

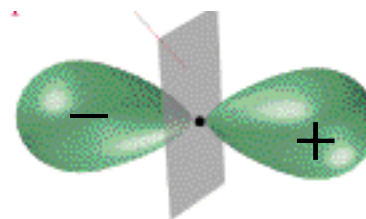
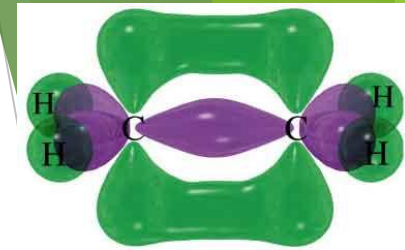
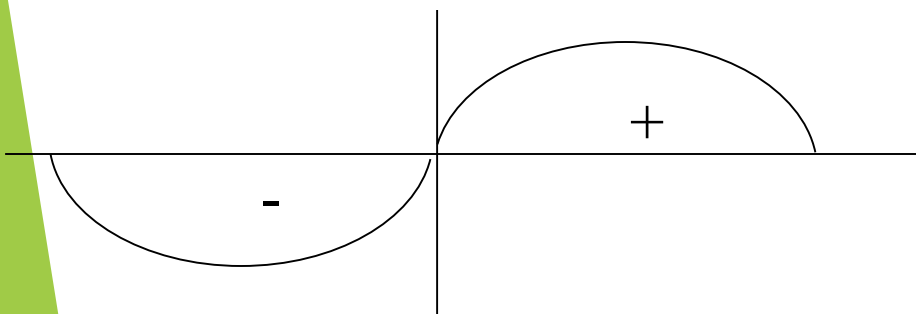
# Chapter 2

# Structure and Properties of Organic Molecules

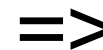
*Organic Chemistry*, 5<sup>th</sup> Edition  
L. G. Wade, Jr.

# Wave Properties of Electrons

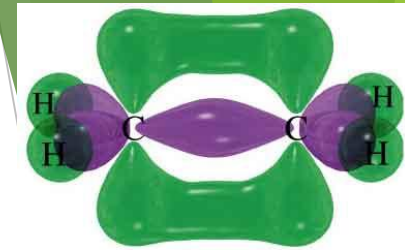
- ▶ Standing wave vibrates in fixed location.
- ▶ Wave function,  $\psi$ , mathematical description of size, shape, orientation
- ▶ Amplitude may be positive or negative
- ▶ Node: amplitude is zero



the  $2p_x$  orbital



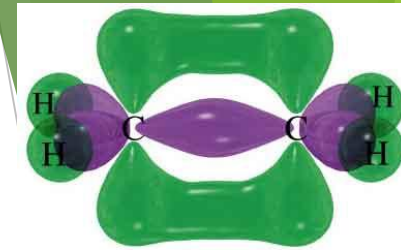
# Wave Interactions



- ▶ Linear combination of atomic orbitals
  - ▶ between different atoms is bond formation
  - ▶ on the same atom is hybridization.
- ▶ Conservation of orbitals
- ▶ Waves that are in phase add together. Amplitude increases.
- ▶ Waves that are out of phase cancel out.

=>

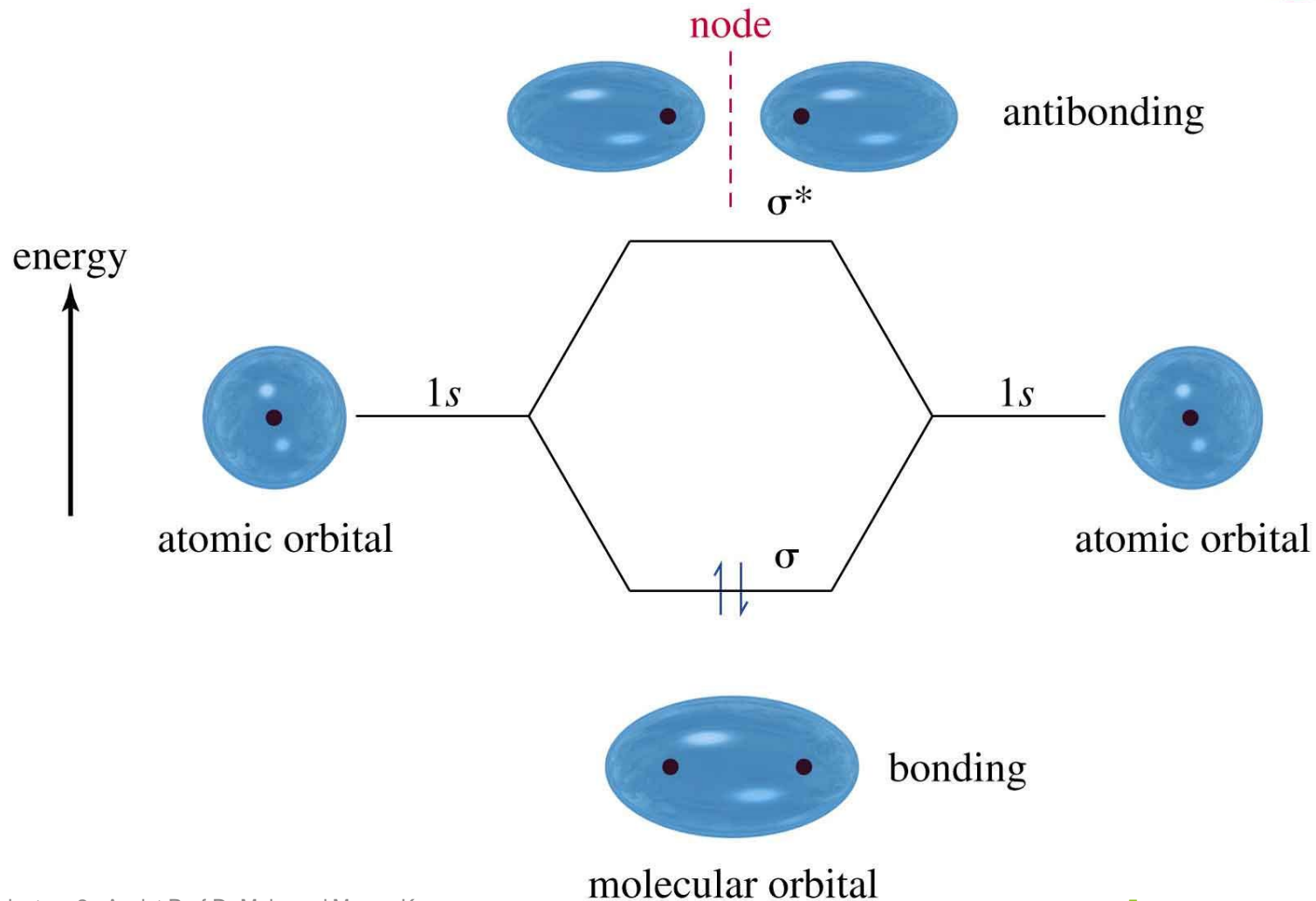
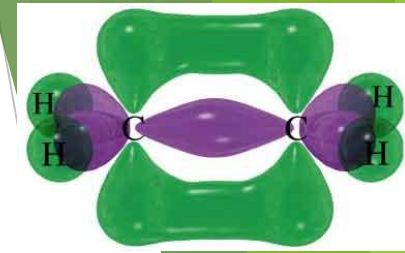
# Sigma Bonding



- ▶ Electron density lies between the nuclei.
- ▶ A bond may be formed by  $s-s$ ,  $p-p$ ,  $s-p$ , or hybridized orbital overlaps.
- ▶ The bonding MO is lower in energy than the original atomic orbitals.
- ▶ The antibonding MO is higher in energy than the atomic orbitals.

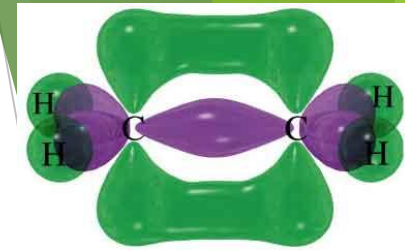
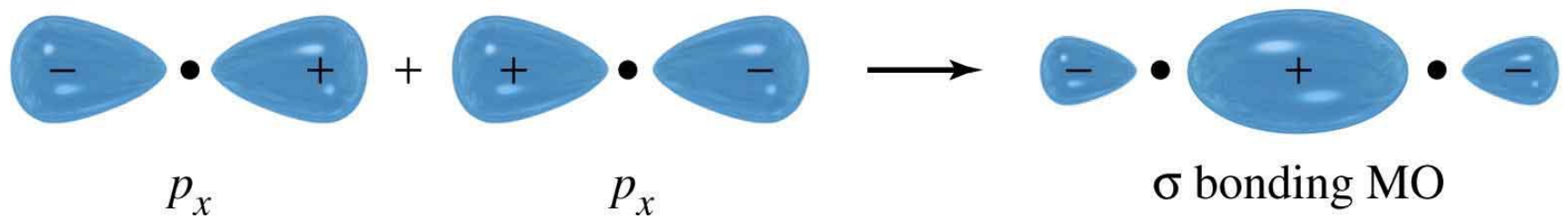
=>

# H<sub>2</sub>: s-s overlap

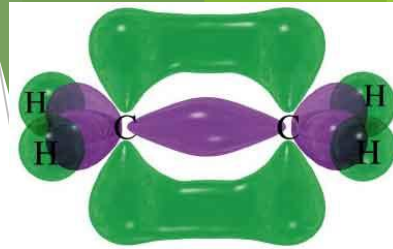


# $\text{Cl}_2$ : $p$ - $p$ overlap

Constructive overlap along the same axis forms a sigma bond.



# HCl: $s$ - $p$ overlap

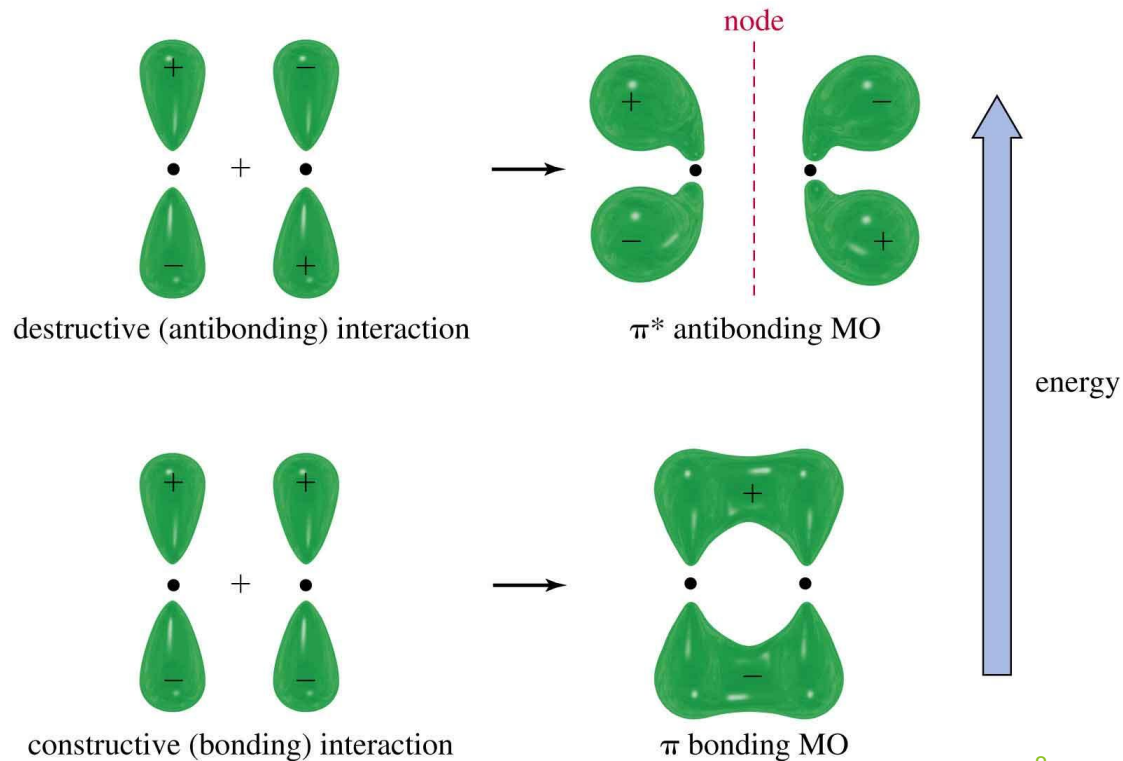
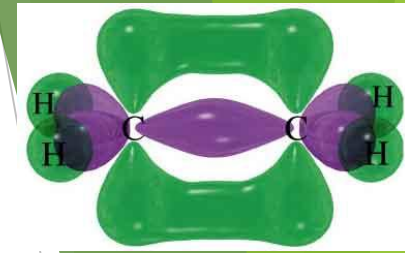


Question:

Draw the predicted shape for the bonding molecular orbital and the antibonding molecular orbital of the HCl molecule.

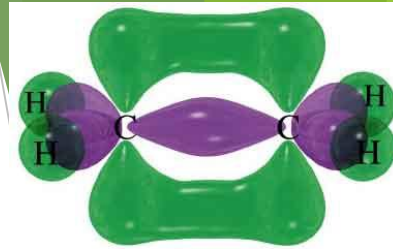
# Pi Bonding

- ▶ Pi bonds form after sigma bonds.
- ▶ Sideways overlap of parallel  $p$  orbitals.

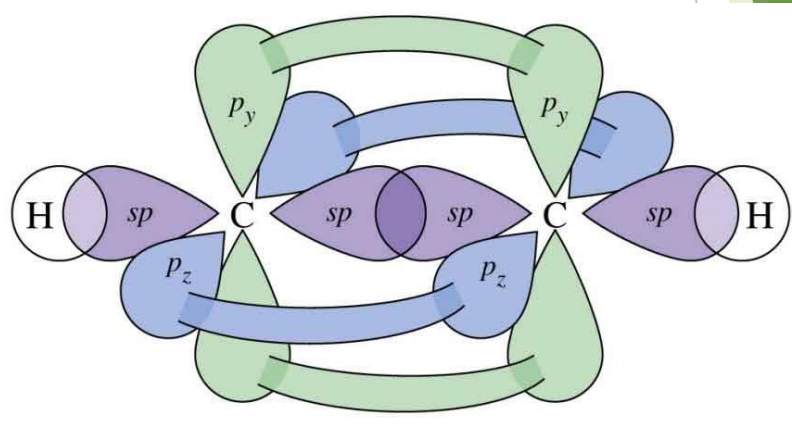
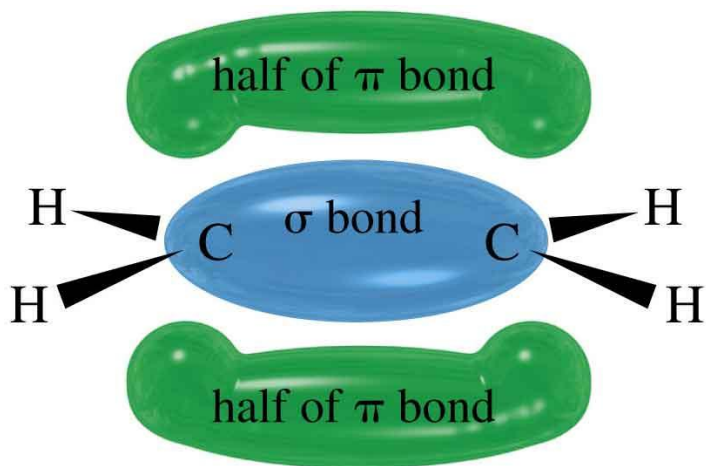




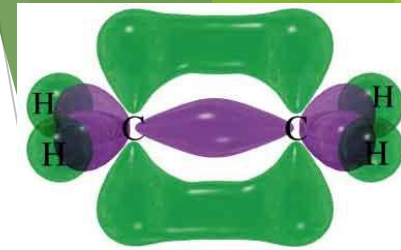
# Multiple Bonds



- ▶ A double bond (2 pairs of shared electrons) consists of a sigma bond and a pi bond.
- ▶ A triple bond (3 pairs of shared electrons) consists of a sigma bond and two pi bonds.



# Molecular Shapes



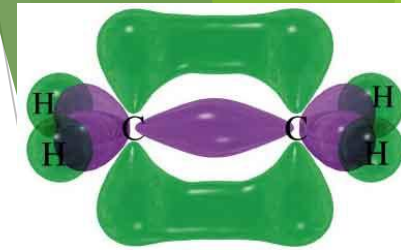
- ▶ Bond angles cannot be explained with simple  $s$  and  $p$  orbitals. Use VSEPR theory.

Valence shell electron pair repulsion (**VSEPR**) **theory** is a model used in chemistry to predict the geometry of individual molecules from the number of electron pairs surrounding their central atoms. It is also named the Gillespie-Nyholm**theory** after its two main developers.

- ▶ Hybridized orbitals are lower in energy because electron pairs are farther apart.

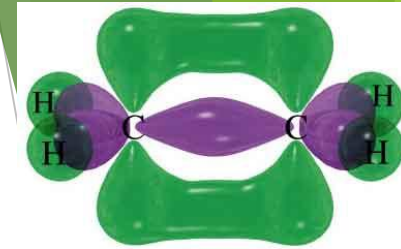
=>

# HYBRIDIZATION



- 1) ONE COMBINES S AND P ORBITALS ON SAME ATOM
- 2) FOR ANY SECOND-ROW ELEMENTS (C, N, O) AN S ORBITAL MUST INCLUDED IN THE COMBINATION
- 3) THE NUMBER OF ORBITALS COMBINED = NUMBER OF SIGMA BONDS AND LONE PAIR ELECTRONS ON ATOM
- 4) THE RESULTING HYBRIDIZED ORBITALS ARE SEPARATED FROM EACH OTHER AS MUCH AS POSSIBLE

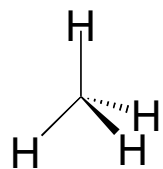
# SP<sup>3</sup>



Case I - 4 sigma bonds

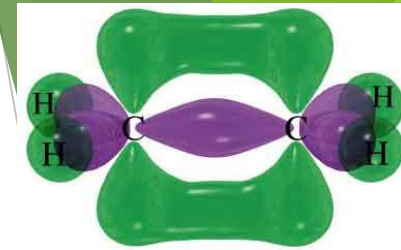
Tetrahedron Bond angle 109°

Consider methane

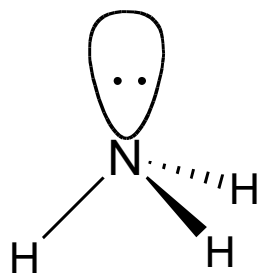


HINT: never put a bond between the two bonds in the plane of the paper.

# Case 2



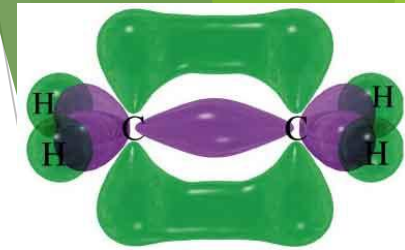
3 Sigma bonds and one lone pair



Geometry? pyramidal      WHY?

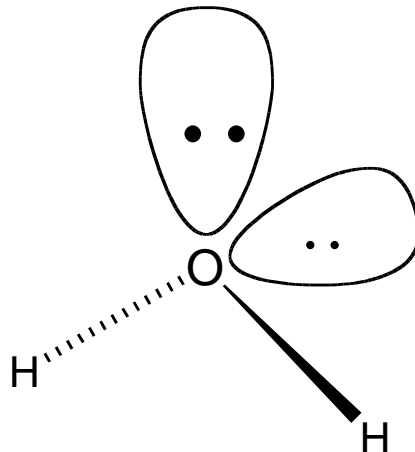
See nucle, not electrons

# Case 3



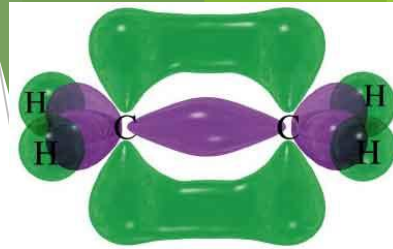
2 sigma bonds and 2 lone pair

Consider dimethyl ether CH<sub>3</sub>OCH<sub>3</sub>



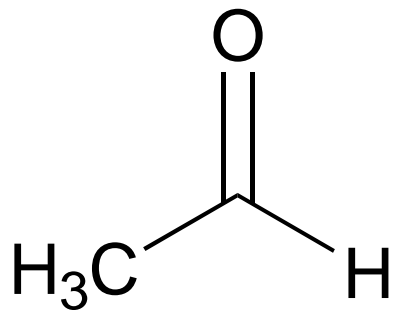
**BENT**

# $sp^2$ Hybrid Orbitals



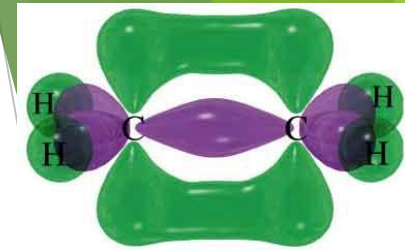
- ▶ combination of an s orbital with 2 p orbitals - three  $sp^2$  hybrid orbitals

trigonal planar:  $120^\circ$  bond angles.



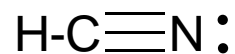
Carbon has 3 sigma and one pi bond

# *sp* Hybrid Orbitals



Combine one s 2 with one p 2 sigma orbital

Linear  $180^\circ$

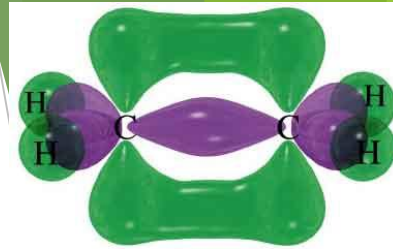


Note: both C and N are *sp* hybridized

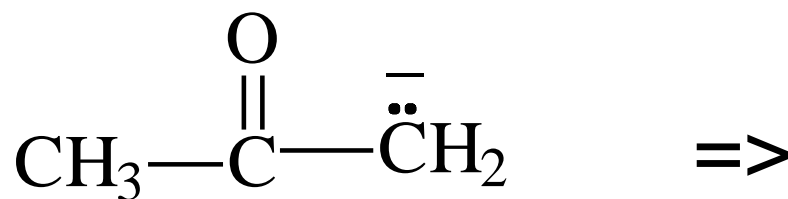


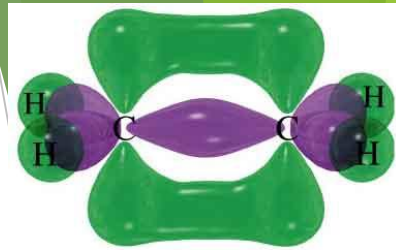


# Sample Problems



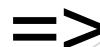
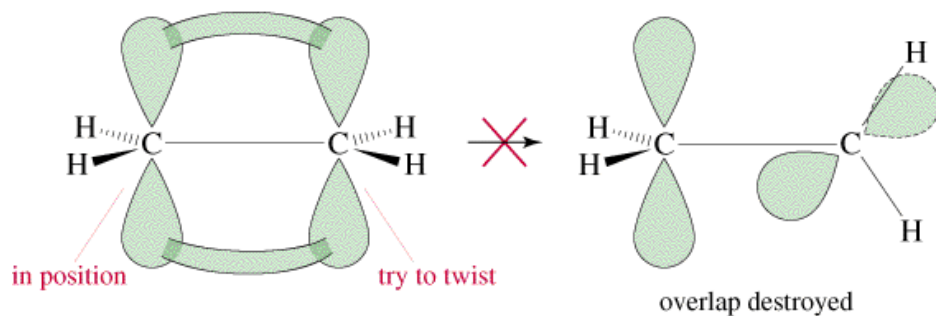
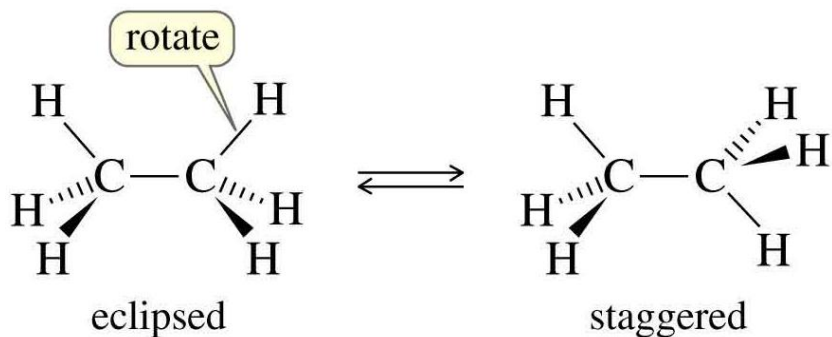
- ▶ Predict the hybridization, geometry, and bond angle for each atom in the following molecules:
- ▶ **Caution! You must start with a good Lewis structure!**
- ▶  $\text{NH}_2\text{NH}_2$
- ▶  $\text{CH}_3\text{-C}\equiv\text{C-CHO}$



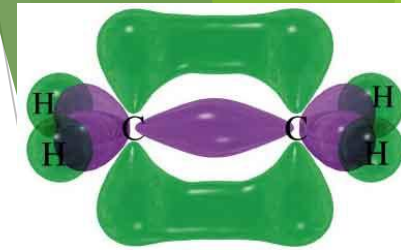


# Rotation around Bonds

- ▶ Single bonds freely rotate.
- ▶ Double bonds cannot rotate unless the bond is broken.

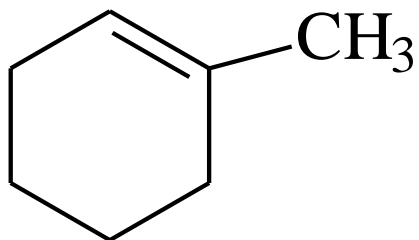
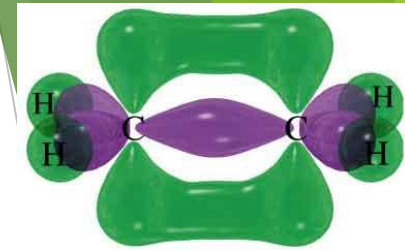


# Isomerism

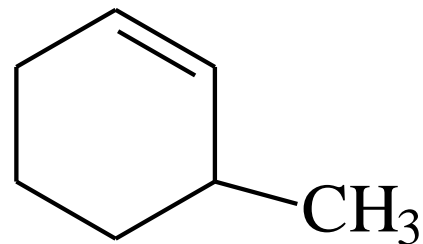


- ▶ Molecules which have the same molecular formula, but differ in the arrangement of their atoms, are called **isomers**.
- ▶ Constitutional (or structural) isomers differ in their bonding sequence.
- ▶ Stereoisomers differ only in the arrangement of the atoms in space. =>

# Structural Isomers

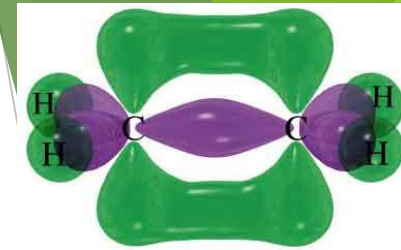


and



$\Rightarrow$

# STEREISOIMERS



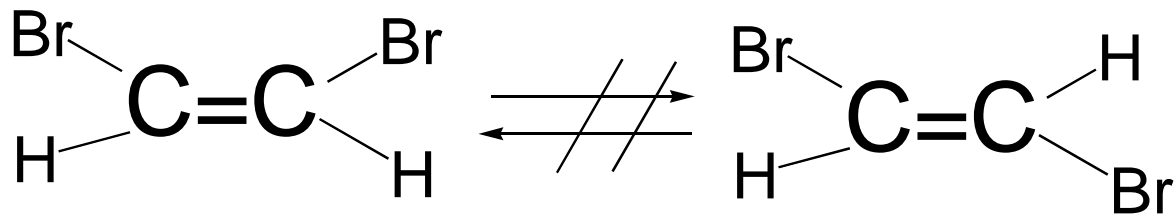
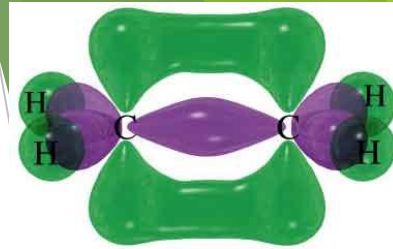
different structures but are alike with respect to which atoms are attached to which other atoms.

ARISES WHEN THERE IS RESTRICTED ROTATION

**Pi BOND** Two different groups attached to both carbons in pi bond

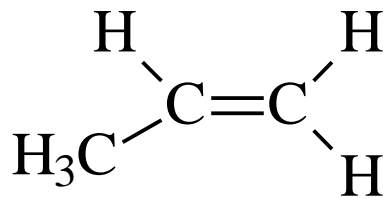
**RING** Two different groups attached to two ring carbons

# EXAMPLES



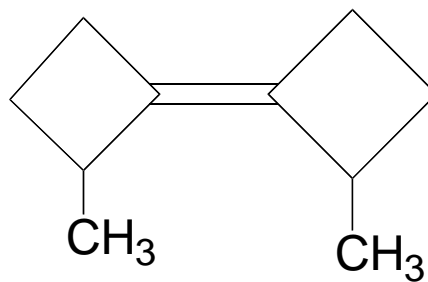
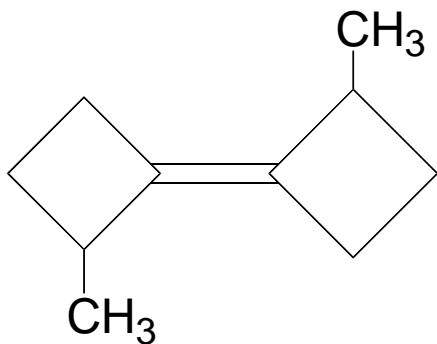
CIS - same side

TRANS - across

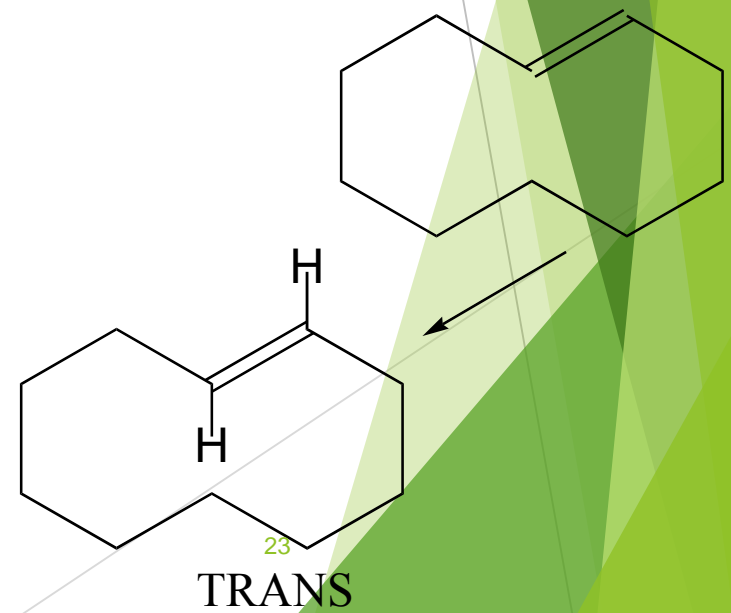
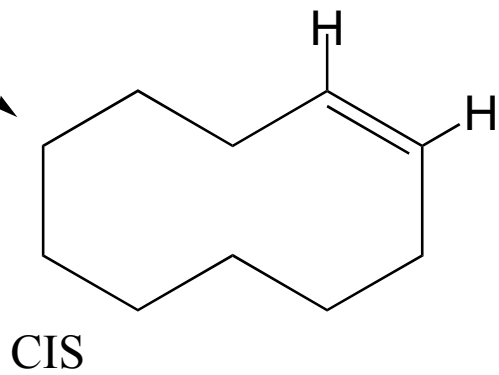
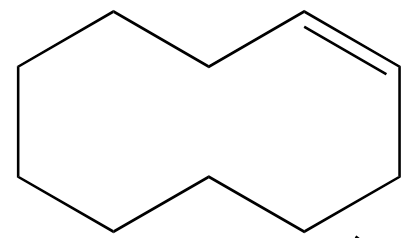
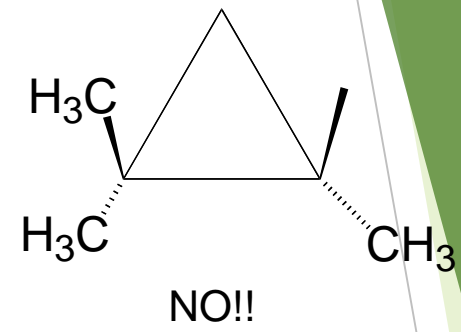
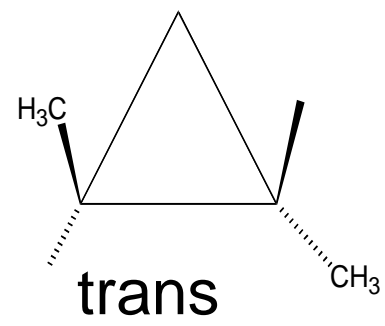
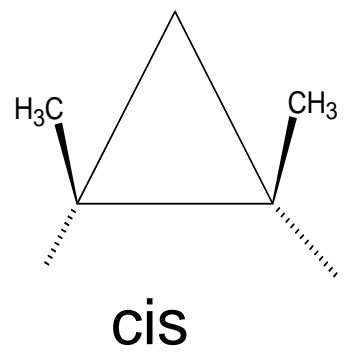
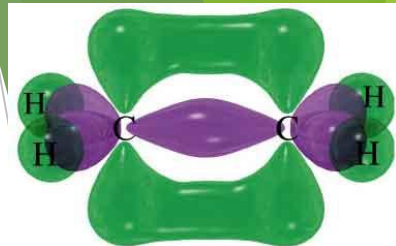


No cis-trans isomers possible

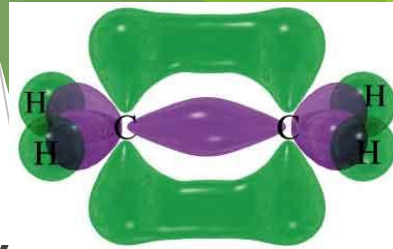
⇒



# EXAMPLES - RINGS

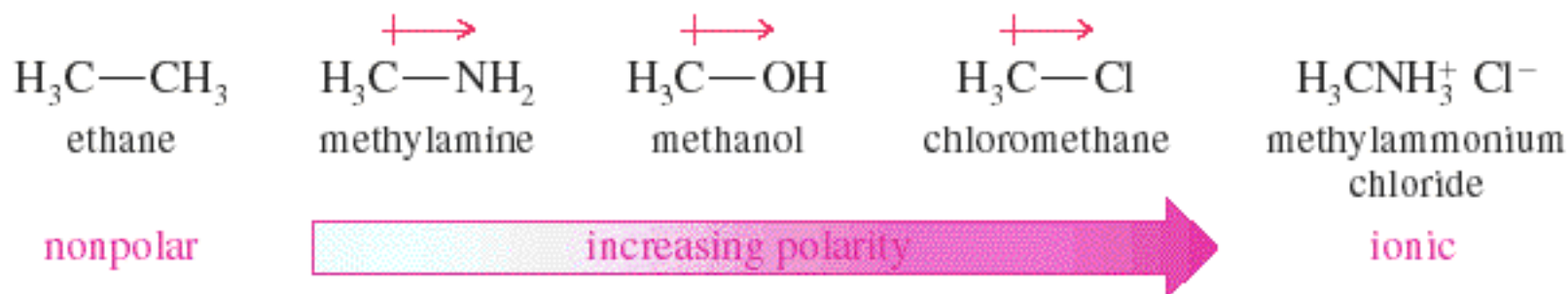


# Bond Dipole Moments



- ▶ are due to differences in electronegativity.
- ▶ depend on the amount of charge and distance of separation.
- ▶ In debyes,

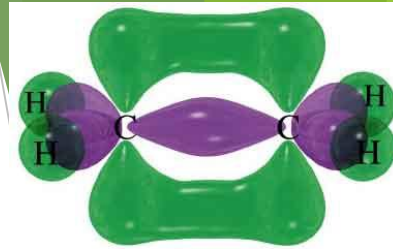
$$\mu = 4.8 \times \delta (\text{electron charge}) \times d (\text{angstroms})$$



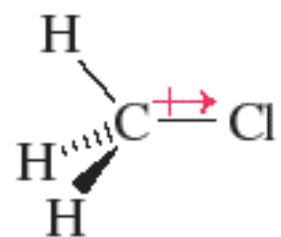
$\Rightarrow$



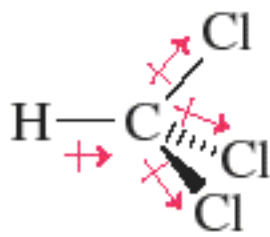
# Molecular Dipole Moments



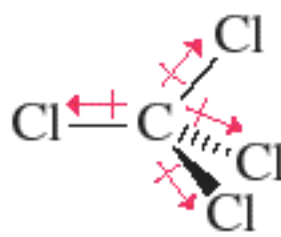
- ▶ Depend on bond polarity and bond angles.
- ▶ Vector sum of the bond dipole moments.
- ▶ Lone pairs of electrons contribute to the dipole moment.



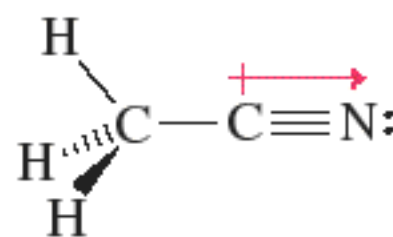
$\mu = 1.9 \text{ D}$   
chloromethane



$\mu = 1.0 \text{ D}$   
chloroform



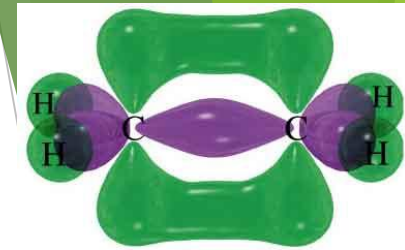
$\mu = 0$   
carbon tetrachloride



$\mu = 3.9 \text{ D}$   
acetonitrile

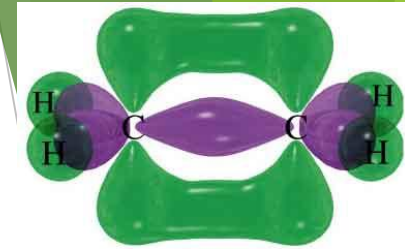
$\Rightarrow$

# Intermolecular Forces



- ▶ Strength of attractions between molecules influence m.p., b.p., and solubility; esp. for solids and liquids.
- ▶ Classification depends on structure.
  - ▶ Dipole-dipole interactions
  - ▶ London dispersions
  - ▶ Hydrogen bonding

=>

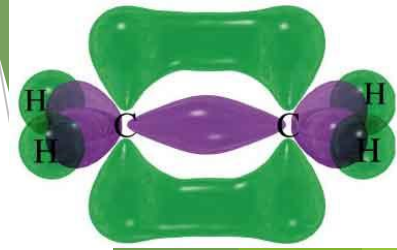


# Dipole-Dipole Forces

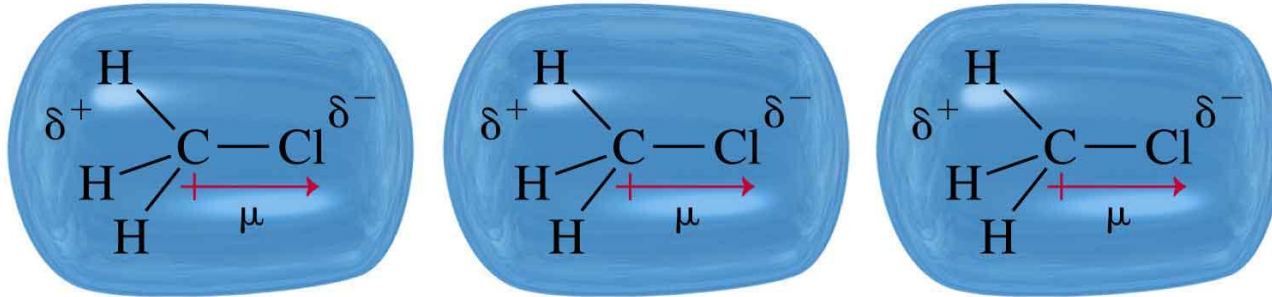
- ▶ Between polar molecules
- ▶ Positive end of one molecule aligns with negative end of another molecule.
- ▶ Lower energy than repulsions, so net force is attractive.
- ▶ Larger dipoles cause higher boiling points and higher heats of vaporization.

=>

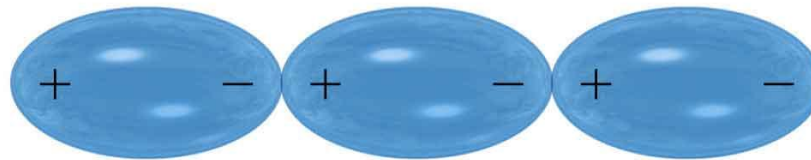
# Dipole-Dipole



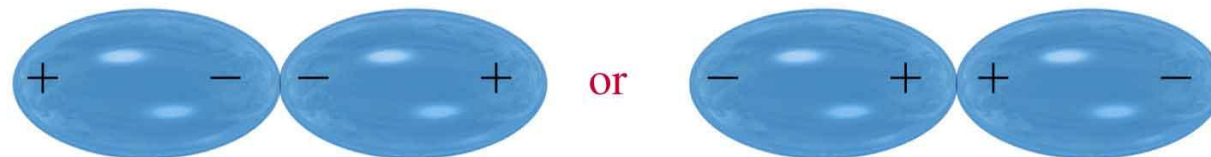
*attraction (common)*



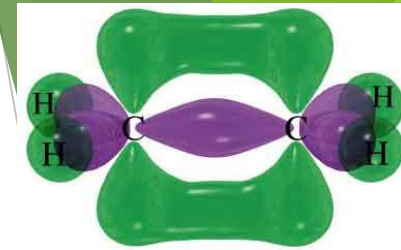
*symbolized by*



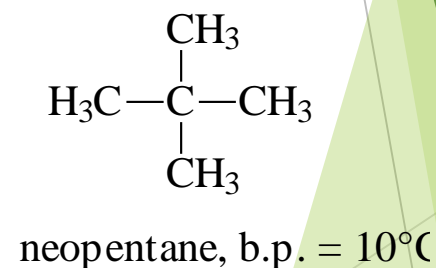
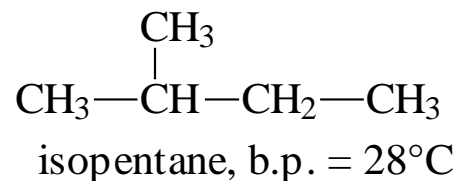
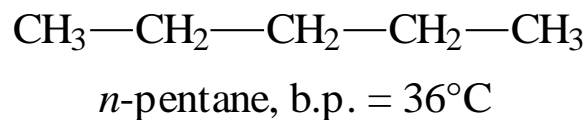
*repulsion (uncommon)*



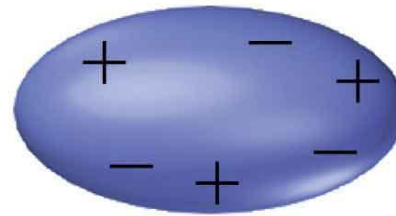
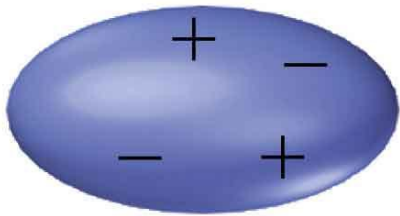
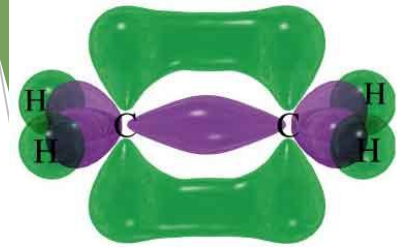
# London Dispersions



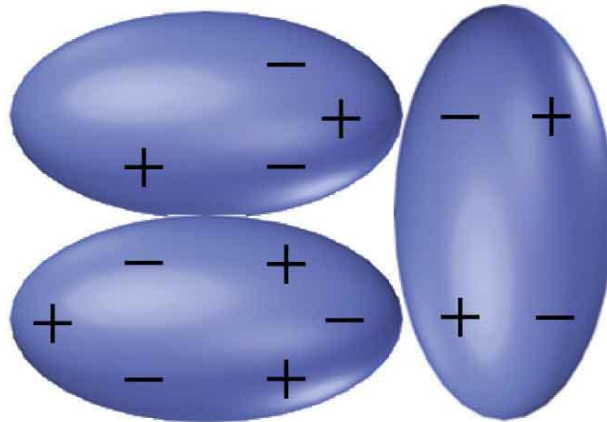
- ▶ Between nonpolar molecules
- ▶ Temporary dipole-dipole interactions
- ▶ Larger atoms are more polarizable.
- ▶ Branching lowers b.p. because of decreased surface contact between molecules.



# Dispersions



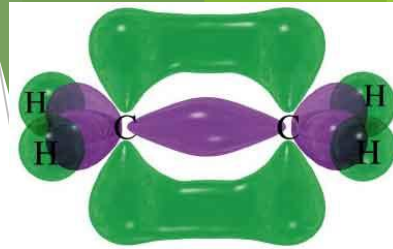
random temporary dipoles when separated



correlated temporary dipoles when in contact

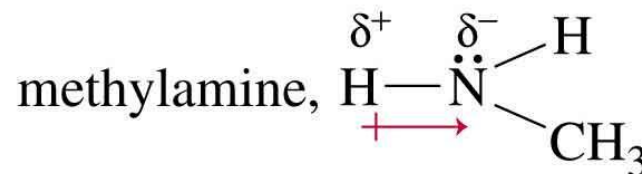
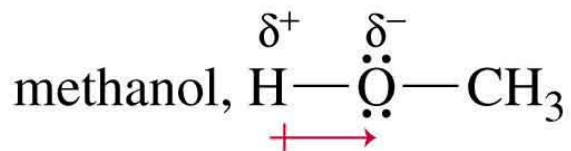
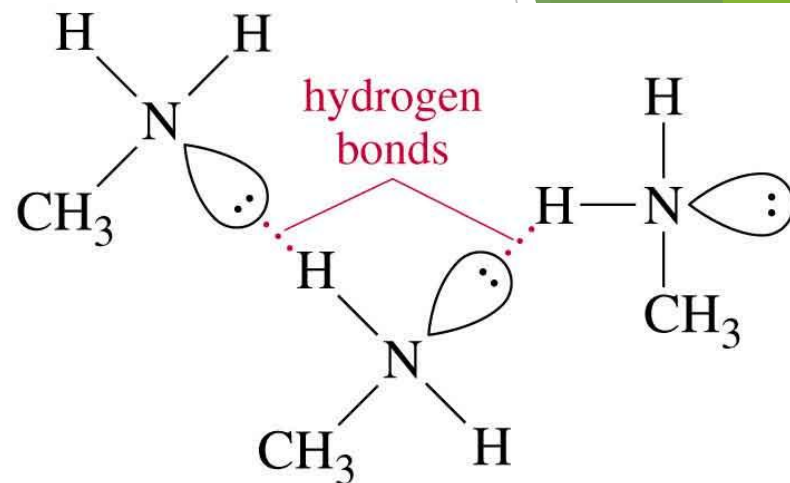
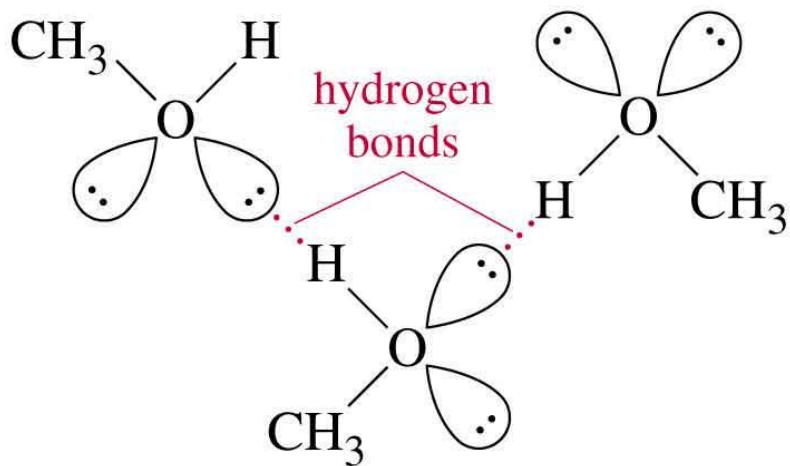
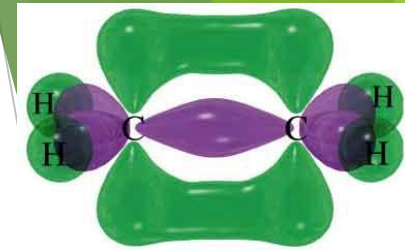


# Hydrogen Bonding



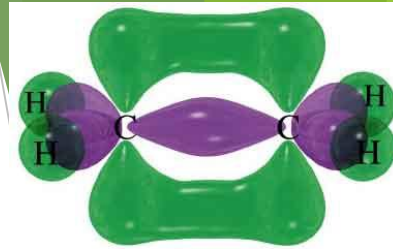
- ▶ Strong dipole-dipole attraction
- ▶ Organic molecule must have N-H or O-H.
- ▶ The hydrogen from one molecule is strongly attracted to a lone pair of electrons on the other molecule.
- ▶ O-H more polar than N-H, so stronger hydrogen bonding  
=>

# H Bonds





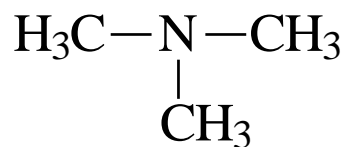
# Boiling Points and Intermolecular Forces



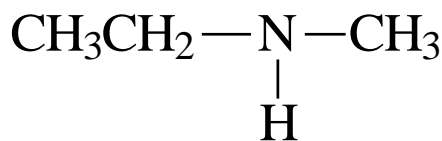
ethanol, b.p. = 78°C



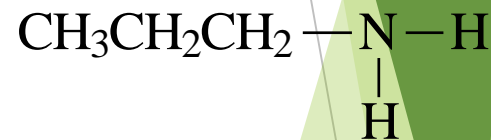
dimethyl ether, b.p. = -25°C



trimethylamine, b.p. 3.5°C



ethylmethylamine, b.p. 37°C



propylamine, b.p. 49°C



ethanol, b.p. = 78°C

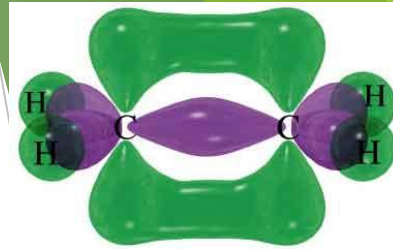


ethylamine, b.p. 17°C

=>

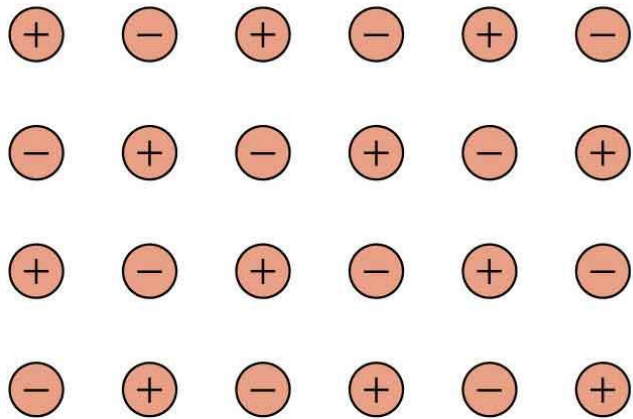
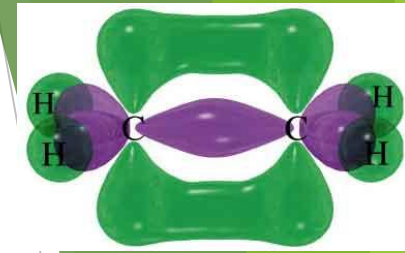
33

# Solubility

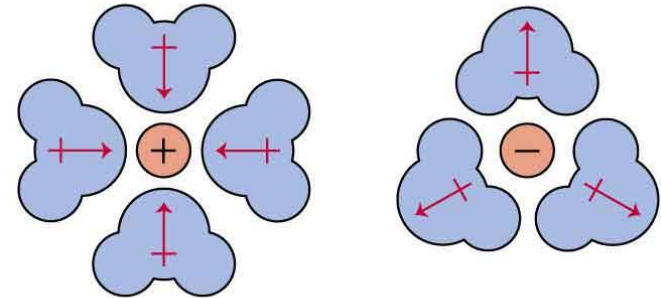


- ▶ Like dissolves like
  - ▶ Polar solutes dissolve in polar solvents.
  - ▶ Nonpolar solutes dissolve in nonpolar solvents.
  - ▶ Molecules with similar intermolecular forces will mix freely.
- =>

# Ionic Solute with Polar Solvent



ionic crystal lattice

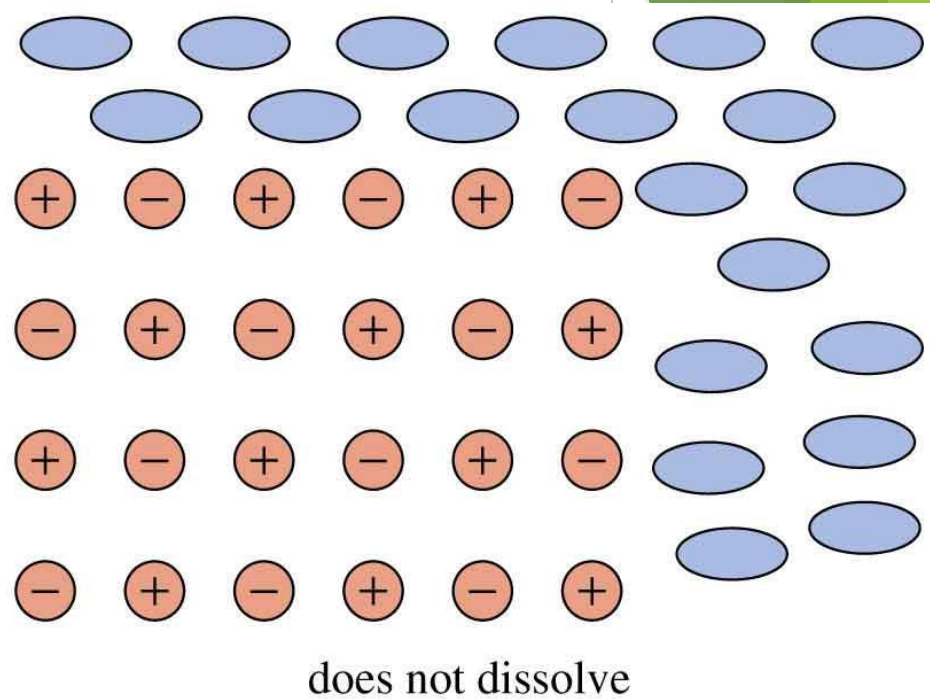
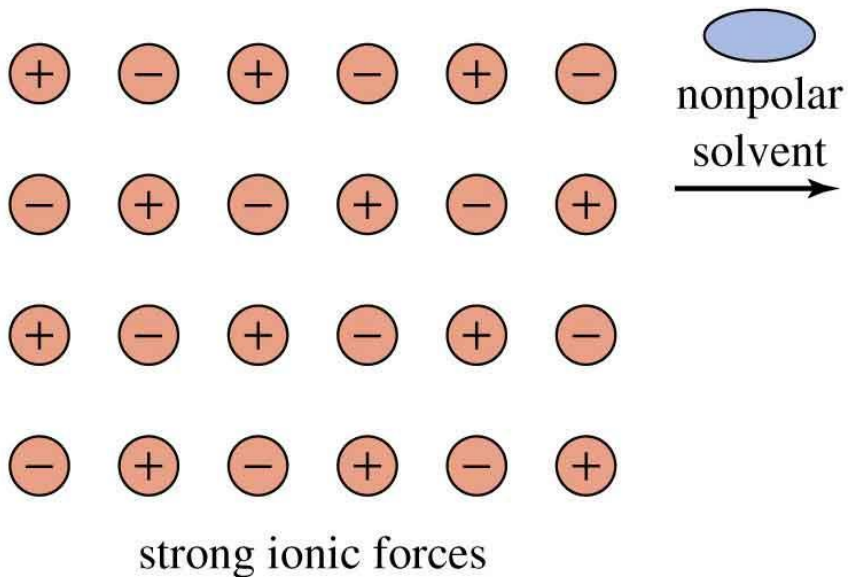
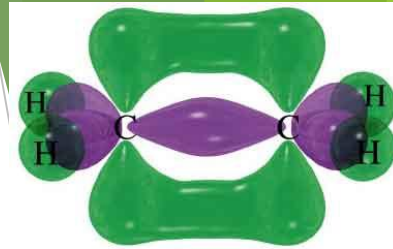


hydrated ions  
(dissolves)

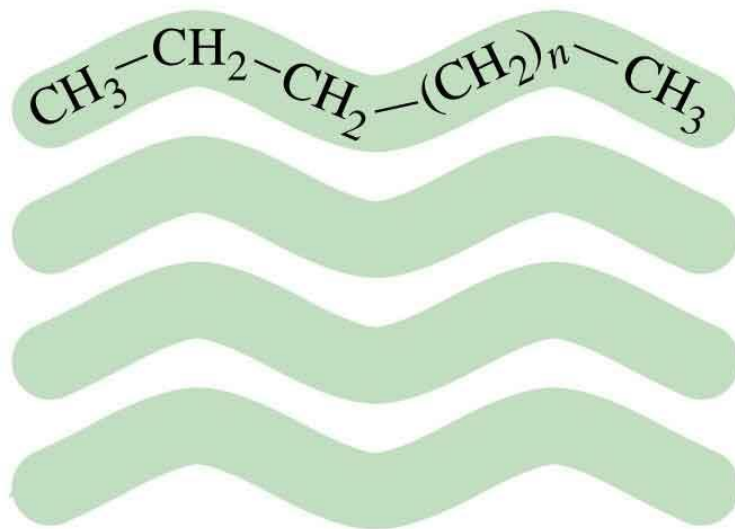
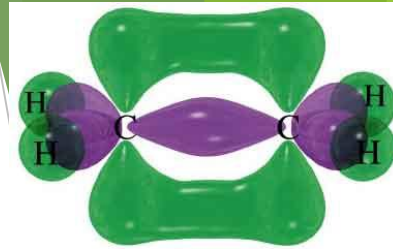
Hydration releases energy.  
Entropy increases.



# Ionic Solute with Nonpolar Solvent

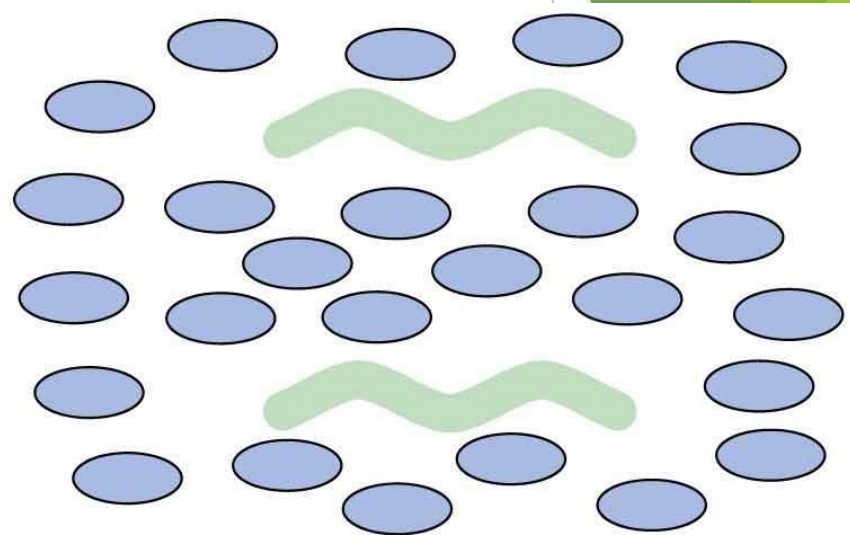


# Nonpolar Solute with Nonpolar Solvent



nonpolar solid  
(weak intermolecular forces)

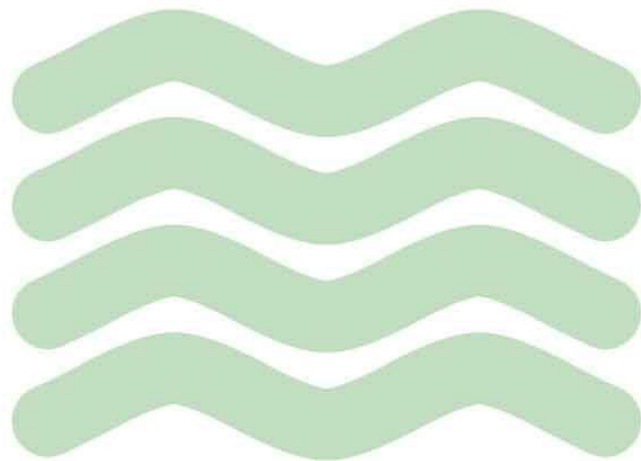
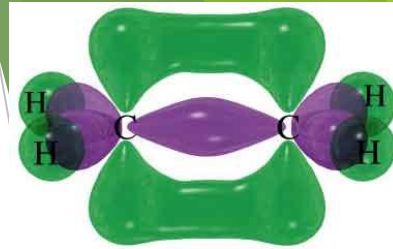
nonpolar  
solvent  
→



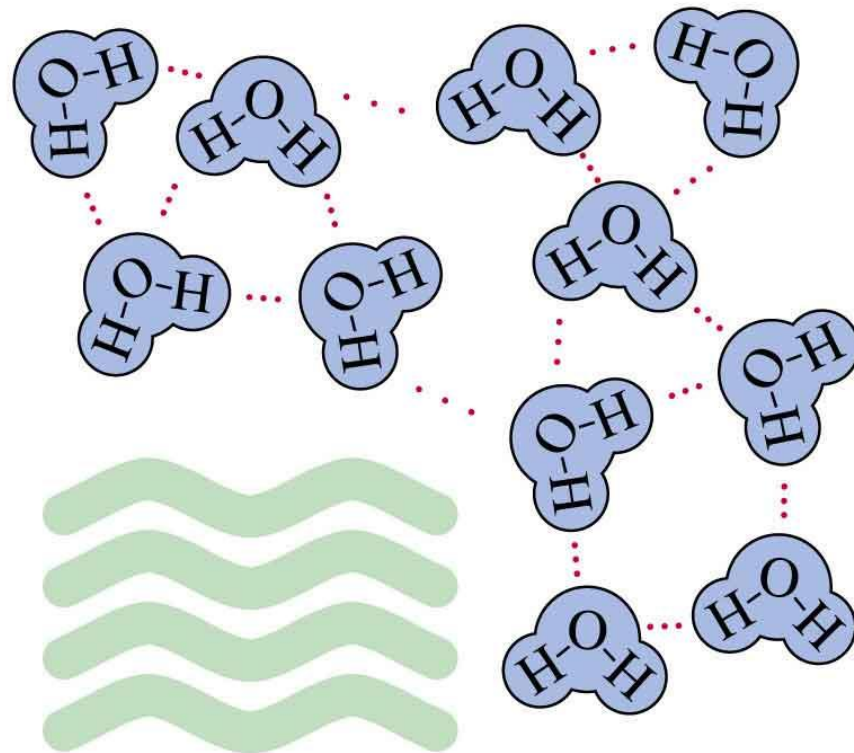
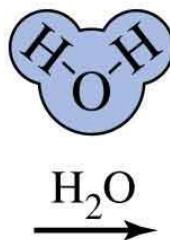
dissolves



# Nonpolar Solute with Polar Solvent



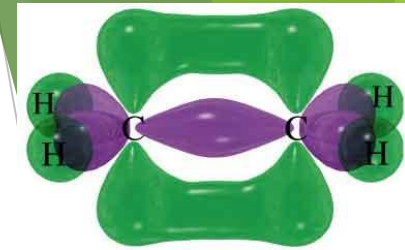
nonpolar solid



does not dissolve



# Classes of Compounds



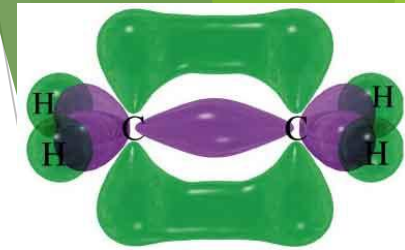
- ▶ Classification based on **functional group**
- ▶ Three broad classes
  - ▶ Hydrocarbons
  - ▶ Compounds containing oxygen
  - ▶ Compounds containing nitrogen

=>

# Hydrocarbons

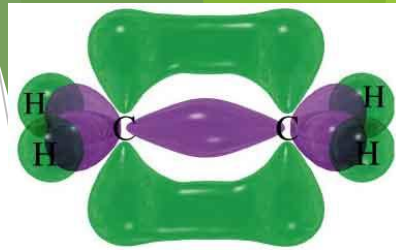
- ▶ Alkane: single bonds,  $sp^3$  carbons
- ▶ Cycloalkane: carbons form a ring
- ▶ Alkene: double bond,  $sp^2$  carbons
- ▶ Cycloalkene: double bond in ring
- ▶ Alkyne: triple bond,  $sp$  carbons
- ▶ Aromatic: contains a benzene ring

=>

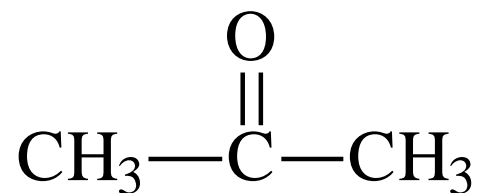
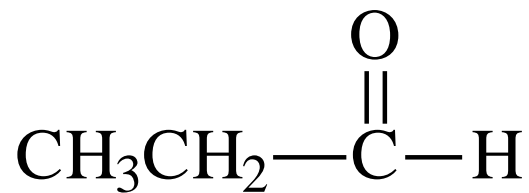




# Compounds Containing Oxygen

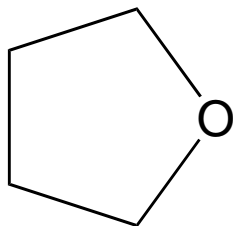
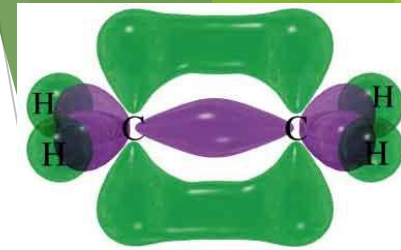


- ▶ Alcohol: R-OH
- ▶ Ether: R-O-R'
- ▶ Aldehyde: RCHO
- ▶ Ketone: RCOR'



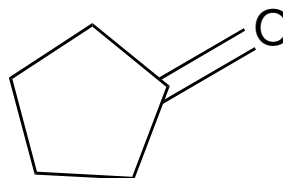
=>

# Cyclic ethers and ketones



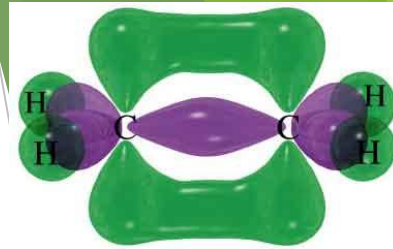
THF

(tetrahydrofuran)

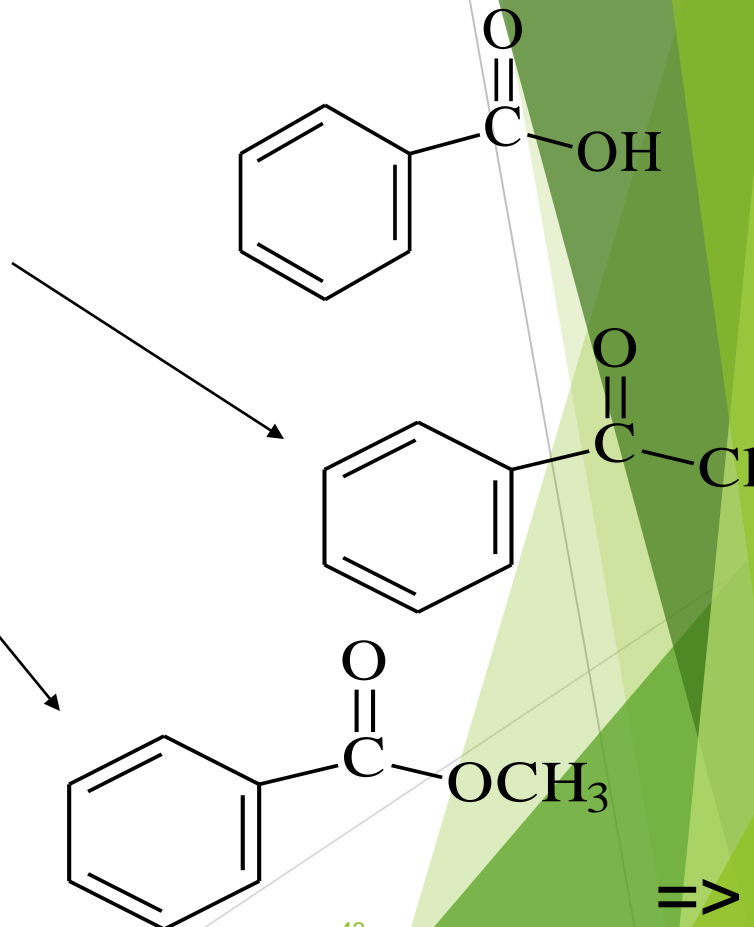
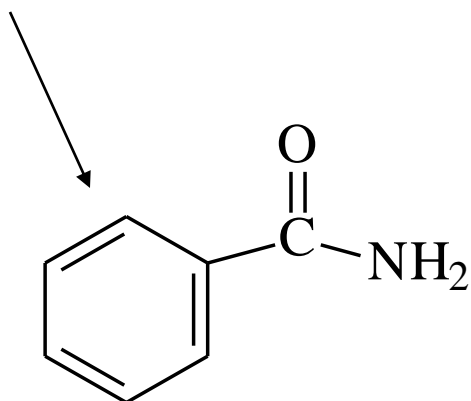


cyclopentanone

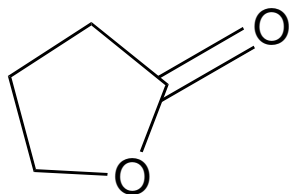
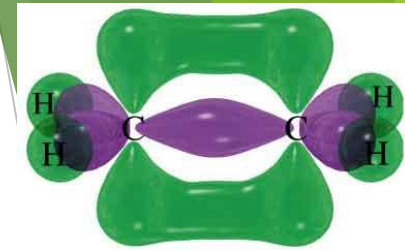
# Carboxylic Acids and Their Derivatives



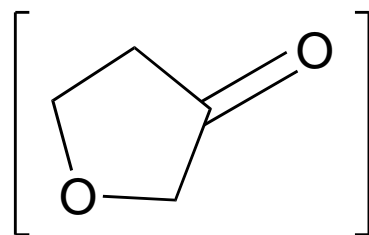
- ▶ Carboxylic Acid:  $\text{RCOOH}$
- ▶ Acid Chloride:  $\text{RCOCl}$
- ▶ Ester:  $\text{RCOOR}'$
- ▶ Amide:  $\text{RCONH}_2$



# Cyclic esters

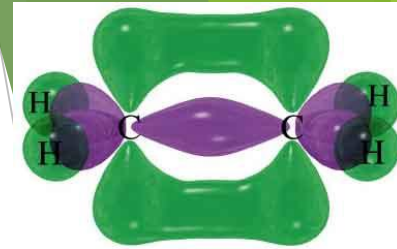


Cyclic ester

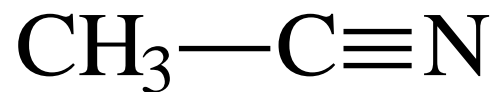
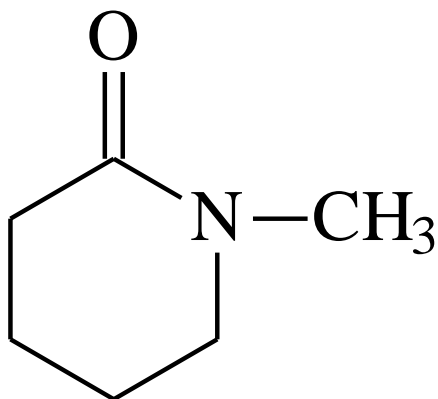


(cyclic ether and cyclic ketone)

# Compounds Containing Nitrogen



- ▶ Amines:  $\text{RNH}_2$ ,  $\text{RNHR}'$ , or  $\text{R}_3\text{N}$
- ▶ Amides:  $\text{RCONH}_2$ ,  $\text{RCONHR}$ ,  $\text{RCONR}_2$
- ▶ Nitrile:  $\text{RCN}$



=>