

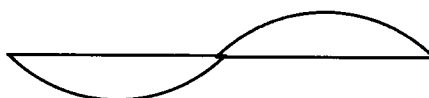
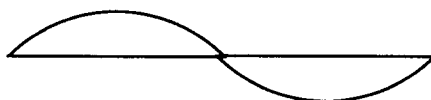
Chapter 2: Structures and Properties of Organic Molecules

Wave Properties of Electrons in Orbitals: H : H ?

standing wave

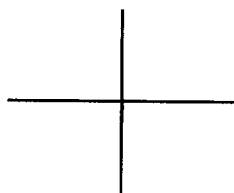
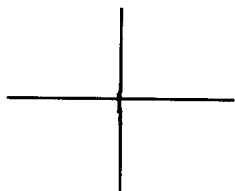
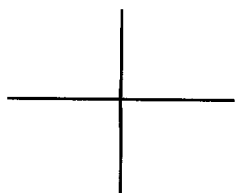
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guitar string analogy:



wave function (Ψ):

Ψ^2 :



Linear Combination of Atomic Orbitals:

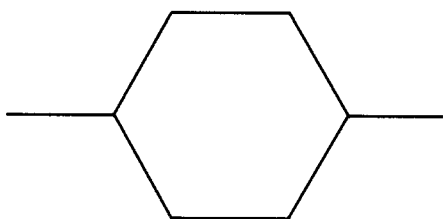
1. Combine orbitals on different atoms
2. Combine orbitals on the same atom

Molecular Orbitals



wave functions can be combined in 2 ways:

1. constructively (in phase, signs match) - wave functions reinforce each other -
2. destructively (out of phase, opposite signs) - wave functions cancel out -



To explain bonding in some molecules (H_2 , F_2 , HF), we can overlap the simple **s** orbitals and/or **p** orbitals of the atoms involved.

Examples: H_2 (above), F_2 - overlap a **p** orbital from each atom (p.42)
 HF - overlap the **s** orbital of H with a **p** orbital of F (p.42)

In each of the above molecules, the direct "end to end" overlap of the orbitals results in the formation of a **sigma bond** -

pi (π) bond -

Let's attempt to use the simple LCAO method to explain bonding in CH_4 .

First, some observations:

4 equivalent carbon - hydrogen bonds (carbon forms bonds to 4 atoms)

109.5° HCH bond angles - tetrahedral geometry

Types of orbitals available for overlap? - Determine electron configuration:

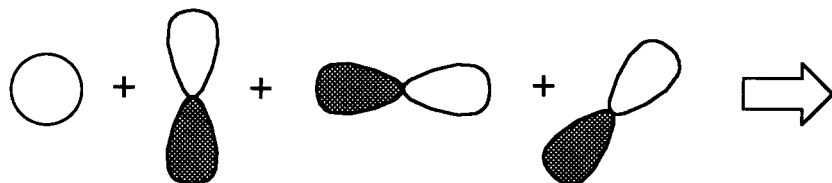
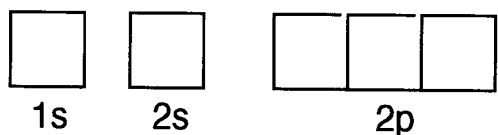
Carbon:



Will overlap of these orbitals provide a molecule that fits the observations?

We need 4 equivalent orbitals on carbon:

of hybrid orbitals formed = # of atomic orbitals mixed

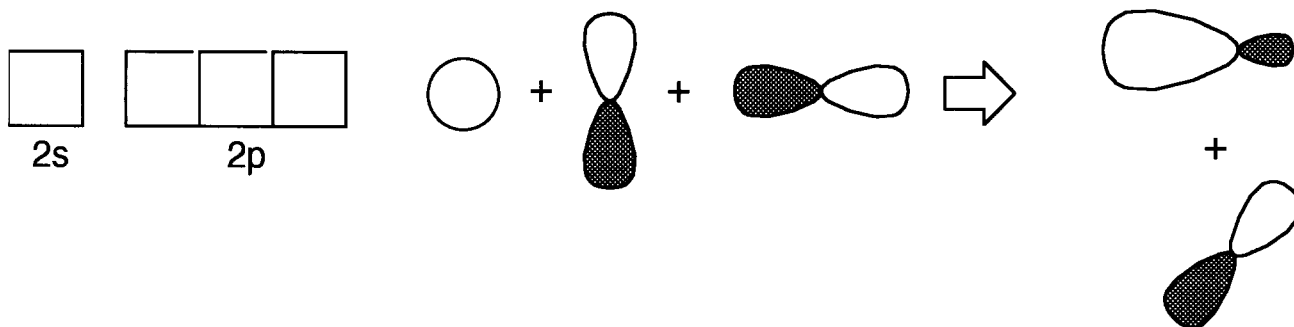


Bond angles? **VSEPR**

Another Example: Ethane CH_3CH_3

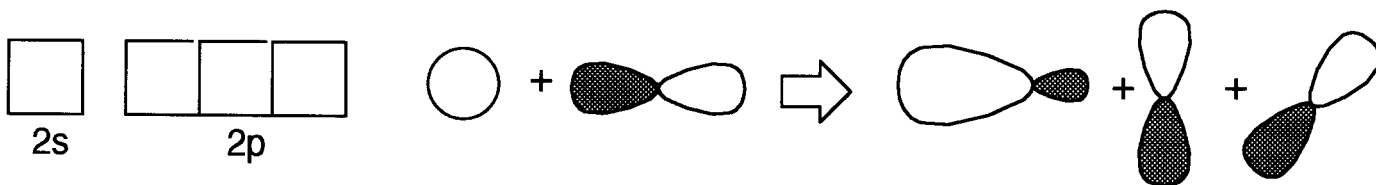
Bonding in Ethene (ethylene): CH_2CH_2

observations: each carbon forms bonds with 3 atoms
shorter C-C bond than ethane's
approx. 120° bond angles - trigonal planar geometry

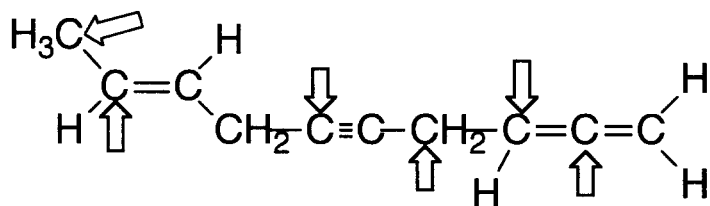


Bonding in Ethyne (acetylene): CHCH

observations: each carbon forms bonds with 2 atoms
shorter C-C bond than ethene's
 180° bond angles - linear geometry



Example: choose hybridization for the carbons indicated



Hybridization of Heteroatoms

Nitrogen: NH_3

Oxygen: H_2O

Boron: BF_3

Hybridization Summary:

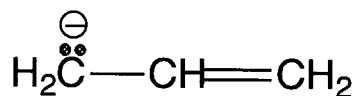
- to determine the hybridization for an atom, add the # of atoms bonded to the number of lone pairs
- hybridization dictates geometry/bond angles

if total = 4

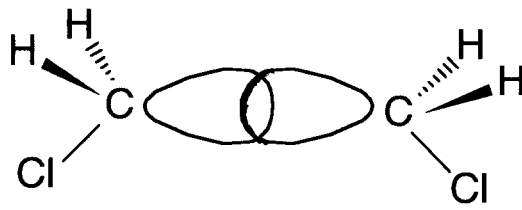
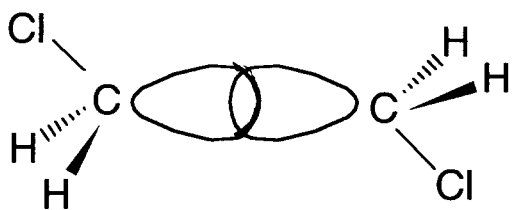
if total = 3

if total = 2

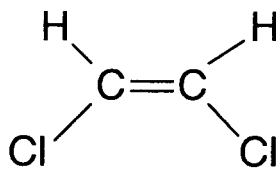
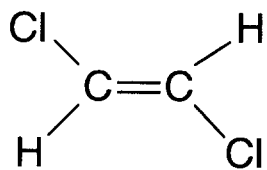
Last Example (for now)



Free Rotation Around Single Bonds:



Restricted Rotation Around Double Bonds:



Systematic Isomer Hunt

1. Determine the unsaturation number using the formula
$$\text{UN} = \frac{\# \text{C} \times 2 + 2 - \# \text{H}}{2}$$

The following modifications to the formula are sometimes necessary:

- a. if the molecular formula contains a halogen atom, count it as a hydrogen
- b. if the molecular formula contains oxygen, ignore it
- c. if the molecular formula contains nitrogen, subtract the # of nitrogens from the number of hydrogens

The unsaturation number gives an idea of how many multiple bonds or rings are present in the compound. Each pi bond is 1 point of unsaturation and each ring is 1 point of unsaturation.

Example: An unsaturation number (UN #) of 1 means that the compound has 1 double bond or 1 ring. A UN # of 2 means that the compound has 2 double bonds, or 1 double bond and 1 ring, or 2 rings, or 1 triple bond.

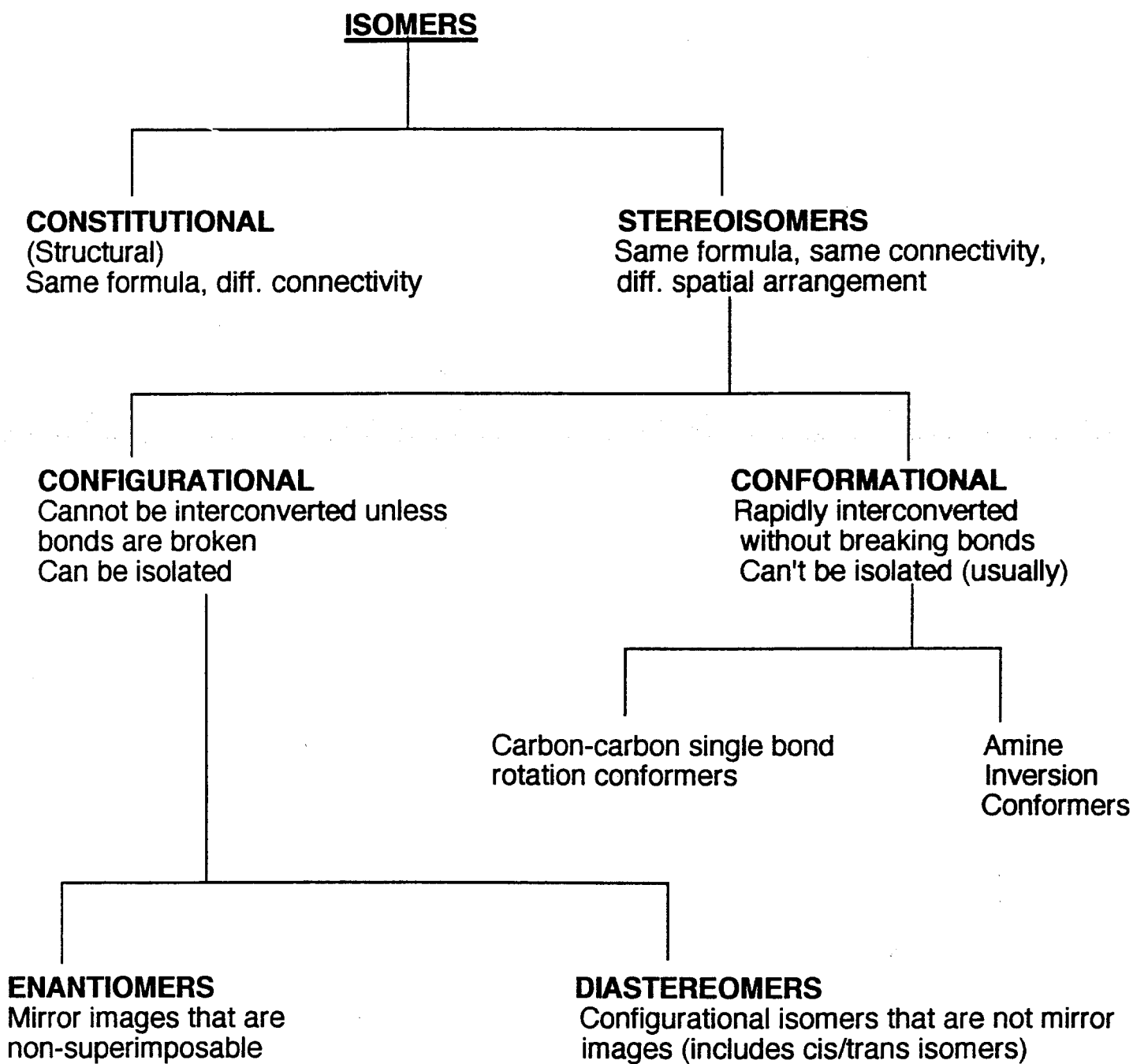
2. Look for structural isomers first.
 - a. Draw the longest continuous carbon chain (or the largest ring) first. (In cases of double/triple bonds, place those bonds in as many different positions in the chain as possible.)

 - b. Chop off one carbon and place that carbon in as many different positions on the parent chain as possible. (or construct ring with one less carbon and place one carbon on the ring)

- c. Chop off two carbons from the longest continuous chain found in a. and place both carbons in as many different positions as possible.

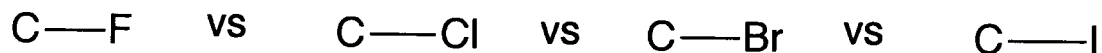
 - d. Continue this process until no longer possible. You now have all possible carbon skeletons.

 - e. If the molecular formula contains atoms other than carbon and hydrogen, you must know something about the functional groups possible for those atoms. In simple cases such as alkyl halides and alcohols, place the halogen or the OH group in as many different positions as possible on each of the carbon skeletons found in steps a.-d.
-
2. After all structural isomers have been found, look for geometric (cis/trans) isomers.
-
-
3. After all geometric isomers have been found, look for enantiomers.



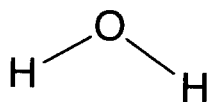
Polarity of Bonds and Molecules

bond dipole moment (μ) = $\delta \times \text{distance}$



Molecular Dipole Moment - vector sum of individual bond dipole moments in the molecule - indicates overall polarity of the molecule

Examples:



Which is more polar, NH_3 or BF_3 ?

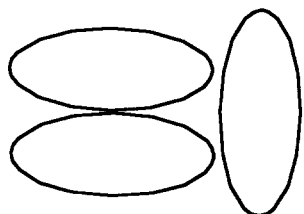
Intermolecular Attractions and Repulsions: (Predicting physical properties)

1. dipole - dipole forces: forces between polar molecules



2. London Dispersion Forces: attractive force between nonpolar molecules
a temporary, induced dipole





- brief lifetime
- change continuously
- Net result is attraction.

How strong are London dispersion forces?

Do nonpolar molecules have low boiling points?

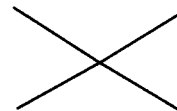
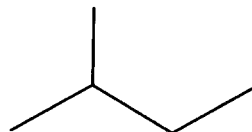
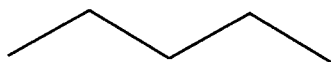
(see boiling point graph p. 89)

Strength of London dispersion forces depends on close surface contact of the molecules.

Surface area -

Branching -

Examples:



3. H Bond: a particularly strong dipole-dipole attraction
(Inter NOT Intramolecular)

occurs between:



∴O, N or F



Example:



Solubility: "Like dissolves like"

solute---solute + solvent---solvent \longrightarrow solvent---solute

Polar compounds

Nonpolar compounds

POLARITY EFFECTS on SOLUBILITIES

T6

