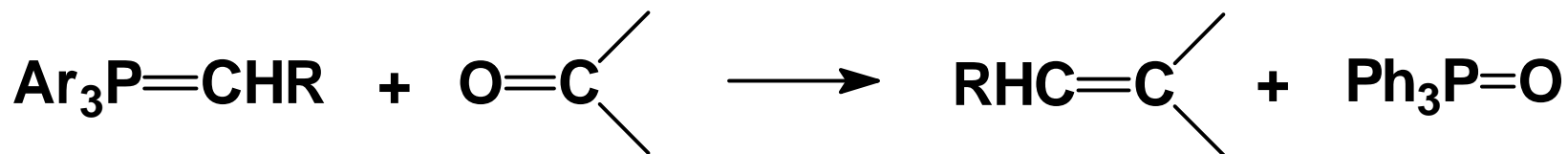
Useful in organic chemistry to convert alcohols to alkyl halides without forming a carbocation intermediate.



Phosphorus Ylids:

("ill-eds")

Wittig Reagent
1979 Nobel Prize



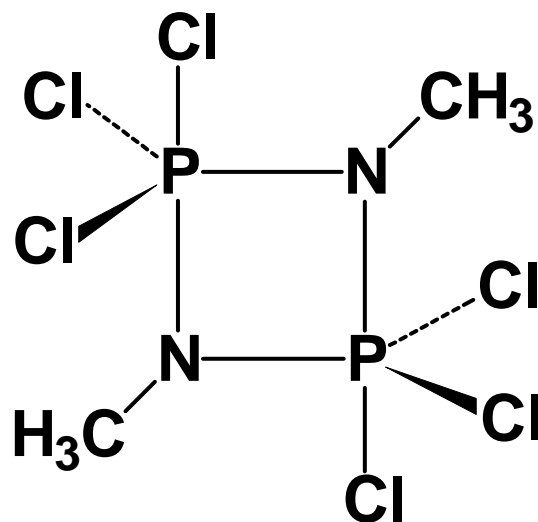
Phosphorus-Nitrogen - Phosphazanes

P(V) Most common.

Have formally P-N single bonds.



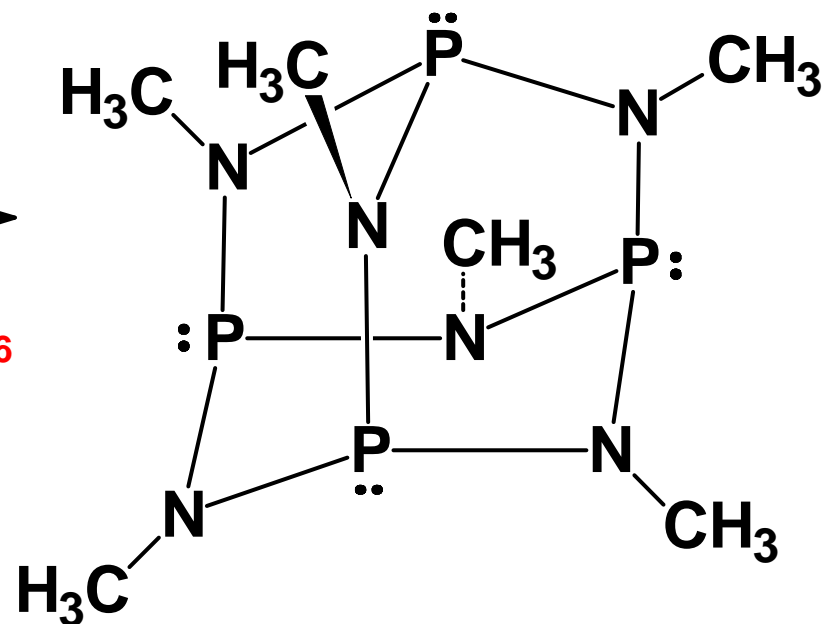
The phosphorus atom is trigonal bipyramidal, the axial P-N bond is longer than the equatorial bond.



P(III)

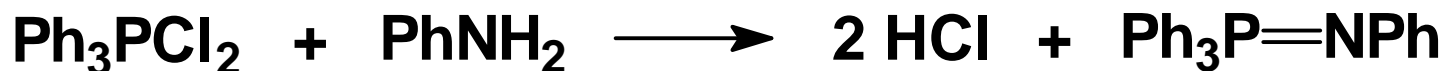


Isoelectronic with P₄O₆ adamantane structure.



Phosphorus-Nitrogen - Phosphazenes

P(V) **Most common. Have formally P-N double bonds.**



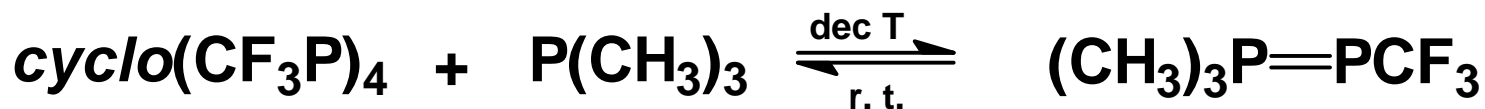
The "bistriphenylphosphine immonium" ion is an excellent counter-ion for stabilizing transition metal carbonyl anions, many salts become "air stable".

The $d\pi-p\pi$ double bond, unlike in allene need not be 180° . For example:

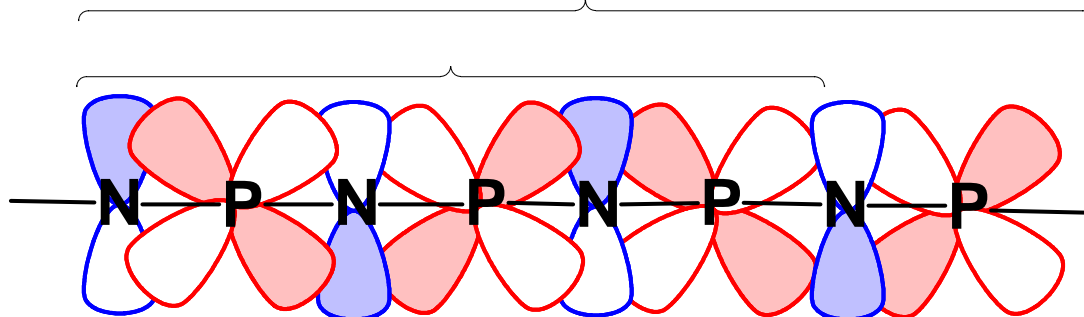
$[\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3]$ Two molecules in unit cell, each different. $\angle_{\text{PCP}} = 130^\circ \& 144^\circ$

Other Species: $\text{P}=\text{C}$ $\text{P}\equiv\text{C}$ $\text{P}=\text{P}$

$\text{R}-\text{C}\equiv\text{P}$: $\text{R} = \text{H}, \text{Bu}^t, \text{F}, \text{CF}_3$ **Unstable wrt polymerization, as a ligand will displace ethylene.**



Phosphazenes - Bonding



For a 6-membered ring symmetry is broken!

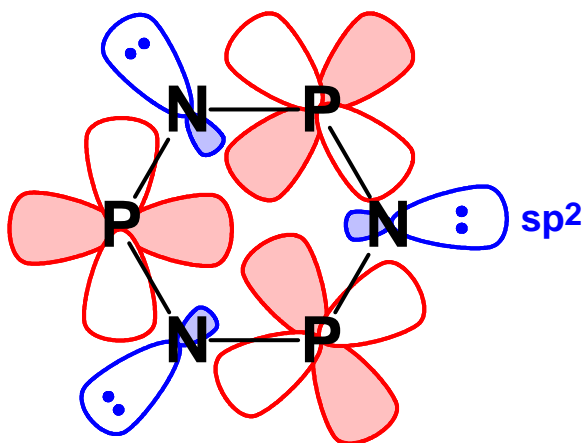
For an 8-membered ring symmetry is unbroken!

Trimers are planar.

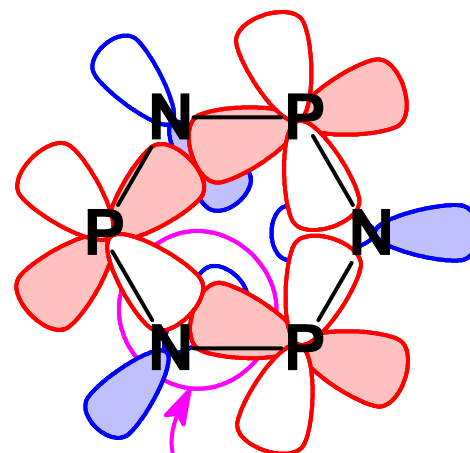
Tetramers are mostly non-planar. Planarity is not necessary for $d\pi-p\pi$ conjugation.

$[\text{NPF}_2]_4$ is planar!

Trimers may use an "exocyclic" conjugation.

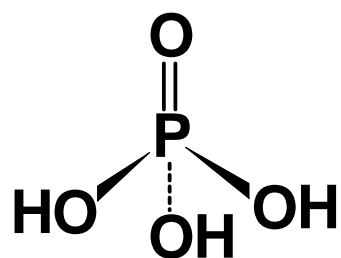


Symmetry is unbroken!

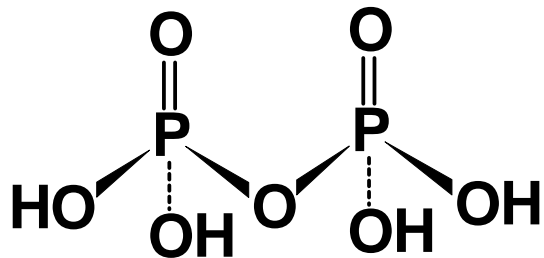


Symmetry is broken!

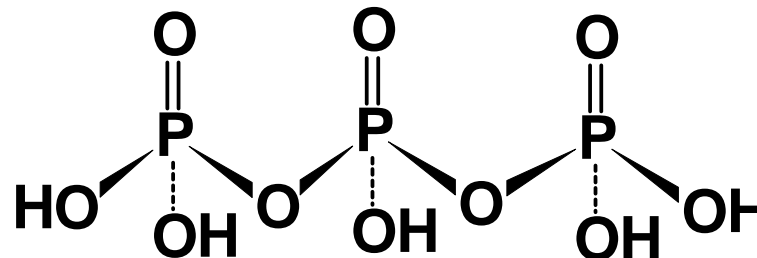
Oxoacids of Phosphorus(V)



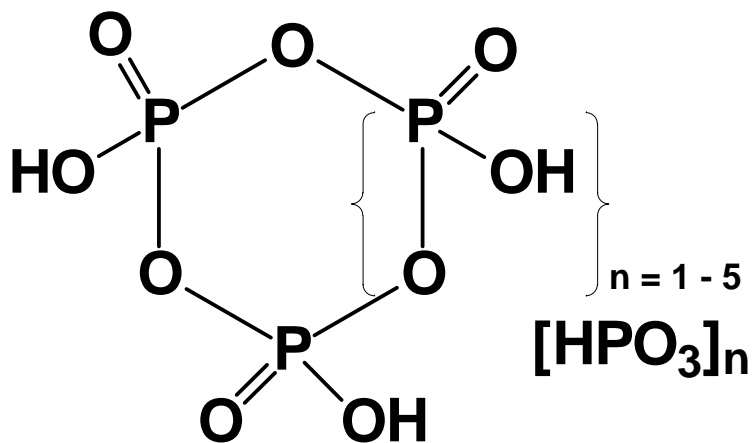
Orthophosphoric
Acid



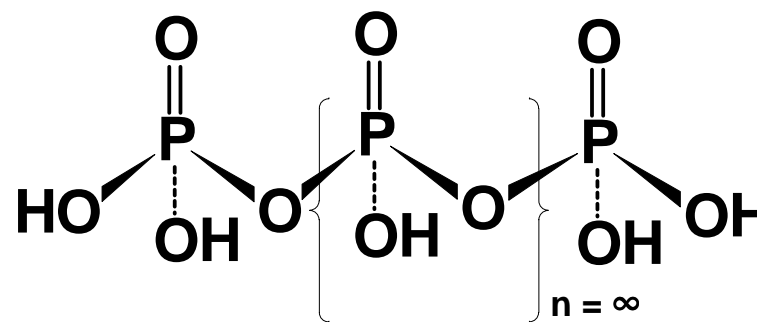
Diphosphoric Acid
Pyrophosphoric Acid



Triphosphoric Acid



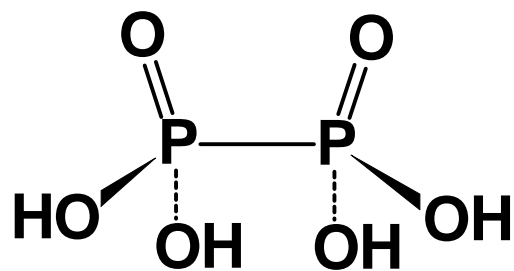
Cyclotriphosphoric Acid
Trimetaphosphoric Acid



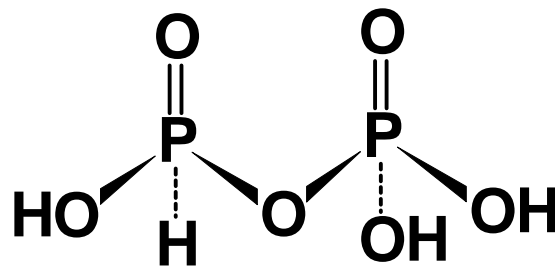
H_3PO_3 Polyphosphoric Acid
Metaphosphoric Acid

Polyphosphoric acids do not hydrolyze rapidly in water. Sometimes very slowly.
Poly phosphoric acids strongly influence the properties of water.

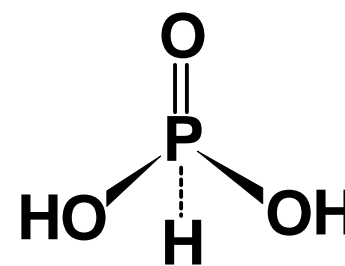
Oxoacids of Phosphorus(IV)-(III)



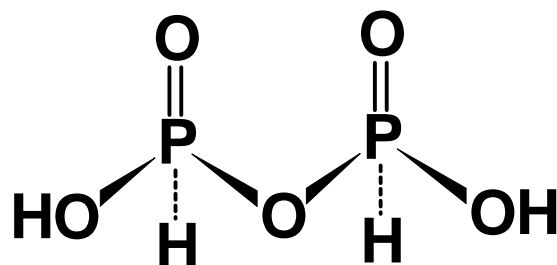
Hypophosphoric Acid
Diphosphoric(IV) Acid



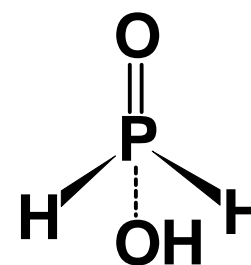
Isohypophosphoric Acid
Diphosphoric(III-V) Acid



Phosphonic Acid
Phosphorous Acid



Diphosphonic Acid
Pyrophosphorous Acid



Phosphinic Acid
Hypophosphorous Acid