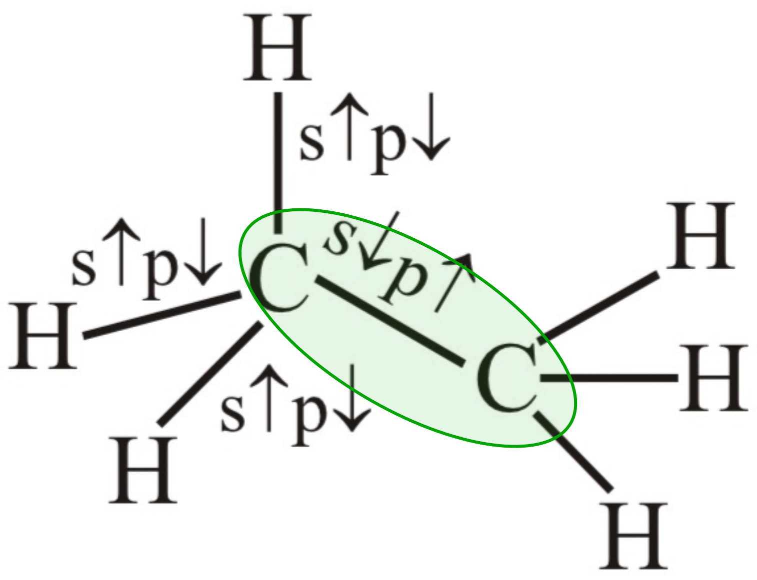
Application of Bent's Rule

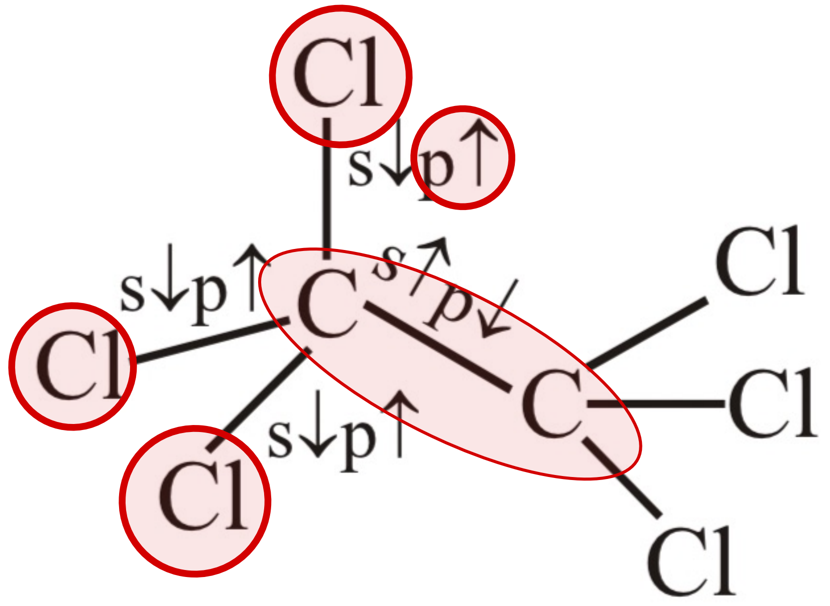
(Q)

Compare C–C bond length in C_2H_6 and C_2Cl_6

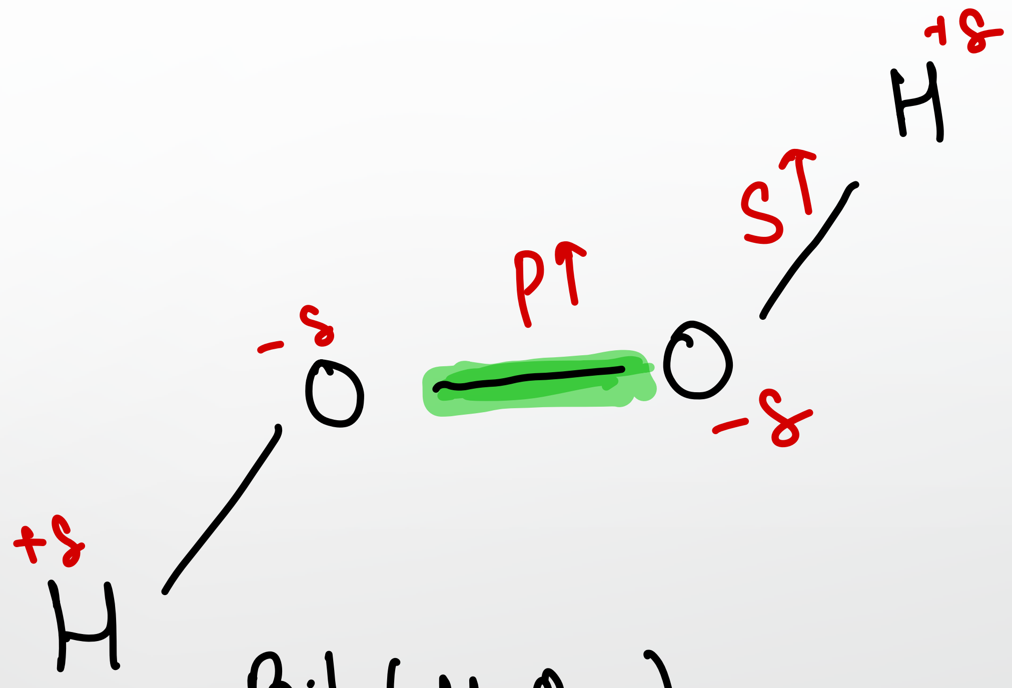
In C_2H_6 and C_2Cl_6 both carbon atom are sp^3 hybrid and there is no lone pair of electron on central atom, but all the four sp^3 hybrid orbital around any of the carbon are non-equivalent.

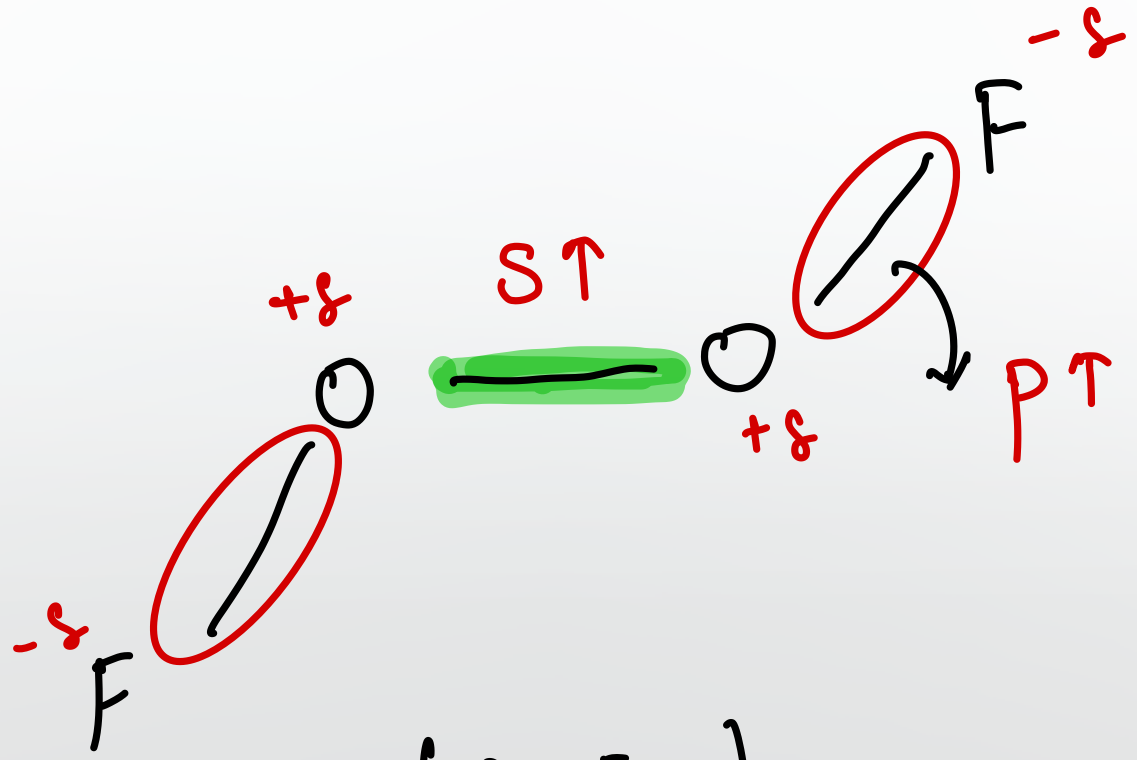
In C_2H_6 molecule, to one of the C-atom three hydrogen atom (less electronegative) and one carbon atom (more electronegative than H) is attached. According to Bent rule, more electronegative carbon will overlap with that hybrid orbital has less character of s-character.





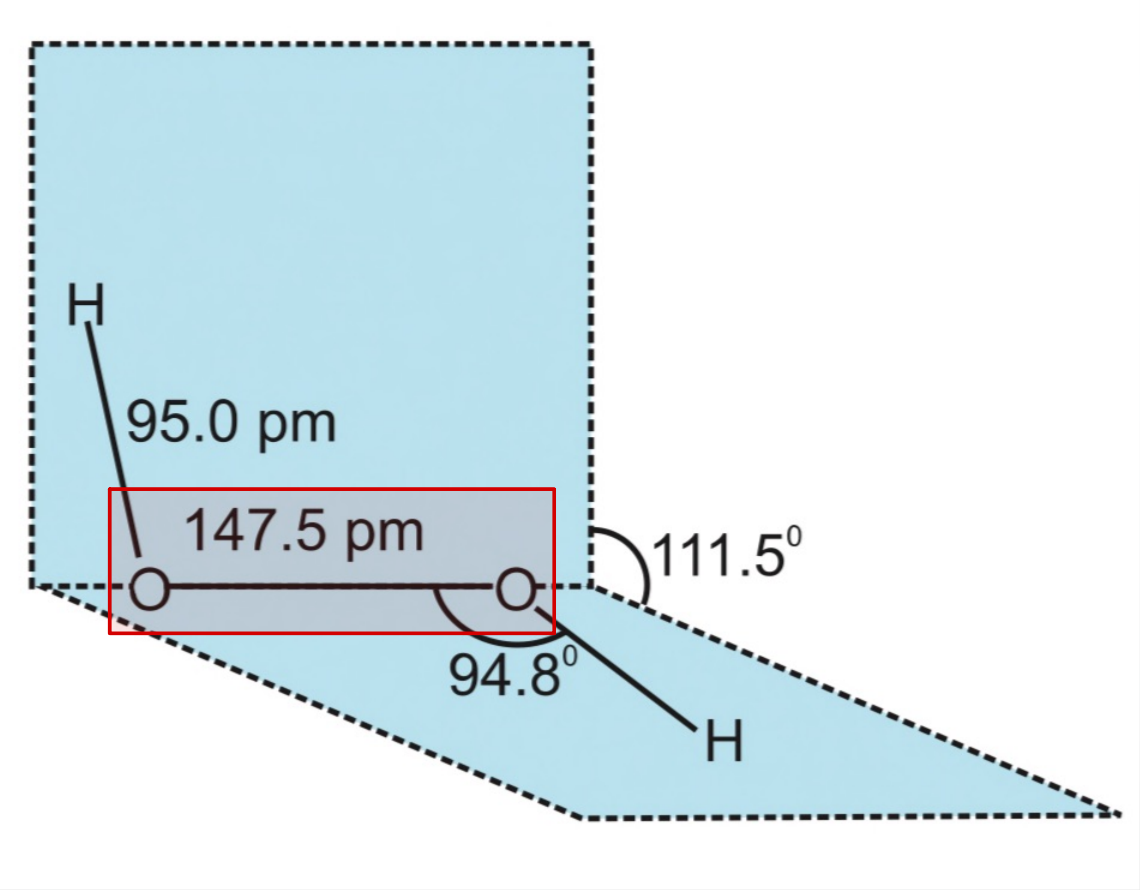
(Q) compare 'O-O' bond length in H2O2 and O2F2.

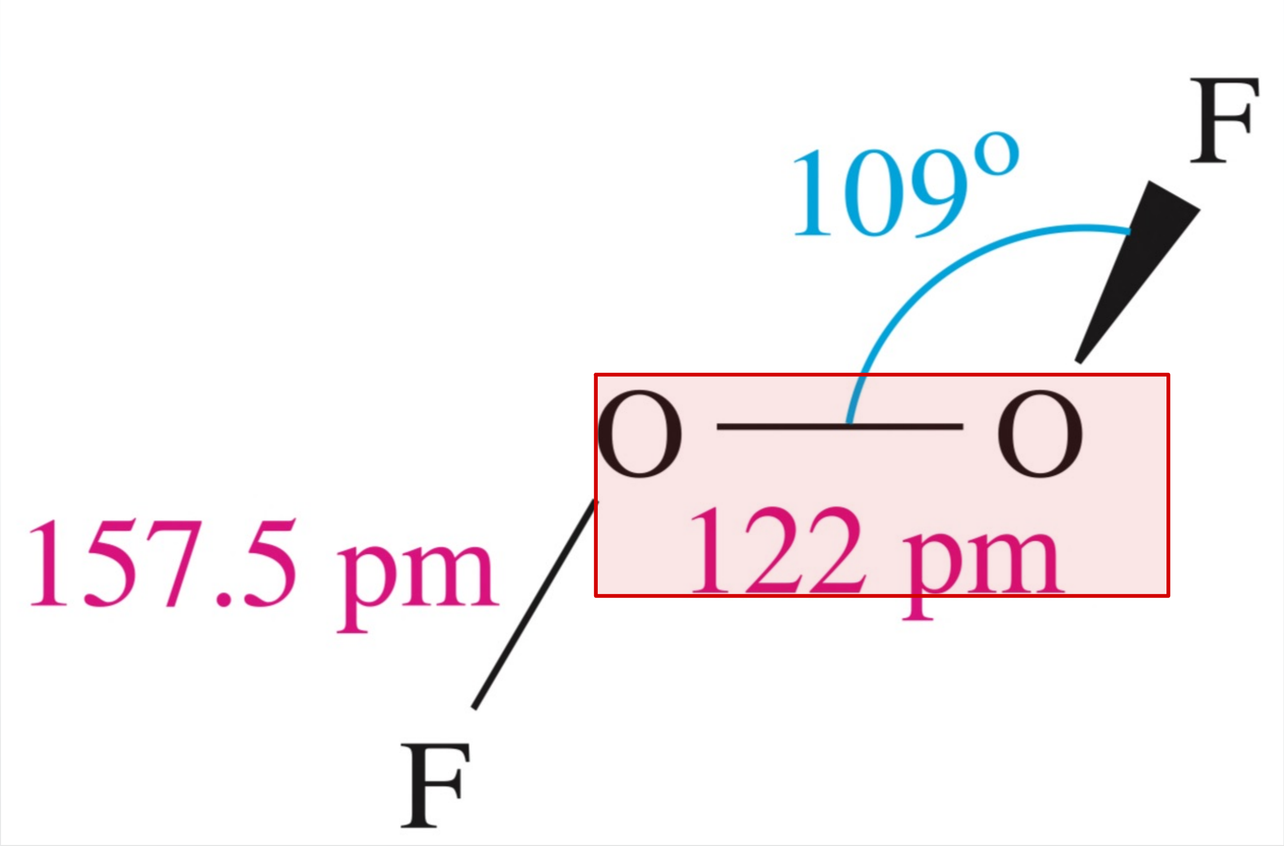




B.L (H_2O_2) > B.L (O_2F_2)

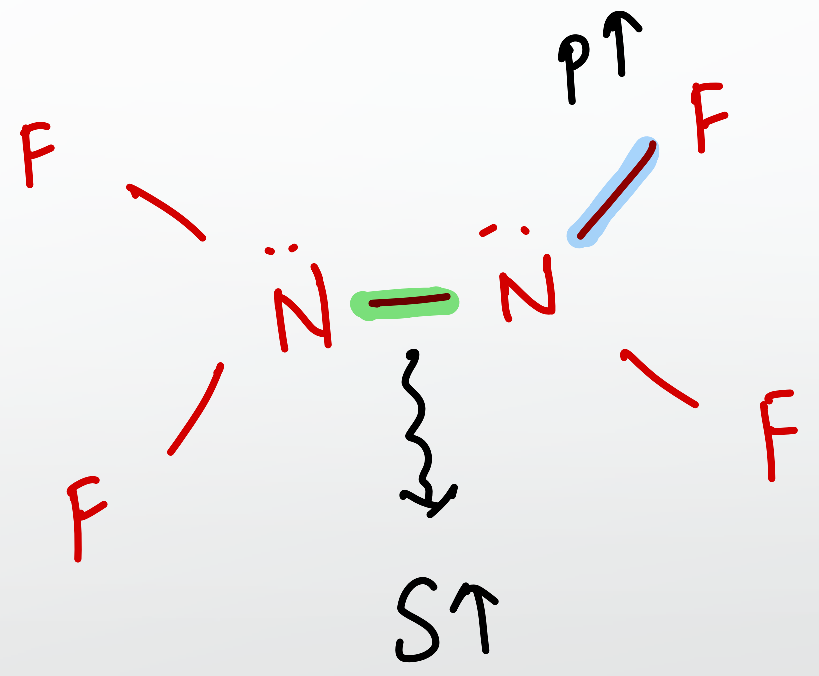
(O - O) (O - O)


H
95.0 pm
147.5 pm
111.5°
O
O
94.8°
H


F
109°
O
O
157.5 pm
122 pm
F

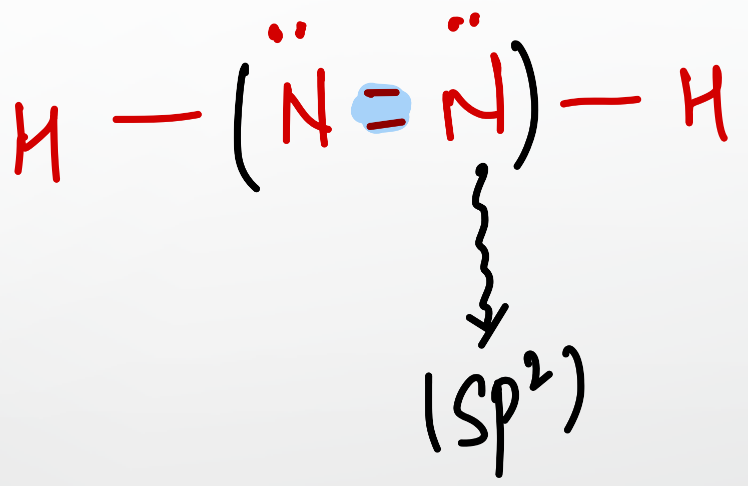
Chemical Bonding

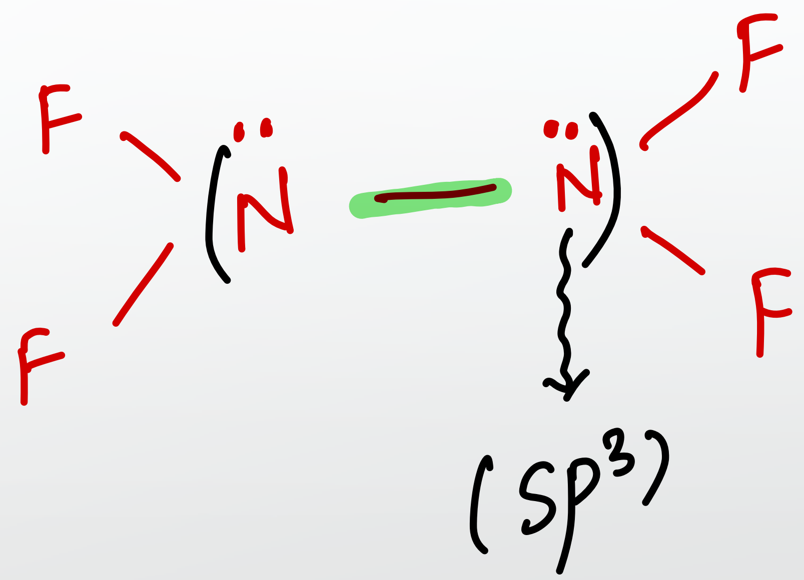
(Q) compare N-N bond length in N2H4 and N2F4



$$B.L\,(N-N)_{N_2H_4} > B.L\,(N-N)_{N_2F_4}$$

(Q) Compare N-N bond length in N2H2 and N2F4.

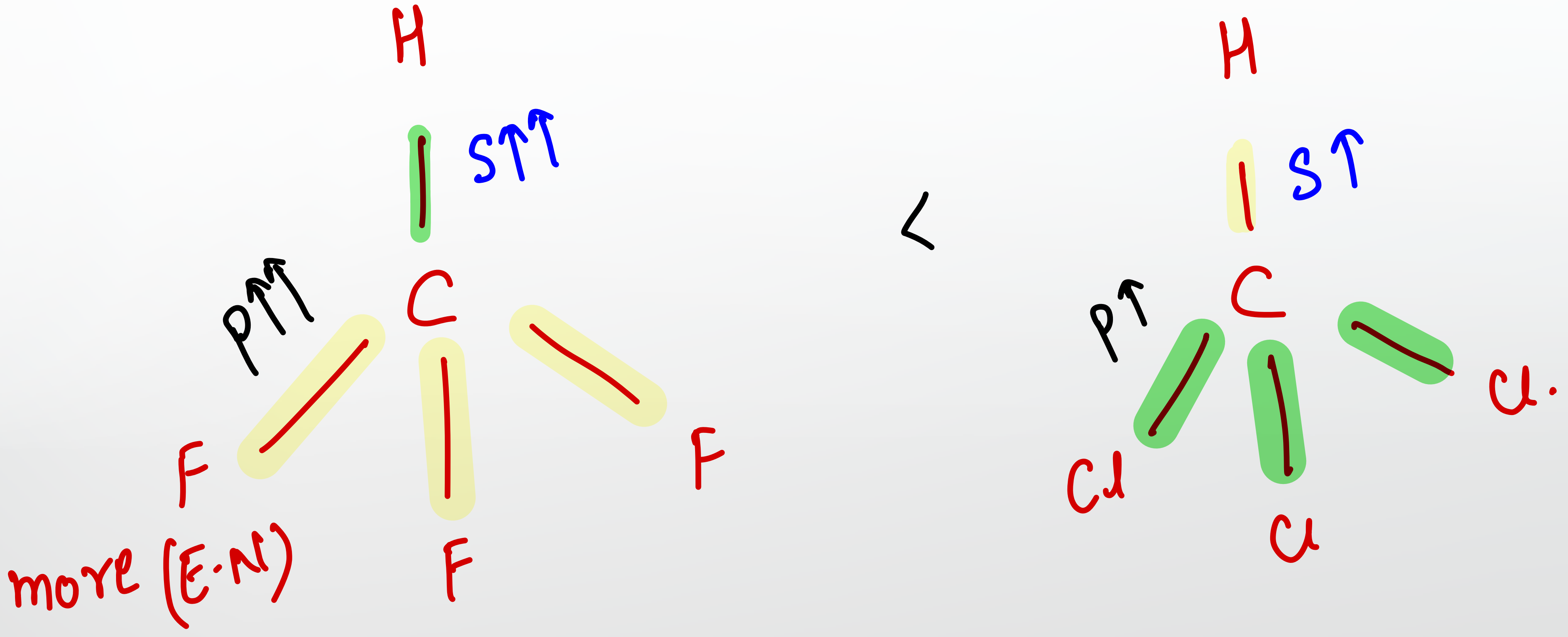




$$B.L\ (N-N)_{N_2H_4} < B.L\ (N-N)_{N_2F_4}$$

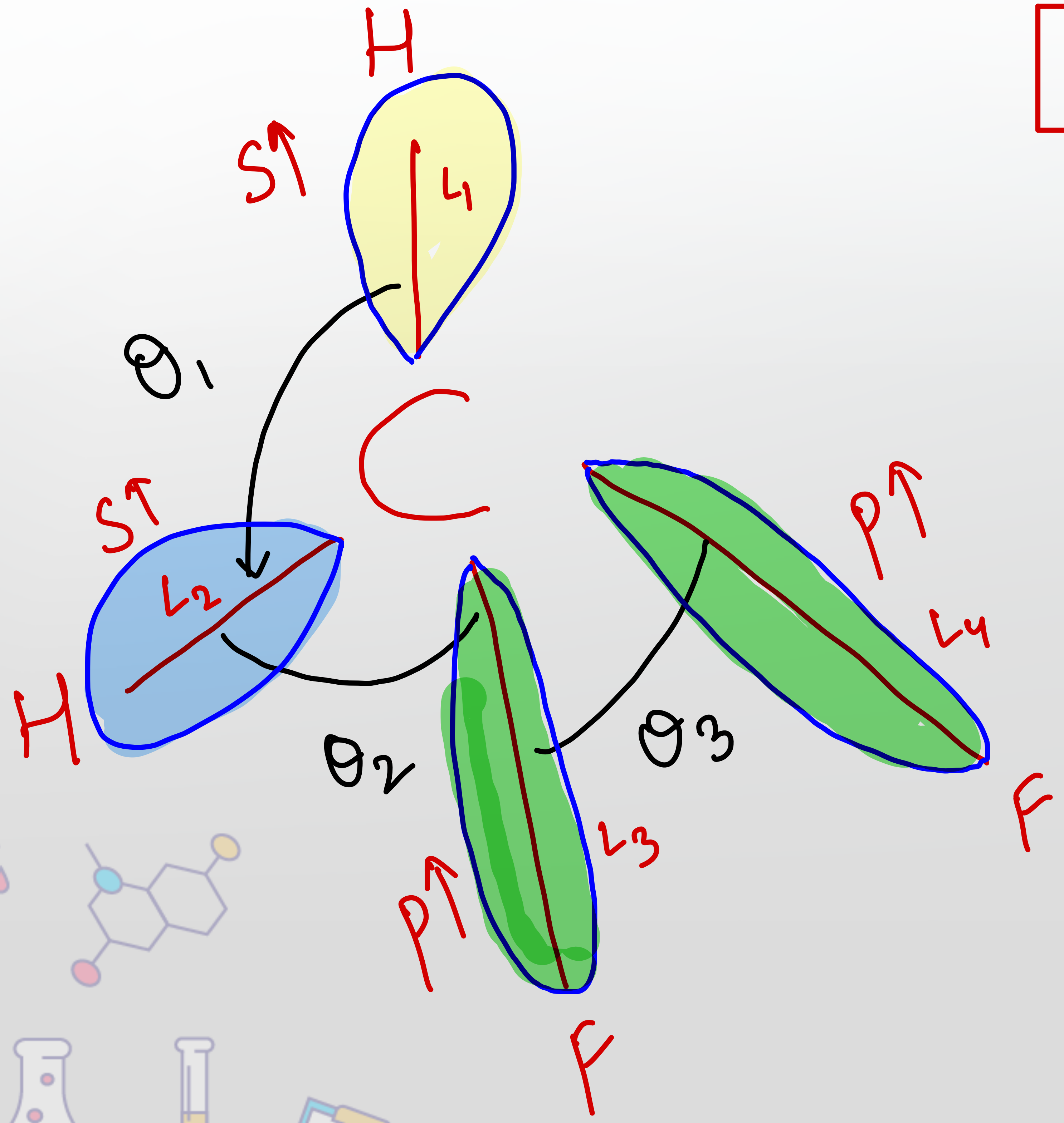
Note: double bond always less than single bond

(Q) Compare 'C-H' bond length in F3CH and Cl3CH.



$B.L\ (\text{'C-H'})_{CHF_3} < B.L\ (\text{'C-H'})_{CHCl_3}$

(Q) compare '$H\hat{C}H$' , '$H\hat{C}F$' , $F\hat{C}F$' in CH2F2

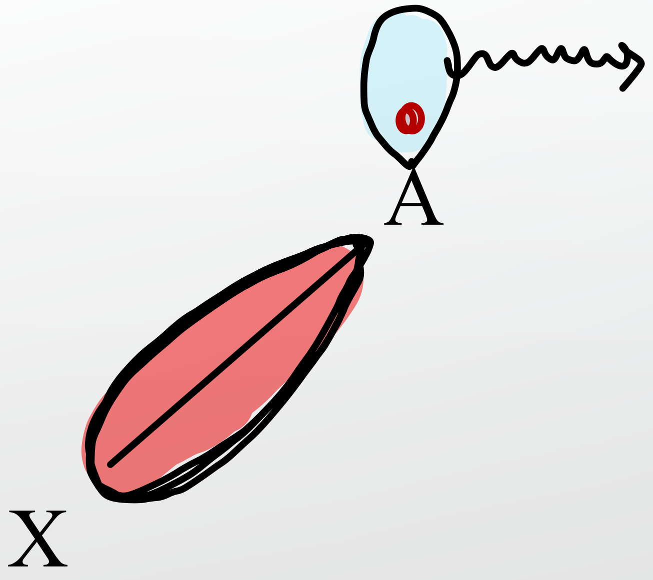


$$\boxed{\theta_1 > \theta_2 > \theta_3}$$

		S% Character
Sp	BA 180°	50
Sp²	BA 120°	33.33%
Sp³	BA 109°28'	25%

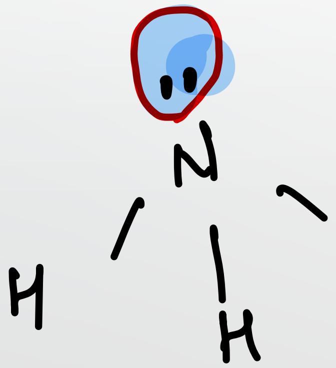
Hybridisation in odd electron species

Odd e species : $\dot{N}O$, $\dot{N}O_2$, $\dot{Cl}O_2$, $\dot{Cl}O_3$, $\dot{C}F_3$, $\dot{C}H_3$



orbital.

SN = σ Bond + lp. [Hybrid orbital]

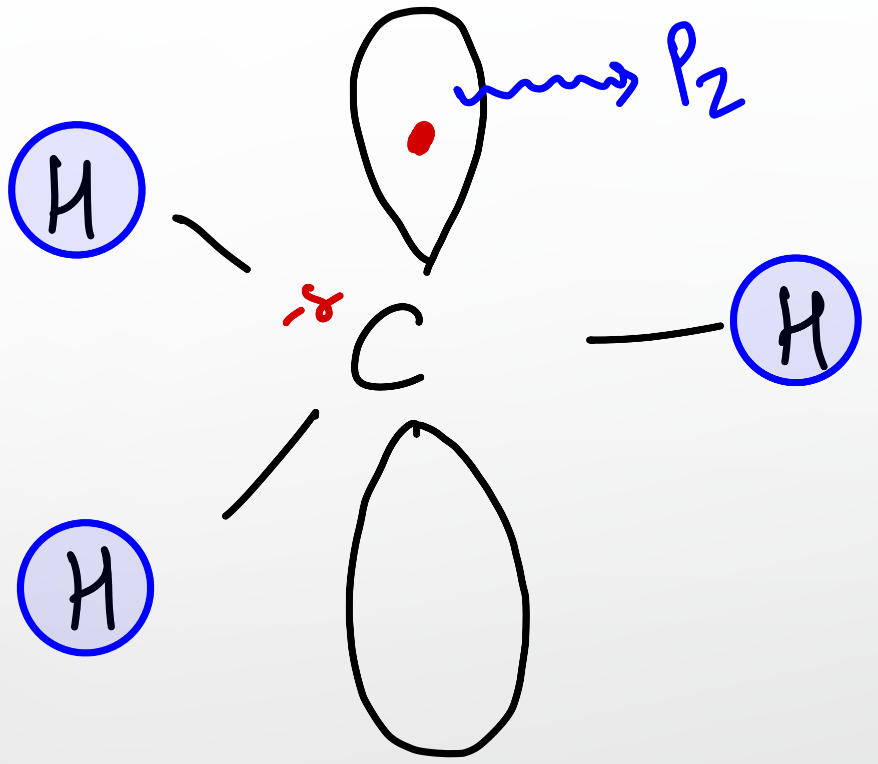


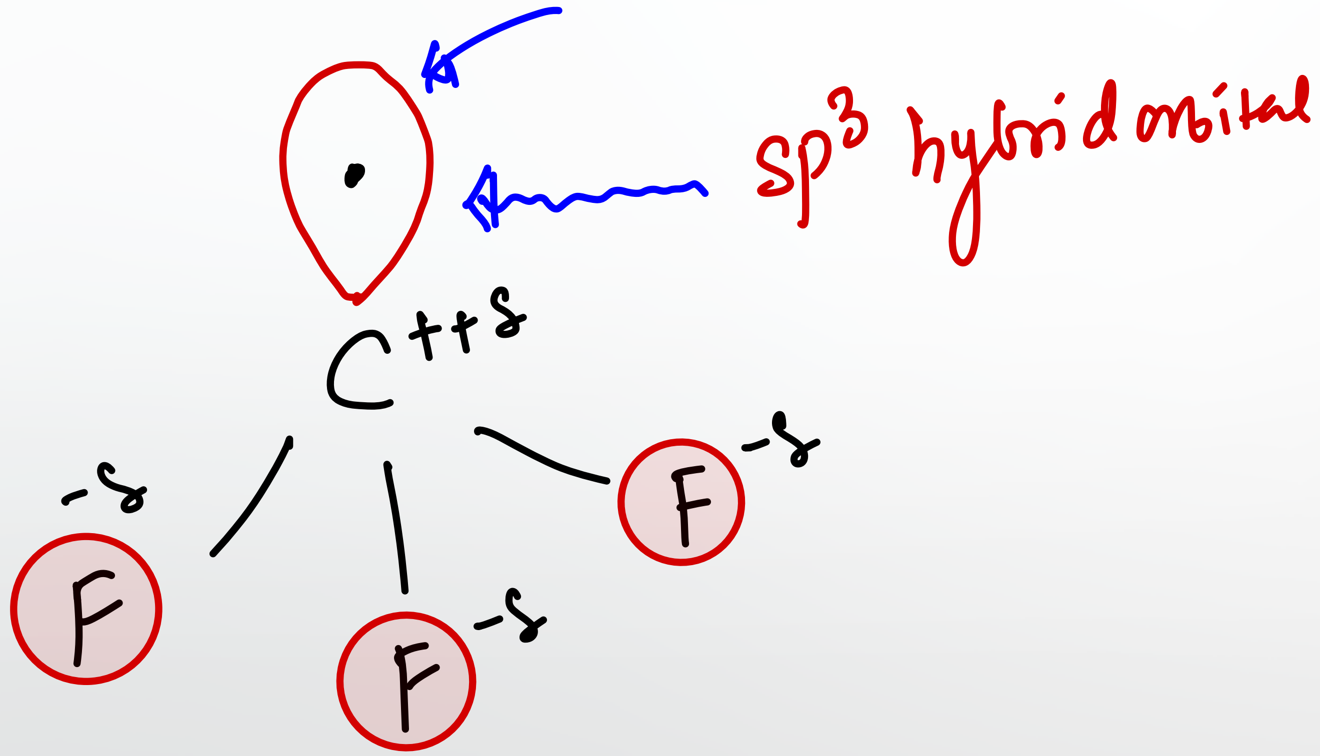
SN = 3+1 = 4

Hyb : sp^3

* If the Surrounding atom / peripheral atom is more electronegative it increases P character in A-X bond and hence increases S character in orbital of odd electron and make orbital to participate in hybridisation

(Q) what would you expect to be the shape of $\dot{C}H_3$ and $\dot{C}F_3$ free radical





$\dot{C}H_3$:

SN = 3

Hyb: sp^2 $(S + P_x + P_y)$

Shape: Trigonal planar.

$\dot{C}F_3$:

SN: 4

Hyb: sp^3

Shape: Trigonal pyramidal.

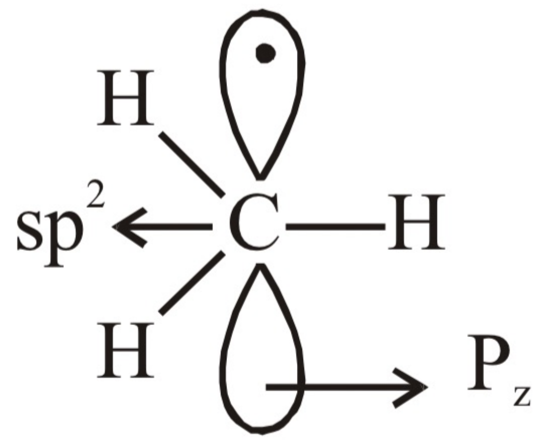
$\dot{C}H_3$:

Bond angle = 120°

Hybridisation = sp^2

Shape = planer

Structure :



Free electron in pure P atomic orbital

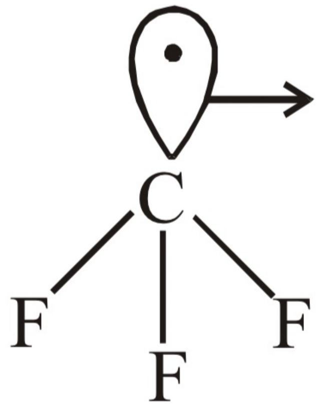
$\dot{C}F_3$:

Bond angle = 109°28'

Hybridisation = sp^3

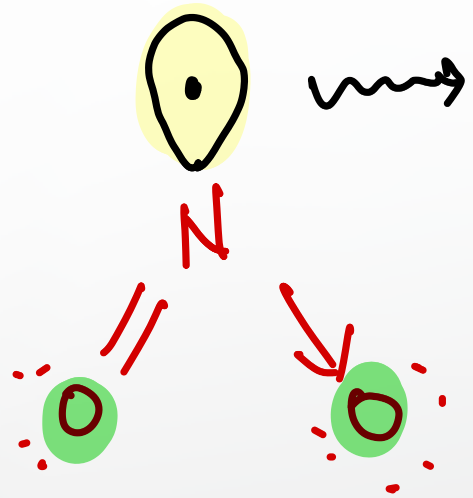
Shape = pyramidal

Structure :



free electron present in one sp^3 hybrid orbital

(Q) find the hybridisation and geometry of NO2.



participates in hybridization

(free e^- in sp^2 hybrid orbital)

Hyb: sp^2

Geo: V|Bent.

example:

* Homolytic clevage.
* Heterolytic clevage.

① Heterolytic

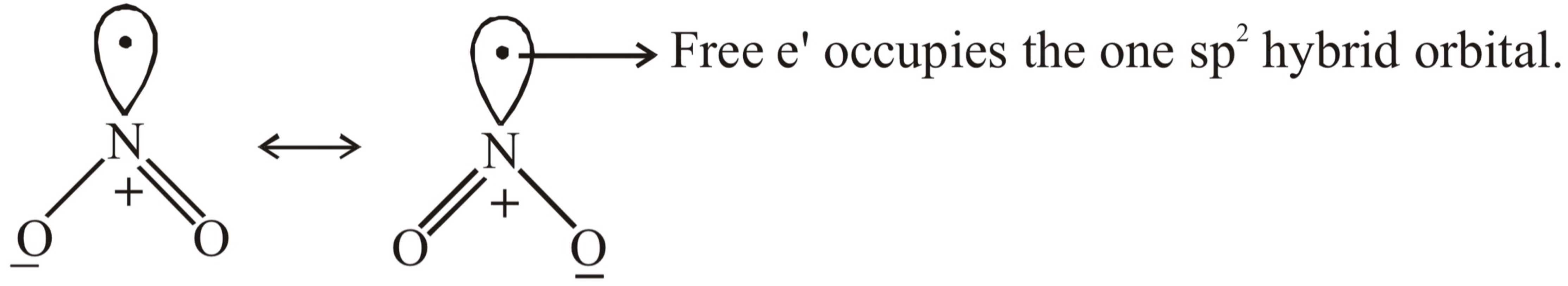
$$X : Y \longrightarrow X^+ + Y^-$$

(less EN) (more EN)

$$H_3C : CH_3 \longrightarrow H_3C^+ + {}^-CH_3$$

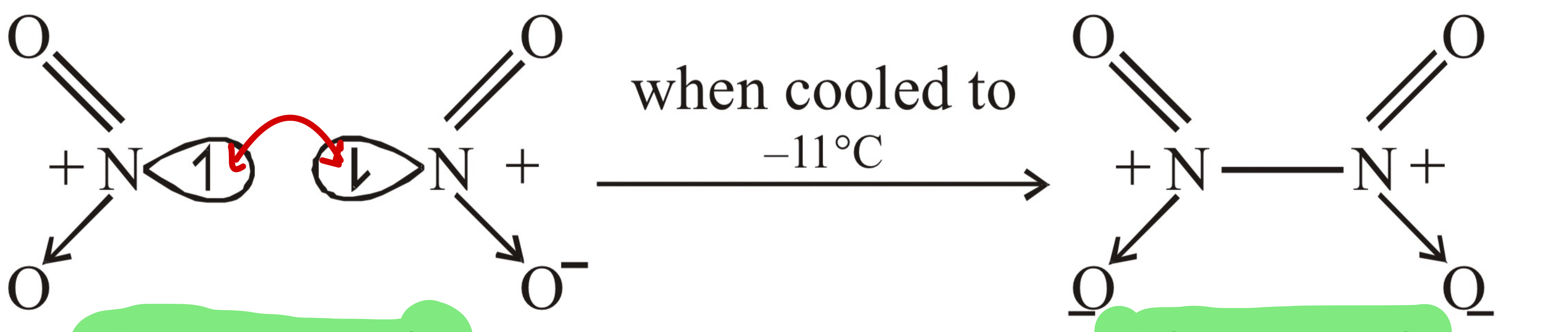
② Homolytic

$$H_3C - CH_3 \longrightarrow 2(\cdot CH_3)$$


Free e' occupies the one sp² hybrid orbital.

Nitrogen(IV) oxide exists as an equilibrium mixture of the brown NO_2 radical and its colourless dimer, N_2O_4 (dinitrogen tetroxide):

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K = 0.115 \text{ at } 25°C$$



Paramagnetic (unpaired electron) Brown colour gas

Diamagnetic (no unpaired electron) white coloured solid

Polymer

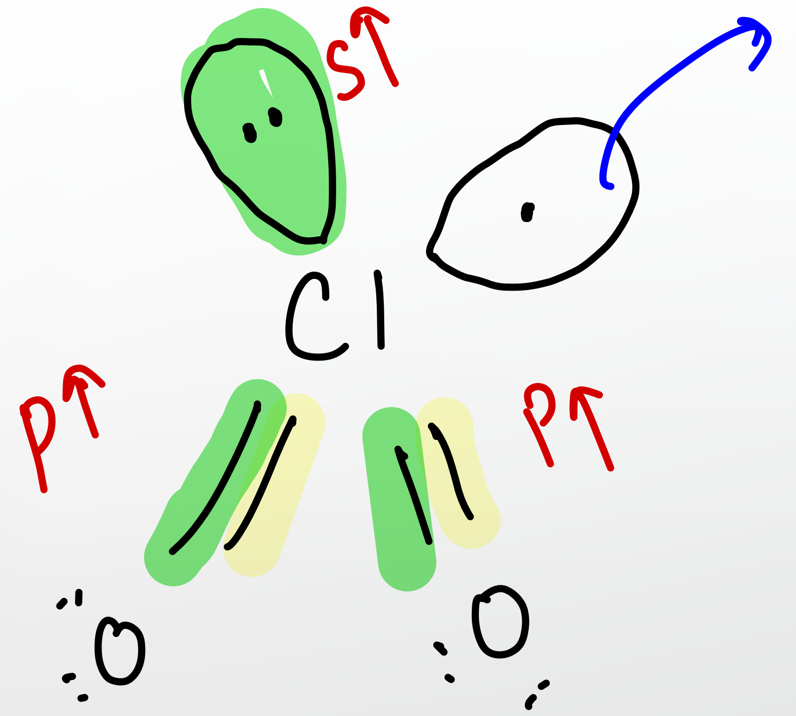
① $(CH_2 = CH_2)_n$ monomer Ethene

$\downarrow$

$+CH_2 - CH_2+_n$ polymer poly ethene

(Q) Find the hybridisation of ClO2.

Sol:)



EN (3.5)

E.N (Cl) = 3.0

Hyb: sp^2

G.S Cl [Ne] $3s^2$ $3p^5$

↑↓ | ↑↓ | ↑↓ | ↑

E.S Cl [Ne] $3s^2$ $3p^2$ $3d^1$

↑↓ | ↑↓ | ↑ | ↑ | ↑ | | | |

E.S Cl [Ne] $3s^2$ $3p^3$ π $3d^2$

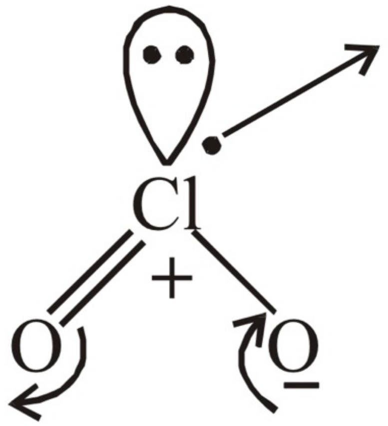
↑↓ | ↑ | ↑ | ↑ | ↑ | ↑ | | |

sp^2 π

odd e^- (delocalised in d orbital)

Note: ClO_2 does not dimerise because odd electron undergoes delocalisation (in its own vacant 3d-orbital)

Structure :

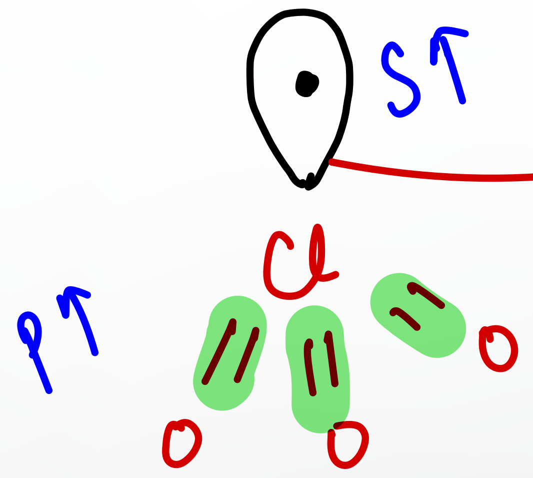


The free electron resides at the 3d-orbital of Cl-atom.

Since the free electron is delocalised in d-orbital, it's dimear formation tendency is very less as compared to NO_2.

(Q) find hybridisation of ClO3 will it have tendency to dimerise?

Ans:)



participates in hybridization.

Hybridization : sp^3

odd e^- localized.

yes, tendency to dimerize.

(3) **ClO_3 :**

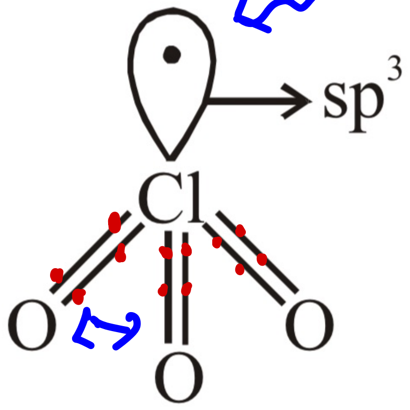
Bond angle = 119°

Hybridisation = sp^3

Shape = pyramidal

← sp^3 hybrid orbital.

Structure :



$$2ClO_3 \xrightarrow[\text{dimerises}]{\text{readily}} Cl_2O_6$$