

Bent's rule

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Bent proposed following rules to explain the non-equivalent nature of hybrid orbitals -

1. The more electronegative atom demands greater electron density from the central atom.
2. Greater is the p-character of a hybrid orbital then lesser is its electronegativity.
3. The central atom directs greater p and less s-character and lesser p and greater s-character in hybrid orbitals directed towards more or less electronegative substituent respectively.

The hybrid orbitals of C-atom in $\text{H}_3\text{C}-\text{Cl}$ directed towards H-atom should have more than 25% s-character while those directed towards Cl-atom should have less than 25% s-character.

The $\text{F}-\text{C}-\text{F}$ bond angle in CH_2F_2 is less than 109.5° , it indicates that the s-character is less than 25% but $\text{H}-\text{C}-\text{H}$ bond angle is larger and the C-H bond has more s-character.

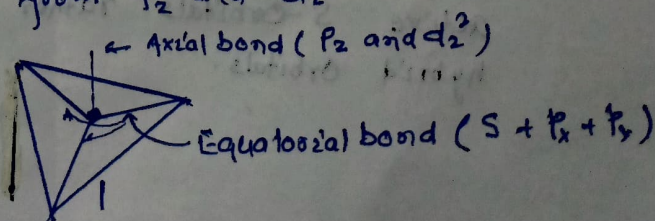
s-character increases then bond angle widens

For example: -

Molecules: -	H_2O	NH_3
s-character: -	104.5°	107.3°
Bond angle: -		

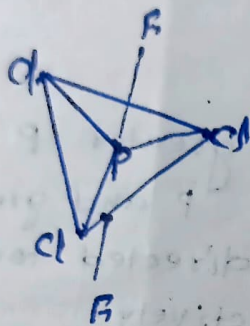
Bent's rule states that more electronegative substituent tends to attach itself with an orbital having less s-character while a less electronegative substituent tends to attach itself with the orbital having more s-character.

In a trigonal bipyramidal structure, the three equatorial bonds are formed from the hybrid orbitals having contribution from s, p_x and p_y orbitals while the two axial bonds are formed from the hybrids having contributions from p_z and d_z^2 .



[PF_2Cl_3]

As we know in PF_2Cl_2 the two F atoms attach themselves to two axial bonds (where no contribution from s-orbital) and the three Cl atoms go to equatorial position where $\frac{1}{3}$ rd s-character.



In CH_2F_2 , the H-C-H bond angle is 111.9° but F-C-F bond is 108.3° .

From Bent rule, F-C-F bond angle is smaller than symmetrical bond angle of 109.28° , indicating that the C-F bonds involve hybrid orbitals of carbon with less than 25% s-character.

... involved in hybridisation: —