Ch 2 Structure and Properties of Organics

2.1-6 3-D Structure, Hybridization, and Orbitals

2.4,6 "VSEPR" and Molecular Shape: <u>V</u>alence <u>S</u>hell <u>E</u>lectron <u>P</u>air <u>R</u>epulsion

Concept: electron groups repel, determine structure

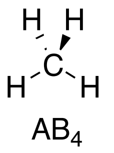
4 electron groups: tetrahedral, 109° angle
3 electron groups: trigonal planar, 120° angle
2 electron groups: linear, 180° angle

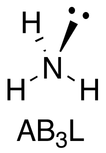
2 Types of "Electron Groups"

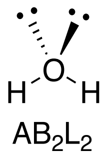
1. "B" = bonds to other atoms.
    - Whether it's a single, double, or triple bond, it still counts as one "electron group" or one "bond group"
2. "L" = Lone pairs

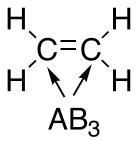
B+L	Electron Geometry	Bond Angle	Hybridization	Remaining P-orbitals
4	Tetrahedral	≈109°	sp^3	0
3	Trigonal Planar	≈120°	sp^2	1
2	Linear	≈180°	sp	2

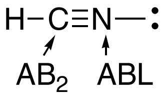
EXAMPLES

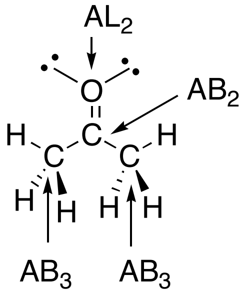












2.5 DRAWING 3-D

Guidelines for Drawing Models:

A. In-Plane/Out-of-Plane

- Designate an atom **in front** of plane with a **wedge**
- Designate an atom **behind** plane with a **hash**
- Designate an atom **in the plane** plane with a **straight line**

B. 3-D Perspective

1. Keep as many atoms as possible in a single plane (plane of the paper) by zig-zagging. Connections within the paper are drawn with straight lines.
2. Use wedges to indicate atoms that are in front of the plane.
3. Use hashes to indicate atoms behind the plane.

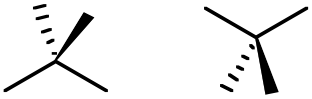
C. For any tetrahedral atom, only 2 attachments can be in the plane, 1 must be in front, and 1 behind.

-if the two in the plane are “down”, the hash/wedge should be up

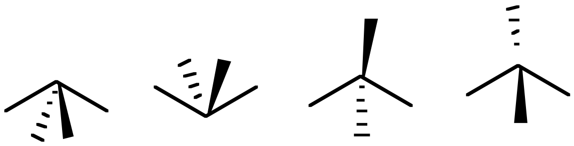
-if the two in plane are “up”, the hash/wedge should be down.

-the hash/wedge should never point in same direction as the in-plane lines, or else the atom doesn’t looks tetrahedral

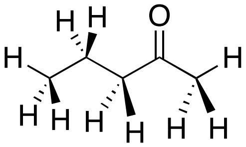
-for polyatomic molecules, it is strongly preferable to NOT have either of the in-plane atoms pointing straight up. Straight-up in-plane atoms do not lend themselves to extended 3-D structures.

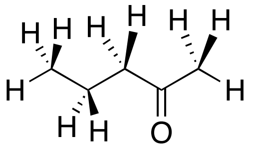


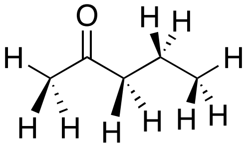
Good! Look tetrahedral

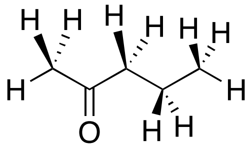


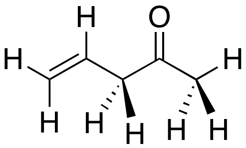
Bad! These don' t look tetrahedral!

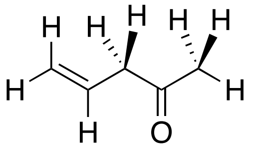


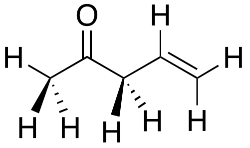


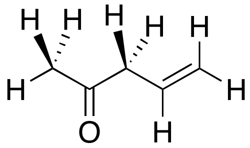












Draw:

C_2H_6

C_4H_{10}

CH_3COCH_3

$CH_3CH{=}CHCl$

Hybrid Orbitals; π bonding (Chapter 2.1-4)

1s + 3p → 4 sp^3 hybrids 109°

1s + 2p (+ 1 unhybridized p)→ 3 sp^2 hybrids (+ 1 unhybridized p) 120º
1s + 1p (+ 2 unhybridized p's)→ 2 sp hybrids (+ 2 unhybridized p's) 180º

Why does hybridization occur?

- Hybrid orbitals are big and point in one direction. Their **directionality** leads to **better overlap** which leads to **strong bonds**.
- Hybrid orbitals leads to nice VSEPR angles

If hybridization is so great, why aren't pure monatomic atoms hybridized?

- For an isolated atom, having 1 s and 3 p atomic orbitals is better than 4 sp^3 hybrid orbitals
- However, when covalent bonds can result, the small price of hybridizing is paid off a thousandfold by the payoff of making strong, good VSEPR bonds

If hybridization is so great, why aren't all carbons sp^3 hybridized? Why do some stay sp^2 or sp, and withhold some p orbitals from hybridization?

- p orbitals are withheld from hybridization for the sole purpose of using them to make π bonds.
- Only when double bonds or triple bonds are involved is the hybridization less than the full sp^3
- Each π bond requires the attached atoms to use p orbitals

2 Kinds of Covalent Bonds

- sigma (σ) bonds: electron density is along the axis between the nuclei
  - -σ bonds always involve the overlap of s or s-containing hybrids (s, sp, sp^2, sp^3)
- pi (π) bonds: electron density is either above/below or before/behind, but not along the internuclear axis
  - π bonds involve the overlap of parallel p orbitals

The first bond in any bond (whether single, double, or triple), is a σ bond. The "extra" bonds in a double or triple bond are π bonds.

Bond	**σ**	**π**
Single	1	0
Double	1	1
Triple	1	2

π bonds are weaker and more reactive than σ bonds. Most organic reactions involve π bonds

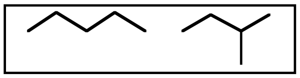
2.7-2.8 Bond Rotations, Structural Isomers, and Stereoisomers

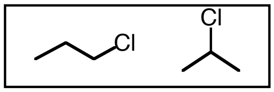
Rotation is allowed for single bonds
- No bonds break, the sigma bond is fine

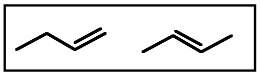
Rotation is forbidden for double bonds
- The p-bond overlap breaks, between the two p orbitals that need to be parallel

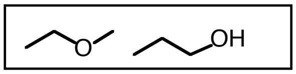
isomers-different compounds with the same molecular formula.

structural isomers (or constitutional isomers)-isomers that have their atoms connected in a different order.

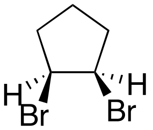




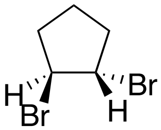




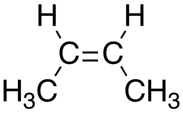
stereoisomers (or configurational isomers)-isomers in which atoms are joined in the same order but differ in the way their atoms are arranged in space.
- Stereoisomers have the same condensed formula (if not, they aren't stereoisomers)
- Stereoisomers can not be interconverted by bond rotation or by being turned over
- If two things can be interconverted by bond rotation or being turned over, then they aren't stereoisomers!
- Stereoisomers are subdivided into two categories: **enantiomers** and **diastereomers**.
  - o **Diastereomers**: have **cis/trans** relationship



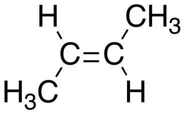
cis



trans

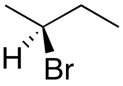


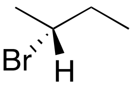
cis



trans

  - o **Enantiomers**: have **mirror image** (left hand/right hand) relationship





Problem: For the following pairs of structures, classify whether they are related as **same**, **structural isomers**, or **stereoisomers**.

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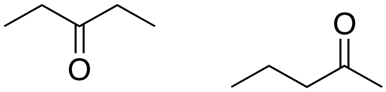

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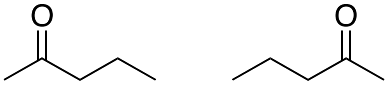
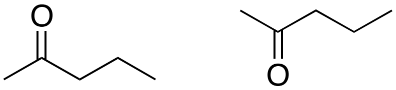
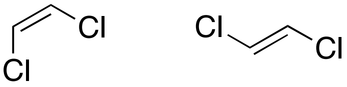
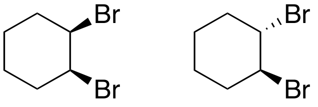


c.


d.


e.


f.


g.


h.


2.9 Polarity

-molecular dipole: vector sum of bond and lone-pair dipoles

A simple molecule is totally nonpolar only if:

1. Central atom has no lone pairs
2. All attached atoms are the same

Practical:

- Lone pairs and O-H or N-H bonds usually dominate
- C-C, C-H, and C-halogen bonds are practically nonpolar or at best only weakly polar

Problems: Classify as totally nonpolar or polar.

a. CO_2 b. CCl_4 c. CH_4 d. C_4H_{10}

e. H_2O f. NH_3 g. CH_3CH_2OH h. $CHCl_3$

2.10 Intermolecular Forces and Boiling Points

1. Hydrogen bonds (O-H or N-H)
2. Dipole-Dipole
    - Much weaker than hydrogen bonds
3. London Forces
    - Increases with increasing molecular weight

Intermolecular Forces impact:

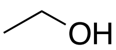
1. Boiling points and melting points
2. Solubility

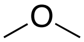
For Boiling Points:

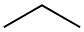
1. If weight is about equal → H-bonder > polar > nonpolar
2. If H-bonding/polarity is comparable: high mw > lower mw

Problem: Rank the boiling points, 1 being highest

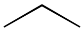
a.

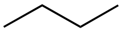


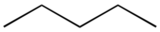




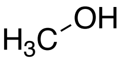
b.

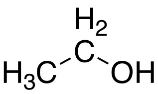






c.


$H_3C{-}OH$


$H_3C{-}CH_2{-}OH$

2.11 Polarity and Solubility

2 Practical Rules:

1. The more N's or O's in a molecular, the greater it's water solubility
2. The more C's, the lower it's water solubility

Facts/Theory

1. "Like dissolves like"
    - enthalpy and entropy factors

Good solubility	Bad solubility
a. Polar solvent-polar solute	a. Polar solvent-nonpolar solute
b. Nonpolar solvent-nonpolar solute	b. Nonpolar solvent-polar solute

2. Water is very polar

3. Any molecules with N or O can H-bond with water (even if it can't necessarily H-bond itself) (Rule 1)

4. Adding C's adds C-C, C-H nonpolar bonds → reduces water solubility (Rule 2)

5. Hydrocarbons and halocarbons are insoluble in water
    - Many other organics have low solubility in water
    - Depends on the ratio of nonpolar/polar, N or O to C

Problems: Circle the more water soluble of the following pairs:

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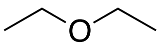

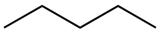

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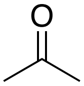

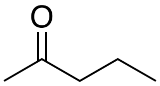

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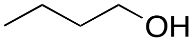
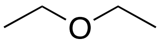




Problem: Box the higher boiling in each pair. Does water solubility and boiling point always correspond? Why or why not?

Classification of Organic Compounds. The Functional Groups (Sections 2-12-14)

Hydrocarbons: C + H only

0. Alkanes and Cycloalkanes

a. Single bonds only
b. Names end "ane" (methane, ethane, propane, etc.)
c. "cycloalkanes": carbon rings
d. alkanes are considered "nonfunctional"
    - no reactive π-bonds, lone pairs, heteroatoms, or highly polar bonds
e. an "**alkyl group**" is part of a molecule that contains only C, H, and single bonds.
    1. Basically a part of the molecule that isn't going to be very reactive or "functional"
    2. Symbol: R

1. Alkenes C=C

a. contain C=C double bond
b. names end "ene" (ethane, propene, butene, etc.)
c. double bonds can't rotate
    a. rotation is allowed for single bonds, but is forbidden for double bonds
    b. Why:
        1. a single bond (σ) can rotate freely without compromising orbital overlap
        2. But a π-bond cannot rotate freely, because π -overlap breaks
        - The two π -bonded atoms have parallel and overlapping p orbitals. To rotate the bond completely breaks the π -bond half-way through the rotation.
        - The energy price is thus way too high.
d. Restricted rotation results (sometimes) in cis/trans isomers

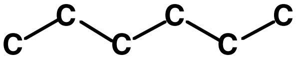
e. A π -bond is much weaker than a σ-bond, and thus is far more reactive. Thus, an alkene is viewed as a "functional group" because it reacts ("functions")
f. Functional groups and "R" groups:

2. Alkynes: Triple bonds

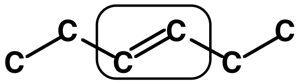
Name end "yne"

3. Aromatics or Arenes: Resonance

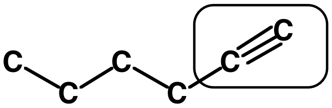
Twelve To Remember: The Functional Groups



0. Alkane
-all single bonds
-no heteroatoms

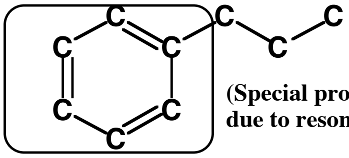


1. Alkene
-C=C double bond



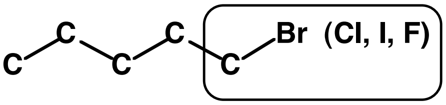
2. Alkyne
-triple bond

Tip: A-E-I
so alkane, alkene, alkyne

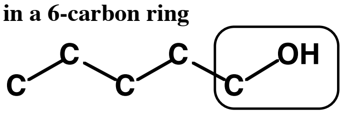


(Special properties due to resonance)

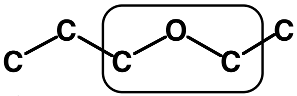
3. Arene
-alternating double bonds
in a 6-carbon ring



4. Haloalkane

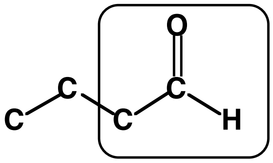


5. Alcohol
-oxygen
-OH
-single bonds

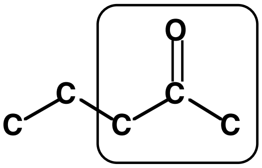


6. Ether
-oxygen
-no OH
-single bonds

Alcohols and Ethers Can be Seen as H_2O Derivatives: Oxygen Molecules With Single Bonds Only
Tip: A before E

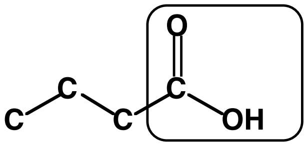


7. Aldehyde
-oxygen
-C=O double bond
-one H connected to C=O

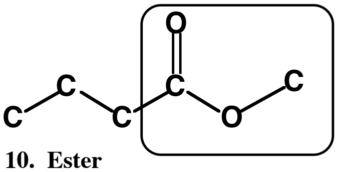


8. Ketone
-oxygen
-C=O double bond
-two C's connected to C=O

Aldehydes and Ketones Have C=O (Carbonyl) Double Bonds
Tip: A before kEy;
Aldehyde has less C's attached to C=O

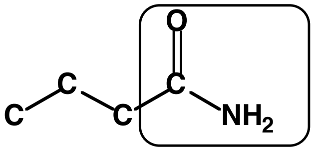


9. (Carboxylic) Acid
-2 oxygens
-C=O double bond, with O-H directly attached

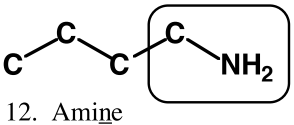


10. Ester
-2 oxygens
-C=O double bond, with O-C directly attached

A(cid) before E(ster)



11. Ami<u>d</u>e
-one nitrogen, one C=O
-C=O double bond, with N directly attached
-"D" for C=O <u>d</u>ouble bond



12. Ami<u>n</u>e
-one nitrogen, no C=O
-"N" for <u>N</u>o C=O double bond

N compounds

4. Haloalkanes R-X
   a. bonds are polarized: R group is δ+, halogen is δ-
   b. C-X bonds are often rather weak and breakable = "functional"

Oxygen Compounds

5. Alcohols ROH
   a. Oxygen hybridization and shape: sp^3, tetrahedral electron geometry, bent/angular atomic geometry, approximately 109º bond angle
   b. contain OH group attached to an sp^3 carbon
   c. names end "ol" (methanol, ethanol, etc.)
   d. Polarity: oxygen is δ-, attached hydrogen and carbon are δ+
   e. Hydrogen-bonding: impacts boiling point and water solubility
   f. Oxygen lone pairs
   - Capable of hydrogen bonding to water hydrogens
   - Capable of interacting with strong acids (Bronsted acids or Lewis acids = "electrophiles")
   g. The O-H bond is polarized enough so that alcohols are slightly acidic
   - Not enough to ionize at all in neutral water, or to any significant degree in NaOH/water
   - But acidic enough so that they can be deprotonated by less stable R^- or R_2N^- anions to form RO^- anions

6. Ethers ROR
   a. Oxygen hybridization and shape: sp^3, tetrahedral electron geometry, bent/angular atomic geometry, approximately 109º bond angle
   b. Don't hydrogen-bond themselves, so lower boiling than ROH of equal weight.
   c. Oxygen lone pairs do hydrogen-bond to water hydrogens, so decent water solubility
   d. Relatively low reactivity

7,8. Aldehydes, Ketones C=O

Aldehydes Ketones

   a. Have C=O group = **"carbonyl group"**
   b. Carbonyl carbon: sp^2, trigonal planar, 120º bond angles
   c. The carbonyl always has two other attachments, of which:
      - Formaldehyde has 2 H's attached to carbonyl
      - Aldehydes have one H attached to carbonyl
      - Ketones have no H's attached to carbonyl.
   d. Carbonyl bond is strongly polarized
      - Highly reactive
      - Highly electrophilic

9. Carboxylic Acids:

- Strong polarity and resonance stabilization of conjugate anions make these fairly acidic.
- Extremely important role in biological pH and biochemistry

10. Esters

- without OH bond, esters don't have the hydrogen bonding or acidity of carboxylic acids
- reactivity is similar to aldehydes and ketones, dominated by carbonyl

Nitrogen Compounds

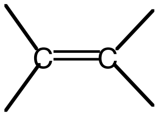
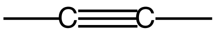
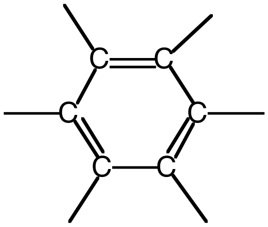
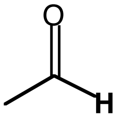
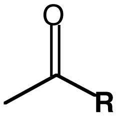
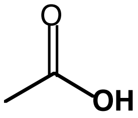
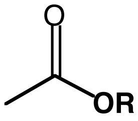
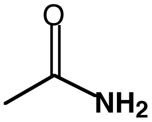
11. Amines

- polar
- usually hydrogen bonders
- Nitrogen lone pairs are basic (primary chemical and biological role)
- Many drugs are amines

12. Amides

- polar
- proteins and enzymes consist of multiple amides
- nitrogen is flat, sp^2, trigonal planar, thanks to resonance
- Nitrogen lone pair is **not** basic

The Functional Groups, R-Z

Functional Group Z	Name	Suffix (or Prefix) Used in Systematic Name
-R	Alkane	-ane
	Alkene	-ene
	Alkyne	-yne
	Arene	not responsible
-X (Cl, Br, I, or F)	Haloalkane	halo-
-OH	Alcohol	-ol
-OR	Ether	not responsible
	Aldehyde	-al
	Ketone	-one
	Carboxylic Acid	-oic acid
	Ester	-oate
	Amide	-amide
$-NH_2$	Amine	amino-

Nomenclature Review	
methan-	1C
ethan-	2C
propan-	3C
butan-	4C
pentan-	5C
hexan-	6C
heptan-	7C
octan-	8C
nonan-	9C
decan-	10C