<u>Ch. 1 Intro and Review</u> <u>1.1 Intro to Organic Chemistry</u> "Organic":

"Organic Chemistry":

- Focus on carbon, with H, N, O, and halogens all major contributors
- Biochemicals are all carbon-based
 - Food, hair, skin, muscles, etc.
 - Clothes, plastics, fuels, etc.

The abundance of carbon, by mass:

Universe	<<0.1%	
Earth	<1%	
Body	18% (60% of body mass is water)	
Non-water body mass	45%	
	•	

>90% of known molecules are organic!

Why is carbon so special?

1. Versatile bonding! 4 covalent bonds per carbon enables:

a.

b.

- 2. Modest Electronegativity enables:
 - a. strong bonds to other C's, H's, and other nonmetals

Orbitals and Bonding: Review (Chapter 1:2-5)

- 1. Atomic orbitals for 2nd-row elements (C, N, O):
- Note: for organic, we won't need to fuss with d or f orbitals
- 2. Valence electrons: electrons in an atom's outside shell
- **3.** Octet Rule: atoms transfer or share electrons to obtain a filled shell (which is 8 for C, N, O, halogen)
 - Note: <u>never</u> draw C, N, or O with > 8 electrons!!!
- 4. Bond Types:

Donu	rypes.	
a.	Covalent bonds	H ₂
•	Between <u>nonmetals</u>	
•	Involve shared electrons	H ₂ O
b.	<u>Ionic</u> :	
•	Negligible sharing of electrons	
•	Metals transfer electron(s) to nonmetal	LiF
•	If formula has a <u>metal</u> , assume <u>ionic</u>	
	bonding	
•	Special case of ionic bonding in absence	
	of metals: ammonium salts	NH ₄ Cl

Normal Bonding (Chapter 1)

Summary of Normal, Ideal Bonding (No Formal Charge)

Summary of rorman racar Doname (110 Formar Charge)							
	Valence	Valence	Lone				
	Electrons	Bonds	Pairs				
	4	4	0				
—N—	5	3	1				
-o:	6	2	2				
Н—	1	1	0				
:CI	7	1	3				

<u>Rules for Drawing Lewis structures for organic molecules: (Ch 1:4,5)</u>

- 1. Try to provide normal bonding for C, N, O atoms **<u>if possible</u>**. (Works > 95% of time)
- 2. Double or triple bonds will often be involved.
 - Double or triple bonds are often required to achieve normal bonding.
- 3. In any formula that has a charge, there will always be an atom with that formal charge.
- 4. In any formula that includes a metal, assume ionic bonding.
 - Assume positive charge for the metal,
 - Assume negative charge for the organic portion.
- 5. Do not draw bonds between nonmetals and metals, as if they were covalently bound.
- 6. Be sure to specify the formal charge on any atom that has formal charge.
- 7. Always be aware of how many lone pairs are on any atom
 - Note: We will often omit lone pairs. But you must know when they are there!

Lewis Structure Practice

- 1. Draw Lewis structures for the following formulas: (Include lone pairs or formal charges if necessary)
 - a. CH₃CH₃ b. CH₃CH₂OH

c. CO₂

d. HCN

e. CH₃CHO

f. NaOCH₃

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Formal Charge (Section 1.7): When an atom does not have its normal bonding

- Atoms with formal charge dominate reactivity. Therefore the ability to recognize and identify atoms with formal charge is really important!
- <u>Skills</u>:
 - 1. Identify the formal charge for any atom that does not have normal bonding
 - 2. Identify the number of bonds and lone pairs associated with any atom whose formal charge is specified
- Note: <u>Designation of formal charge is required</u>. If you don't write the charge sign next to an atom that should have formal charge, you will lose test points!

Formal Charge Equations:

- 1. FC = group # (bonds + unshared e's) (use to calculate FC)
- 2. Group # FC = bonds + unshared electrons (given formal charge, use to find lone pairs)

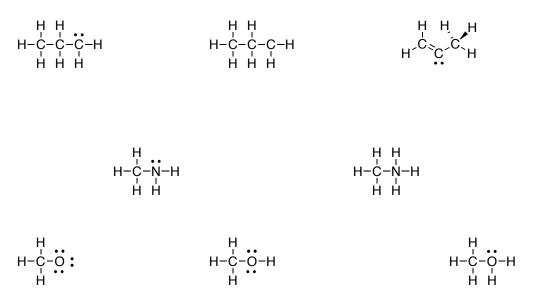
	memorize)
С	4 bonds \leftarrow neutral
	3 bonds and zero lone pairs \leftarrow cation +1
	3 bonds and one lone pair \leftarrow anion -1
Ν	4 bonds $\leftarrow \rightarrow$ cation +1
	3 bonds and one lone pair \leftarrow neutral
О	3 bonds and one lone pair \leftarrow cation +1
	2 bonds and 2 lone pairs \longrightarrow neutral
	1 bond and three lone pairs \iff anion -1

FORMAL CHARGE

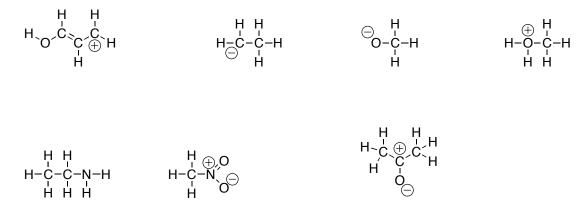
# of Bonds	С	Ν	0	F
4	0	+1		
3	-1 or	0	+1	
	+1			
2		-1	0	
1			-1	0

Formal Charge Practice (Section 1.7)

1. Assign any *formal charges* to atoms that need them:



2. Fill in lone pairs on any atoms that need them (whether atoms with formal charge or neutral atoms):



Notice: With the exception of carbocations, all other C/N/O atoms end up with a combined total of four when you sum up their bonds and lone-pairs. So apart from carbocations, if you know the number of bonds, you can fill in the correct number of lone pairs without even thinking much!

Electronegtivity and Bond Polarity (Section 1.6)

Electronegativity: the ability to "hog" electrons in covalent bonds -when two atoms are unequal, one will always attract bond electrons more strongly than the other -the more electronegative atom has a δ - charge, the less electronegative atom a δ + charge

H 2.2		С	N	0	F	Patterns: 1. Increases left to right 2. Increases bottom to top
		2.5	3.0	3.4	4.0	3. C-H bond are pretty comparable, essentially nonpolar
					Cl 3.2	 C-other non-metal, C is always less electronegative, δ+ on C C-metal, C is always more
					Br 3.0	electronegative, δ- on C
					I 2.7	

<u>1.8 Ionic Structures</u>

- **1.** If you see a metal in a formula, treat it as ionic rather than covalent/molecular
 - a. -always put a positive charge on the metal
 - b. -never draw a "bond" between the metal and the non-metal
 - **c.** -always figure there must be a negative charge on the non-metal portion of the formula, with a formal negative charge on something
- 2. The one time you see ions without metals is with ammonium ions

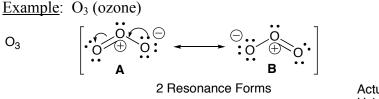
LiOH

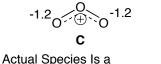
NaH

NH₄OCH₃

Resonance Structures (Section 1:9)

Sometimes a single Lewis structure does not provide an adequate picture.





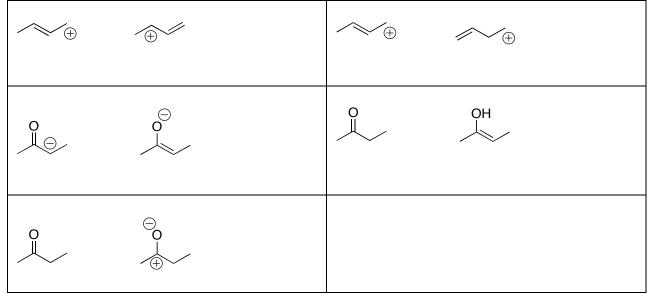
Hybrid of the Resonance Forms

Notes/observations:

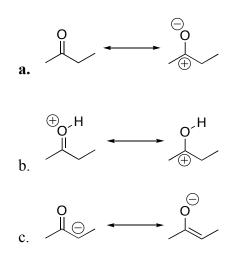
- 1. Neither form **A** nor **B** can avoid formal charges.
 - The majority of resonance situations have some formal charge involvement
- 2. The <u>real molecule</u> is <u>hybrid</u>: see picture C
 - The central oxygen has + charge
 - Each of the outside oxygens is -1/2
 - Both of the bonds to the outside oxygens are equal in length/strength
 - The actual length/strength of the oxygen-oxygen bonds reflect 1.5 bonds (shorter and stronger than single bonds; longer and weaker than double bonds)
- 3. Why not just draw the hybrid?
 - Hard to do, without first working through resonance structures first.
 - Hard to keep track of the electrons, which is essential for understanding reactivity
- 4. When are Two Structures related as Resonance Structures?
 - Atoms must be connected in exactly the same way. Resonance forms differ <u>only in the</u> <u>placement of electrons.</u>
 - If two Lewis structures have the same atomic connectivity, but differ <u>only</u> in the placement of some electrons, they are related as resonance structures.
 - If the placement/connectivity of atoms differ, then the two structures are <u>not resonance</u> <u>structures (they may perhaps be related as "isomers", see later.)</u>
 - KEY: FOR RESONANCE STRUCTURES, ELECTRONS MOVE BUT ATOMS DO NOT MOVE. IF ATOMS MOVE, YOU DON'T HAVE RESONANCE STRUCTURES
 - Note: The real molecule is represented by the hybrid, and electrons are not actually jumping back and forth.
- 5. Resonance, when it exists, involves the delocalization of electrons and charge
 - In ozone, instead of one of the outside oxygens getting stuck with a full negative charge, that negative charge is shared with the other outside oxygen, and both have a more manageable 1/2 charge
 - This delocalization of electrons/charge is stabilizing.
 - KEY: RESONANCE IS STABILIZING
- 6. Resonance, when it exists, always involves electrons in double bonds and/or lone pairs (π electrons)
- 7. One of the most frequent resonance situations we'll see is when you a charged atom attached to a double bonded atom ("allylic" situation")
- 8. When resonance structures are equal in stability, the hybrid is the average of the resonance forms
- 9. When resonance structures are unequal, the more stable structure dominates the hybrid
 - <u>Ranking Stability:</u>
 - More bonds \rightarrow more stable (but don't exceed octet rule!). (Priority rule)
 - Bonds being equal (tiebreaker rule): <u>negative charge</u> is better on <u>more electronegative</u> atom; <u>positive charge</u> is better on less electronegative atom

Resonance Problems

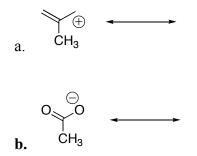
1. Which of the following are related as resonance structures?



2. Which Resonance Structure is Better and would make a more than 50% contribution to the actual hybrid? Why, bonds or electronegativity?



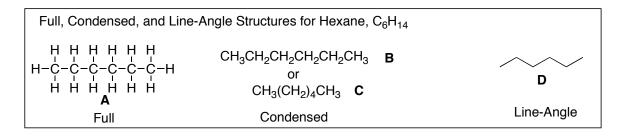
3. Draw a resonance structure for the following



Structural Formulas (Section 1-10)

- 1. Full Structural Formulas
- 2. Condensed Formulas
- 3. Line-Angle (Skeletal) Formulas

Since organic structures are large and complex, full Lewis structures are often a hassle. You'll need to be proficient in both condensed and line-angle formulas.



Condensed Formulas: Central atoms are shown with attached atoms, essentially in sequence

- Challenges:
 - 1. Handling parentheses
 - 2. Handling double and triple bonds
 - 3. Handling branches
 - 4. Handling ketones/aldehydes/esters/amides/carboxylic acids
 - 5. In general, recognizing when an oxygen is double-bonded off a carbon, and when it is single bonded both to carbon and to something else.

Line-Angle (Skeletal) Formulas:

- 1. Each vertex represents a carbon
- 2. C-H bonds are often omitted: assume enough H's to give four bonds or the appropriate formal charge
- 3. Oxygen and Nitrogen atoms must be specified, and O-H and N-H bonds are not omitted
- Line-angle formulas are routinely the fastest and cleanest to draw.
- Line-angle is essential and optimal for showing 3-dimensional organic shape.

Formula Practice (Section 1-10)

3. Time race: Draw as many copies of C_6H_{14} hexane as you can in 20 seconds:

Full:

Condensed:

Line-Angle:

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4. Draw the full structure, given the condensed structure. (Note:

 $\mathrm{CH}_3\mathrm{CH}_2\mathrm{OH}$

(CH₃)₂CHCH₂NH₂

CH₂CHCl

CH₃CHO

 CH_3CO_2H

5. Fill in the full structure, including attached hydrogens and attached lone pairs, for the following line-angle structures. If given a condensed structure, convert it to a line-angle.

 \triangle `OH <u>___</u> $\overline{\oplus}$ o↓

CH₃CH₂CH₂CH₂CH₃

 $CH_{3}CO_{2}H \\$

Acid-Base Chemistry (Section 1-12-14)

Acidity/Basicity Table

Entry	<u>Class</u>	Structure	<u>Ka</u>	<u>Acid</u> Strength	Base	<u>Base</u> <u>Strength</u>
1	Strong Acids	H-Cl, H ₂ SO ₄	10 ²		СІ [⊖] , но-\$-0 0 0	
2	Hydronium	H ₃ O ⁺ , ROH ⁺ cationic	10 ⁰		H ₂ O, HOR neutral	
3	Carboxylic Acid	R OH	10-5		RLOO	
4	Ammonium Ion (Charged)	R, H R ^N R Charged, but only weakly acidic!	10 ⁻¹²		$ \begin{array}{c} R \\ N \\ R^{\bullet} R \\ \text{Neutral, but basic!} \end{array} $	
5	Water	НОН	10 ⁻¹⁶		_{HO} Θ	
6	Alcohol	ROH	10 ⁻¹⁷		RO ^Ө	
7	Ketones and Aldehydes	Ομαμ	10 ⁻²⁰		O a o	
8	Amine (N-H)	(iPr) ₂ N-H	10 ⁻³³		(iPr) ₂ N [⊖] Li [⊕]	
9	Alkane (C-H)	RCH ₃	10-50		RCH₂⊖	

Quick Checklist of Acid/Base Factors

- 1. Charge
- 2. Electronegativity
- 3. Resonance/Conjugation
- 4. Hybridization
- 5. Impact of Electron Donors/Withdrawers
- 6. Amines/Ammoniums
- When a neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.

More Detailed Discussion of Acid/Base Patterns/Factors to remember

- 1. Charge: all else equal, cations are more acidic than neutrals, and anions more basic than neutrals.
- 2. Electronegativity:
 - Acidity: H-X (halogen) > H-O > H-N > H-C
 - Basicity: $X \stackrel{\Theta}{\sim} < O \stackrel{\Theta}{\sim} < N \stackrel{\Theta}{\sim} < C \stackrel{\Theta}{\sim}$
 - Anion Stability: $X \xrightarrow{\Theta} O > N \xrightarrow{\Theta} C \xrightarrow{\Theta}$
 - Why: <u>The more stable the anion Z⁻ that forms, the more acidic the parent H-Z will</u> <u>be</u>. All acids H-Z must give up H⁺. The better off the resulting anion Z⁻ is, the more willing H-Z will be to sacrifice H⁺.
 - The anion stability directly correlates the love for electrons.
 - Notice three things:
 - ANION STABILITY and the ACIDITY OF A NEUTRAL ACID PRECURSOR ARE DIRECTLY RELATED.
 - ANION STABILITY and the BASICITY OF THE ANION ARE INVERSELY RELATED (more stable anion, less basic anion)
 - ANION BASICITY AND THE ACIDITY OF THE CONJUGATE ACID ARE INVERSELY RELATED (the stronger the acidity of the parent acid, the weaker the basicity of the conjugate anion)
 - KEY: WHEN THINKING ABOUT ACIDITY AND BASICITY, FOCUS ON THE ANION. THE STABILITY OF THE ANION DETERMINES ACID/BASE BEHAVIOR.
- 3. Resonance/Conjugation: Since anion resonance is stabilizing, <u>an acid that gives a</u> <u>resonance-stabilized anion is more acidic.</u> And an anion that forms with resonance will be more stable and less basic.

• Oxygen Series Examples:
Acidity: sulfuric acid > carboxylic acid > water or alcohol
Anion Basicity:
$$HO - \stackrel{O}{=} - \stackrel{O}{=} \stackrel{O}{$$

- Note: Resonance is often useful as a tiebreaker (for example, molecules in which both have O-H bonds and both have equal charge, so that neither the charge factor nor the electronegativity factor could predict acidity/basicity)
- NOTE: Resonance can sometimes (not always) trump electronegativity or even charge.
 - Example of resonance versus charge: A carboxylate anion, with serious resonance stabilization, ends up being so stabilized that it is even less basic than a neutral, uncharged amine! A hydrogen sulfate anion from sulfuric acid is less basic than not only neutral amines but also neutral oxygen (water, etc.)
- 4. Hybridization: For lone-pair basicity, (all else being equal), $sp^3 > sp^2 > sp > p$
- 5. Electron donating/electron withdrawing substituents:

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- Electron withdrawing substituents stabilize anions, so they increase neutral acidity and decrease anion basicity
- Electron donating substituents will destabilize anions, so they decrease neutral acidity and increase anion basicity.
- 6. Ammonium Cations as Acids and Neutral Amines as Bases
 - Neutral amines are more basic than any neutral oxygen (electronegativity factor), and more basic than some resonance-stabilized oxygen anions.
 - Ammonium cations are more acidic than neutral nitrogen compounds or most neutral oxygen compounds, but less acidic than oxygens that give resonance-stabilized anions. (In this case, resonance factor trumps the charge factor).

Acid/Base Problems

 Choose the More Acidic for Each of the Following Pairs: Single Variable Problems

 1.
 $^{\mathsf{NH}_3}$ \oplus NH_4

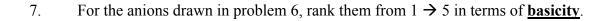
 2.
 $\stackrel{\frown}{\mathsf{OH}_2}$ \bigcirc OH

 3.
 \bigcirc OH \bigcirc CH_3

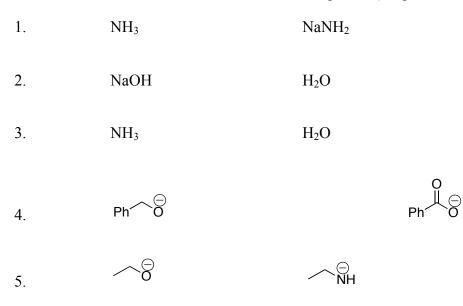
4. Он Лон



6.	Rank the Acidity f	rom 1 → 5, 1 b	eing most acidic. (Think Anion	! And Draw Anion!)
	•		Q	
HF	H_2O	CH ₃ NH ₂	H´ `OH	CH_4



Choose the More **Basic** for Each of the Following Pairs (Single Variable)



Predicting Acid/Base Equilibria: Any acid base equilibrium favors the side that has the more stable, less reactive base

6. Draw arrow to show whether equilibrium favors products or reactants. (Why?)

a.
$$H_2O + \overset{\bigcirc}{} NH_2$$

b. $H_2O + \overset{\bigcirc}{} H_2 \overset{\bigcirc}{} OH + NH_3$
 $\overset{\bigcirc}{} OH + H \overset{\bigcirc}{} OH$
 $\overset{\bigcirc}{} OH + H \overset{\bigcirc}{} OH$
 $\overset{\bigcirc}{} OH + H \overset{\bigcirc}{} OH$

Gene

 $HA + B^{\ominus} \longrightarrow A^{\ominus} + BH$

Stronger acid \rightarrow weaker conjugate base Weaker acid \rightarrow stronger conjugate base

- Acid-base reactions always favor formation of the weaker acid and weaker base ٠
- The weaker acid and weaker base are always on the same side
- The more stable anion is the weaker base

THEREFORE:

- The equilibrium will always favor the WEAKER, MORE STABLE ANION
- IF YOU CAN IDENTIFY WHICH ANION IS MORE STABLE, YOU CAN PREDICT • THE DIRECTION THE REACTION WILL GO.
- This logic can be used to predict whether an anion can successfully deprotonate a neutral • species.
- 7. Can $H_3C \ominus$ deprotonate H_2O ?

Some Arrow-Pushing Guidelines (Section 1.14)

- 1. Arrows follow electron movement.
- 2. Some rules for the appearance of arrows
 - The arrow must begin from the electron source. There are two sources:
 - a. An atom (which must have a lone pair to give)
 - b. A bond pair (an old bond that breaks)
 - An arrow must always point directly to an <u>atom</u>, because when electrons move, they always go to some new atom.
- 3. Ignore any Spectator Atoms. Any metal atom is always a "spectator"
 - When you have a metal spectator atom, realize that the non-metal next to it must have negative charge
- 4. Draw all H's on any Atom Whose Bonding Changes
- 5. Draw all lone-pairs on any Atom whose bonding changes
- 6. <u>KEY ON BOND CHANGES</u>. Any two-electron bond that changes (either made or broken) must have an arrow to illustrate:
 - where it came from (new bond made) or
 - an arrow showing where it goes to (old bond broken)

7. <u>Watch for Formal Charges and Changes in Formal Charge</u>

- If an atom's charge <u>gets more positive</u> ⇒ it's donating/losing an electron pair ⇒ <u>arrow must emanate from that atom or one of it's associated bonds.</u> There are two "more positive" transactions:
 - <u>When an anion becomes neutral</u>. In this case, an arrow will emanate from the atom. The atom has donated a lone pair which becomes a bond pair.
 - <u>When a neutral atom becomes cationic</u>. In this case, the atom will be losing a bond pair, so the arrow should emanate from the bond rather than from the atom.
- If an atom's charge <u>gets more negative</u> ⇒ it's accepting an electron pair ⇒ <u>an</u> <u>arrow must point to that atom</u>. Ordinarily the arrow will have started from a bond and will point to the atom.

8. <u>When bonds change, but Formal Charge Doesn't Change, A "Substitution" is</u> <u>Involved</u>

- Often an atom gives up an old bond and replaces it with a new bond. This is "substitution".
- In this case, there will be an incoming arrow pointing directly at the atom (to illustrate formation of the new bond), and an outgoing arrow emanating from the old bond that breaks

Examples of "Arrow Pushing" and "Mechanism" (Section 1-14)

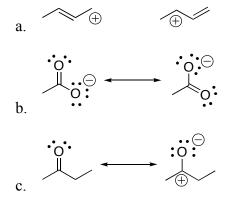
HOCH₃ + HO[⊕] + CH₃Br Reaction:

Mechanism, with arrows to show how electrons move, how the new bond forms, and how an old bond breaks:

$$HO: + H-C - Br: \longrightarrow HO - C - H + Br: \square$$

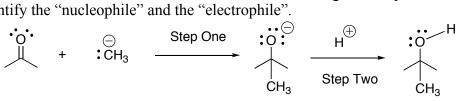
Notes:

- Arrows are drawn to show how electron pairs are moving as new bonds form or old bonds break.
- Mechanisms help us to understand and generalize when and why bonds make or break, so that we can understand when and why reactions will occur and what products will form.
- Each arrow always goes from an electron source (either an atom with a lone pair or else a bond pair) to an acceptor atom
- Terms:
 - a. "<u>Nucleophile</u>" = source of electon pair ("Lewis base") ("Lewis acid")
 - b. "**Electrophile**" = acceptor
- c. An arrow always proceeds from a nucleophile and points toward an electrophile.
- d. Arrow-pushing is very helpful in relating two resonance structures
- 1. Use arrows to show how the electrons "move" from the first to the second resonance structures:



2. Use arrows to show the mechanism for the following acid-base reaction.

3. Use arrows to show the mechanism for the following two-step reaction. For the first step, identify the "nucleophile" and the "electrophile".



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Ch 2 Structure and Properties of Organics

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

<u>2.4,6 "VSEPR" and Molecular Shape:</u> <u>Valence Shell Electron Pair Repulsion</u>

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

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

EXAMPLES

H H H ^C H AB ₄	H_) H ^{_N} ∖H AB₃L	H ^O H AB ₂ L ₂	$\begin{array}{c} H \\ C = C \\ H \\ AB_3 \end{array}$	H−C≡N—: ≁ ↓ AB ₂ ABL	AL_{2} H_{C} H_{C} H_{H} H_{H} H_{H} AB_{3} AB_{3}
--------------------------------------------	-------------------------------------------	----------------------------------------------------	--------------------------------------------------------	---------------------------------------	--------------------------------------------------------------------

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

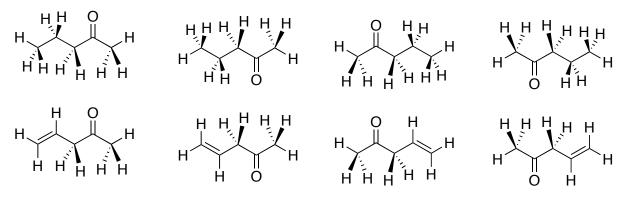
-for polyatomic molecules, it is strongly preferable to NOT have either of the in-plane atoms pointing straight up. Straight-up in-plane atoms do not lend themselves to extended 3-D structures.





Good! Look tetrahedral

Bad! These don't look tetrahedral!



Draw: C_2H_6

 $C_{4}H_{10}$

CH₃COCH₃

CH₃CH=CHCl

Hybrid Orbitals; π bonding (Chapter 2.1-4) $1s + 3p \rightarrow 4 sp^3$ hybrids

 $1s + 2p (+ 1 \text{ unhybridized } p) \rightarrow 3 \text{ sp}^2 \text{ hybrids } (+ 1 \text{ unhybridized } p) 120^{\circ}$ 1s + 1p(+2) unhybridized $p's \rightarrow 2$ sp hybrids (+2 unhybridized p's)) 180°

- Why does hybridization occur?
 Hybrid orbitals are big and point in one direction. Their <u>directionality</u> leads to <u>better overlap</u> which leads to strong bonds.
- Hybrid orbitals leads to nice VSEPR angles

- <u>If hybridization is so great, why aren't pure monatomic atoms hybridized?</u>
 For an isolated atom, having 1 s and 3 p atomic orbitals is better than 4 sp³ 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 sp³ •
- 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 $-\sigma$ bonds always involve the overlap of s or s-containing hybrids (s, sp, sp², sp³)
- 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 σπ

Single 0 1 Double 1 1 Triple 1 2

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

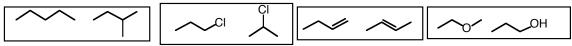
2.7-2.8 Bond Rotations, Structural Isomers, and Stereoisomers

Rotation is <u>allowed</u> for <u>single</u> 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

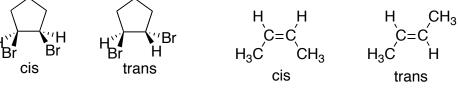
isomers-different compounds with the same molecular formula.

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



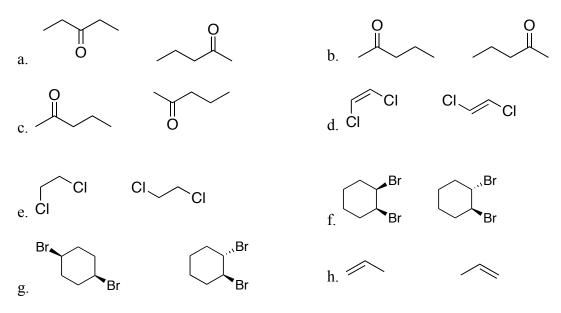
stereoisomers (or configurational isomers)-isomers in which atoms are joined in the same order but differ in the way their atoms are arranged in space.

- Stereoisomers have the same condensed formula (if not, they aren't stereoisomers)
- Stereoisomers can <u>not</u> 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.
 - **<u>Diastereomers</u>**: have <u>cis/trans</u> relationship



• Enantiomers: have mirror image (left hand/right hand) relationship H Br Br H

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



Chem 350 Jasperse Ch. 2 Notes

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

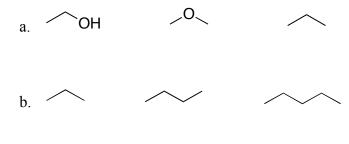
Intermolecular Forces impact:

- 1. Boiling points and melting points
- 2. Solubility

For Boiling Points:

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

Problem: Rank the boiling points, 1 being highest





2.11 Polarity and Solubility

2 Practical Rules:

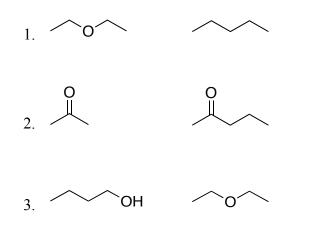
- 1. The more N's or O's in a molecular, the greater it's water solubility
- 2. The more C's, the lower it's water solubility

- Facts/Theory 1. "Like dissolves like"
 - enthalpy and entropy factors ٠

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 \rightarrow 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:



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

<u>Classification of Organic Compounds</u>. 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 "<u>alkyl group</u>" is <u>part</u> 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

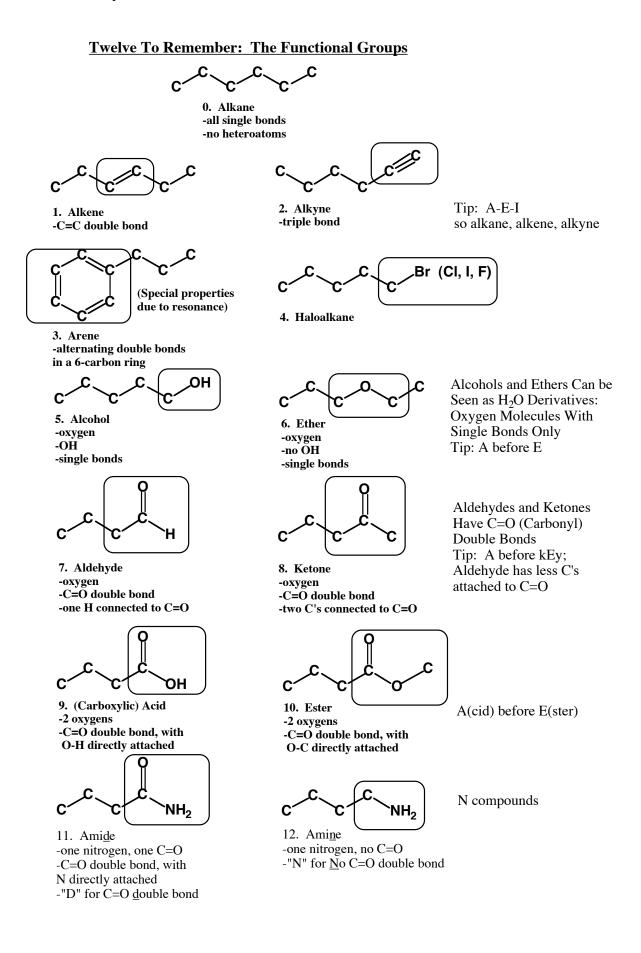
<u>1. Alkenes C=C</u>

- a. $\operatorname{contain} \overline{C} = C$ 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



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

R-X

Oxygen Compounds

5. Alcohols ROH

- a. Oxygen hybridization and shape: sp³, tetrahedral electron geometry, bent/angular atomic geometry, approximately 109° bond angle
- b. contain OH group attached to an sp³ 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 R₂N⁻ anions to form RO⁻ anions

6. Ethers ROR

- a. Oxygen hybridization and shape: sp³, tetrahedral electron geometry, bent/angular atomic geometry, approximately 109° 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 = <u>"carbonyl group"</u>
- b. Carbonyl carbon: sp^2 , trigonal planar, 120° 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 <u>not</u> basic

The Functional Groups, R-Z

Ine Functional Group Z Name		Suffix (or Prefix) Used in Systematic Name	Nomenclature Review	
-R	Alkane	-ane	methan- 1C	
	Alkene	-ene	ethan- 2C propan- 3C butan- 4C pentan- 5C hexan- 6C	
	Alkyne	-yne	heptan- 7C octan- 8C nonan- 9C decan- 10C	
	Arene	not responsible		
-X (Cl, Br, I, or F)	Haloalkane	halo-		
-OH	Alcohol	-ol		
-OR	Ether	not responsible		
Й	Aldehyde	-al		
R	Ketone	-one		
ОН	Carboxylic Acid	-oic acid		
OR	Ester	-oate		
NH ₂	Amide	-amide		
-NH ₂	Amine	amino-		

# C's	Name	Formula	Bp (°C)	Structure
1	Methane	CH ₄	-162	Н-(СН ₂)-Н
2	Ethane	C_2H_6	-89	H-(CH ₂) ₂ -H
3	Propane	C_3H_8	-42	H-(CH ₂) ₃ -H
4	Butane	C_4H_{10}	0	H-(CH ₂) ₄ -H
5	Pentane	$C_{5}H_{12}$	36	H-(CH ₂) ₅ -H
6	Hexane	$C_{6}H_{14}$	69	H-(CH ₂) ₆ -H
7	Heptane	$C_{7}H_{16}$	98	H-(CH ₂) ₇ -H
8	Octane	$C_{8}H_{18}$	126	H-(CH ₂) ₈ -H
9	Nonane	$C_{9}H_{20}$	151	H-(CH ₂) ₉ -H
10	Octane	$C_{10}H_{22}$	174	H-(CH ₂) ₁₀ -H

ALKANE NAMES, Formulas, Properties (Memorize) (Sections 3.2,4)

Notes: (Including some alkane properties, Section 3.5)

- 1. Memorize names
- 2. Names all end in "ane"
- 3. From 5 up, come from Greek
- 4. Boiling points: more C's \rightarrow high boiling point (London force)
- 5. Formula: for acyclic alkanes $\rightarrow C_{\rm N}H_{2\rm N+2}$
 - Basically 2H per carbon (2N), plus 2 extra H's at the ends (+2)
 - Branched isomers for acyclic alkanes still have C_NH_{2N+2}
- 6. <u>Cyclic Alkanes</u>: names start in "cyclo" (cyclopentane, cyclooctane, etc.)
- 7. Formula for <u>cvclic alkanes \rightarrow C_NH_{2N}</u>
 - Basically 2H per carbon (2N), but without the extra two H's at the ends
 - Cyclic alkanes with side-chains still have C_NH_{2N}
- 8. Solubility: nonpolar
 - \rightarrow insoluble in water
 - \rightarrow soluble in nonpolar, hydrophobic solvents
- 9. Density: < 1 (less than water)
 - \rightarrow float on top of water

Industrial Alkan	$\underline{cs}(J.J)$		
Name	# C's	Boiling Range	Use
Natural Gas	C_1 - C_3	Gas	Fuel
	(70% methane)		
"Petroleum Gas"	C_2-C_4	<30°	Heating, Gas
Propane	C ₃	-42°	Propane tanks,
			camping, etc.
Gasoline	C ₄ -C ₉	30-180°	Car fuel
Kerosene	C_8-C_{16}	160-230°	Jet fuel
Diesel	C_{10} - C_{18}	200-320°	Truck fuel
Heavy Oils	C_{16} - C_{30}	300-450°	
Motor Oils		High temp	
Paraffin		Vacuum	
Asphalt		Never Distills	
Coke		Never Distills	

Industrial Alkanes (3.5)

Nomenclature of Alkanes (Sections 3.3-4)

Systematic IUPAC Rules for Branched and Substituted Alkanes

- 1. Longest continuous C-chain \rightarrow "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:

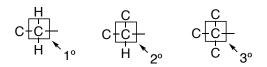
- Hyphenate numbers
- Do not put a space between substituents and the core name

H₃C CH_3 CH-H₃C-C-Memorize H₃C ĊH₂ Isopropyl t-butyl or tert-butyl CH₃ H_2 C_CH H₃C H₃C CH₃ Others H_{2} s-butyl n-propyl isobutyl n-butyl (n for "normal")

Special Names for Some 3 or 4-carbon Substituents

Another Classification System

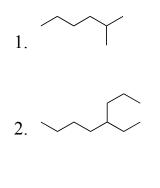
Primary (1°): with one attached carbon Secondary (2°): with two attached carbons Tertiary (3°): with three attached carbons

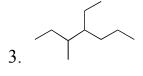


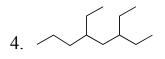
Very Complex Substituents (Not responsible)

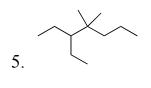
Substituent: (1-ethyl-2,3-dimethylpentyl) Overall: 9-(1-ethyl-2,3-dimethylpentyl)nonadecane

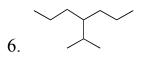
Nomenclature Example Problems

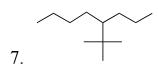


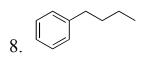






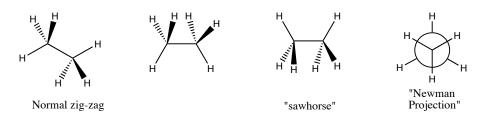






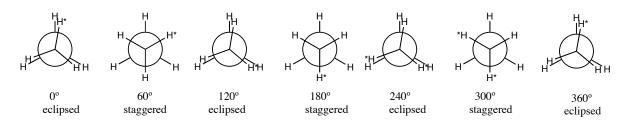
Structure, Conformations of Acyclic Alkanes (3.7)

A. "Conformations" = "Conformers" = "Rotamers" = different 3-D arrangements resulting from rotation around a single bond



B. "Newman Projections": look straight down one C-C bond

- If both bonded carbons are tetrahedral, there will be three bonds extending from the front carbon, and three more bonds extending from the back carbon
- Terms:
 - **<u>Dihedral angle</u>**: angle between a bond on the front atom relative to a bond on the back atom
 - Eclipsed: when bonds are aligned. 0°, 120°, 240°, 360° dihedral angles
 - **Staggered**: when bonds are as far apart as possible: 60°, 180°, 300°
 - Skew: anything else in between the eclipsed and staggered extremes

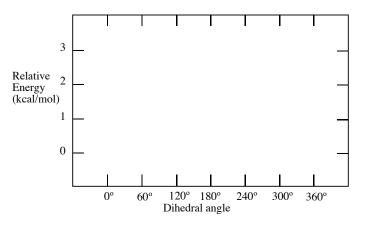


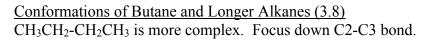
Energy: Staggered best, eclipsed worst

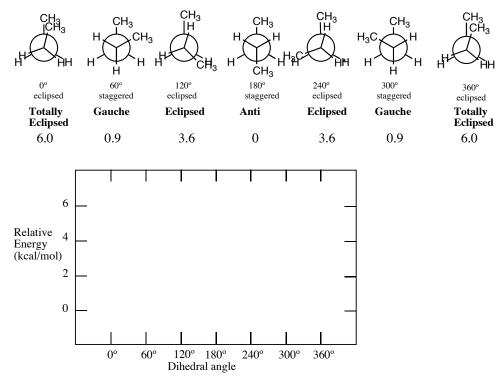
• Why: <u>Torsional strain</u>. **Repulsion between bonding electron pairs** is reduced in the staggered conformation, and is worst in the eclipsed conformation.

<u>Rotation Barrier</u>: energy gap between the best and worst conformation when you go through a full 360° rotation (as would take place in a full bond rotation)

• Draw in Entergy diagram:







Questions

- 1. Draw the energy diagram
- 2. What would be the rotation barrier?

Strain Energy Factors:

- 1. <u>**Torsional**</u> strain (why all of the eclipsed type conformations are worse). Repulsion between bonded electrons
- 2. <u>Steric</u> strain: When atoms themselves get too close. Atom-atom repulsion.
- 3. <u>Angle</u> strain: When bond angles can't achieve ideal VSEPR angles. (No angle strain in ethane or butane)

Total Strain =	Torsional strain (are any bonds eclipsed?)
	+ Steric strain (are any atoms too close)
	+ Angle strain (are any bond angles forced to be other than ideal?)

Questions

- 1. In general, why are staggered better than eclipsed?
- 2. Why is eclipsed better than totally eclipsed?
- 3. Why is anti better than gauche?
- 4. Why is gauche better than eclipsed?
- 5. Why is anti better than totally eclipsed?

Summary

- 1. Anti < gauche < eclipsed < totally eclipsed
- 2. Steric and torsional reasons
- 3. The bulkier a substituent, the greater the steric strain in eclipsed and totally eclipsed conformations

Skills. Be Able to:

- 1. predict relative rotation barriers
- 2. write a conformational analysis (rotation/energy diagram)
- 3. draw Newman pictures for any bond in any structure
- 4. identify anti/gauche/eclipsed/totally eclipsed conformations

Steps to Drawing Newman Structure:

- 1. Draw a circle (back carbon) with a dot in the middle
- 2. Add three sticks extending from the periphery of the circle, with one of them straight up
- 3. Add three sticks extending from the center dot (front carbon) to illustrate the bonds radiating from the front carbon

$$\bigcirc \longrightarrow H^{\operatorname{CH_3}}_{\operatorname{H}} \longrightarrow H^{\operatorname{CH_3}}_{\operatorname{H}} \xrightarrow{\operatorname{CH_3}}_{\operatorname{H}} \xrightarrow{\operatorname{CH_3}}_{\operatorname{H}}$$

Problems

1. Rank the rotation barriers for the following, relative to the indicated bonds

 CH_3-CH_3 \uparrow \uparrow \uparrow

Draw Newman projections for the best and worst conformations of the structure shown, relative to the indicated bond. Use the 3rd carbon in the back.

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<u>Higher Alkanes</u> -for any alkane, anti conformations best = zig-zag layout

<u>3.10 Cycloalkanes</u> Nomenclature: cyclopropane, cyclobutane, etc..

General formula: C_NH_{2N} -this is also true for cycloalkanes with chain(s) attached

3.11 Substituted Cycloalkanes and cis/trans Isomers in Disubstituted Cycloalkanes Nomenclature:

- Monosubstituted: alkylcycloalkane
- Disubstituted: cis- (or trans-)-x-alkyl-y-alkylcycloalkane
 - 1. "Cis"-same side "trans" opposite sides
 - 2. Number ring so as to minimize numbers

	Total Ring	Strain	Main
	Strain	Per	Source
Ring Size	(kcal/mol)	CH_2	Of Strain
3	28	9	Angle Strain
4	26	7	Angle Strain
5	7	1	Torsional Strain (eclipsing)
6	0	0	STRAIN FREE
7	6	1	Torsional Strain (eclipsing)

Torsional Strain (eclipsing)

1

3.12 Ring Stability and Ring Strain (Section 4.4-8)

8

10

Structural Isomer Problems (3.2, 3.10)

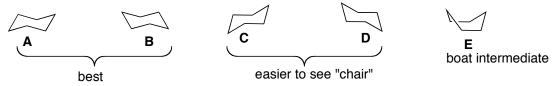
- <u>Check formula first</u>. Is it an acyclic molecule (C_NH_{2N+2}) , or not? $(C_NH_{2N}$ could be a cyclic alkane, or perhaps an alkene ...)
- **<u>Be systematic</u>**. Try the longest possible chain (or largest ring size) first, then systematically shorten it and find the branched isomers.
- Avoid duplicates!
- Beware of things that look different but are really the same thing.
- 1. Draw all structural isomers of C₇H₁₆. (Be systematic; no duplicates!)

2. Draw all structural isomers of C₇H₁₄. (Be systematic; no duplicates!)

3.13 Cyclohexane Chair Conformations

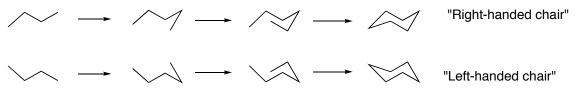
- Cyclohexane has no angle strain or torsional strain
- Cyclohexane has perfect 109° angles with staggered, non-eclipsed C-C bonds
- Obviously it is not flat (natural angle for a flat cyclohexane would be 120°)

Chair Conformations:



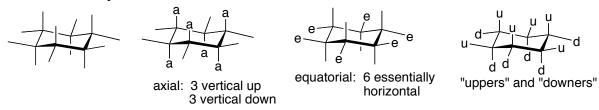
- Chairs A and B are constantly interconverting via "boat" E
- A and **B** are best to draw and work with.
- But C/D make it easier to visualize why it's called a "chair": 4 carbons make the seat of the chair, one makes backrest, one a footrest.

Process for Drawing Both Chairs:



- 1. Draw a 4-carbon zig-zag. It helps if your left-most carbon is a little lower than your 3rd carbon
- 2. Add a 5th carbon and 6th carbon, but don't have them exactly underneath the 2nd and 3rd carbons.
- 3. Connect the 6^{th} carbon to the orginal 1^{st} carbon
 - For a "left-handed chair", start up and zig-zag down.

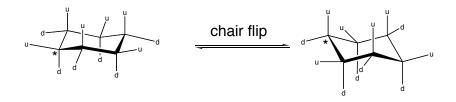
"Axial" and "Equatorial" Positions for Substituents



- 1. Each carbon has one axial and one equatorial H's
- 2. Always have six axial attachments
- 3. 3 axials up (on alternating carbons)

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- 4. 3 axials down (on alternating carbons)
- 5. Always have six equatorial attachments
- 6. For processing cis/trans problems, it's helpful to recognize "upper" from "downer" positions
- 7. When a chair flips, what was equatorial becomes axial, and what was axial becomes equatorial

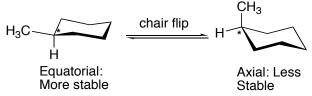


Drawing equatorial and axial bonds:

- Make axial straight up or straight down (3 each)
- Make equatorial bond lines almost exactly horizontal
- Equatorials are easiest to draw on left and right-most carbons

Drawing Mono- and DiSubstituted Cyclohexanes (Sections 3-14,15)

• Always attach the first substituent onto the leftmost carbon (easiest to draw)



- Draw in the H on any substituted carbon, but skip on H-only carbons
- Equatorial is better than axial for steric reasons. In the axial configuration, the substituent has destabilizing steric interactions
 - 2 extra gauche interactions, and 1,3-diaxial interactions
- For disubstituted chairs, let the cis/trans relationship guide whether the second substituent should be in an "upper" or "lower" position relative to the original substituent.
- If one substituent is bigger than the other, the most stable chair will always have the larger substituent equatorial

Questions:

- 1. Draw both chair forms for cis-2-methyl-1-isopropylcyclohexane.
- 2. Which is the best chair for cis-2-methyl-1-isopropylcyclohexane?
- 3. Draw both chair forms and identify the best chair for trans-2-methyl-1isopropylcyclohexane.
- 4. Which is more stable, cis- or trans-2-methyl-1-isopropylcyclohexane?
- 5. Then answer the same questions for the 1,3- and 1,4- isomers.

