Bents Rule

M. Sc. : CC – 1/CSIR NET
(Inorganic Chemistry)

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BENT RULE
Henry Bent (1926-2015)

More En element prefers to stay at axial position with greater P character & develope more ionic nature where as L.P. electron/less electronegative atom prefers to stay at equatorial position with more S-character & develope more covalent nature. It is also known as Apicophilicity.
This rule can be explained by Bent equation

Equivalent hybrid orbital SP (180^0), SP^2 (120^0), SP^3 (109.5^0), SP^3d^2 (90^0) non equivalent hybrid orbital SP^3d (90^0 & 120^0), SP^3d^3 (90^0 & 72^0)

$$\text{Cos}\theta = \frac{S}{S-1}$$

Where θ =Angle
S= %S character

For axial
θ = 120^0

$$\text{Cos}120 = \frac{S}{S-1}$$

$$\frac{-1}{2} = \frac{S}{S-1}$$

$-S+1 = 2S$

$3S = +1$

$$\text{There } S = \frac{1}{3} = 33.3\%$$

For axial
θ =90^0

$$\text{Cos}\theta = \frac{S}{S-1}$$

$$0 = \frac{S}{S-1}$$

$$S = 0 = 0\%$$

For axial
θ = $109^0 28'$

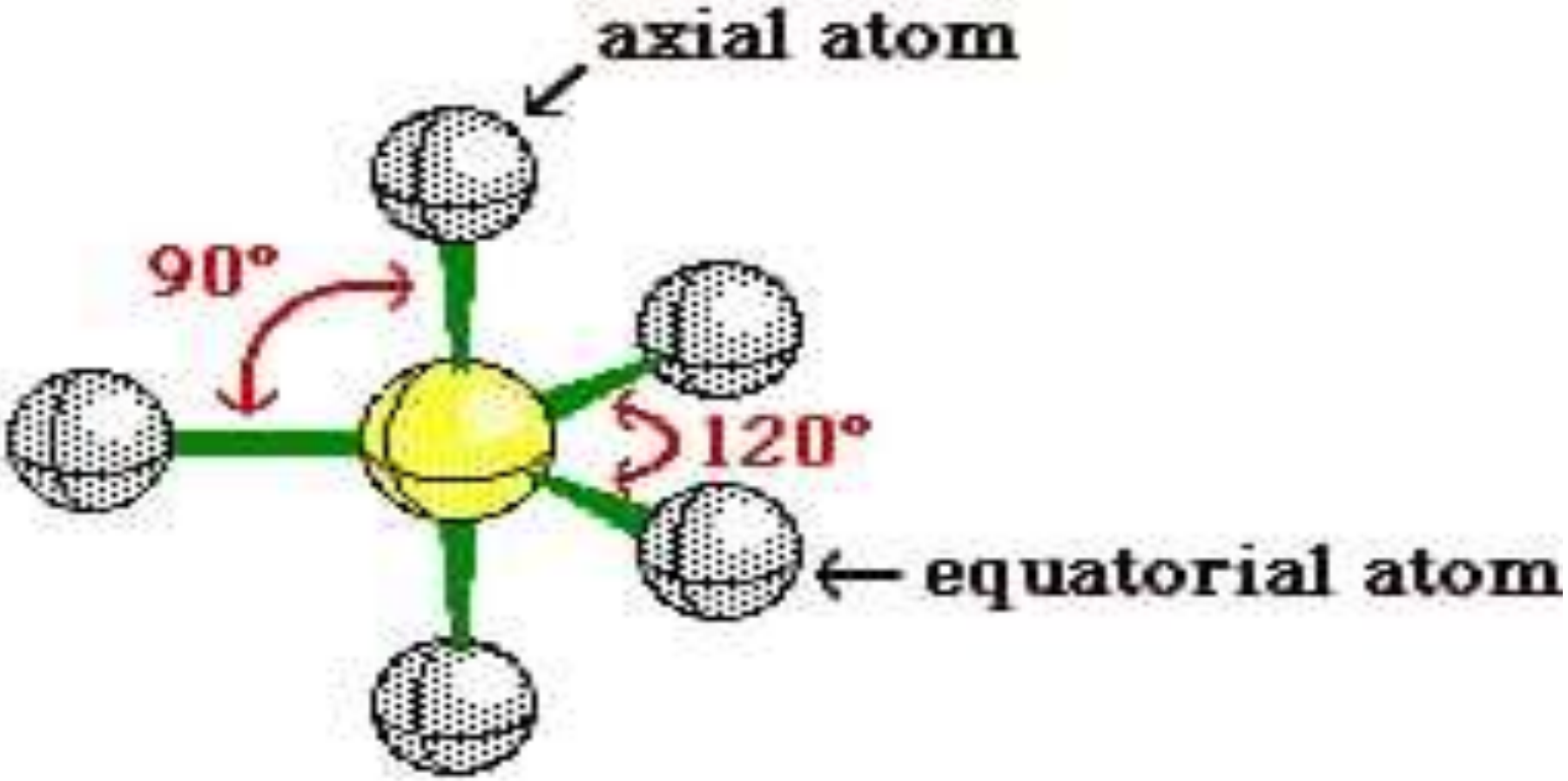
$$\text{Cos}\theta = \frac{S}{S-1}$$

θ = 25%

Hence % S Character in Equatorial > axial
More in S character more in bond angle

Cause of Preference/Apicophilicity

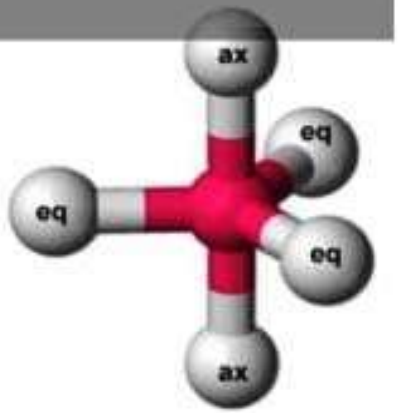
In molecule of non equivalent hybrid orbital have apiece (axial) & equatorial position & have different bond angle with different stabilities.



The bond angle between apical and equatorial bonds is only 90°, while that between equatorial bonds is 120°. Axial atom is surrounded by 3 equitorial atoms with more steric hinderence but equitorial atoms surrounded by only 2 axial atoms & with less steric hinderence Therefore, bulky substituents prefer the equatorial position to avoid the steric repulsion. π-donating ligands also prefer the equatorial position, because they can interact with the anti-bonding orbital (σ* orbital) of the equatorial bonds

Example

Shape of PCl_3F_2



As per VSEPR rule :

Central atom P: No. of valance electrons = **5e**

Other atoms Cl: 3 × 1 electron = **3e**

Other atoms F: 2 × 1 electron = **2e**

Total Number of electrons = 5e+5e = 10e

Number of electron pair = 10e/2 = 5

Number of bond pairs = 5 and Number of lone pairs = 0

Prediction of shape = Trigonal bipyramidal (TBP)

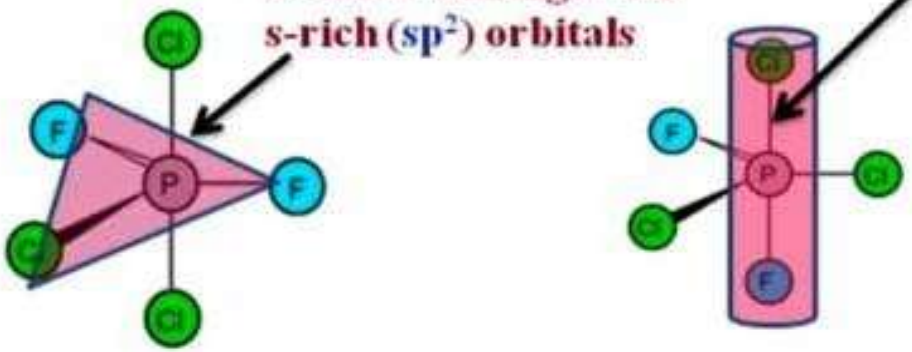
Hybridisation = [sp^3d = sp^2 (trigonal planar) + pd (linear)]

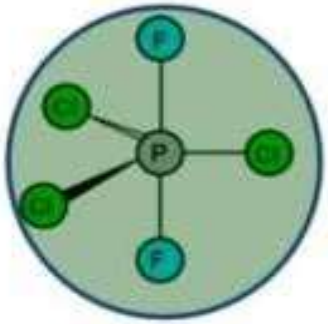
Possible Structure / arrangements of atoms :

electronegetivity Cl < F

Equatorial position = bonded through the s-rich (sp^2) orbitals

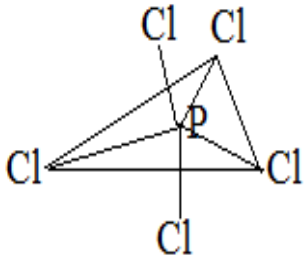
Axial position = bonded through the s-poor (pd) orbitals



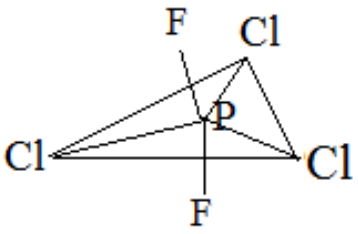


Actual arrangements of the atoms

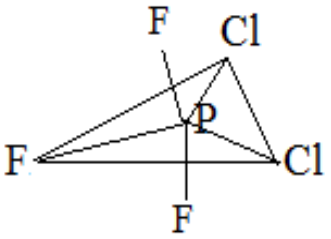
PCl_5



PCl_3F_2

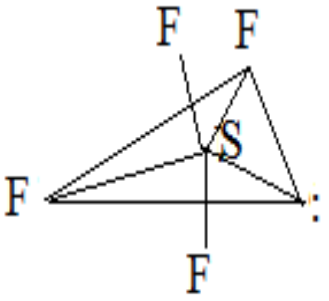


PCl_2F_3

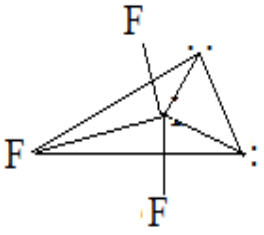


More En at axial

SF_4

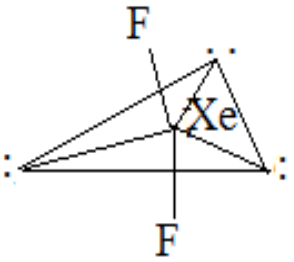


ClF_3



L. P. at equatorial

XeF_2

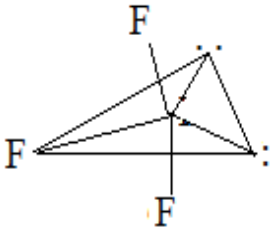


ClF_3

Orbital needed = valence of central atom +Bonded atom/2

7+3/2 = 5 therefore Hybridization – Sp^3d

So shape – TBP



% S character proportional closeness to the nucleus

Proportional En

% P character proportional longevity

a (no S character) > e

Modified Bents Rule

P refers to stay more spacious position i.e. more bond angle

$120^0 > 90^0 > 72^0$)

Let us consider

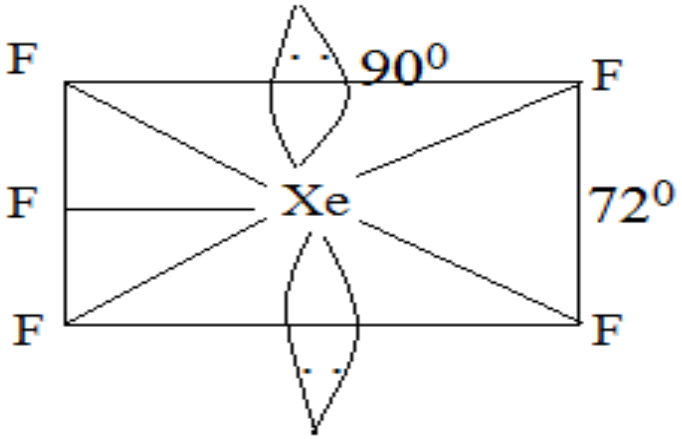
XeF_5

Orbital needed = $\frac{8+5+1}{2}$

7 (5 L.P.+ 2 L.P)

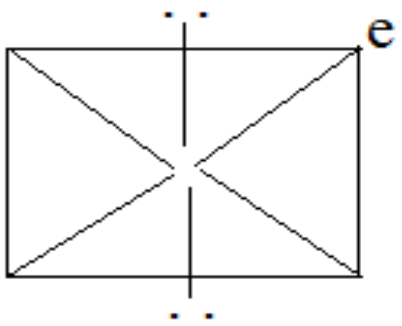
Hybridization – Sp3d3

Shape – Pentagonal Bipyramidal (PBP)



So, L.P. goes to axial position

Octahedral



Here axial feels less tension so L.P stay at axial

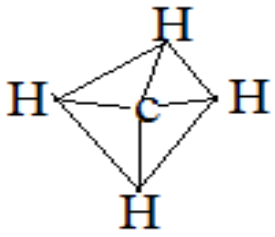
Significance of Bents Rule

Bents Rule explain the ionic & covalent nature of bonded atoms in a molecule & it also explain bond angle of bonded atoms in a molecule due to more S & P Character

- % S is closer to the nuclear has low energy than P orbital
- More S % , have shape like S orbital
- More P % , have shape like P orbital
- More S % increases in Hybrid orbital it is bulkier & shorts.
- More P character increases bond length & it is thinner & longer.

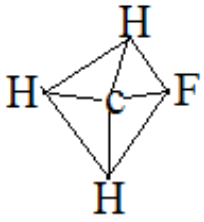
CH_4

SP^3



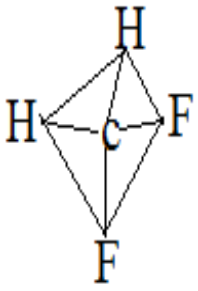
Same S Character
Same Bond angle

CH_3F



Less S Character C-F bond than HC-H bond
Bond angle HC-F < H-C-H

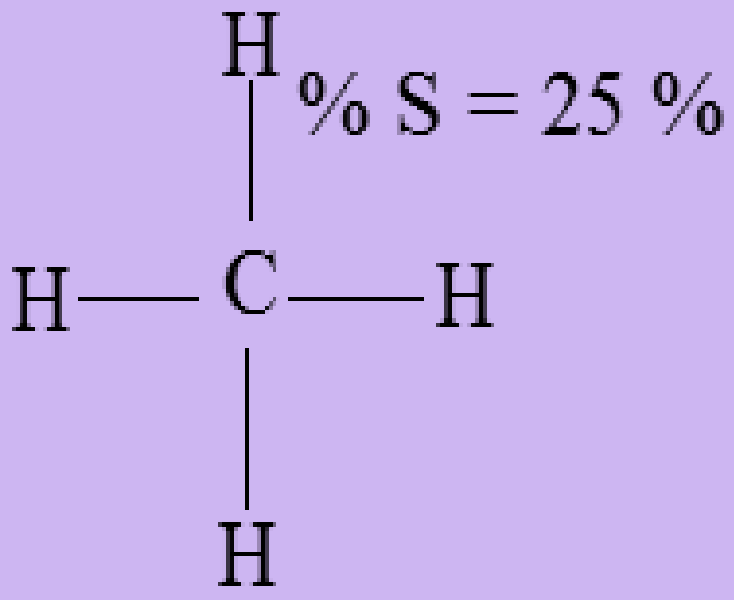
CH_2F_2



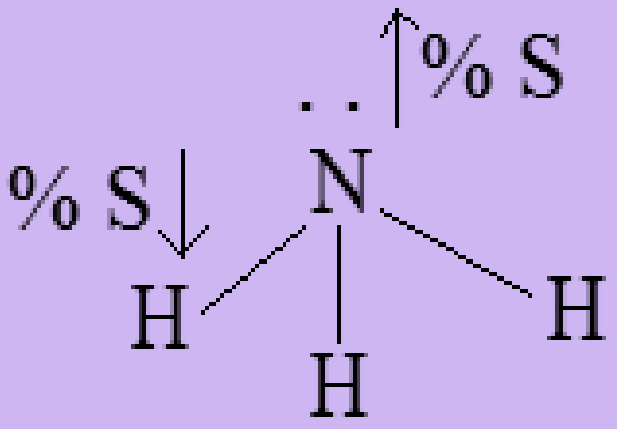
P character in C-F > C-H

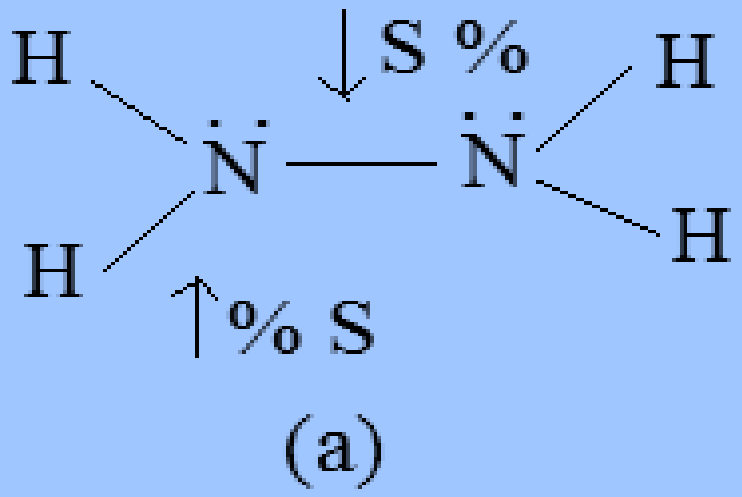
- More S Character proportional closer to the nucleus proportional less repulsion proportional more bond angle proportional less Hybrid energy proportional prefer at equatorial position TBP
- More P character means far from the nucleus
- More repulsion
- More hybrid energy proportional smaller bond angle

CH_4

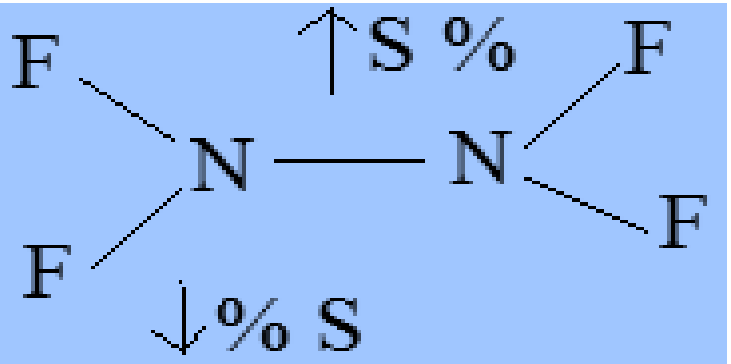


NH_3





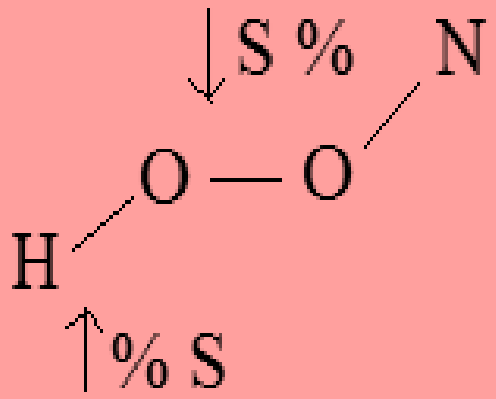
(a)



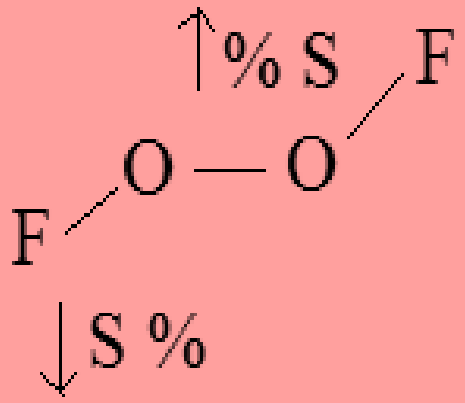
(b)

N-N bond length (b) < (a)

(therefore % S character Proportional closer to the nucleus



(a)



(b)

More % of S character Close to the nucleus i.e. O-O bond length of b < a

Thank You