

Equivalent and Non equivalent Hybrid Orbitals: Bent's Rule, idea of Berry's Pseudorotation and Apicophilicity

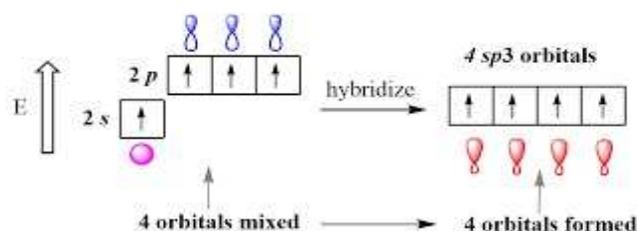
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Hybridisation: Mixing of different atomic orbitals having comparable energy resulting an equal no of new orbitals with mixed character.

- ❖ Hybrid orbital undergo better overlap → form stronger bonds with other atoms than the pure orbitals → provided **most stable geometry** for a molecule.
- ❖ Generally hybrid orbitals are **mostly equivalent**. (Some exceptions are also there)
- ❖ The energy released by the formation through hybrid orbitals greater than the energy required for promotion of pure orbital for hybridisation.



To explain the nature of bonding in Covalent molecules and also predict some properties as :

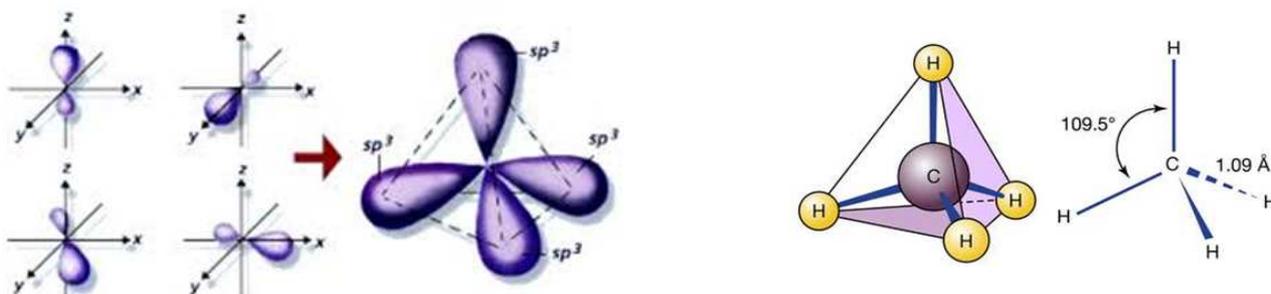
- | | |
|---------------------|--------------------------------------|
| ➤ bond length | ♣ bond strength |
| ➤ bond polarity | ♣ direction / bond moments |
| ➤ bond angle | ♣ shape / structure of the molecules |
| ➤ chemical property | ♣ reactivity |

Some Aspects

One misconception: Shape or Structure of the molecule can be determined from the **Hybridisation** of the central atom.

Example: In CH_4 molecule, since **hybridisation** of C is sp^3 , hence its shape is **Tetrahedral**.

- ❖ **Reality:** CH_4 is **tetrahedral** in shape because it possesses **lowest energy content** in this shape depending on **bond Energies** and **electron pair repulsions**.
- ❖ *Theoretical as well as some experimental findings* denoted that **hybridisation** of C atom of CH_4 molecule is sp^3 and for this hybridisation the probable structure is **tetrahedral**.



- ❖ The amount of **hybridisation** can be explained that **hybrid orbital** permits the *wider distribution of electronic charge cloud* and *more effective overlap* is denoted by **overlap integral [S]**.
- ❖ When we move from **pure atomic orbitals** to any **hybrid orbital** the overlap integral changed and its value indicates the amount of **hybridisation**.
- ❖ From hybridisation we can get some idea of bond properties as mentioned above.

Relation between hybridisation and bond angle:

$$\cos\theta = \frac{S}{S-1} = \frac{P-1}{P}$$

Where, θ = bond angle between two hybrid orbitals and S and P = fractional s and p character of the bond.

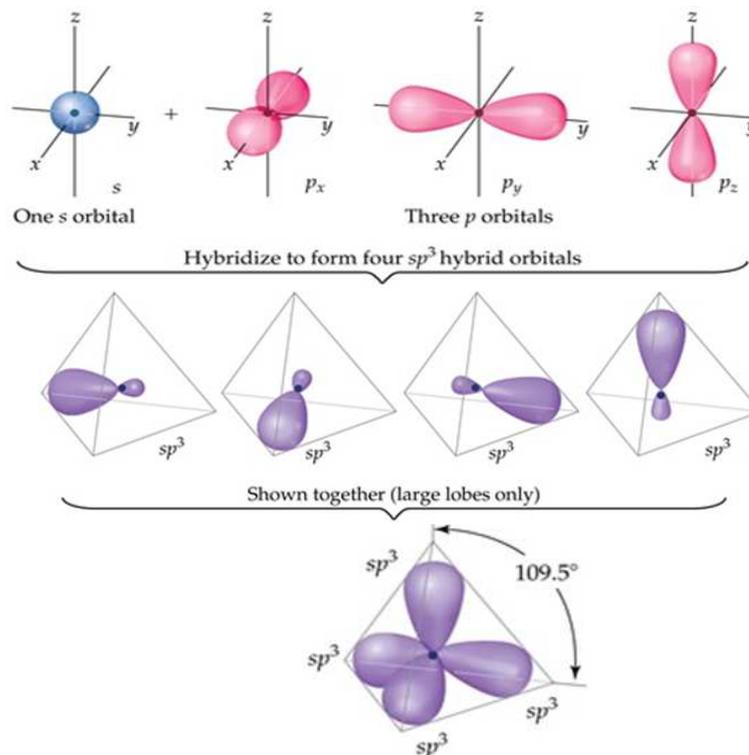
Electron pair, Shape, bond angle and Hybridization correlation:

The total peripheral electron number or steric number is the key number from which Ideal shape of the molecule and Hybridization of the central atom can be predicted:

Sl. No	Steric no. (SN)	Valance Shell e-pair	Ideal shape	Hybridization	Ideal Bond Angle
1.	2	2	Linear	sp	180°
2.	3	3	Trigonal Planar	sp ²	120°
3.	4	4	Tetrahedral	sp ³	109.5°
4.	4	4	Square Planar	sp ² d/ dsp ²	90°
5.	5	5	Trigonal bipyramidal	sp ³ d/dsp ³	120°, 90°
6.	6	6	Octahedral	sp ³ d ²	90°
7.	7	7	Pentagonal bipyramidal	sp ³ d ³	72°, 90°

Equivalent hybrid orbitals: Hybrid orbitals where the ratios of participating atomic orbitals are same for all the orbitals called Equivalent hybrid orbitals.

sp³ hybridisation : For sp³ hybridisation 4 atomic orbitals as one s orbital, three p orbitals are involved to produce 4 sp³ hybrid orbitals.



All 4 new orbitals are equally same sp^3 character

- ❖ Geometry = Regular Tetrahedron
- ❖ Bond angle = 109.5°
- ❖ Bond length = Single bond

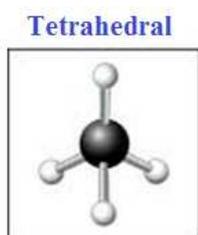
Non Equivalent hybrid orbitals: Hybrid orbitals where the ratios of participating atomic orbitals are different or not same for all the orbitals called non Equivalent hybrid orbitals.

1. Presence of lone pair of electrons

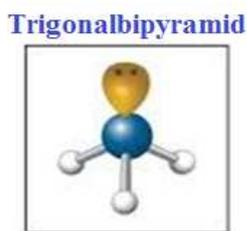
For CH_4 molecule according to VSEPR model possess 4 b.p. and 0 l.p.,

Hence all 4 orbitals possess sp^3 hybrid orbitals and all are equivalent but for NH_3 Or H_2O , in both the molecule the central atom possess sp^3 hybridisation, but N bear 3 b.p.s, 1 l.p. and for O bear 2 b.p.s. , 2 l.p.s respectively.

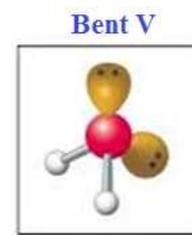
For both the cases l.p. of e bearing hybrid orbital and bond pair bearing orbital are not **equivalent**.



CH_4
l.p. = 0



NH_3
l.p. = 1



H_2O
l.p. = 2

2. Presence of dissimilar atoms rather than central atoms:

Again for the CH_4 like molecule the CH_2F_2 molecule dissimilar atoms are attached with the central atom C having sp^3 hybridisation and 0 l.p. present.

In this case all 4 hybrid orbitals are not equally sp^3 hybrid orbitals. The hybrid orbitals of 2C–H bonds are physically and chemically different than the hybrid orbitals of 2C–F bonds.

Hybridisation and shape of CH_4 molecule

As per VSEPR rule:

Central atom C : No. of valance electrons = 4e

Other atoms H: 4×1 electron = 4e

Total Number of electrons = $4e+4e = 8e$

Number of electron pair = $8e/2 = 4$

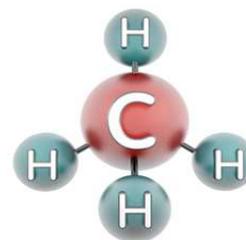
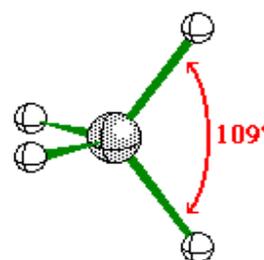
Prediction of shape and hybridisation = Tetrahedron

Number of bond pairs = 4 and Number of lone pairs = 0

Using box diagram the hybridisation is $[\text{sp}^3] = 4$ equivalent hybrid orbitals

Actual Shape of the molecule = Tetrahedron

Bond Angle : 109.5°



Hybridisation and shape of CH_2F_2

As per VSEPR rule :

Central atom C : No. of valance electrons = 4e

Other atoms 2H: 2×1 electron = 2e

2F : 2×1 electron = 2e

Total Number of electrons = $4e+4e = 8e$

Number of electron pair = $8e/2 = 4$

Prediction of shape = Tetrahedral and hybridisation = $[\text{sp}^3]$

Number of bond pairs = 4 and Number of lone pairs = 0

Actual Shape of the molecule should be = Tetrahedral

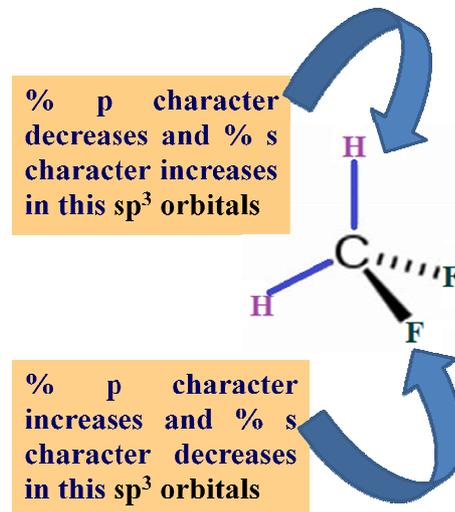
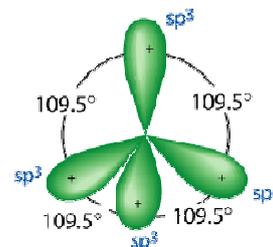
and Bond Angle : 109.5°

➤ But the real case is something different :

$\angle\text{HCH} = 111.9^\circ$ and $\angle\text{FCF} = 108.3^\circ$

C–H = 108.64pm[CH_4] and C–H = 108.67pm[CH_2F_2]

C–F = 132.32pm [CF₄] and C–F= 135.09pm[CH_2F_2]



Electronegativity difference $F > H$

With increases % s character of hybrid sp^3 orbitals bond length diminished and b.p.-b.p. repulsion enhanced and hence bond angle.

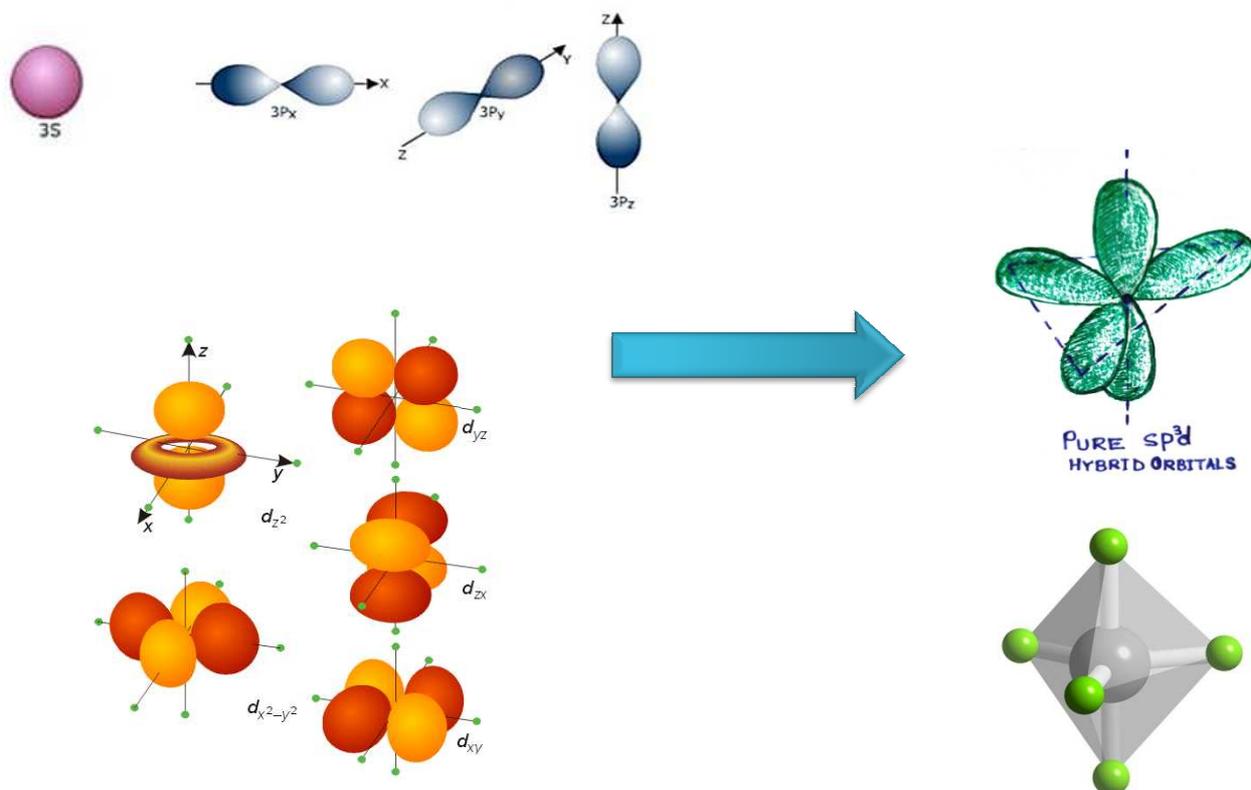
With increases % p character of hybrid sp^3 orbitals bond length become larger and b.p.-b.p. repulsion minimised and hence bond angle.

Certain Hybridization scheme inherently possesses non Equivalent hybrid orbitals:



Prediction of shape for this hybridisation = Trigonal bipyramid [TBP]

Here the central atom must be the member of the period whose principal quantum no. 3, that it must have 3s, 3p and 3d orbitals.



If these 5 orbitals get hybridized equivalently then we should have 5 equivalent sp^3d hybrid orbitals.

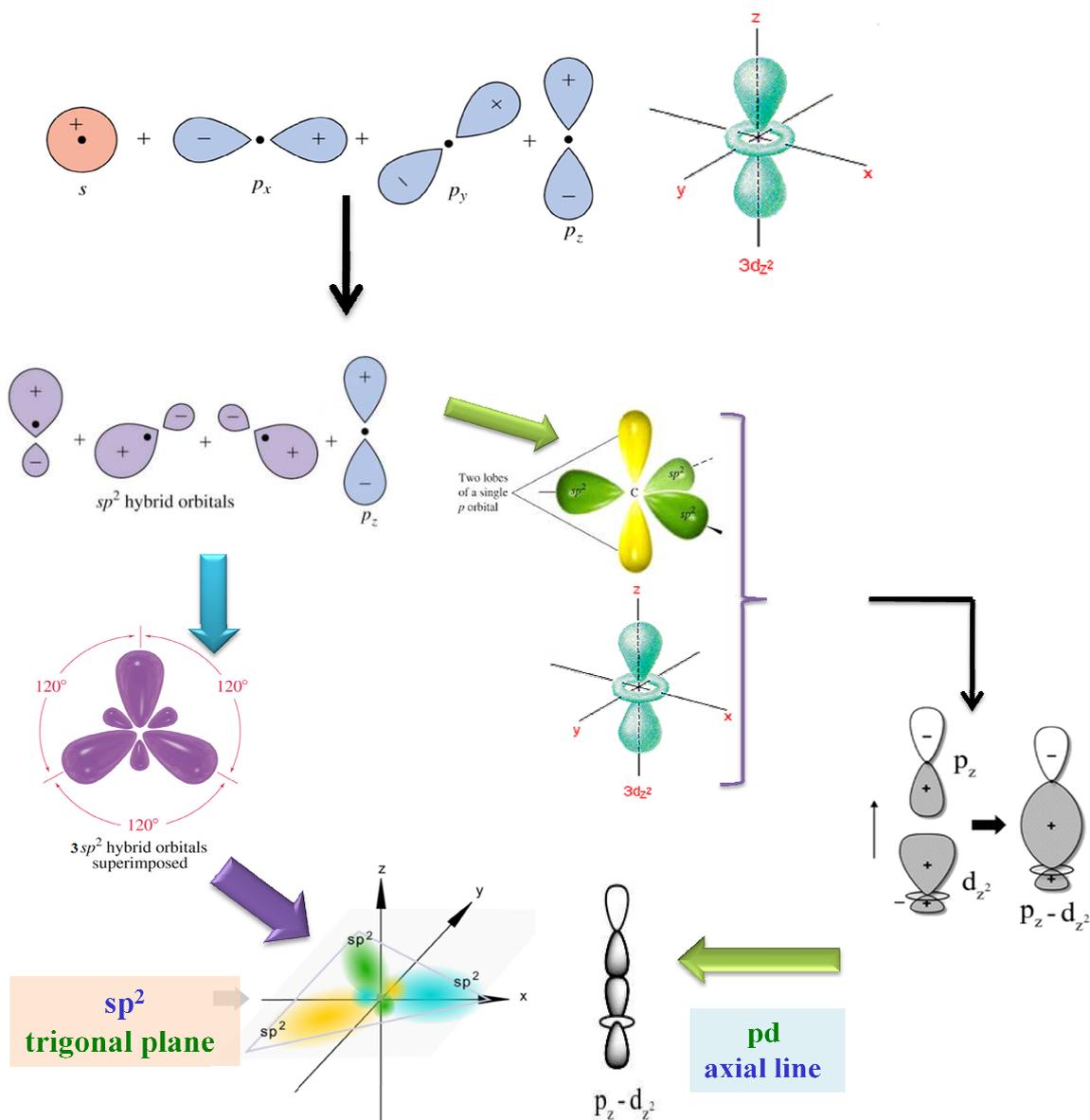
The sp^3d hybridization is a combination of 2 sets: [i] a set of 3 sp_xp_y hybrid orbitals distributed in the equatorial xy plane forming a trigonal plane and [ii] a set of 2 $p_z-d_z^2$ hybrid orbitals oriented in axial position forming a linear shape passing through the centre of the trigonal plane.

sp^3d hybridization:

For this sp^3d hybridization we can divide it in two parts : $sp^2 + pd$

[a] the trigonal plane = sp^2

[b] the axial line = pd



Bond Angle and % s / % p characters:

sp^3d hybrid orbitals can be split as $sp^2 + pd$.

$$\cos\theta = \frac{S}{S-1} = \frac{P-1}{P}$$

§ Experimentally, the angle between equatorial substituents is 120° .

$$S(f_s) = \cos\theta / (\cos\theta - 1)$$

\therefore Fraction of s -character in equatorial positions [trigonal planar e] with $\theta = 120^\circ$ is,

$$S(f_s) = \cos(120) / (\cos 120 - 1)$$

$$= (-1/2) / (-1/2 - 1) \quad [\cos(120) = -1/2]$$

$$= (-1/2) / (-3/2) = 1/3 = 0.33.$$

which indicates that for equatorial positions angle between bonds are 120° and the amount of **s character** of the orbitals = **0.33 or ~ 33% and ~ 66% p character**.

We know that it is **sp^2 orbitals** which have **33% s - character**, so the equatorial hybrid orbitals are sp^2 hybridized.

§ **Again** we know experimentally, that the angle with **axial substituents is 90°** . So,

$$\begin{aligned} S(f_s) &= \cos\theta / (\cos\theta - 1) \\ &= \cos 90 / \cos 90 - 1 \\ &= 0 / (0 - 1) \\ &= 0 \end{aligned}$$

So, the amount of **s - character** in **axial orbitals** is zero i.e the **pd part** (no s character) occupies the axial position.

Hybridisation and shape of PCl_5

As per VSEPR rule :

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

Other atoms Cl: 5×1 electron = 5e

For neutral molecule : 0e

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

Number of electron pair = 10e/2 = 5

Prediction of shape and hybridisation = Trigonal bipyramidal (TBP)

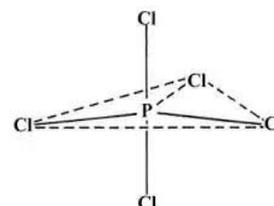
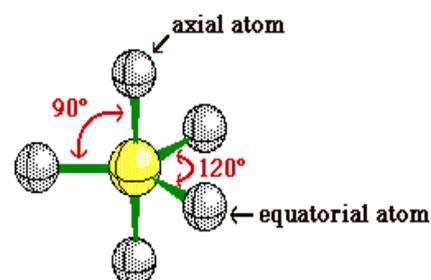
$[sp^3d = sp^2$ (trigonal planar) + pd (linear)]

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

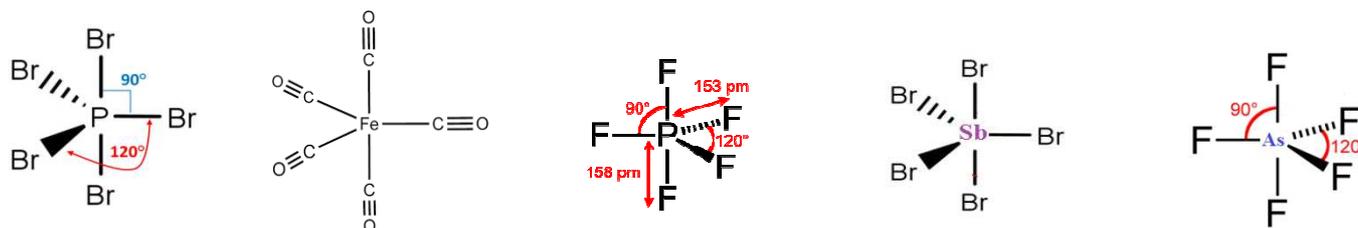
Actual Shape of the molecule depending on e-e repulsion and stability = **Trigonal bipyramidal (TBP)**

Since all other atoms are same Cl, all of them are occupied in these 5 positions of TBP geometry.

Bond Angle : 120° (eq-eq), 180° (ax-ax), 90° (eq-ax)



Other PCl_5 like Molecules having sp^3d hybridization



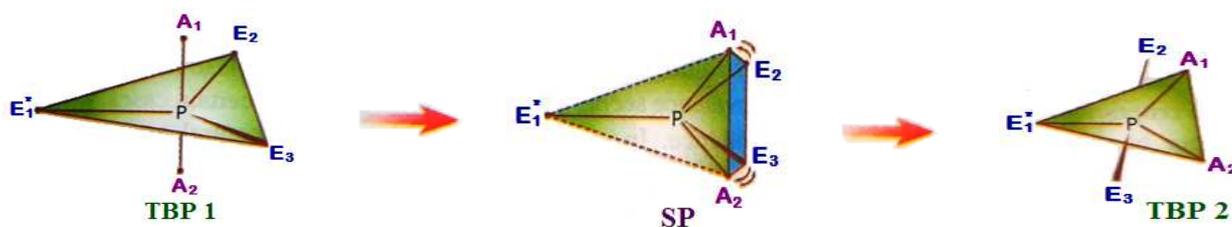
Berry's Pseudorotation

The rapid interchange of axial and equatorial group in TBP structure may be explained in terms of interchange mechanism suggested by R.S. Berry 1960.

According to this proposed mechanism molecules having AX_5 type with no lone pair of electrons in the central atom having sp^3d hybridisation adopted generally TBP structure. Such structures of this stoichiometry are not very stable and may be interconverted to others structure with comparable energy.

A TBP structure may readily converted to a square pyramid [SP] transition state and again converted to new TBP structure. During this process one of the equatorial group remain rigid in its position and acts as a pivot, while the other two equatorial groups interchange their position with the axial groups and a new TBP structure generated.

In this mechanistic process 4 groups are interchange their position by rotation about an axis passing through the pivot and the central atom. For these AX_5 type of molecule two TBP arrangements are related to each other by simple rotation and this process is called Berry Pseudorotation. The process can take place very rapidly because of the similarity in energy between TBP and SP structure.



- For example PF_5 molecule the exchange of two equatorial ^{19}F to axial ^{19}F in PF_5 is too rapid to monitor with ^{19}F nmr spectroscopy.
- Hence presence of other atoms e.g. Cl, PCl_2F_3 the rate of exchange is more slower specially at low temperature and can be distinguished different peaks of ^{19}F during this rotation TBP to SP to TBP.

What about the molecules having sp^3d hybridization but holding different other atoms:



Here 2 different types of atoms [F and Cl] are attached with the central atom P

Both these atoms have different electronegativity $F \gg Cl$.

Hence there orbital occupancy must be different.

Substituents at the trigonal plane [equatorial position] = bonded through the s-rich (sp^2) orbitals = the bond length with metal ion must be shorter.

Substituents at the linearly coordinated [axial position] = bonded through the s-poor (pd) orbitals = the bond length with metal ion must be longer.

Bent's Rule

It is the preference of atoms having different electronegativity to occupy the hybrid orbitals which are non equivalents: different s-character and different p-character.

[i] More electronegative substituents prefer hybrid orbitals of the central atom with greater p-character and less s-character.

[ii] Less electronegative substituents prefer hybrid orbitals of the central atom with greater s-character and less p-character.

[iii] The central atom involved hybrid orbitals with higher s-character to develop higher covalence and less s-character in the bond with greater ionic character.

[*J. Chem. Educ.*, **1960**, 37, 616–624], [*Chem. Rev.* **1961**, 61, 275 – 311]

Hybridisation and 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 = $5e + 5e = 10e$

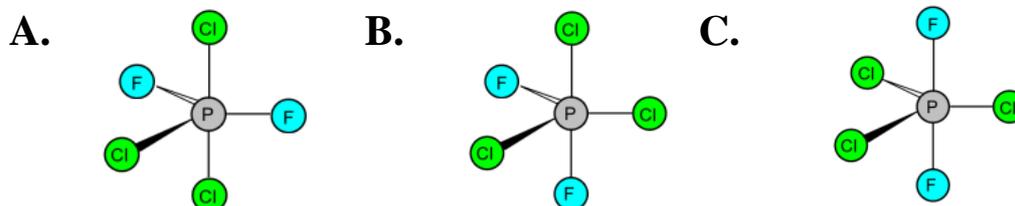
Number of electron pair = $10e/2 = 5$

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

Prediction of shape and hybridisation = Trigonal bipyramidal (TBP)

$[\text{sp}^3\text{d} = \text{sp}^2$ (trigonal planar) + pd (linear)]

Possible Structure / arrangements of atoms : Trigonal bipyramidal (TBP)



Electronegativity of $\text{Cl} < \text{F}$, and according to Bent's Rule, depending on hybrid orbitals electronegativity, here the structure C. Having both F atoms occupied in the axial positions is the correct structure.

Apicophilicity

Apicophilicity: It is the propensity of more *electronegative* substituents to search for the low *electronegative* $[\text{p}_z\text{d}_z^2]$ apical orbitals in the TBP structures.

This phenomenon is well demonstrated in a series of oxysulfuranes type of compounds by Martin.

[*Science*, **1983**, 221, 509–514]