Bent's rule

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 H_3C-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 F-C-F bond angle in CH_2F_2 is less than 109.5°. it indicates that the S-character is less than 25% but H-C-H bond angle is larger and the C-H bond has more S-Character.

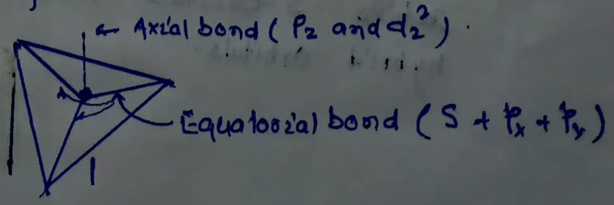
S-character Increases then bond angle widen

for example: -

Molecules :-	H_2O		NH_3
S-character :-		S-Character increases →	
Bond angle :-	104.5°	→	107.3°

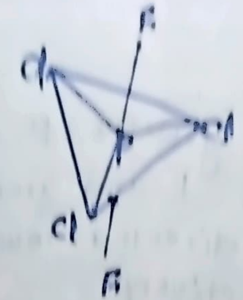
Bent's rule states that more electronegative substituent tends to attach itself with an Orbital having less S-Character while a less electronegative substituent tends to attach itself with the Orbital having More S-character.

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 [illegible] F atoms attach themselves to two axial bonds (where no contribution from S-orbital) and the three Cl atoms go to the equatorial position which have [illegible] 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.

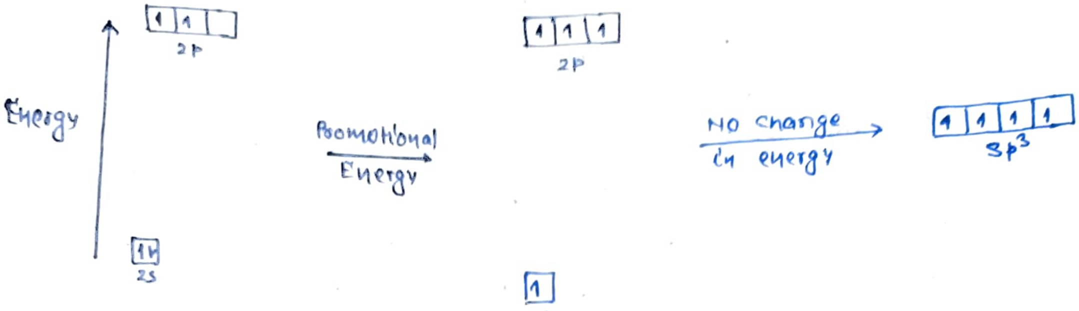
Energetics involved in hybridisation:—

When a set of hybrid orbitals is formed by a linear combination of atomic orbital, the energy of the resulting hybrid is a weighed average of the energies of the participating atomic orbitals.

For example:- When carbon forms four co-valent bonds, although there is promotional energy from the configuration $1s^2\ 2s^2\ 2p^2$ to $1s^2\ 2s^1\ 2p^3$ this is independent of the hybridisation to the valence state.

In the Phosphorus atom, there is little initial promotional energy. The ground state is trivalent, as is valence state. Here, any hybridisation will cost energy as a filled 3S orbital is raised in energy and half filled 3p orbitals are lowered in energy. This energy of hybridisation is of the order of magnitude of bond energies and thus be important in determining the structure of molecules. It is responsible for the tendency of some lone pairs to occupy spherical nonstereochemically active S-orbitals rather than stereochemically active hybrid orbitals.

For example, the hydrids of group VA (15) and VIA (16) are found to have bond angles considerably reduced as one progresses from the first element in each group to those that follow.



(Hybridisation of C-atom)

$NH_3 = 107^\circ$, $PH_3 = 93.8^\circ$, $AsH_3 = 91.8^\circ$ $SbH_3 = 91.3^\circ$

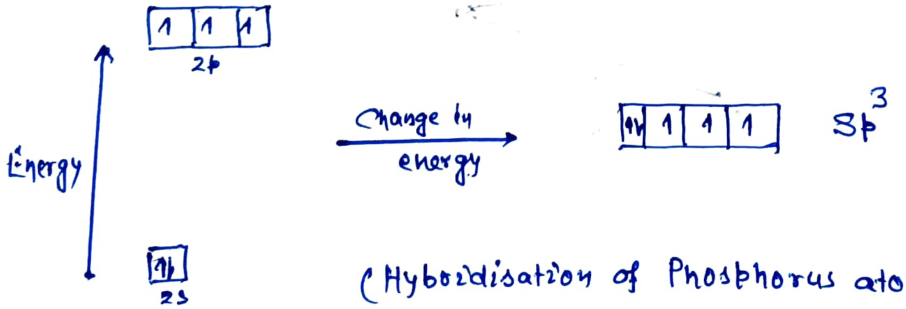
$H_2O = 104.5^\circ$ $H_2S = 92^\circ$ $H_2Se = 91^\circ$ $H_2Te = 89.5^\circ$

Any energy factor that favours reduction in bond angle in these compounds is the hybridisation which cost about 600 kJ mol^{-1} to hybridise the central Phosphorus atom.

From the standpoint of this energy factor alone, the most stable arrangement would be utilising pure p-orbitals in bonding and letting the lone pair occupy a pure S-orbital. This tendency is opposed by the repulsion of electrons, both bonding and non bonding favouring approximately tetrahydral geometry.

In case of small atoms like N and O the steric effect are more pronounced.

However, In the larger atoms such as P, As, Sb, S, Se, Te the steric effects are some what relaxed, allowing the reduced hybridisation energy of more p-character in the bonding orbitals to come into play.



(Hybridisation of Phosphorus atom)

Anothers factor which affect the most stable arrangement of the atom is the variation of bond energy with Hybridisation.

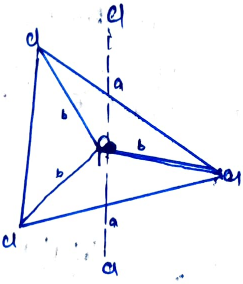
The directed lobes of sp-hybrid orbitals overlap more effectively than the undirected 1s-orbitals, the two lobed p-orbitals, or the diffused d-orbitals.

The increased overlap results in stronger bonds. Thus, the molecule is forced to choose between higher promotional energy and better overlap for an S-rich hybrid orbital or lower promotional energy and poorer overlap for an S-poor hybrid.

An sp^3d hybrid orbital set may be considered to be a combination of $P_z d_{z^2}$ hybrids and $sp_x p_y$ hybrids. The former make two linear hybrid orbitals bonding axially and the latter from the trigonal, equatorial bonds.

The sp^3 hybrid orbitals are capable of forming stronger bonds than those formed by $p_z d_{z^2}$ hybrids.

Thus, the two axial bonds are longer and weaker than three equatorial bonds in TBP geometry with sp^3d hybridisation.

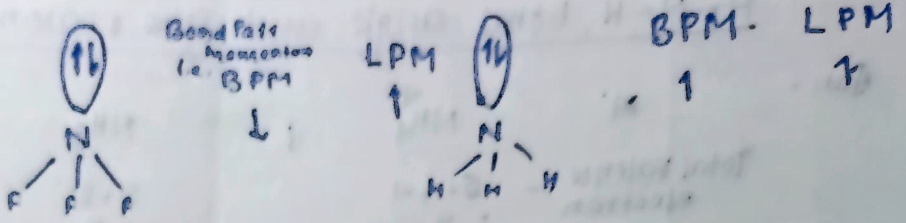


a = 214 pm

b = 202 pm.

Explain:- Bond angle in NF_3 is smaller than NH_3

Ans:- Both NF_3 and NH_3 have a pyramidal structures:-



F is more electronegative than N, but H is less electronegative than N

Element :-	F	N	H
Electronegativity:-	4.0	3.5	2.1

Electronegativity in decreasing order

Hence Bond Pair momentum (BPM) and Lone pair momentum (LPM) in NH_3 are working in same direction, but in NF_3 they work in opposite directions.

Hence Bond angle in NF_3 is smaller than NH_3