



Study of Bent Rule and Energetics of Hybridization

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Introduction : Hybridisation is the concept of mixing atomic orbitals into new hybrid orbitals with different energies, shapes, etc. than the component atomic orbitals. When a set of hybrid orbital is constructed by a linear combination of atomic orbitals, the energy of the resulting hybrids is a weighted average of the energies of the participating atomic orbitals. This energy of hybridization is of the order of magnitude of bond energies and can thus be important in determining the structure of molecules.

Bent rule encompasses the relationships between bond polarity (ligand electronegativity) and central -atom geometry through their mutual connection to central-atom hybridization.

Key Words : Bent rule , Hybridisation, orbitals

According to hybridisation atomic orbitals combine and redistribute their energies to form hybrid orbital. These are identical with respect to energy, shape etc. Shapes of the hybrid orbital depends upon contribution of s, p orbitals and its affect 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".

s orbitals has low energy than p orbital.

More s character decrease the energy of bonding orbitals and hence they have shaped more like a s orbital. More p character increase the energy of bonding orbitals and hence they have shaped more like a p orbitals.

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.

The most stable arrangement would be to utilize pure p orbitals for bonding and letting the lone pair into the pure s orbital.

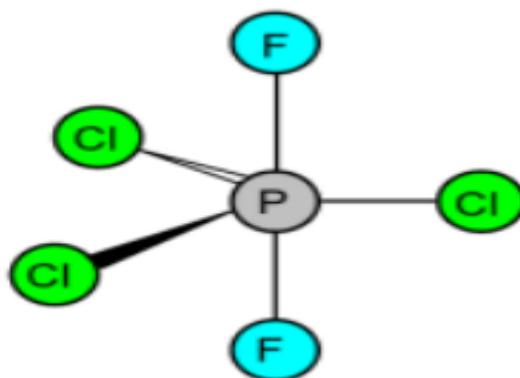
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s-Orbitals are more penetrating and electron density is less available for bonding. Thus, more electronegative atoms would be able to withdraw more electron density from p orbitals than from



s orbitals.

we can also describe bent rule as “More electronegative substituents prefer hybrid orbitals having less s-character and more electropositive substituents prefer hybrid orbitals having more s-character.”

Examples of Bent Rule and Energetics of Hybridization

1. sp^3d Hybridisation in PCl_xF_{5-x} : In sp^3d Hybridisation one s, three p and one d-orbitals form 5 sp^3d hybridised orbital. All these five hybrid orbitals are not of the same type so they can be divided into two non-equivalent sets. The first set is known as equatorial set of orbitals. It is formed from one s, one p_x and one p_y orbitals. The second set is known as axial set. It is formed from one p_z and one d orbitals. It is experimentally observed that the more electronegative substituent occupies the axial position (as it has less s character) that is f and less electronegative substituents is equatorially situated that is cl.
2. Less bond angle in CH_2F_2 : In the case of sp^3 hybridisation, CH_4 or CCl_4 formed tetrahedral geometry with bond angle 109.5° . But in the case of CH_2F_2 , the F-C-F bond angle is less, this explained on the basis of Bent's rule. F is more electronegative than H so F-C-F s-character is less than 25% while in H-C-H it is more than 25%. Due to less s-character bond angle is less in CH_2F_2 .



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