

→ Concept of Energetics of Hybridisation

According to hybridisation, atomic orbitals combine and redistribute their energies to form hybrid orbitals. These are identical with respect to energy, shape etc. Shape of the hybrid orbital depends upon contribution of s, p, d-orbitals and it affects the energy of hybridisation. Bent's rule states that "Atomic s-character tends to concentrate in orbitals that are directed toward electropositive groups and atomic p-character tends to concentrate in orbitals that are directed toward electronegative groups."

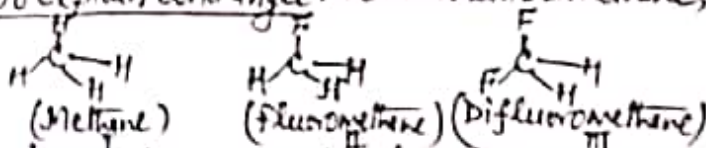
1. s-orbitals has low energy than p-orbital.
2. More s-character decrease the energy of bonding orbitals and hence they have shape more like a s-orbital. More p-character increase the energy of bonding orbitals and hence they have shape more like a p-orbitals.
3. s-orbitals are closer to the nucleus, so it stabilize the lone pair. Due to more s-character less repulsion and less hybridisation energy, and less bond angle, vice versa is true for more p-character.
4. The most stable arrangement would be to utilize pure p-orbitals ~~for~~ bonding and letting the lone pair into the pure s-orbital.
5. s-orbitals are more penetrating and electron density is less available for bonding. Thus more electronegative atom would be able to withdraw more electron density from p-orbitals than from s-orbitals.

⇒ Bent rule

In Chemistry, Bent rule describes and explains the relationship between the orbital hybridisation of central atoms in molecules and the electronegativities of substituents. This rule was stated by Jerry Bent as follows: "Atomic s-character tends to concentrate in orbitals that are directed toward electropositive groups and atomic p-character tends to concentrate in orbitals that are directed toward electronegative groups." According to this rule-

- (1) lone pair tends to occupy that hybrid orbital where there is more s-character/less p-character.
- (2) more electronegative neighbouring substituent tends to overlap with that orbital of central atom which has more p-character.
- (3) Multiple bond tends to occupy that hybrid orbital which has more s-character.
- (4) % s-character increases, bond angle <sup>increases</sup> while p-character decreases, bond angle <sup>decreases</sup>, i.e., bond angle  $\propto$  s-character  $\propto \frac{1}{p\text{-character}}$
- (5) % s-character decreases with the increase of electronegativity of groups/elements.

Applications/Explanations: 1. To explain bond angle: let us consider methane, fluoromethane and difluoromethane.

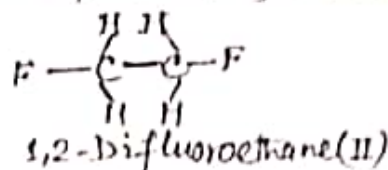
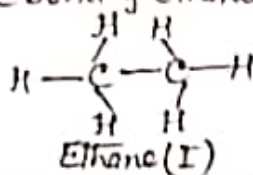


We know, bond angle decreases with the increase of % s-character. In case of methane (I), bond angles remain same (109°28') as % s-character of C-H bond is same

In fluoromethane (II), F is more electronegative than H. % s-character is not same. % s-character of C-F bond decreases while % s-character of C-H bond increases. So,  $\angle \text{FCFH}$  is less than  $109^\circ 28'$  and  $\angle \text{HCH}$  is more than  $109^\circ 28'$ . The molecule is distorted tetrahedral.

In difluoromethane (III), two more electronegative element (F) present. % s-character of C-F bond more decreases and % s-character of C-H bond more increases. So,  $\angle \text{FCF}$  or  $\angle \text{FCH}$  is more less than  $109^\circ 28'$  &  $\angle \text{HCH}$  is more, larger than  $109^\circ 28'$ .

2. To explain bond strength: Bond strength increases with the increase of % s-character of the bond. For example, C-C bond of 1,2-difluoroethane is stronger than C-C bond of ethane. This can be explained as follows:

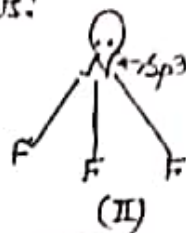
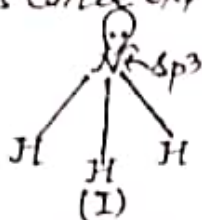


In ethane (I), C-atoms are  $sp^3$  hybridised, and has 25% s-character. All the six C-H bonds have same % s-character.

In 1,2-dichloroethane (II), two C-F and four C-H bonds are present. % s-character of C-F bond decreases more while % s-character of C-H bond increases. There increase the s-character of C atoms/C-C bond from 25% (i.e., s-character > 25%).

So, C-C bond in 1,2-difluoroethane (II) is more stronger than that of ethane (I).

3. To explain basic character/strength: Basic character/strength decreases with the increase of % s-character. For example,  $\text{NF}_3$  is weaker Lewis acid than  $\text{NH}_3$ . This can be explained as follows:



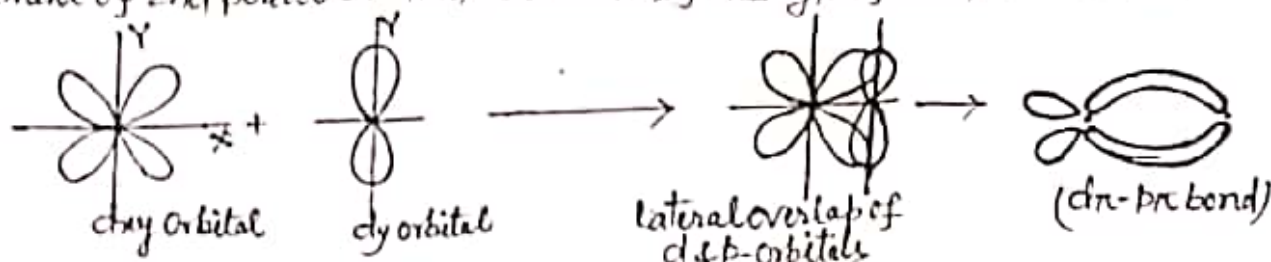
F is more electronegative than H.  $\text{NF}_3$  (II) has three N-F bonds & one  $sp^3$  hybrid orbital containing unbonded electron pair (lone pair). Since N-F bond has less s-character than that of N-H bond (I), and lone pair containing  $sp^3$  hybrid orbital at N atom of  $\text{NF}_3$  has large % s-character than that of  $\text{NH}_3$  (I). So,  $\text{NF}_3$  is weaker Lewis base than  $\text{NH}_3$ .



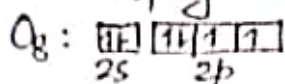
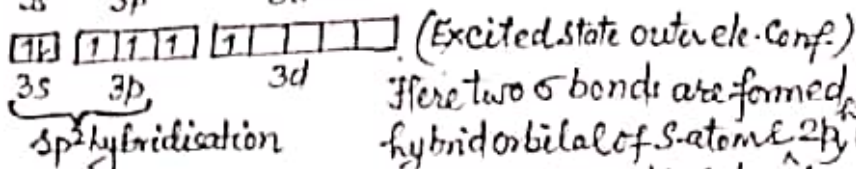
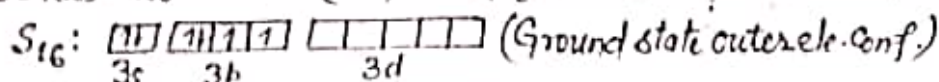
→ dn-pπ bond:

A covalent bond formed by lateral or side wise overlap of d- and p-orbitals is called dn-pπ bond.

In dn-pπ bond, dxy orbital of one element of 3rd period and p orbital of another element of 2nd period involved. Formation of this type of bond shown below:

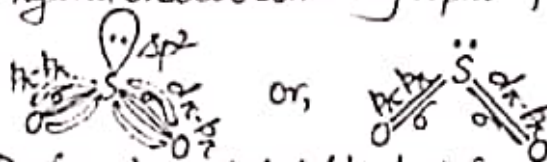


For examples, (1) Formation of SO<sub>2</sub>: In SO<sub>2</sub> molecule, S-atom is sp<sup>2</sup> hybridised. It has two σ-bonds (S-O), one pπ-pπ and one dn-pπ bond. This can be explained as:

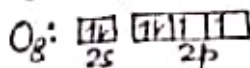
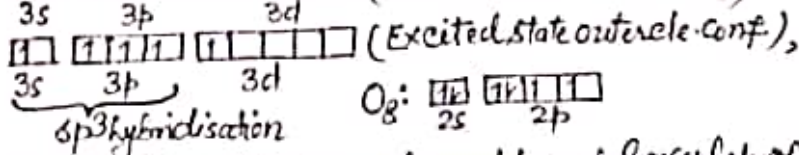
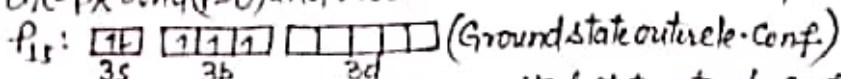


Here two σ bonds are formed by axial overlap of <sup>half-filled</sup> sp<sup>2</sup> hybrid orbital of S-atom & <sup>half-filled</sup> 2p orbital of O-atom. One π-bond is formed by lateral overlap of 3p<sub>z</sub> (unhybridised) orbital of S-atom and 2p<sub>z</sub> orbital of O-atom. Another

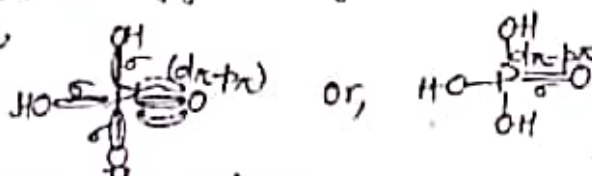
π-bond is formed by lateral overlap of unhybridised 3d<sub>xy</sub> orbital of S-atom & 2p<sub>z</sub> orbital of second oxygen atom. One sp<sup>2</sup> hybrid orbital containing a pair of electrons remains unbonded (called lone pair).



2. Formation of H<sub>3</sub>PO<sub>4</sub>: In H<sub>3</sub>PO<sub>4</sub> molecule, P-atom is sp<sup>3</sup> hybridised. It has one dn-pπ bond (P=O) and rest σ-bonds. This can be explained as follows:



Here four P-O (sigma) bonds are formed by axial overlap of half filled sp<sup>3</sup> hybrid orbital of P-atom and half filled 2p orbitals of O-atoms. One π-bond (P=O) is formed by lateral overlap of unhybridised half filled 3d<sub>xy</sub> orbital of P-atom and 2p<sub>z</sub> orbital (half-filled) of one O-atom



1. Q. Explain dn-pπ bond in SO<sub>3</sub> & H<sub>2</sub>SO<sub>4</sub> molecules.

2. Q. Illustrate dn-pπ bond in N(SiH<sub>3</sub>)<sub>3</sub> molecule.