Allotropes of Phosphorus

- Phosphorus has at least 12 allotropes.
- Most common are white and red phosphorus. Black phosphorus is most stable.
- White phosphorus (P_4) ignites spontaneously in air. Used in military weapons and smoke devices. Highly toxic, reactive with halogens and metals.
  Synthesis:

$$\overset{+5}{2\,Ca_3(PO_4)_2} + 6\,SiO_2 + 10\,\overset{+0}{C} \xrightarrow{1700\ K} \overset{+0}{P_4} + 6\,CaSiO_3 + 10\,\overset{+2}{CO}$$

Oxidation State

Oxidant: P in $Ca_3(PO_4)_2$ Reductant: C

- Red phosphorus structure consists of chains, perpendicularly cross-linked at the P'-P'' junction (the P'' is in a different chain). Not toxic, less reactive than white form toward halogens and metals, and also less flammable. Synthesis:

$$\text{White P} \xrightarrow[\text{inert atmosphere}]{540\ K} \text{Red P}$$

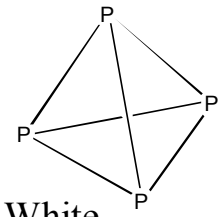
- Black phosphorus is similar to graphite in structure and physical properties (black, smooth, and electrically conductive). Not toxic, nonflammable, chemically inert up to high temperatures. Synthesis:

$$\text{White P} \xrightarrow[12{,}000\ atm]{\Delta} \text{Black P}$$

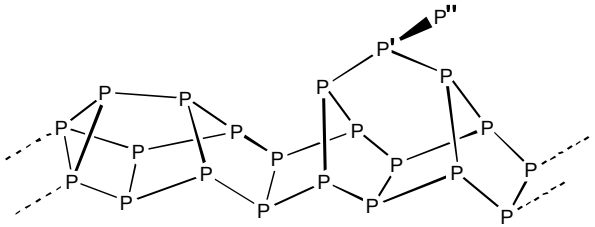
- Disproportionation of P_4:

$$\overset{+0}{P_4} + 3\,NaOH + 3\,H_2O \xrightarrow{\Delta} 3\,NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$$

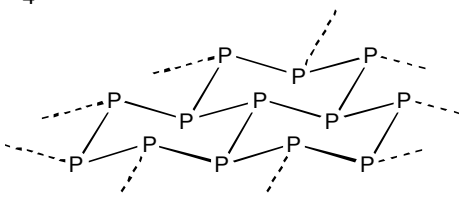
Oxidant and Reductant: P_4



White



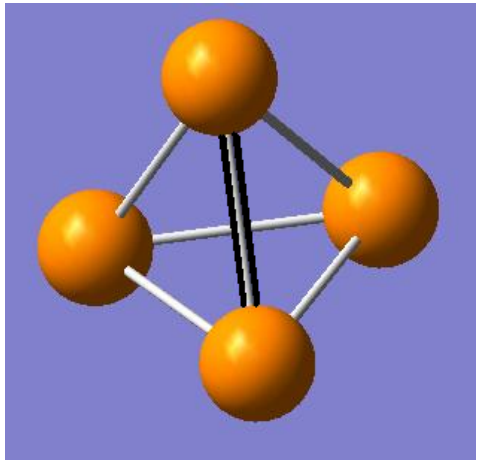
Red


Black

Reference: Housecroft and Sharpe, *Inorganic Chemistry*, 3rd ed., 2008.

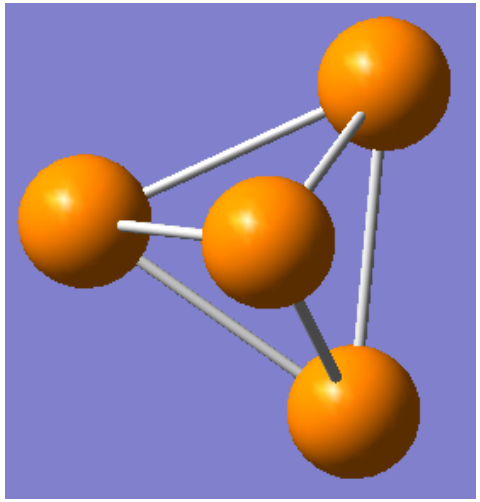
White Phosphorus

- P_4 has T_d symmetry:

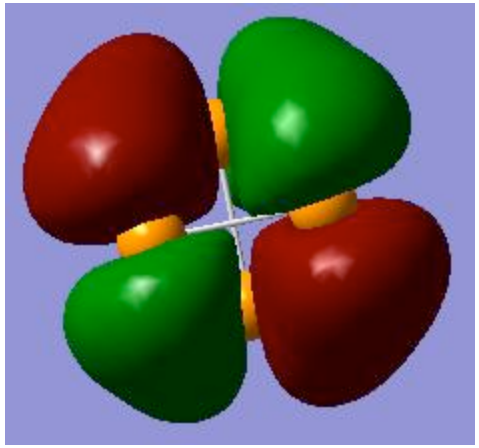


S_4 axis straight down into paper.

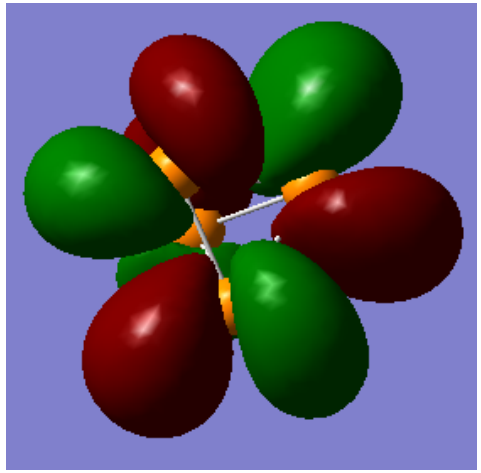
σ_d plane perp. to paper, through bolded bond.



C_3 axis straight down into paper.



HOMO, mix of bonding and antibonding. Notice increased electron density between some P atoms and decreased density between others.



LUMO, antibonding. Notice nodes of electron density between P atoms.