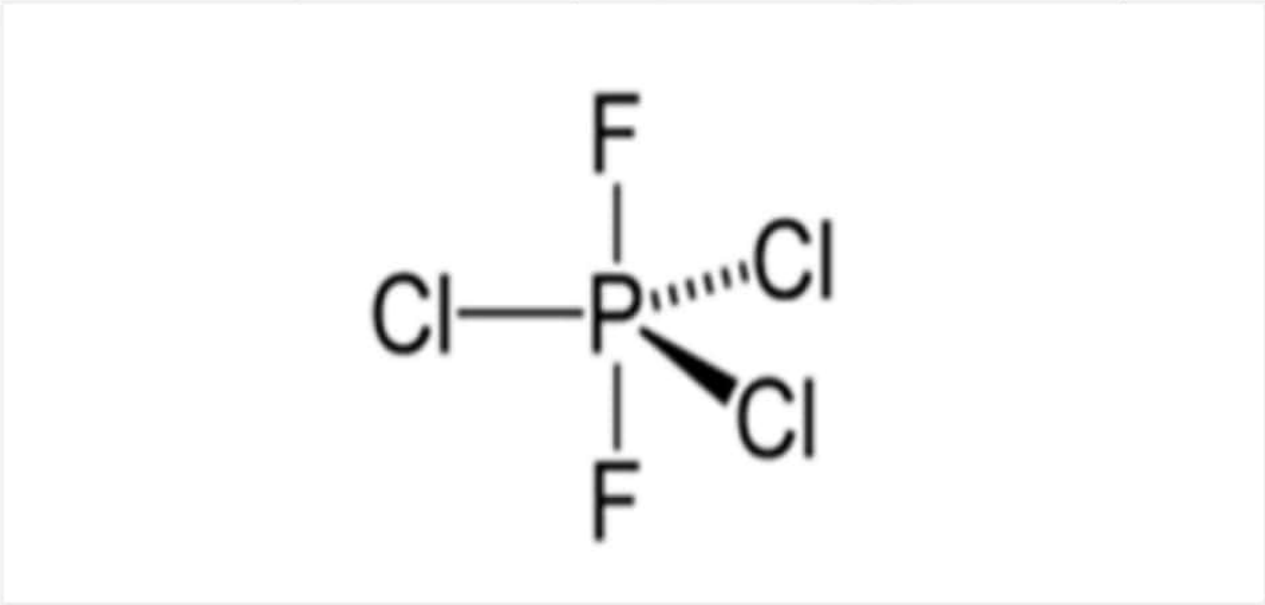
BENT'S RULE OF HYBRIDISATION:

CONCEPTUAL FACT: The more electronegative atom prefer to stay in that hybrid orbital having less S-character or more p- character and more electropositive atom prefer to that hybrid orbital which have more S-character or less p-character.

EXPLAINATION: The more electropositive atom or group will withdraw the bond pair more from central atom. it is easy when hybrid orbital is having less S-character and more P-character .

S-orbital is closer to the nucleus so it electronegativity is more than p-orbital.

ILLUSTRATIVE EXAMPLE (1): PCl_3F_2 (sp^3d Hybridization) and TBP (Trigonal bi pyramidal)



Where angle < F-P-F =180 and <Cl-P-Cl =120 two P-Cl bond is axial while three P-Cl bond is equatorial

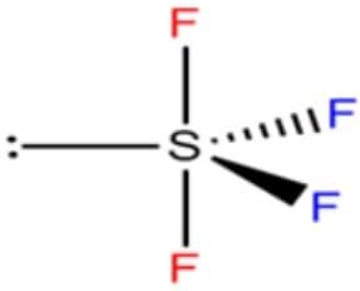
(1) APICOPHIOLICITY IN TBP GEOMETRY:

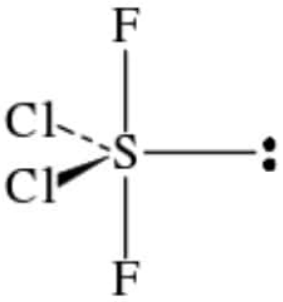
(1) Trigonal bipiramidal geometry more electronegative atom prefers to stay in low electronegative $P_Z dz^2$ orbital of sp^3d hybridization. You can also say that more electronegative atom prefer that hybrid orbital having low s-character or no s-character.

(2) If electronegativity difference between central atom and surrounding atom is large then due to polarity some ionic character is developed and covalent character decreased.

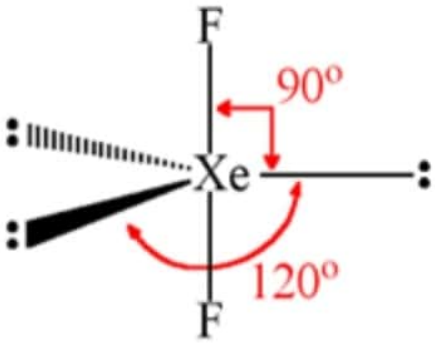
(4) **Position of lone pair:** Bent rule is very important in predicting position of lone pair. lone pair is attracted by only one nucleus while bond pair is attracted by two nucleuses. Central atom hold lone pair cloud tightly if central atom is having more S-Character.

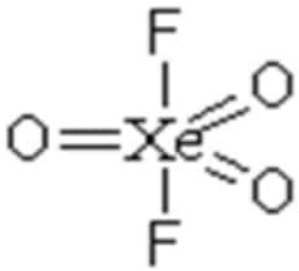
ILLUSTRATIVE EXAMPLE (2): SF_4 (Sp3d) TBP and SF_2Cl_2 (Sp3d)





ILLUSTRATIVE EXAMPLE (3): XeF_2 and XeO_3F_2





(2) ORBITAL ANALYSIS (CALCULATION OF (% S) AND %P) CHARACTER:

$$\text{Cos } \theta = \frac{s}{s-1} = \frac{p-1}{p}$$

where (s + p= 1)

Valid for → $(90 < \theta < 120)$

$SP^3d \cong SP^{2+}Pd$

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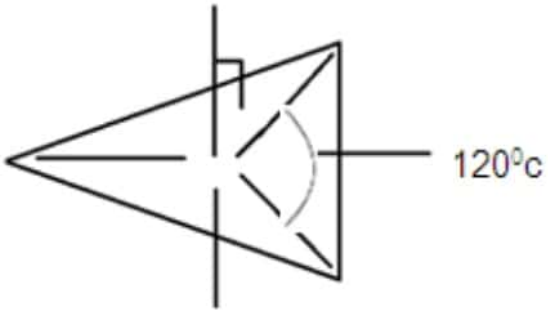

S% character is equatorial orbital at1 20^0c :

$$\cos\theta = \frac{s}{s-1}$$

$$\cos 120 = \frac{3}{s-1} \qquad \cos 120 = -\frac{1}{2}$$

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

$$2s = 1\text{-}s$$

$$3s = 1$$

S = 1/3 = 0.33 or 33.33% S. character

S% character for orbital at 90^0 C:

$$\text{Cos}\theta = 90 \qquad \cos 90 = 0$$

$$\text{Cos}90 = \frac{S}{S-1}$$

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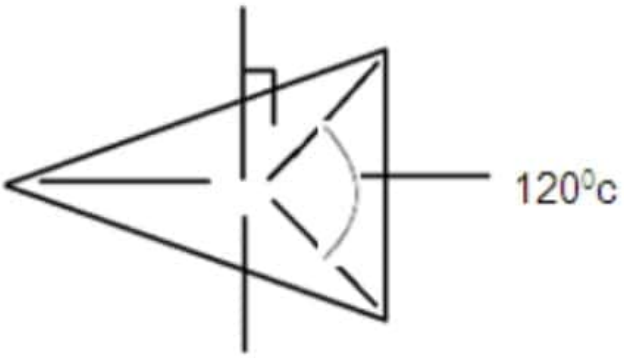

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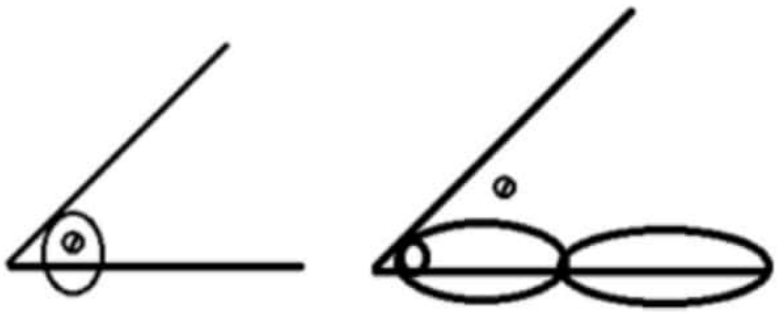
S = 0.00% Zero % S-Character

(3) EFFECT OF THE STRAINGTH OF COVALENCY:

(Alternate Statement of bent)

RULE: The more electronegative atom not only prefer to stay in that orbital which having less % S character (more p-character) but it also decreases % S-character and increases % P-character in its attached orbital from the central atom depending on circumstance.

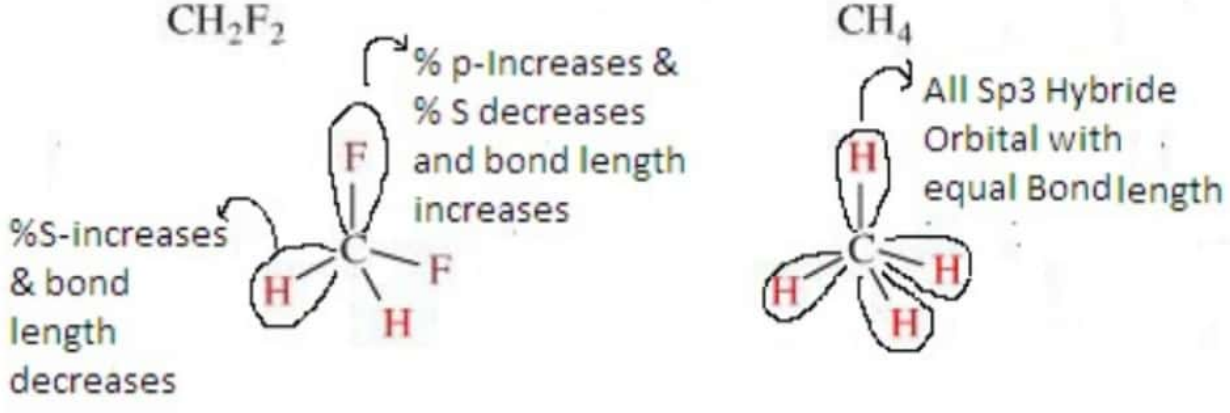
$$\% S \propto \text{Bond angle} \propto \text{bond straight} \propto \frac{1}{\text{Bond length}}$$



s- Orbital p-Orbital

On increasing % s character in hybrid orbital , the bond length decreases while bond angle increases.

ILLUSTRATIVE EXAMPLE (3): : Explain C-H bond length of CH4 is longer than C-H bond length of Difloromethan (CH_2F_2) ?



EXCEPTIONS OF BENT'S RULE:

(1): Bent's rule is applicable in those molecules where **central atoms are same and** they are also in same Hybridization. For example N-N bond length cannot be compared in N_2H_4 and N_2O_4 using Bent rule.

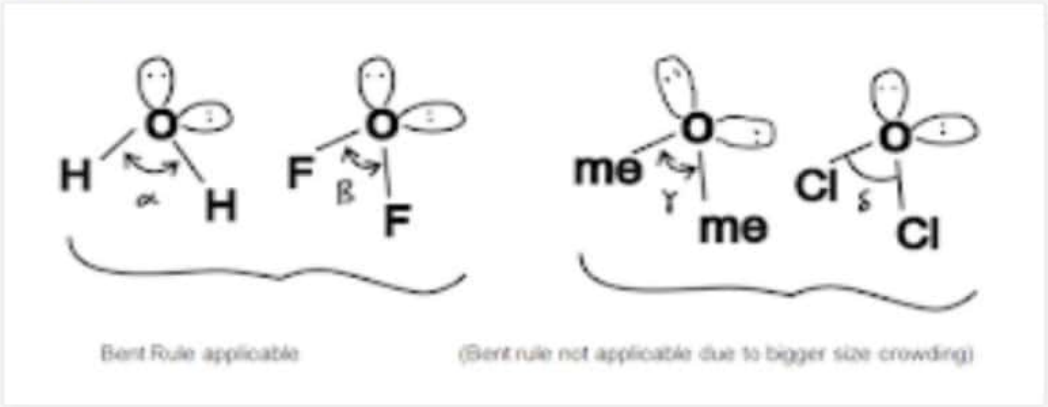
ILLUSTRATIVE EXAMPLE (4): Arrange PF_3 ASH_3, PH_3, NH_3, H_2Se in decreasing order by Bent's rule here we used **DRAGO'S RUEE"**

SOLUTION: $NH_3 > NF_3 > PF_3 > PH_3 > AsH3 > H_2Se$

(2): Bent's rule violets in those molecules where steric factor's plays dominating rule.

ILLUSTRATIVE EXAMPLE (5): Compared Bond angle among H_2O OF_2, OMe_2, OCl_2

SOLUTION:



$$\delta > \gamma > \alpha > \beta$$

ILLUSTRATIVE EXAMPLE (6): IN CH_2SF_4

Axial bond < F-S-F = β

Equatorial bond F-S-F = α

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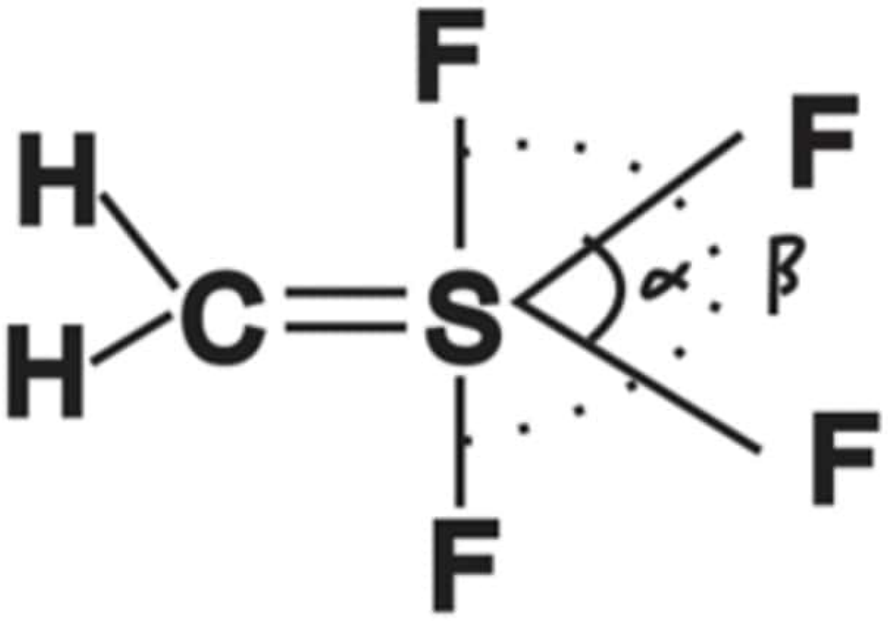
Axial bond < F-S-F = β

Equatorial bond F-S-F = $\propto$

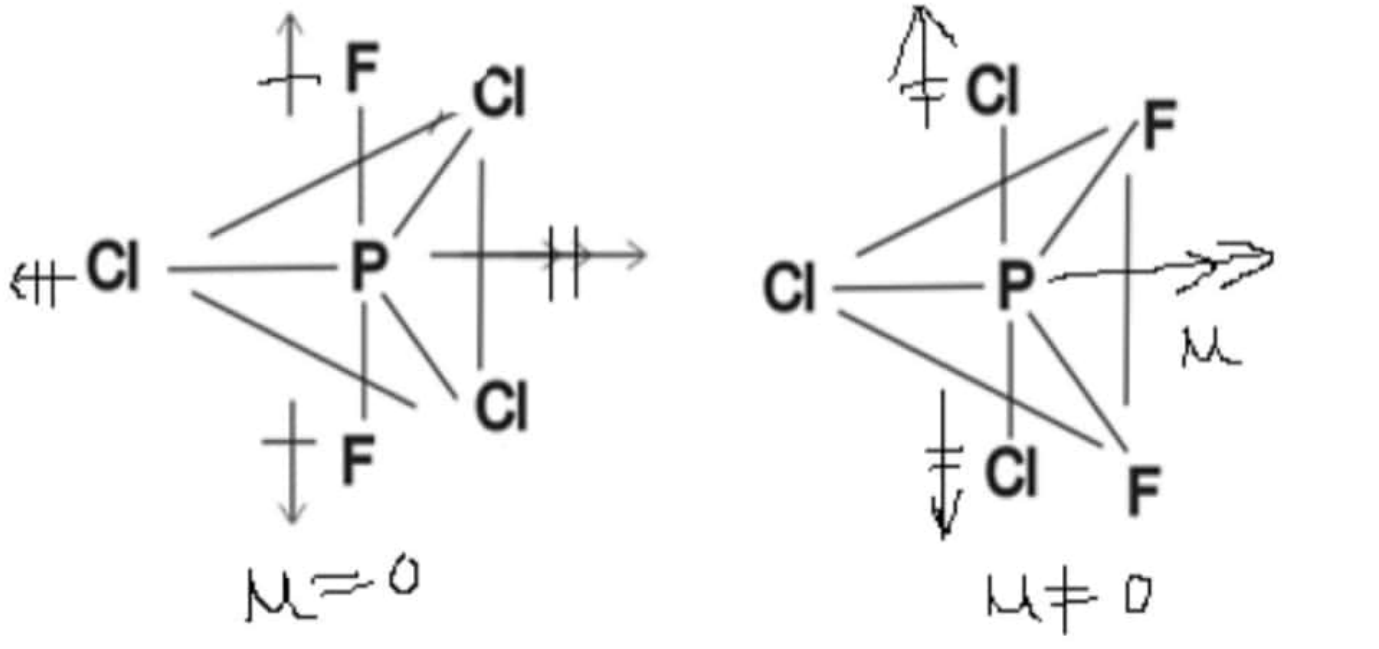


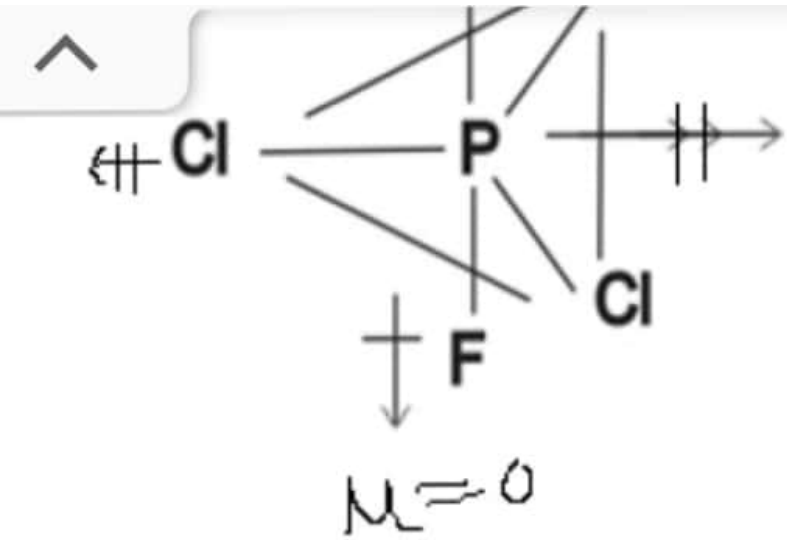
TRATIVE EXAMPLE (7): Compare Dipole moment of following compound pairs

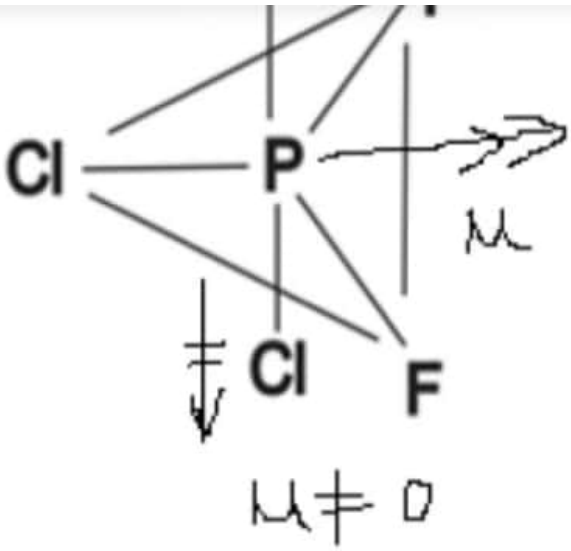
(1) Dipole moment of PCl_2F_3 is non zero while dipole moment of PCl_3F_2 is zero why?
(2) Dipole moment of $P(CH_3)_2(CF)_3$ is non zero while dipole moment of $P(CH_3)_2(CF_3)_2$ is zero why?

SOLUTION: According to bent rule more electronegative atom or group attached those orbital have minimum S- character there in Trigonal bipiramidal (TBP) Geometry we known that axial orbital hare no S- character so F and $-CF_3$ are attached with axial positions.

(1) :







(2)