Date: / /

Equivalence and Noneequivalence of the Hybrid Orbitals:

Hybrid orbitals

- Equivalent: sp, sp^2, sp^3 and sp^3d^2
- Noneequivalent: sp^3d and sp^3d^3

Noneequivalent Hybrid Orbitals

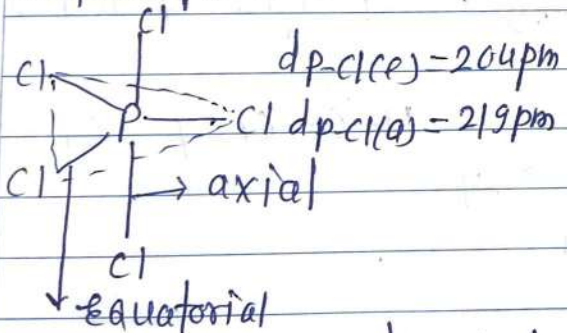
sp^3d

i) $sp^2 + pd$ TBP → axial hybrid orbitals

↓

xy plane

Equatorial plane



Note: In a TBP geometry, in terms of VSEPR each axial e⁻ pair experiences repulsions at 90° from 3 equatorial pairs while each equatorial pair experiences 2 such repulsions from the axial pairs. It makes the axial bond relatively larger.

sp^3d^3

$sp^2d^2 + pd$

xy plane (Basal plane) → $(s + p_x + p_y + d_{xy} + d_{x^2-y^2})$ +

Perpendicular to basal plane along the axial direction (+z & -z axis) → $(p_z + d_{z^2})$

(ii) sp^3d (Square Pyramidal)

- $s + p_x + p_y + d_{x^2-y^2}$ hybrid orbital → Lying on basal plane (i.e. xy plane)
- p_z pure orbital → Perpendicular to xy plane

TBP ⇌ SP

Bery Pseudorotation

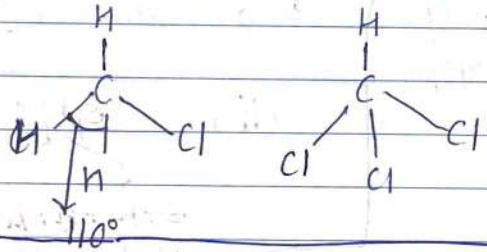
Date: / /

Presence of nonequivalent group and lone pairs:

sp^3d and sp^3d^3 shows that these hybrid orbitals are nonequivalent from the standpoint of their genesis. But equivalent hybrid orbitals (e.g sp^3 hybrid orbitals) may become nonequivalent, if the atoms or groups binding with the central differ significantly in electronegativity. Even in some cases when some of the hybrid orbitals are occupied by the lone pairs, the equivalent hybrid orbitals may lose their equivalent character in the compound formed.

e.g. CH_4 & CCl_4 all bond angles are 109.5°

CH_3Cl and $CHCl_3$ Bond angles ≠ 109.5°



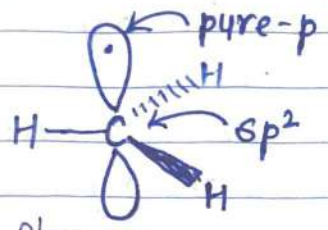
$H-\hat{C}-Cl \neq Cl-\hat{C}-Cl$

Bond Angles in (s+p) Combination:

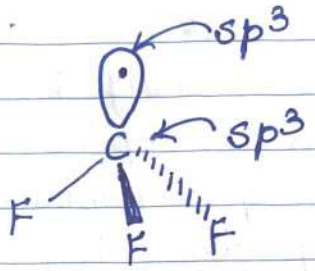
Hybridization	% Character		Angle
	s	p	
sp (linear)	50	50	180
sp^2 (Trigonal planar)	33.33	66.66	120
sp^3 (Td)	25	75	109.5°
p^2 (i.e. 2 pure p-orbitals	0	100	90

Date / /

CH_3 radical Vs. CF_3 radical:



Planar
sp^2 hybridised
Odd unpaired $\bar{e}$ is housed in pure p-orbital



Pyramidal
sp^3 hybridised
∴ → Odd unpaired $\bar{e}$ is housed in sp^3 hybrid orbital
→ Because of more electronegativity of F, F directs carbon (central atom) to project s-p hybrid orbital having more p-character.
→ Between sp^3 (75% p) and sp^2 (66.6% p) hybrid orbitals F prefers the sp^3 hybrid orbital of carbon having relatively smaller s-character.

VSEPR Explanation: Because of the slightly higher electronegativity of carbon w.r.t H, the bond pair of C-H bond is slightly attracted towards carbon. Thus the bp-bp repulsion in $\cdot CH_3$ is much higher than that of $\cdot CF_3$. To minimise this bp-bp repulsion in CH_3 it adopts the sp^2 hybridisation where bond angle is higher than that of the pyramidal structure having sp^3 hybridisation.

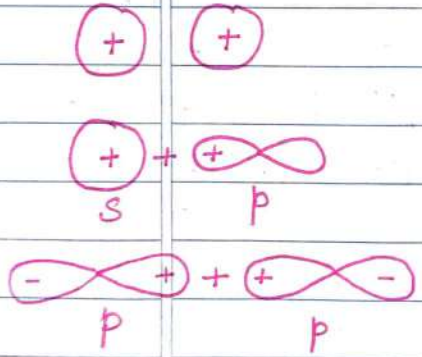
Date: / /

In fact, the CH_2, bp-bp repulsion operates at 120° and the odd electron-bp. repulsion which is relatively less operates at 90°.
In CF_3, bp-bp repulsions are less and it adopts the sp^3 hybridisation and all the repulsions occur at about 109.5°

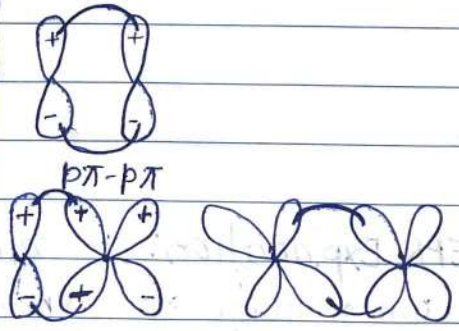
Apicophilicity: The tendency of more electronegative substituents to occupy the axial or apical pd-hybrid orbitals of low electronegativity in TBP geometries is referred to as apicophilicity.

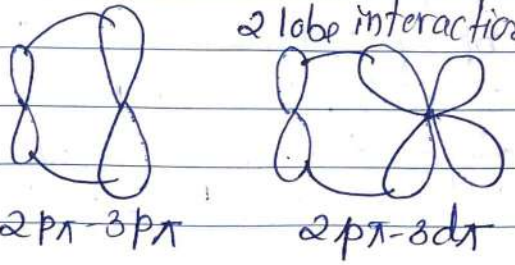
Types of Covalent Bonds:

σ-Bond
- formed by head-on overlap of orbitals
- Electron density is concentrated between two atoms and the line joining the two atom.



π-Bond
- It is formed by sideways overlap of orbitals





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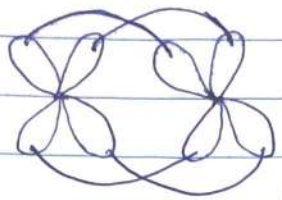


dπ-dπ (4 lobe interaction)
δ-bond

Different Types of overlap of σ-bonds:

- s-s overlap, eg H_2
- s-p overlap, e.g. HX
- p-p overlap, eg. X_2

Keeping the internuclear distance same, the relative strength of bond resulting from three kinds of overlap is

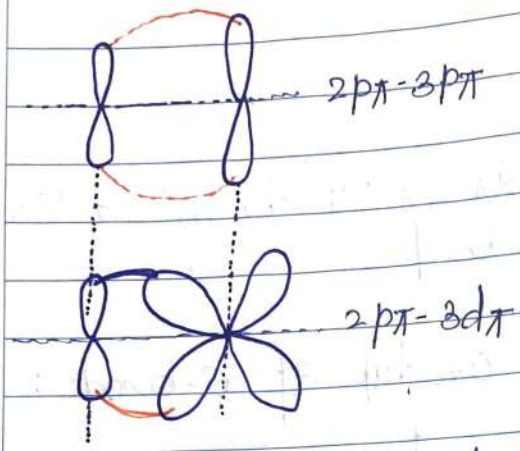
$$s\text{-}s < s\text{-}p < p\text{-}p$$

The order of bond strength can be explained on the basis of the fact that more the area of overlap, higher will be the strength.
Since the p-orbital has directional property, p-p overlap provides more area for overlap for the same internuclear distance.

π-Bond: It is formed by sideways overlap of orbitals. The relative strength of the π bonds increases when the intermolecular distance decreases and the order is:

$$2p\pi\text{-}2p\pi > 2p\pi\text{-}3d\pi > 2p\pi\text{-}3p\pi > 3p\pi\text{-}3p\pi$$

Due to the inclined nature of the d-orbital, it is more close in case of $2p\pi$-$3d\pi$ and strength of bond is more as compared to $2p\pi$-$3p\pi$.



The shape of the molecule is determined by th
σ bond (and lone pairs) but not by the π bonds

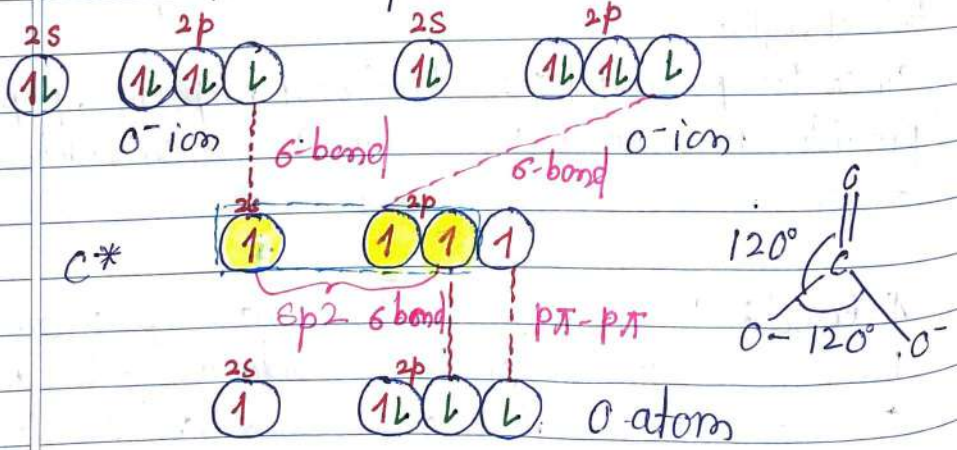
Geometry of Some Ions :

1. CO_3^{2-}

Central atom ⇒ Carbon

$1s^2\ 2s^2\ 2p^2$ G.S.

$1s^2\ 2s\ 2p^3$ E.S.



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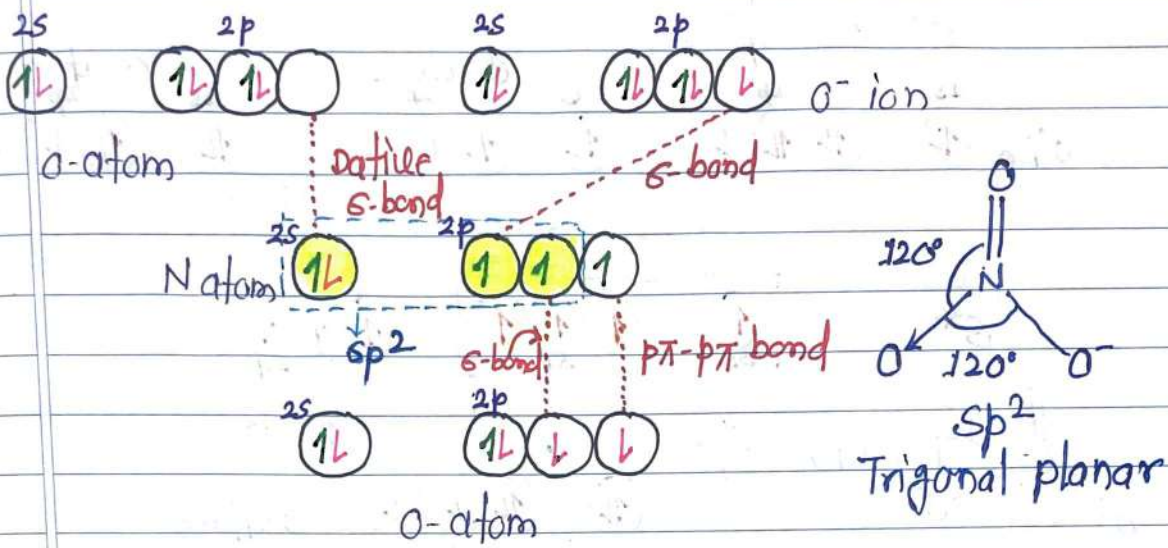
NO_3^- Central atom = N

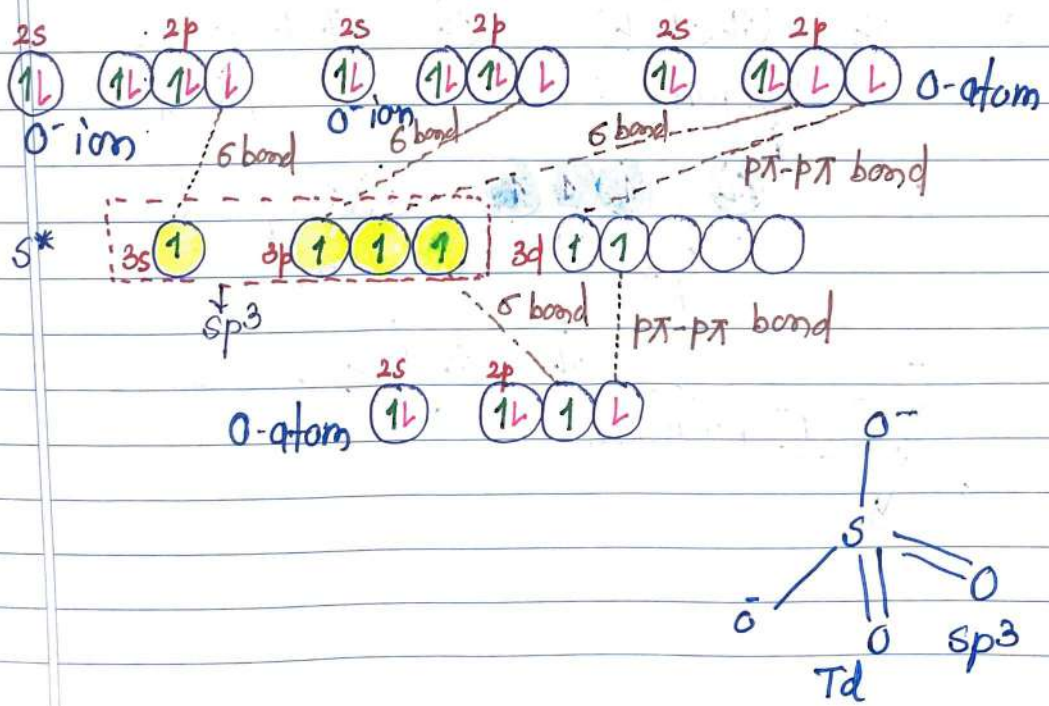
$1s^2\ 2s^2\ 2p^3$ G.S.



SO_4^{2-} Central atom = S

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ G.S.

$1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^3\ 3d^2$ E.S.



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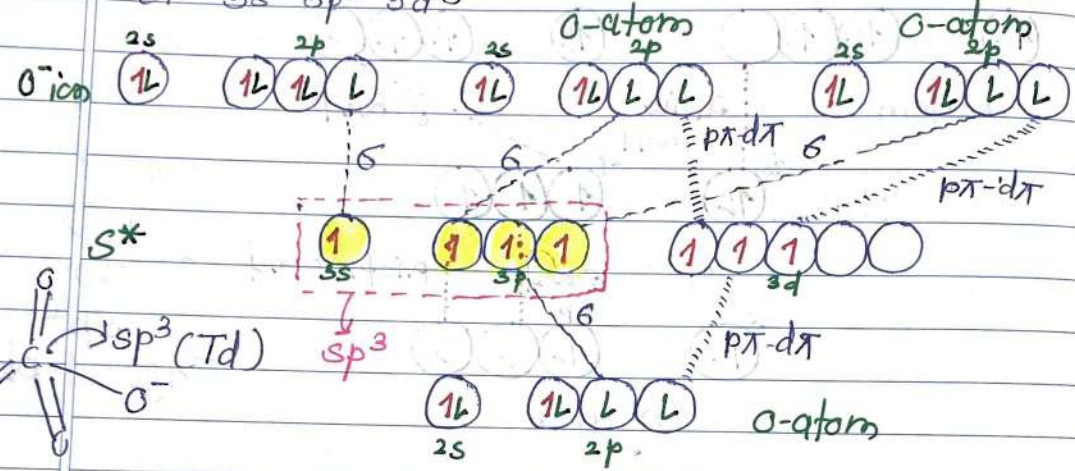
Perchlorate Ion: (ClO_4^-)

Central atom = Cl

Cl $3s^2\ 3p^5$

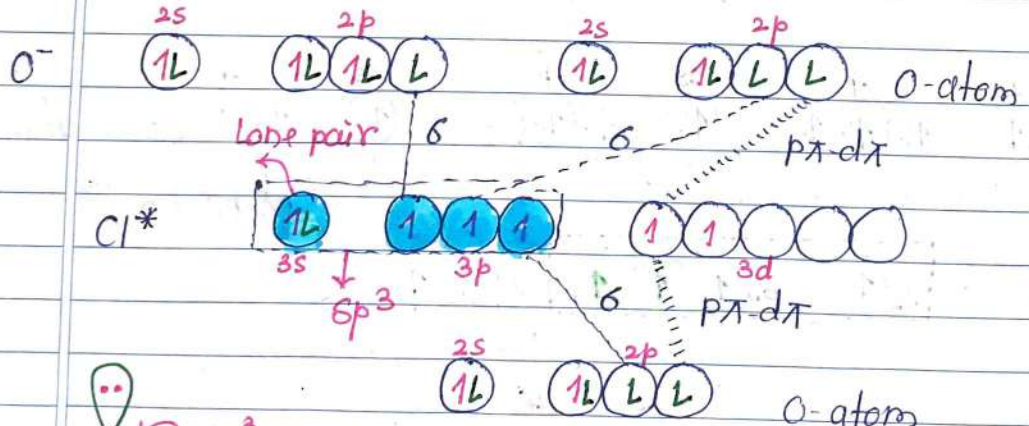
Cl* $3s^1\ 3p^3\ 3d^3$



Chlorate Ion (ClO_3^-): Central atom = Cl

Cl → $3s^2\ 3p^5\ 3d^0$

Cl* → $3s^2\ 3p^3\ 3d^2$



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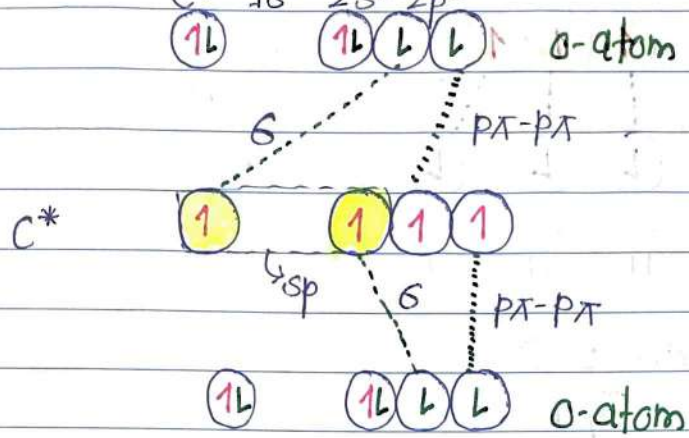
CO_2 Central atom = C

C $1s^2\ 2s^2\ 2p^2$

C* $1s^2\ 2s^1\ 2p^3$



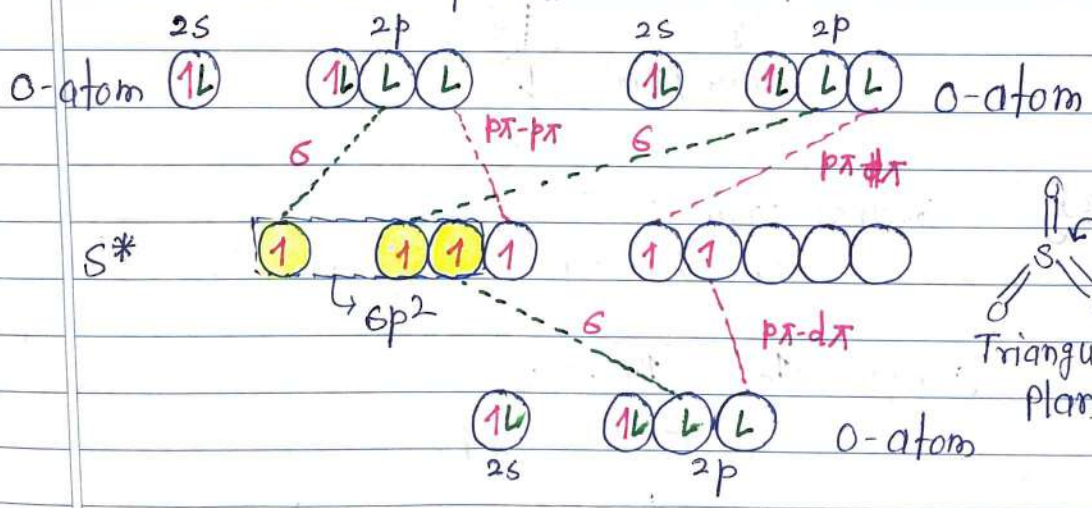
O=C=O

↳sp Linear

SO_3 Central atom = S

S $3s^2\ 3p^4$

S* 3s 3p 3d



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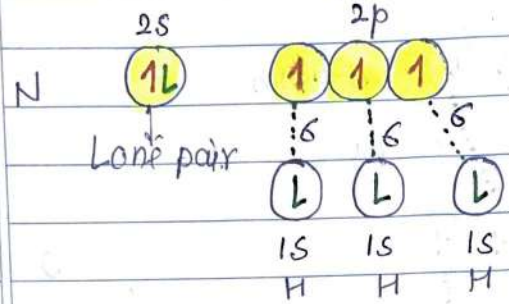
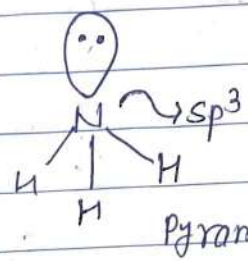
NH_3 Central atom = N

$N = 2s^2\ 2p^3$

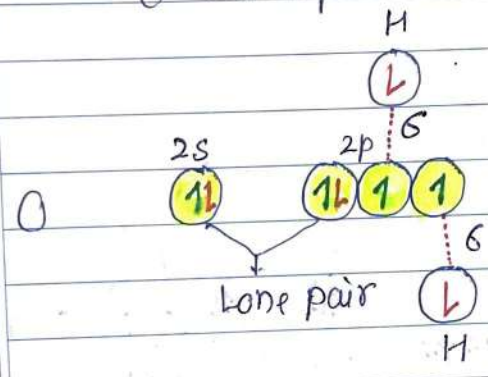


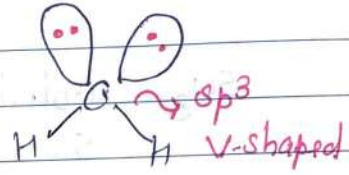


Pyramidal

H_2O Central atom = O

$O\ 2s^2\ 2p^4$





V-shaped

SO_2 Central atom = S

$S = 3s^2\ 3p^4$ $S^* = 3s^2\ 3p^3\ 3d^1$