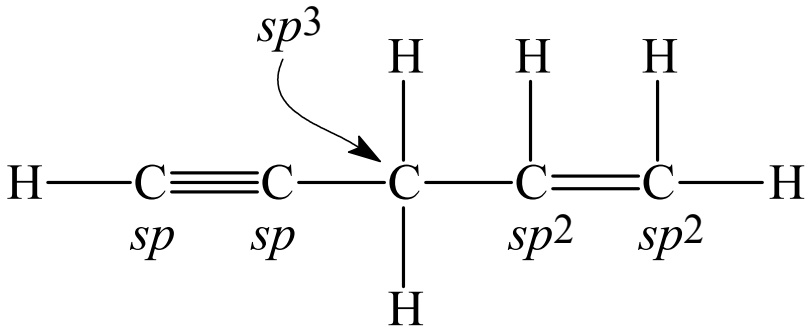
Hybridization and Shape

- The domain geometry and shape about central atoms in a complex molecule can be rationalized in terms of hybridization.

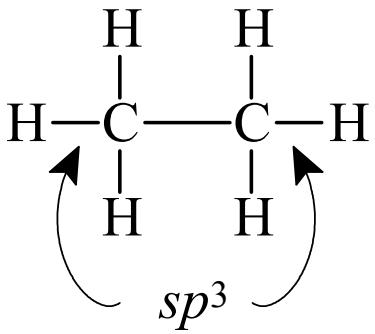
- In the VB model, a sigma bond is always assumed to exist between bonded atoms.

- The directional nature of sigma bonds, often using hybrid orbitals, makes the geometry about a central atom.

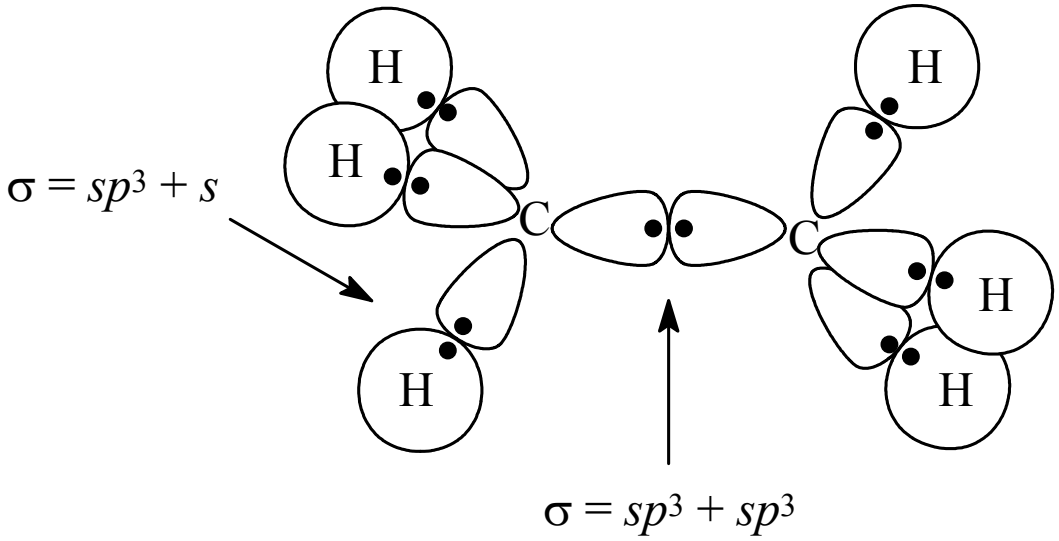


VB Model of Ethane, C_2H_6

Lewis model:



VB model:



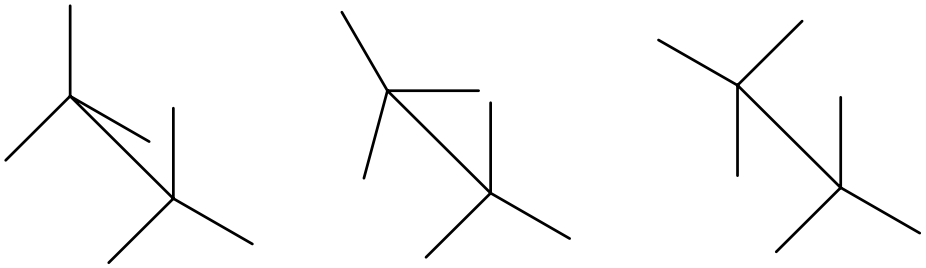
Hindered Rotation in C_2H_6

- Relatively free (slightly hindered) rotation can occur about a single bond axis.

- Hindered rotation leads to stereochemical conformations in ethane.
  - The barrier to rotation is ~12 kJ/mol in C_2H_6.
  - The various fluxional forms are called *conformers*.

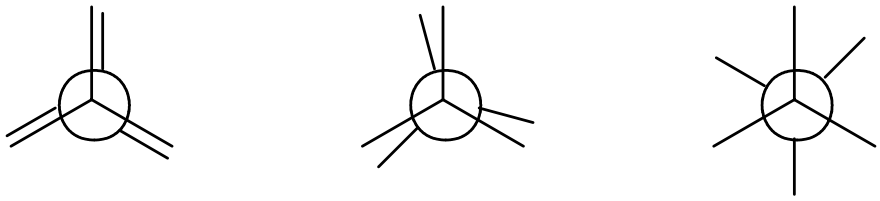
Conformers of Ethane

"Sawhorse" Representations of ethane's conformers:



Eclipsed (highest energy) | Gauche | Staggered (lowest energy)

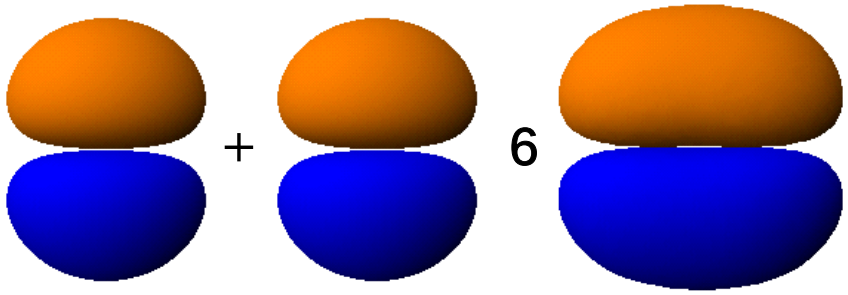
Newman Projections of ethane's conformers:



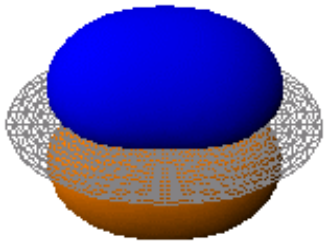
Eclipsed (highest energy) | Gauche | Staggered (lowest energy)

Orbital Overlap in Double and Triple Bonds
Pi Bonding (π bonds)

- Pi bonding results from side-by-side overlap of two orbitals, such as two $2p_x$ or two $2p_y$ orbitals.



Rotated about bond axis to show nodal plane:

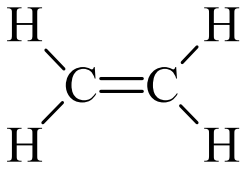


- In the VB approach, there is never a π bond without a σ bond, too.

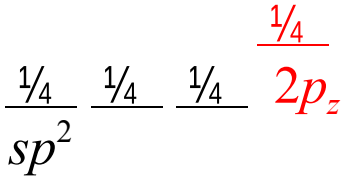
Composition of Bonds by Overlap Type

Bond Type	Composition	Maximum Electron Density
single	σ	along z
double	$\sigma + \pi_x$ or $\sigma + \pi_y$	along z (σ) in xz or yz plane (π_x or π_y)
triple	$\sigma + \pi_x + \pi_y$	along z (σ) in xz plane (π_x) and yz plane (π_y)

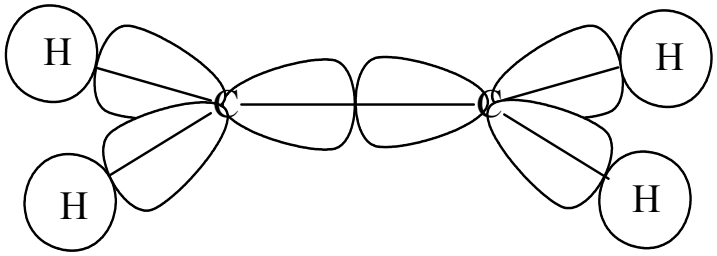
Sigma and Pi Bonding in C_2H_4



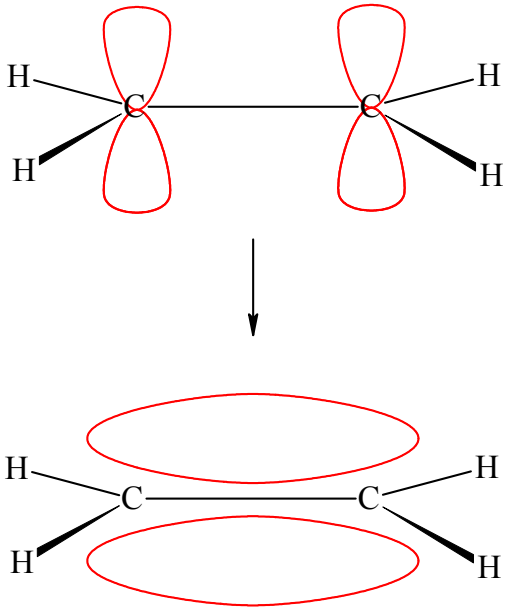
C sp^2 hybridized



Sigma Bonding:



Pi Bonding:

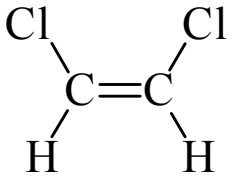


Stereochemical Rigidity and Isomers

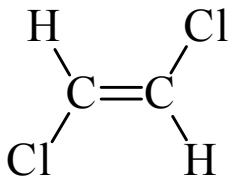
- Rotation is severely restricted about a double bond, creating *stereochemical rigidity* and the possibility of *isomers*.

  Isomers – different compounds with the same molecular formula

  Stereoisomers – isomers that differ only in how their atoms are oriented in space.



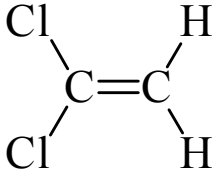
cis



trans

- *Cis-trans* isomers are also called **geometrical isomers**, because they differ in the geometry of the atoms or groups of atoms about the double bond.

- **Structural isomers** (or **constitutional isomers**) have the same formulas but different atoms bonded together.



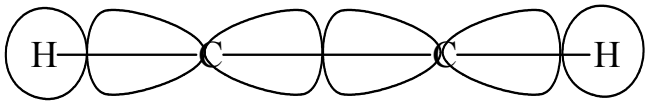
Triple Bond in C_2H_2

$$H{-}C{\equiv}C{-}H$$

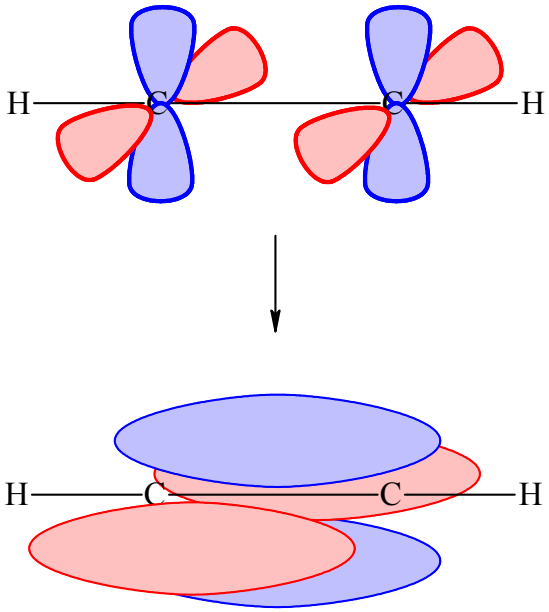
C *sp* hybridized

		¼	¼
¼	¼	$2p_x$	$2p_y$
sp			

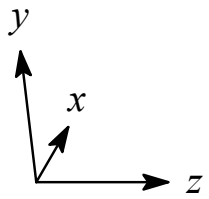
Sigma Bonding:



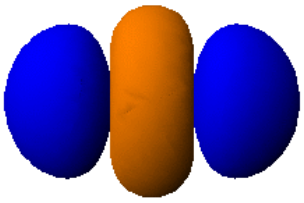
Pi Bonding:



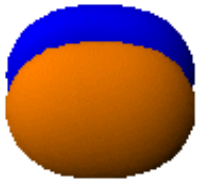
Boundary Surface Models of the Sigma and Two Pi Bonds in C_2H_2



$\sigma(z)$



$\pi(xz)$



$\pi(yz)$