<u>"VSEPR":</u> **<u>V</u>**alence **<u>S</u>**hell **<u>E</u>**lectron **<u>P</u>**air **<u>R</u>**epulsion (Sections 2.4, 2.6)

Concept: electron groups repel, determine structure

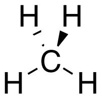
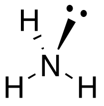
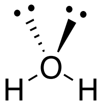
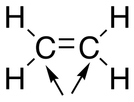
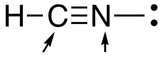
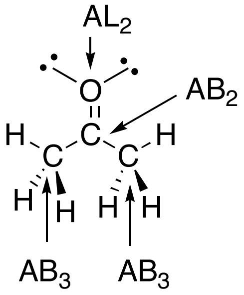
4 electron groups: tetrahedral, 109º angle
3 electron groups: trigonal planar, 120º angle
2 electron groups: linear, 180º angle

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	≈109º	sp^3	0
3	Trigonal Planar	≈120º	sp^2	1
2	Linear	≈180º	sp	2

<u>EXAMPLES</u>

 AB_4	 AB_3L	 AB_2L_2	 AB_3	 AB_2 ABL	

DRAWING 3-D (Section 2.5)

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**

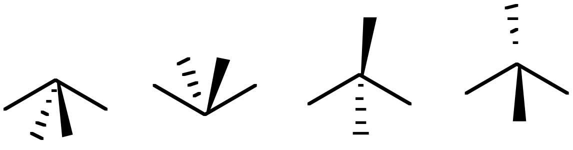
B. 3-D Perspective

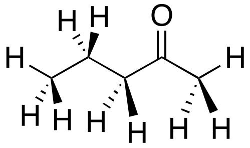
1. Keep as many atoms as possible in a single plane (plane of the paper) by zig-zagging. Connections within the paper are drawn with straight lines.
2. Use wedges to indicate atoms that are in front of the plane.
3. Use hashes to indicate atoms behind the plane.

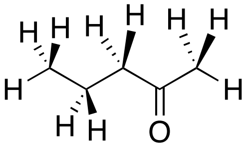
C. For any tetrahedral atom, only 2 attachments can be in the plane, 1 must be in front, and 1 behind.

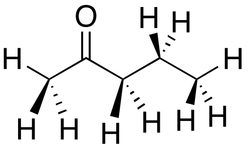
-if the two in the plane are "down", the hash/wedge should be up
-if the two in plane are "up", the hash/wedge should be down.
-the hash/wedge should never point in same direction as the in-plane lines, or else the atom doesn't looks tetrahedral
-for polyatomic molecules, it is strongly preferable to 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.

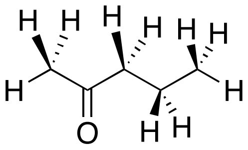

Good! Look tetrahedral

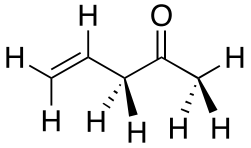

Bad! These don't look tetrahedral!

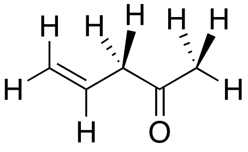


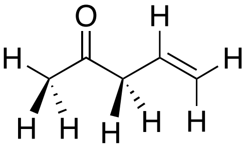


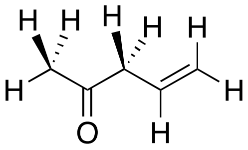






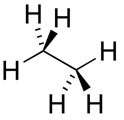




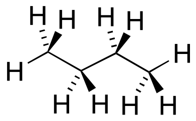


Draw:

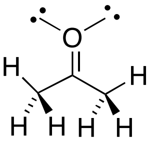
C_2H_6



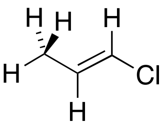
C_4H_{10}



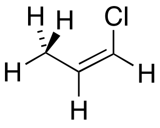
CH_3COCH_3



$CH_3CH{=}CHCl$



or



Hybrid Orbitals (Sections 2.4, 2.6); π bonding (Section 2.3)

1s + 3p → 4 sp^3 hybrids	109°
1s + 2p (+ 1 unhybridized p)→ 3 sp^2 hybrids (+ 1 unhybridized p)	120°
1s + 1p (+ 2 unhybridized p's)→ 2 sp hybrids (+ 2 unhybridized p's)	180°

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.

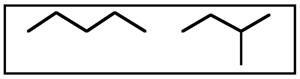
Bond	**σ**	**π**
Single	1	0
Double	1	1
Triple	1	2

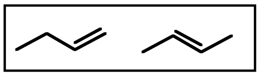
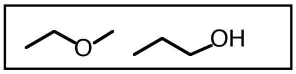
π bonds are weaker and more reactive than σ bonds. Most organic reactions involve π bonds

Classification of Isomers (2.7-2.8)

isomers-different compounds with the same molecular formula.

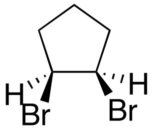
structural isomers (or constitutional isomers)-isomers that have their atoms connected in a different order.



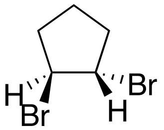




stereoisomers (or configurational isomers)-isomers in which atoms are joined in the same order but differ in the way their atoms are arranged in space.

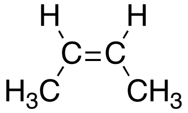
- Stereoisomers have the same condensed formula (if not, they aren't stereoisomers)
- Stereoisomers can not be interconverted by bond rotation or by being turned over
- If two things can be interconverted by bond rotation or being turned over, then they aren't stereoisomers!
- Stereoisomers are subdivided into two categories: **enantiomers** and **diastereomers**.
  - **Diastereomers**: have **cis/trans** relationship



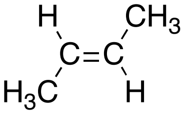
cis



trans

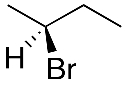


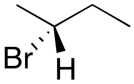
cis



trans

  - **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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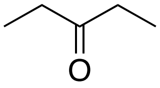
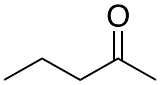
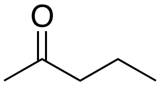
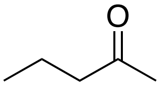


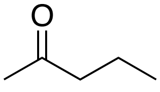


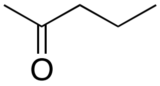
Structural

b.


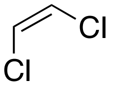


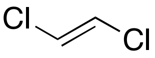
Same

c.


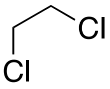


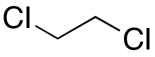
Same

d.


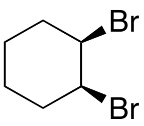


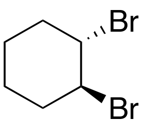
stereoisomer (cis trans diastereomer)

e.


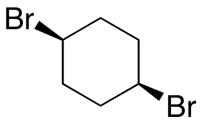


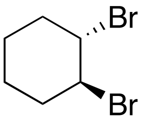
Same

f.


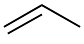
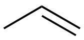


stereoisomer (cis trans diastereomer)

g.




Structural

h.


Same

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}
Nonpolar	Nonpolar	Nonpolar	Nonpolar
e. H_2O	f. NH_3	g. CH_3CH_2OH	h. $CHCl_3$
Polar	Polar	Polar	Weakly Polar

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:

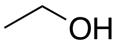
1. Boiling points and melting points
2. Solubility

For Boiling Points:

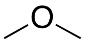
1. If weight is about equal → H-bonder > polar > nonpolar
2. If H-bonding/polarity is comparable: high mw > lower mw

Problem: Rank the boiling points, 1 being highest

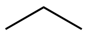
a.



1

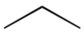


2



3

b.



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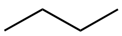
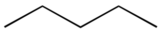
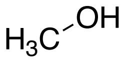


2



1

c.



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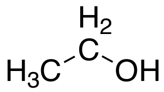


1

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

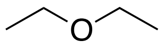
3. Any molecules with N or O can H-bond with water (even if it can't necessarily H-bond itself) (Rule 1)

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:

1.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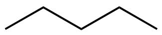
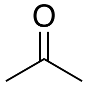

2

2.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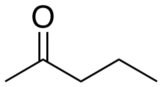
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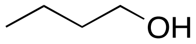
3.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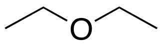
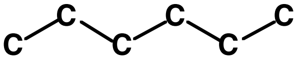

2

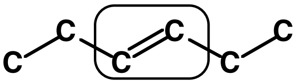
Problem: Box the higher boiling in each pair. Does water solubility and boiling point always correspond? Why or why not?

1 2 Not always, many factors are the same (H-bonding, polarity raises both.
2 1 But extra C's is good for boiling point but bad for water solubility)
1 2

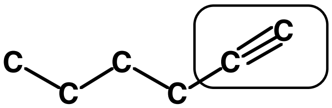
Twelve To Remember: The Functional Groups



0. Alkane
-all single bonds
-no heteroatoms

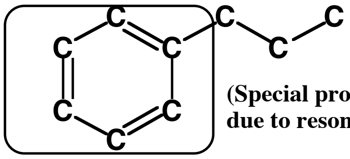


1. Alkene
-C=C double bond



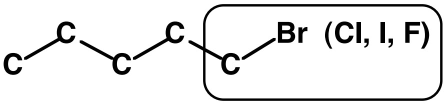
2. Alkyne
-triple bond

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

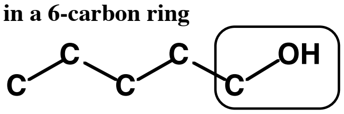


(Special properties due to resonance)

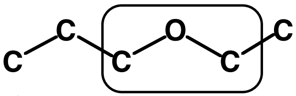
3. Arene
-alternating double bonds in a 6-carbon ring



4. Haloalkane

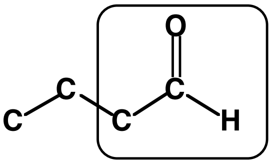


5. Alcohol
-oxygen
-OH
-single bonds

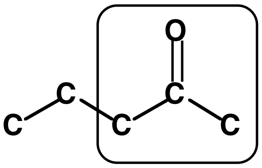


6. Ether
-oxygen
-no OH
-single bonds

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

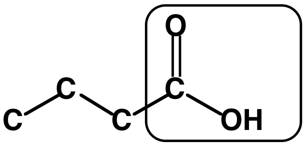


7. Aldehyde
-oxygen
-C=O double bond
-one H connected to C=O

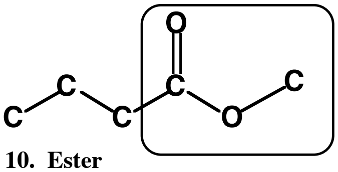


8. Ketone
-oxygen
-C=O double bond
-two C's connected to C=O

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

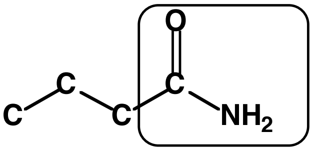


9. (Carboxylic) Acid
-2 oxygens
-C=O double bond, with O-H directly attached

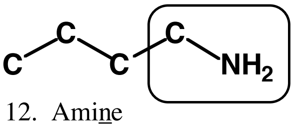


10. Ester
-2 oxygens
-C=O double bond, with O-C directly attached

A(cid) before E(ster)



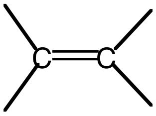
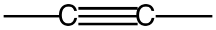
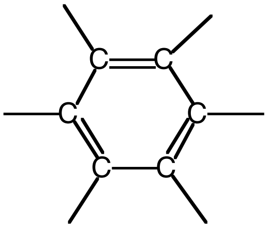
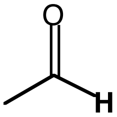
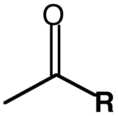
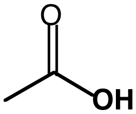
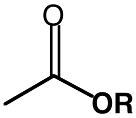
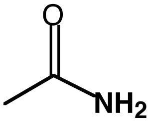
11. Amide
-one nitrogen, one C=O
-C=O double bond, with N directly attached
-"D" for C=O double bond



12. Amine
-one nitrogen, no C=O
-"N" for No C=O double bond

N compounds

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