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

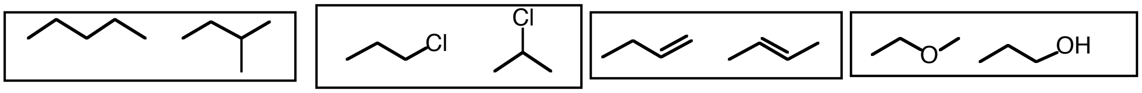
The first bond in any bond (whether single, double, or triple), is a σ bond. The "extra" bonds in a double or triple bond are π bonds.

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

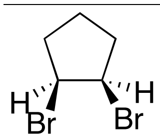
Classification of Isomers (2.7-2.8)
isomers-different compounds with the same molecular formula.

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

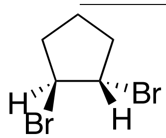


stereoisomers (or configurational isomers)-isomers in which atoms are joined in the same order but differ in the way their atoms are arranged in space.

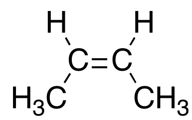
- Stereoisomers have the same condensed formula (if not, they aren't stereoisomers)
- Stereoisomers can not be interconverted by bond rotation or by being turned over
- If two things can be interconverted by bond rotation or being turned over, then they aren't stereoisomers!
- Stereoisomers are subdivided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



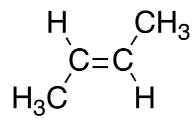
cis



trans

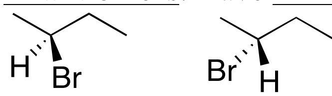


cis

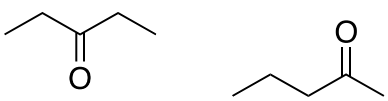


trans

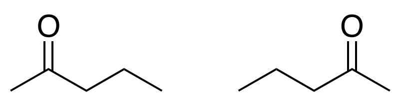
  - **Enantiomers**: have **mirror image** (left hand/right hand) relationship



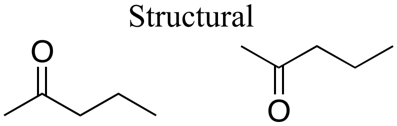
Problem: For the following pairs of structures, classify whether they are related as **same**, **structural isomers**, or **stereoisomers**.

a.


Structural

b.


Same

c.


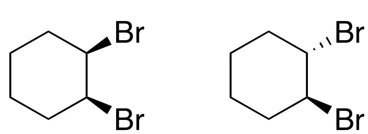
Same

d.

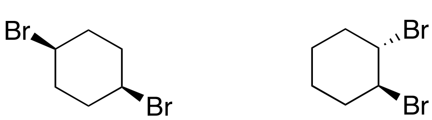

stereoisomer (cis trans diastereomer)

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:

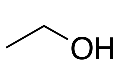
1. Boiling points and melting points
2. Solubility

For Boiling Points:

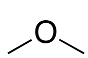
1. If weight is about equal → H-bonder > polar > nonpolar
2. If H-bonding/polarity is comparable: high mw > lower mw

Problem: Rank the boiling points, 1 being highest

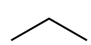
a.



1

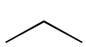


2

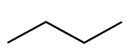


3

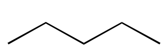
b.



3

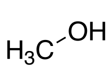


2

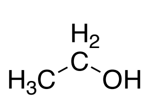


1

c.



2



1

2.11 Polarity and Solubility

<u>2 Practical Rules:</u>
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

<u>Facts/Theory</u>
1. “Like dissolves like”
    - enthalpy and entropy factors

<u>Good solubility</u>	<u>Bad solubility</u>
a. Polar solvent-polar solute	a. Polar solvent-nonpolar solute
b. Nonpolar solvent-nonpolar solute	b. Nonpolar solvent-polar solute

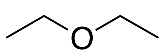
2. Water is very polar

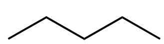
3. Any molecules with N or O can H-bond with water (even if it can’t necessarily H-bond itself) (Rule 1)

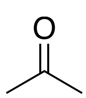
4. Adding C’s adds C-C, C-H nonpolar bonds → reduces water solubility (Rule 2)

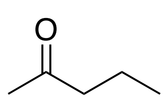
5. Hydrocarbons and halocarbons are insoluble in water
    - Many other organics have low solubility in water
    - Depends on the ratio of nonpolar/polar, N or O to C

<u>Problems</u>: Circle the more water soluble of the following pairs:

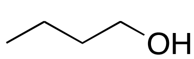
1.


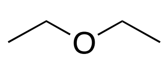
1

2

2.


1


2

3.


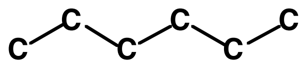
1


2

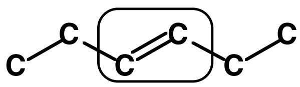
<u>Problem</u>: Box the higher boiling in each pair. Does water solubility and boiling point always correspond? Why or why not?

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

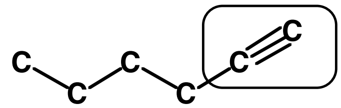
Twelve To Remember: The Functional Groups



0. Alkane
-all single bonds
-no heteroatoms

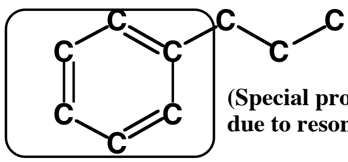


1. Alkene
-C=C double bond



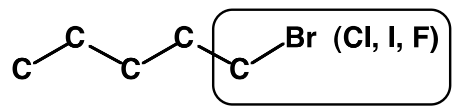
2. Alkyne
-triple bond

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

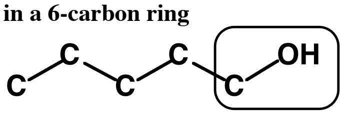


(Special properties due to resonance)

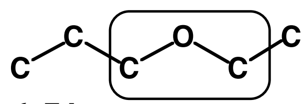
3. Arene
-alternating double bonds in a 6-carbon ring



4. Haloalkane

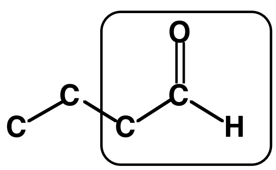


5. Alcohol
-oxygen
-OH
-single bonds

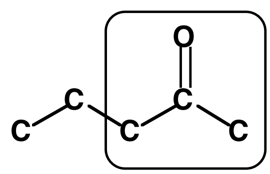


6. Ether
-oxygen
-no OH
-single bonds

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

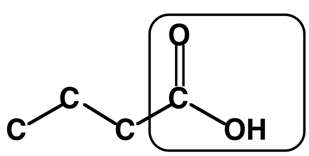


7. Aldehyde
-oxygen
-C=O double bond
-one H connected to C=O

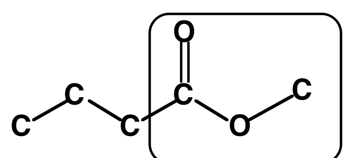


8. Ketone
-oxygen
-C=O double bond
-two C's connected to C=O

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

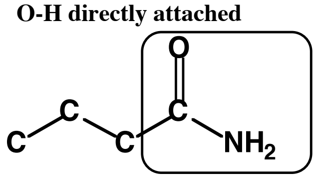


9. (Carboxylic) Acid
-2 oxygens
-C=O double bond, with O-H directly attached

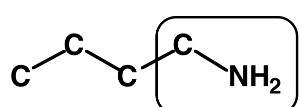


10. Ester
-2 oxygens
-C=O double bond, with O-C directly attached

A(cid) before E(ster)



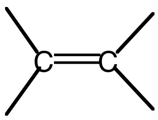
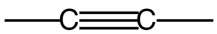
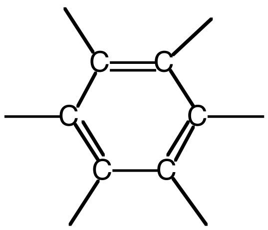
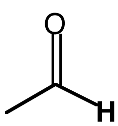
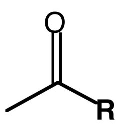
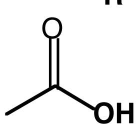
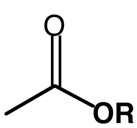
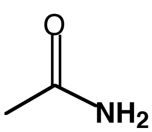
11. Amide
-one nitrogen, one C=O
-C=O double bond, with N directly attached
-"D" for C=O double bond



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

<u>ALKANE NAMES (Memorize)</u> (Sections 3.2)

# C's	Name	Formula	Bp (ºC)	Structure
1	Methane	CH_4	-162	$H\text{-}(CH_2)\text{-}H$
2	Ethane	C_2H_6	-89	$H\text{-}(CH_2)_2\text{-}H$
3	Propane	C_3H_8	-42	$H\text{-}(CH_2)_3\text{-}H$
4	Butane	C_4H_{10}	0	$H\text{-}(CH_2)_4\text{-}H$
5	Pentane	C_5H_{12}	36	$H\text{-}(CH_2)_5\text{-}H$
6	Hexane	C_6H_{14}	69	$H\text{-}(CH_2)_6\text{-}H$
7	Heptane	C_7H_{16}	98	$H\text{-}(CH_2)_7\text{-}H$
8	Octane	C_8H_{18}	126	$H\text{-}(CH_2)_8\text{-}H$
9	Nonane	C_9H_{20}	151	$H\text{-}(CH_2)_9\text{-}H$
10	Octane	$C_{10}H_{22}$	174	$H\text{-}(CH_2)_{10}\text{-}H$

<u>Industrial Alkanes</u> (Sections 3.5)

Name	# C's	Boiling Range	Use
Natural Gas	C_1-C_3 (70% methane)	Gas	Fuel
"Petroleum Gas"	C_2-C_4	<30º	Heating, Gas
Propane	C_3	-42º	Propane tanks, camping, etc.
Gasoline	C_4-C_9	30-180º	Car fuel
Kerosene	C_8-C_{16}	160-230º	Jet fuel
Diesel	C_{10}-C_{18}	200-320º	Truck fuel
Heavy Oils	C_{16}-C_{30}	300-450º	
Motor Oils		High temp	
Paraffin		Vacuum	
Asphalt		Never Distills	
Coke		Never Distills	

<u>Nomenclature of Alkanes</u> (Sections 3.3)

<u>Systematic IUPAC Rules for Branched and Substituted Alkanes (Section 3.3B)</u>

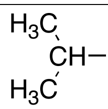
1. Longest continuous C-chain → "core name"
2. Number core chain from an end nearest a substituent
3. Name substituents as "alk<u>yl</u>" groups:
4. Specify the location of substituents using numbers (hyphenate the #'s)
   - If >2 substituents, list alphabetically
   - Use di-, tri-, tetra- if the same substituent is repeated. (But ignore these in alphabetizing).

Punctuation Notes:

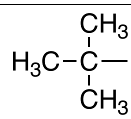
- Hyphenate numbers
- Do <u>not</u> put a space between substituents and the core name

<u>Special Names for Some 3 or 4-carbon Substituents</u>

Memorize

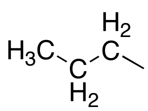


Isopropyl

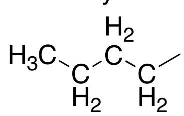


t-butyl or
tert-butyl

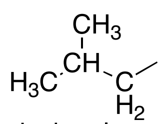
Others



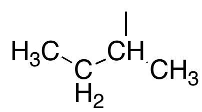
n-propyl
(n for "normal")



n-butyl



isobutyl



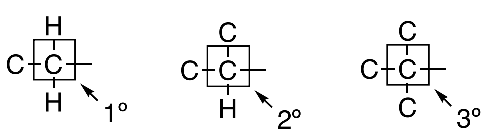
s-butyl

<u>Another Classification System</u>

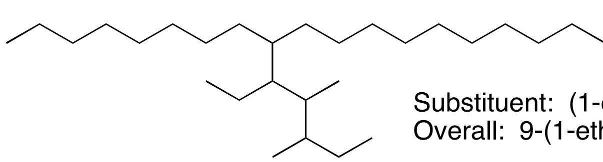
Primary (1°): with one attached carbon

Secondary (2°): with two attached carbons

Tertiary (3°): with three attached carbons



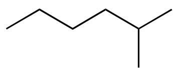
<u>Very Complex Substituents (Not responsible)</u>



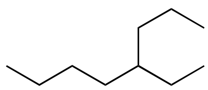
Substituent: (1-ethyl-2,3-dimethylpentyl)

Overall: 9-(1-ethyl-2,3-dimethylpentyl)nonadecane

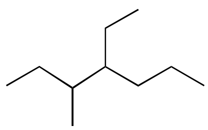
Nomenclature Example Problems (Sections 3.5)

1. 

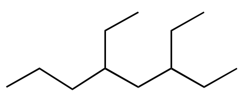
2-methylhexane

2. 

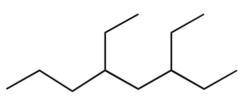
4-ethyloctane

3. 

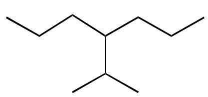
4-ethyl-3-methylheptane

4. 

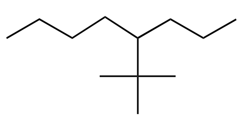
3,5-diethyloctane

5. 

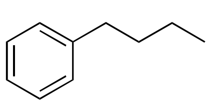
error

6. 

4-isopropylheptane

7. 

4-t-butyloctane

8. 

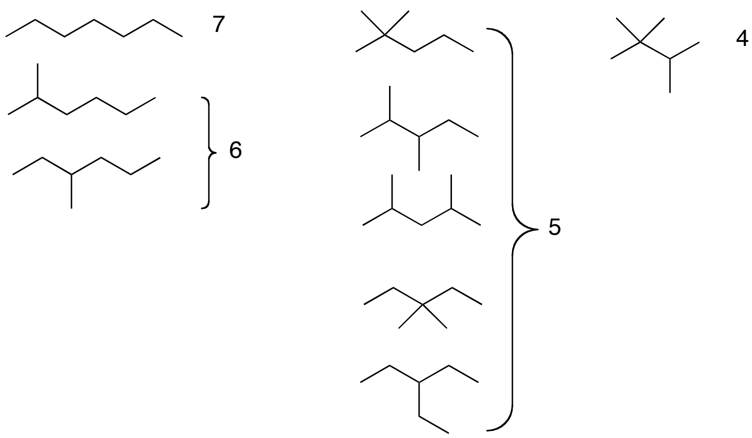
Butylbenzene

Structural Isomer Problems

- **Check formula first**. Is it an acyclic molecule, or not? (Cyclic alkane or an alkene or something…)
- **Be systematic**. Try the longest possible chain (or largest ring size) first, then systematically shorten it and find the branched isomers.
- **Avoid duplicates**!
- Beware of things that look different but are really the same thing.

1. Draw all structural isomers of C_7H_{16}. (Be systematic; no duplicates!)

Formula proves acyclic alkane



2. Draw all structural isomers of C_7H_{14}. (Be systematic; no duplicates!)

Formula proves either a cyclic alkane or an alkene. In addition to the 27 cycloalkanes shown, there are at least another couple dozen alkenes. Notice that these are 27 cycloalkane structure isomers; many of them could also have cis/trans issues, so where I drew just one, you could perhaps actually draw both a cis version and a trans version.