

Ch. 1 Intro and Review**1.1 Intro to Organic Chemistry****“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: **never** draw C, N, or O with > 8 electrons!!!
4. Bond Types:

a. Covalent bonds <ul style="list-style-type: none"> • Between nonmetals • Involve shared electrons 	H ₂ H ₂ O
b. Ionic: <ul style="list-style-type: none"> • Negligible sharing of electrons • Metals transfer electron(s) to nonmetal • If formula has a metal, assume ionic bonding • Special case of ionic bonding in absence of metals: ammonium salts 	LiF NH ₄ Cl

Normal Bonding (Chapter 1)**Summary of Normal, Ideal Bonding (No Formal Charge)**

	Valence Electrons	Valence Bonds	Lone Pairs
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	4	4	0
$\begin{array}{c} \cdot\cdot \\ -\text{N}- \\ \end{array}$	5	3	1
$\begin{array}{c} \cdot\cdot \\ -\text{O}: \\ \end{array}$	6	2	2
H—	1	1	0
$\begin{array}{cc} \cdot\cdot & \cdot\cdot \\ :\text{Cl}- & :\text{Br}- \\ \cdot\cdot & \cdot\cdot \\ \cdot\cdot & \cdot\cdot \\ :\text{I}- & :\text{F}- \\ \cdot\cdot & \cdot\cdot \end{array}$	7	1	3

Rules for Drawing Lewis structures for organic molecules: (Ch 1:4,5)

1. Try to provide normal bonding for C, N, O atoms **if possible**. (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. CH_3CH_3
 - b. $\text{CH}_3\text{CH}_2\text{OH}$
 - c. CO_2
 - d. HCN
 - e. CH_3CHO
 - f. NaOCH_3

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!
- **Skills:**
 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: Designation of formal charge is required. 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. $FC = \text{group \#} - (\text{bonds} + \text{unshared e's})$ (use to calculate FC)
2. $\text{Group \#} - FC = \text{bonds} + \text{unshared electrons}$ (given formal charge, use to find lone pairs)

Practical: (memorize)

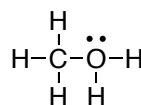
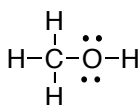
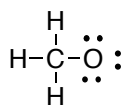
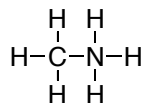
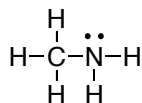
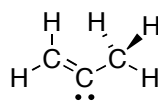
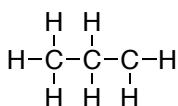
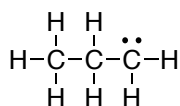
C	4 bonds	↔	neutral
	3 bonds and zero lone pairs	↔	cation +1
	3 bonds and one lone pair	↔	anion -1
N	4 bonds	↔	cation +1
	3 bonds and one lone pair	↔	neutral
O	3 bonds and one lone pair	↔	cation +1
	2 bonds and 2 lone pairs	↔	neutral
	1 bond and three lone pairs	↔	anion -1

FORMAL CHARGE

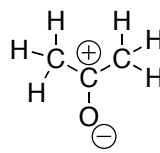
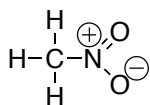
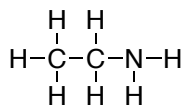
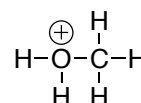
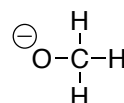
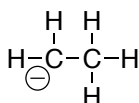
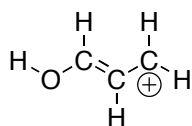
# of Bonds	C	N	O	F
4	0	+1		
3	-1 or +1	0	+1	
2		-1	0	
1			-1	0

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!

Electronegativity 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						Patterns: 1. Increases left to right 2. Increases bottom to top 3. C-H bond are pretty comparable, essentially nonpolar 4. C-other non-metal, C is always less electronegative, δ^+ on C 5. C-metal, C is always more electronegative, δ^- on C
		C 2.5	N 3.0	O 3.4	F 4.0	
					Cl 3.2	
					Br 3.0	
					I 2.7	

1.8 Ionic Structures

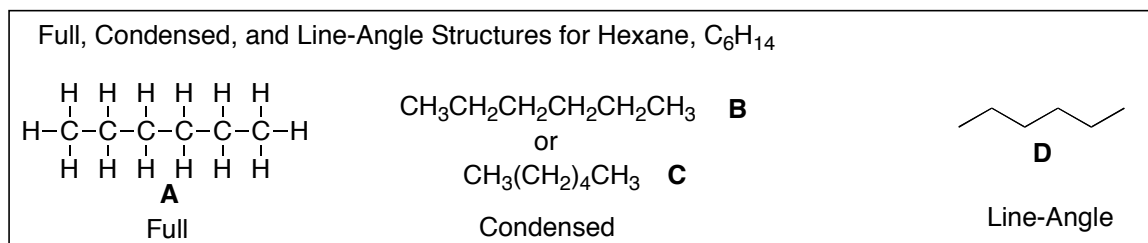
1. If you see a metal in a formula, treat it as ionic rather than covalent/molecular
 - a. -always put a positive charge on the metal
 - b. -never draw a “bond” between the metal and the non-metal
 - c. -always figure there must be a negative charge on the non-metal portion of the formula, with a formal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



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 C₆H₁₄ hexane as you can in 20 seconds:

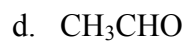
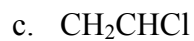
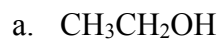
Full:

Condensed:

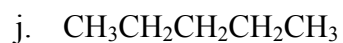
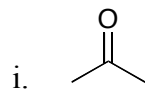
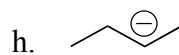
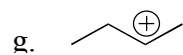
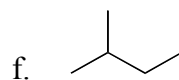
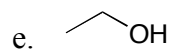
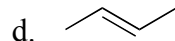
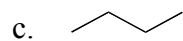
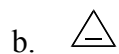
Line-Angle:

Draw the full structure, given the condensed structure.

Point being illustrated



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.

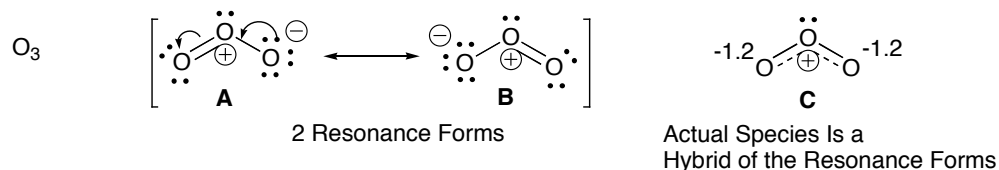


Resonance Structures (Section 1:9)

- Online students, watch: <https://www.youtube.com/watch?v=DTow76zAZ98>

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

Example: O₃ (ozone)



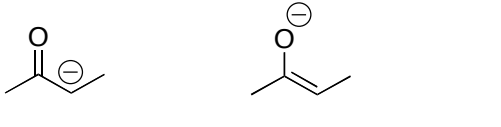
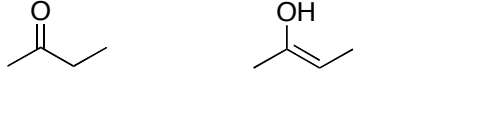
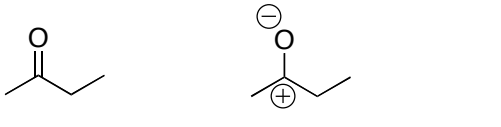


Notes/observations:

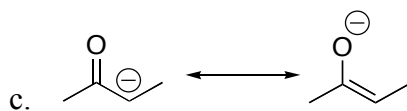
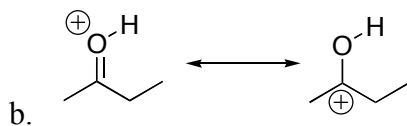
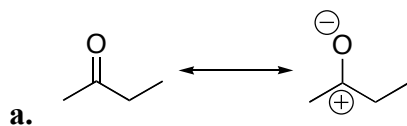
- Neither form **A** nor **B** can avoid formal charges.
 - The majority of resonance situations have some formal charge involvement
 - The real molecule is hybrid: see picture **C**
 - The central oxygen has + charge
 - Each of the outside oxygens is -1/2
 - Both of the bonds to the outside oxygens 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)
 - Why not just draw the hybrid?
 - Hard to do, without first working through resonance structures first.
 - Hard to keep track of the electrons, which help explain reactivity/mechanism
 - Resonance Recognition**: When are Two Structures related as Resonance Structures?
 - Atoms must be connected in exactly the same way.
 - Resonance forms differ **only in the placement of electrons**.
 - If two Lewis structures have the same atomic connectivity, but differ **only** in the placement of some electrons/formal charges, they are related as resonance structures.
 - If the placement/connectivity of atoms differ, then the two structures are not resonance structures (they may perhaps be related as “isomers”, see later.)
- 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.
- Resonance involves the **delocalization** of electrons and charge
 - In ozone, neither outside oxygen gets stuck with a full negative charge. The charge is shared so that both outside oxygens have a more manageable -1/2 charge
 - This delocalization of electrons/charge is stabilizing.
 - **KEY: RESONANCE IS STABILIZING**
 - Resonance always involves electrons in double bonds and/or lone pairs (π electrons)
 - “Allylic resonance”: The most frequent resonance situation is when a charged atom is attached to a double bonded atom
 - When resonance structures are equal in stability, the hybrid is the average of the forms
 - When resonance structures are unequal, the more stable structure dominates the hybrid
 - **Ranking Stability**:
 - **More bonds** \rightarrow more stable (but don't exceed octet rule!). (**Priority rule**)
 - Bonds being equal, consider **electronegativity** (tiebreaker rule):
 - **negative charge** is better on **more electronegative atom**;
 - **positive charge** is better on **less electronegative atom**

Resonance Problems

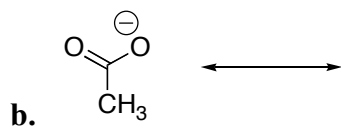
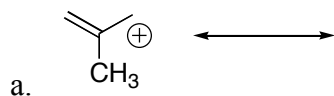
1. Which of the following are related as resonance structures?

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

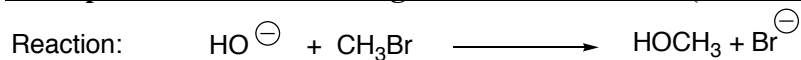


3. Draw a resonance structure for the following

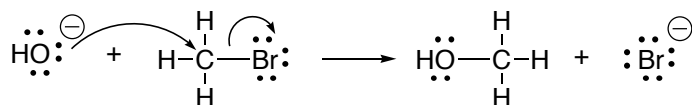


Some Arrow-Pushing Guidelines (Section 1.14)

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 atom, 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. **KEY ON BOND CHANGES.** 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. **Watch for Formal Charges and Changes in Formal Charge**
 - If an atom's charge gets more positive \Rightarrow it's donating/losing an electron pair \Rightarrow arrow must emanate from that atom or one of its associated bonds. There are two “more positive” transactions:
 - When an anion becomes neutral. In this case, an arrow will emanate from the atom. The atom has donated a lone pair which becomes a bond pair.
 - When a neutral atom becomes cationic. 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 gets more negative \Rightarrow it's accepting an electron pair \Rightarrow an arrow must point to that atom. Ordinarily the arrow will have started from a bond and will point to the atom.
8. **When bonds change, but Formal Charge Doesn't Change, A “Substitution” is Involved**
 - 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

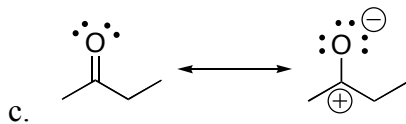
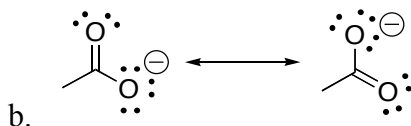
Examples of “Arrow Pushing” and “Mechanism” (Section 1-14)

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

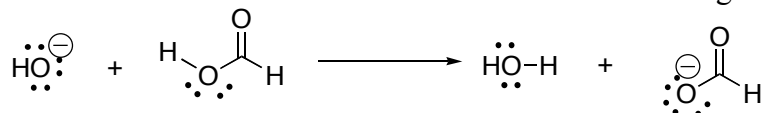


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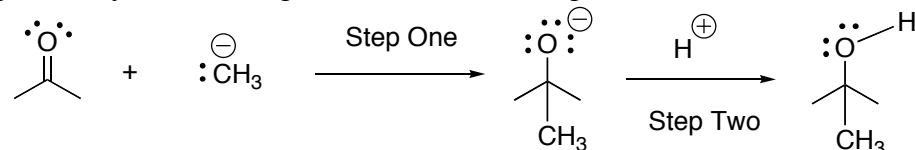
- Arrows are drawn to show how electron pairs are moving as new bonds form or old bonds break.
 - Mechanisms help us to understand and generalize when and why bonds make or break, so that we can understand when and why reactions will occur and what products will form.
 - Each arrow always goes from an electron source (either an atom with a lone pair or else a bond pair) to an acceptor atom
 - **Terms:**
 - a. “**Nucleophile**” = source of electron pair (“Lewis base”)
 - b. “**Electrophile**” = acceptor (“Lewis acid”)
 - 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:



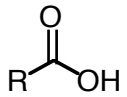
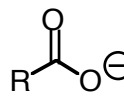
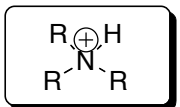
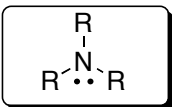
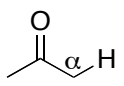
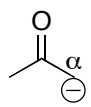
2. Use arrows to show the mechanism for the following acid-base reaction.



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



Acid-Base Chemistry (Section 1-12-14)**Acidity/Basicity Table**

Entry	Class	Structure	K _a	Acid Strength	Base	Base Strength
1	Strong Acids	H-Cl, H ₂ SO ₄	10 ²		Cl [⊖] , HO-S(=O) ₂ -O [⊖]	
2	Hydronium	H ₃ O ⁺ , ROH ⁺ cationic	10 ⁰		H ₂ O, HOR neutral	
3	Carboxylic Acid		10 ⁻⁵			
4	Ammonium Ion (Charged)	 Charged, but only weakly acidic!	10 ⁻¹²		 Neutral, but basic!	
5	Water	HOH	10 ⁻¹⁶		HO [⊖]	
6	Alcohol	ROH	10 ⁻¹⁷		RO [⊖]	
7	Ketones and Aldehydes		10 ⁻²⁰			
8	Amine (N-H)	(iPr) ₂ N-H	10 ⁻³³		(iPr) ₂ N [⊖] Li [⊕]	
9	Alkane (C-H)	RCH ₃	10 ⁻⁵⁰		RCH ₂ [⊖]	

Quick Checklist of Acid/Base Factors

1. Charge
2. **Electronegativity**
3. **Resonance/Conjugation**
4. Hybridization
5. Impact of Electron Donors/Withdrawers
6. Amines/Ammoniums

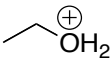


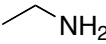
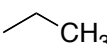


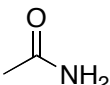
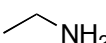
- **When a neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.**

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

- Charge: all else equal, cations are more acidic than neutrals, and anions more basic than neutrals.
- Electronegativity:
 - Acidity: $\text{H-X (halogen)} > \text{H-O} > \text{H-N} > \text{H-C}$
 - Basicity: $\text{X}^- < \text{O}^- < \text{N}^- < \text{C}^-$
 - Anion Stability: $\text{X}^- > \text{O}^- > \text{N}^- > \text{C}^-$
 - Why: **The more stable the anion Z⁻ that forms, the more acidic the parent H-Z will be.** 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.
- Resonance/Conjugation: Since anion resonance is stabilizing, **an acid that gives a resonance-stabilized anion is more acidic.** 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: $\text{HO-SO}_3^- < \text{CH}_3\text{COO}^- < \text{CH}_3\text{CH}_2\text{O}^-$
 - Anion Stability: $\text{HO-SO}_3^- > \text{CH}_3\text{COO}^- > \text{CH}_3\text{CH}_2\text{O}^-$
- 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.)
- Hybridization: For lone-pair basicity, (all else being equal), $\text{sp}^3 > \text{sp}^2 > \text{sp} > \text{p}$
- Electron donating/electron withdrawing substituents:

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

1. NH_3 $\oplus\text{NH}_4$
2.  
3.   
4.  
5.  

6. Rank the Acidity from 1 → 5, 1 being most acidic. (Think Anion! And Draw Anion!)



7. For the anions drawn in problem 6, rank them from 1 → 5 in terms of **basicity**.

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

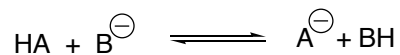


Predicting Acid/Base Equilibria: Any acid base equilibrium favors the side that has the more stable, less reactive base

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



Generic acid/base reaction, with anionic base and neutral acid:



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
- 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 $\text{H}_3\text{C}^\ominus$ deprotonate H_2O ?

Ch 2 Structure and Properties of Organics

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

2.4,6 “VSEPR” and Shape: Valence Shell Electron Pair Repulsion

Online students: watch the following videos: (In face-to-face lecture, I'll probably show some physical models, which will not get displayed in the lecture video. So several minutes in the lecture video will be kind of useless to you without seeing the models. The two videos linked below will give you something as good, or probably better, to view....)

- Online students, watch review of VSEPR logic:
<https://www.youtube.com/watch?v=keHS-CASZfc>
- Online students, watch more video with a bunch of tetrahedral and trigonal atoms, with reference to bond angles and hybridization:
https://mediaspace.minnstate.edu/media/350-T1-VSEPR-Modeling-with-Spartan/1_1andi8t5

Concept: electron groups repel, determine structure

4 electron groups: tetrahedral, 109° angle

3 electron groups: trigonal planar, 120° angle

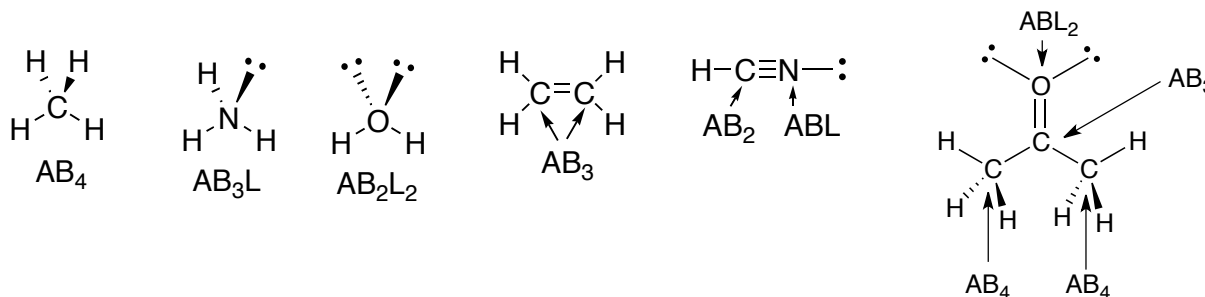
2 electron groups: linear, 180° angle

2 Types of “Electron Groups”

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

B+L	Electron Geometry	Bond Angle	Hybridization	Remaining π -orbitals
4	Tetrahedral	$\approx 109^\circ$	sp^3	0
3	Trigonal Planar	$\approx 120^\circ$	sp^2	1
2	Linear	$\approx 180^\circ$	sp	2

EXAMPLES



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** with a **straight line**

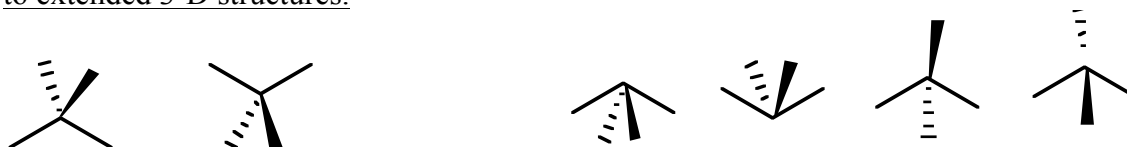
B. 3-D Perspective

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. (Online students:

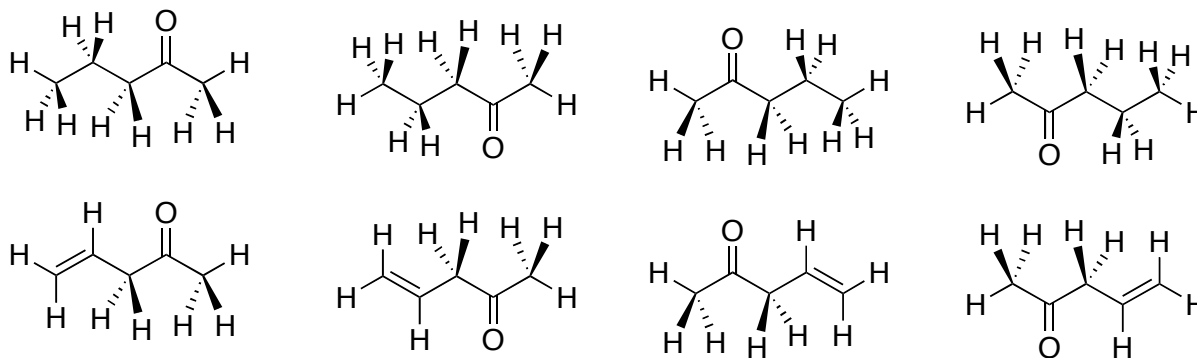
https://mediaspace.minnstate.edu/media/350-T1-VSEPR-Modeling-with-Spartan/1_1andi8t5

- a. -if the two in the plane are “down”, the hash/wedge should be up
- b. -if the two in plane are “up”, the hash/wedge should be down.
- c. -the hash/wedge should never point in same direction as the in-plane lines, or else the atom doesn't look tetrahedral
- d. -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:
C₂H₆

C₄H₁₀

CH₃COCH₃

CH₃CH=CHCl

Hybrid Orbitals; π bonding (Chapter 2.1-4)

$1s + 3p \rightarrow 4 sp^3$ hybrids	109°
$1s + 2p$ (+ 1 unhybridized p) $\rightarrow 3 sp^2$ hybrids (+ 1 unhybridized p)	120°
$1s + 1p$ (+ 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 **directionality** leads to **better overlap** which leads to **strong bonds**.
- Hybrid orbitals leads to nice VSEPR angles

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

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

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

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

2 Kinds of Covalent Bonds

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

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

Bond σ π

Single	1	0
Double	1	1
Triple	1	2

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

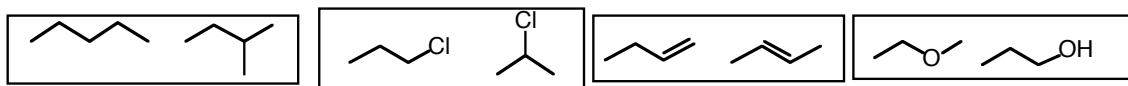
2.7-2.8 Bond Rotations, Structural Isomers, and Stereoisomers

Rotation is allowed for single bonds

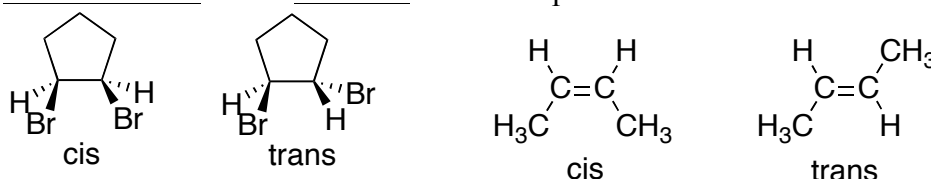
- No bonds break, the sigma bond is fine

Rotation is forbidden for double bonds

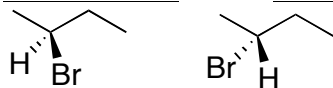
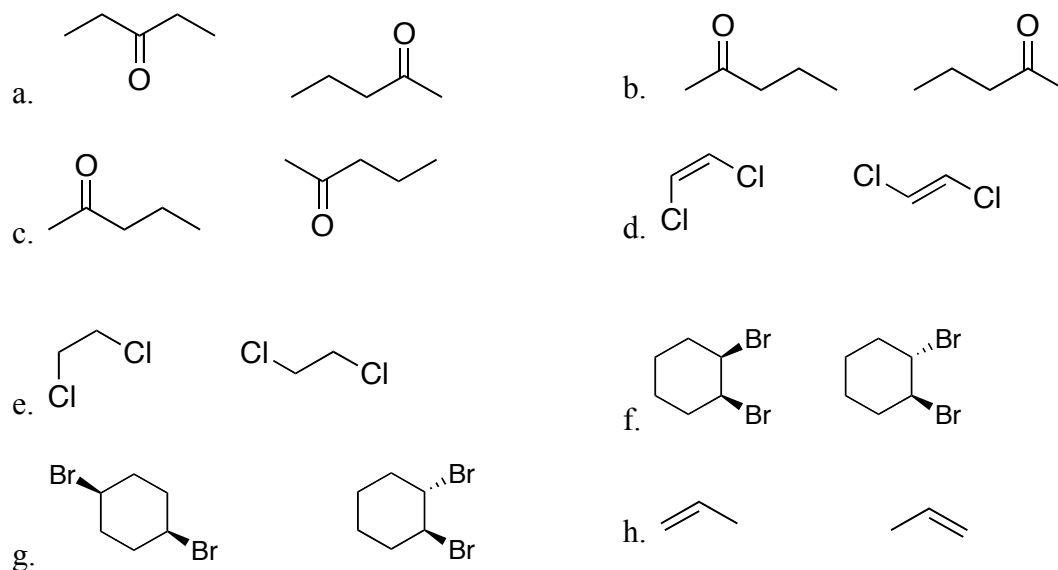
- The π -bond overlap breaks, between the two p orbitals that need to be parallel

isomers-different compounds with the same molecular formula.**structural isomers (or constitutional isomers)**-isomers that have their atoms connected in a different order.**stereoisomers (or configurational isomers)**-isomers in which atoms are joined in the same order but differ in the way their atoms are arranged in space.

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



- **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**.

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. CO₂b. CCl₄c. CH₄d. C₄H₁₀e. H₂Of. NH₃g. CH₃CH₂OHh. CHCl₃

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

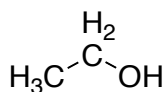
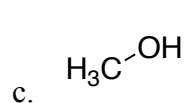
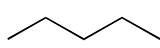
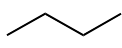
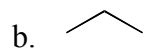
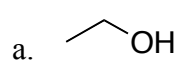
Intermolecular Forces impact:

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



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

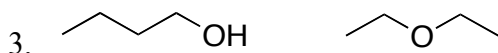
Facts/Theory

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:



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

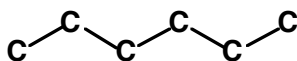
Classification of Organic Compounds. The Functional Groups (Sections 2-12-14)**Hydrocarbons: C + H only****0. Alkanes and Cycloalkanes**

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

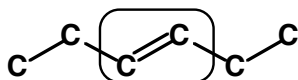
1. Alkenes C=C

- a. contain C=C double bond
- b. names end “ene” (ethane, propene, butene, etc.)
- c. **double bonds can’t rotate**
 - a. rotation is allowed for single bonds, but is forbidden for double bonds
 - b. Why:
 1. a single bond (σ) can rotate freely without compromising orbital overlap
 2. But a π -bond cannot rotate freely, because π -overlap breaks
 - The two π -bonded atoms have parallel and overlapping p orbitals. To rotate the bond completely breaks the π -bond half-way through the rotation.
 - The energy price is thus way too high.
 - d. Restricted rotation results (sometimes) in cis/trans isomers
- e. A π -bond is much weaker than a σ -bond, and thus is far more reactive. Thus, an alkene is viewed as a “functional group” because it reacts (“functions”)
- f. Functional groups and “R” groups:

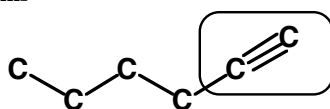
2. Alkynes: Triple bonds Name end “yne”**3. Aromatics or Arenes: Resonance**

Twelve To Remember: The Functional Groups

0. Alkane
-all single bonds
-no heteroatoms

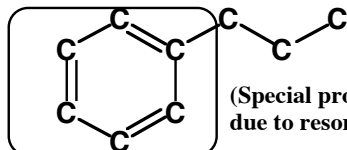


1. Alkene
-C=C double bond



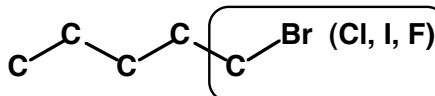
2. Alkyne
-triple bond

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

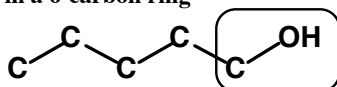


3. Arene
-alternating double bonds
in a 6-carbon ring

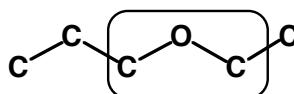
(Special properties
due to resonance)



4. Haloalkane

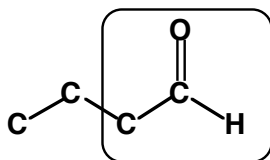


5. Alcohol
-oxygen
-OH
-single bonds

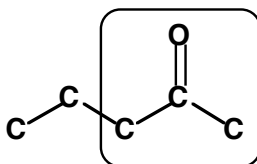


6. Ether
-oxygen
-no OH
-single bonds

Alcohols and Ethers Can be
Seen as H₂O Derivatives:
Oxygen Molecules With
Single Bonds Only
Tip: A before E

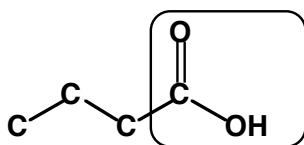


7. Aldehyde
-oxygen
-C=O double bond
-one H connected to C=O

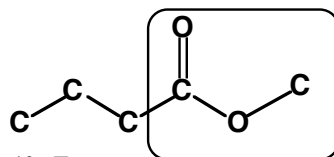


8. Ketone
-oxygen
-C=O double bond
-two C's connected to C=O

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

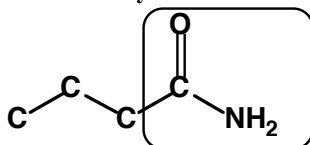


9. (Carboxylic) Acid
-2 oxygens
-C=O double bond, with
O-H directly attached

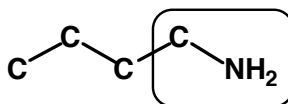


10. Ester
-2 oxygens
-C=O double bond, with
O-C directly attached

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

4. Haloalkanes

R-X

- bonds are polarized: R group is δ^+ , halogen is δ^-
- C-X bonds are often rather weak and breakable = “functional”

Oxygen Compounds

5. Alcohols

ROH

- contain OH group attached to an sp^3 carbon
- names end “ol” (methanol, ethanol, etc.)
- Oxygen hybridization and shape:
 - sp^3 , tetrahedral electron geometry, approximately 109° bond angle
- Hydrogen-bonding: impacts boiling point and water solubility

6. Ethers

ROR

- Oxygen hybridization and shape:
 - sp^3 , tetrahedral electron geometry, approximately 109° bond angle
- Don't hydrogen-bond themselves, so lower boiling than ROH of equal weight.
- Oxygen lone pairs do hydrogen-bond to water hydrogens, so decent water solubility
- Relatively low reactivity

7,8. Aldehydes, Ketones

C=O

AldehydesKetones

- C=O group = “carbonyl group”
- Carbonyl carbon: sp^2 , trigonal planar, 120° bond angles
- 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.
- 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

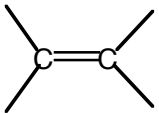

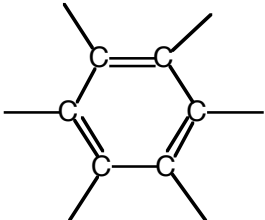
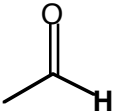
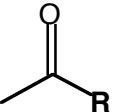
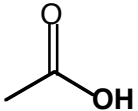
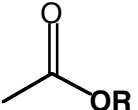
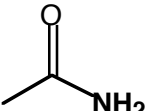
11. Amines

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

12. Amides

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

The Functional Groups, R-Z

Functional Group Z	Name	Suffix (or Prefix) Used in Systematic Name	Nomenclature Review
-R	Alkane	-ane	methan- 1C ethan- 2C
	Alkene	-ene	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	
	Aldehyde	-al	
	Ketone	-one	
	Carboxylic Acid	-oic acid	
	Ester	-oate	
	Amide	-amide	
-NH ₂	Amine	amino-	

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

# C's	Name	Formula	Bp (°C)	Structure
1	Methane	CH ₄	-162	H-(CH ₂)-H
2	Ethane	C ₂ H ₆	-89	H-(CH ₂) ₂ -H
3	Propane	C ₃ H ₈	-42	H-(CH ₂) ₃ -H
4	Butane	C ₄ H 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	Decane	C ₁₀ H ₂₂	174	H-(CH ₂) ₁₀ -H

Notes: (Including some alkane properties, Section 3.5)

- Memorize names
- Names all end in "ane"
- From 5 up, come from Greek
- Boiling points: more C's → high boiling point (London force)
- Formula: for **acyclic alkanes** → C_NH_{2N+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}
- Cyclic Alkanes**: names start in "cyclo" (cyclopentane, cyclooctane, etc.)
- Formula for **cyclic alkanes** → C_NH_{2N}
 - 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}
- Solubility: nonpolar
 - insoluble in water
 - soluble in nonpolar, hydrophobic solvents
- Density: < 1 (less than water)
 - float on top of water

Industrial Alkanes (3.5)

Name	# C's	Boiling Range	Use
Natural Gas	C ₁ -C ₃ (70% methane)	Gas	Fuel
"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	
Asphalt		Never Distills	
Coke		Never Distills	

Nomenclature of Alkanes (Sections 3.3-4)**Systematic IUPAC Rules for Branched and Substituted Alkanes**

1. Longest continuous C-chain → “core name”
2. Number core chain from an end nearest a substituent
3. Name substituents as “alkyl” 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

Special Names for Some 3 or 4-carbon Substituents

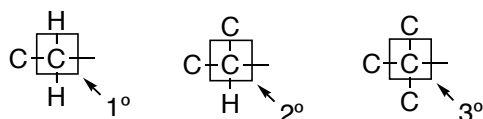
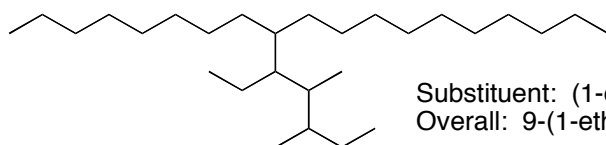
Memorize	$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{CH}- \\ \\ \text{H}_3\text{C} \end{array}$ Isopropyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}- \\ \\ \text{CH}_3 \end{array}$ t-butyl or tert-butyl		Include iso in alphabetizing
Others	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{C}- \\ \quad \\ \text{H}_2 \quad \end{array}$ n-propyl (n for "normal")	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{C}- \\ \quad \quad \\ \text{H}_2 \quad \text{H}_2 \quad \end{array}$ n-butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{CH}-\text{C}- \\ \quad \\ \text{H}_2 \quad \end{array}$ isobutyl	$\begin{array}{c} \\ \text{H}_3\text{C}-\text{C}-\text{CH}-\text{CH}_3 \\ \\ \text{H}_2 \end{array}$ s-butyl

Another Classification System

Primary (1°): with one attached carbon

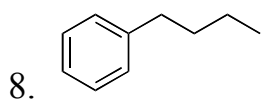
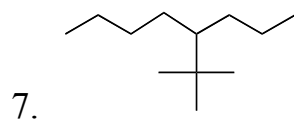
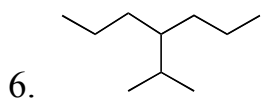
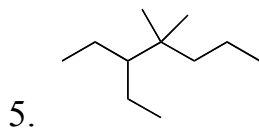
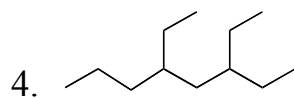
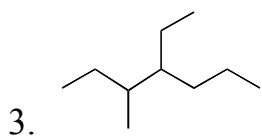
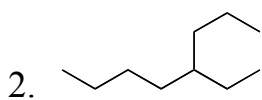
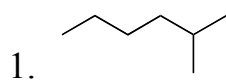
Secondary (2°): with two attached carbons

Tertiary (3°): with three attached carbons

**Very Complex Substituents (Not responsible)**

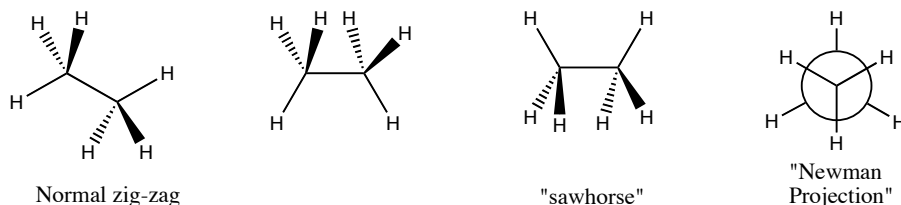
Substituent: (1-ethyl-2,3-dimethylpentyl)

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

Nomenclature Example Problems

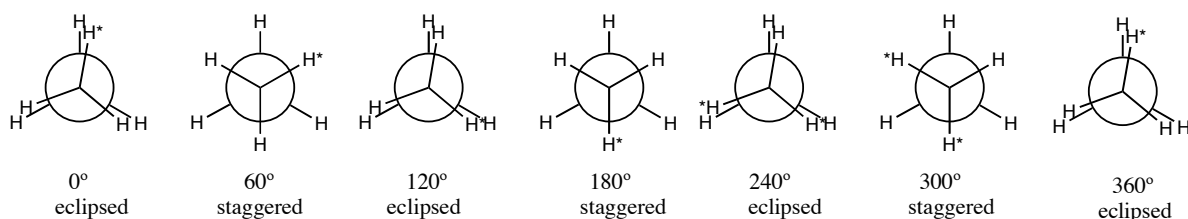
Structure, Conformations of Acyclic Alkanes (3.7)

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

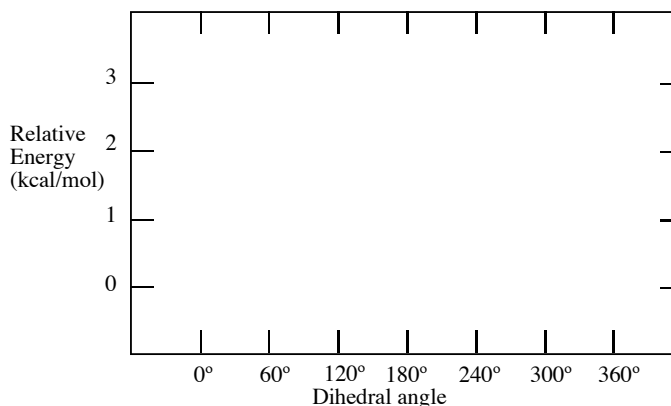
- Online students, watch: <https://www.youtube.com/watch?v=1550xtF-u1k>
 - Online students, watch: <https://www.youtube.com/watch?v=tEXtJLTmdDI>
1. If both bonded carbons are tetrahedral, there will be three bonds extending from the front carbon, and three more bonds extending from the back carbon
 2. Terms:
 1. **Dihedral angle**: angle between a bond on the front atom relative to a bond on the back atom
 2. **Eclipsed**: when bonds are aligned. 0° , 120° , 240° , 360° dihedral angles
 3. **Staggered**: when bonds are as far apart as possible: 60° , 180° , 300°
 4. **Skew**: anything else in between the eclipsed and staggered extremes

**Energy: Staggered best, eclipsed worst**

1. Why: Torsional strain. **Repulsion between bonding electron pairs** is reduced in the staggered conformation, and is worst in the eclipsed conformation.

Rotation Barrier: 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)

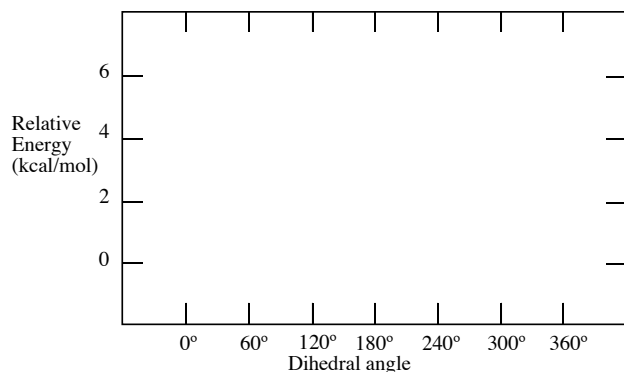
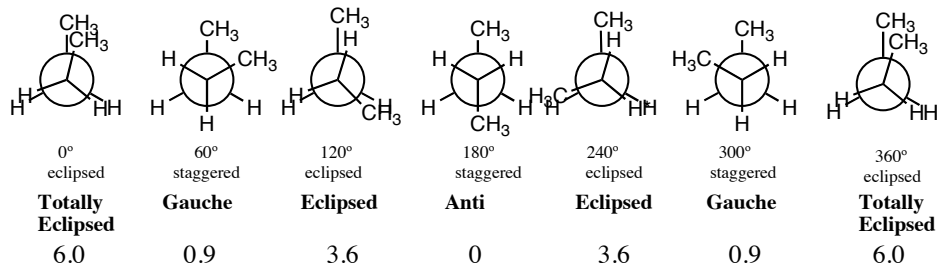
- Draw in Energy diagram:



Conformations of Butane and Longer Alkanes (3.8)

$\text{CH}_3\text{CH}_2\text{-CH}_2\text{CH}_3$ is more complex. Focus down C2-C3 bond.

- Online students, watch: <https://www.youtube.com/watch?v=xXci5VGousQ>

Questions

- Draw the energy diagram
- What would be the rotation barrier?

Strain Energy Factors:

- Torsional** strain (why all of the eclipsed type conformations are worse). Repulsion between bonded electrons
- Steric** strain: When atoms themselves get too close. Atom-atom repulsion.
- Angle** 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

- In general, why are staggered better than eclipsed?
- Why is eclipsed better than totally eclipsed?
- Why is anti better than gauche?
- Why is gauche better than eclipsed?
- Why is anti better than totally eclipsed?

Summary

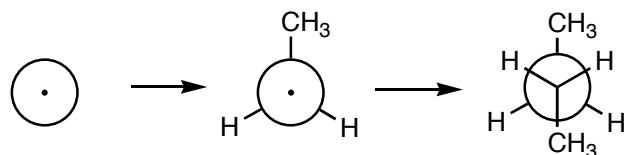
1. Anti < gauche < eclipsed < totally eclipsed
2. Steric and torsional reasons
3. The bulkier a substituent, the greater the steric strain in eclipsed and totally eclipsed conformations

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

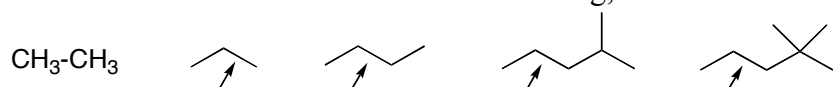
Steps to Drawing Newman Structure:

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



Problems

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



6. 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.

Higher Alkanes

-for any alkane, anti conformations best = zig-zag layout

3.10 Cycloalkanes

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

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

Ring Size	Total Ring Strain (kcal/mol)	Strain Per CH_2	Main Source 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)
8	10	1	Torsional Strain (eclipsing)

Structural Isomer Problems (3.2, 3.10)

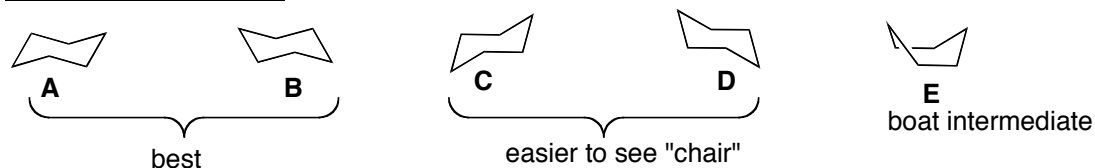
- **Check formula first.** Is it an acyclic molecule (C_NH_{2N+2}), or not? (C_NH_{2N} could be a cyclic alkane, or perhaps an alkene ...)
 - **Be systematic.** Try the longest possible chain (or largest ring size) first, then systematically shorten it and find the branched isomers.
 - **Avoid duplicates!**
 - 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!)

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

3.13 Cyclohexane Chair Conformations

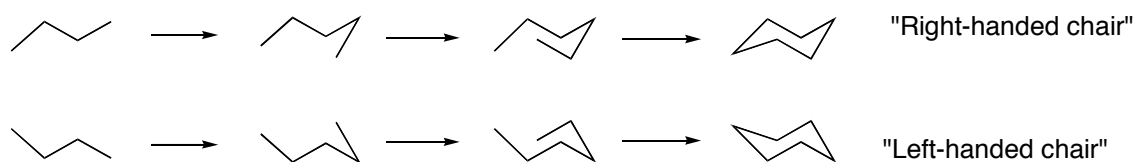
1. Cyclohexane has no angle strain or torsional strain
2. Cyclohexane has perfect 109° angles with staggered, non-eclipsed C-C bonds
3. Obviously it is not flat (natural angle for a flat cyclohexane would be 120°)

Chair Conformations:



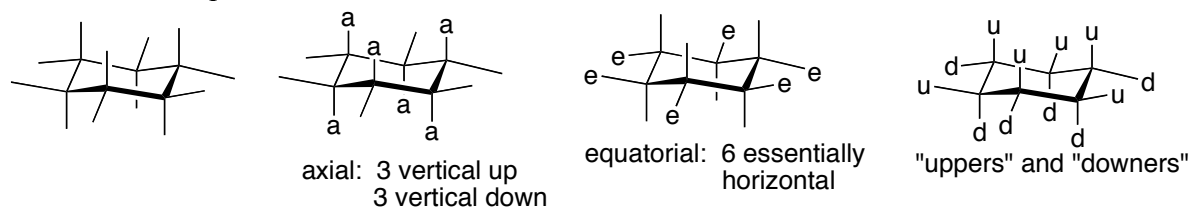
1. Chairs **A** and **B** are constantly interconverting via “boat” **E**
 - Online students: watch https://www.youtube.com/watch?v=6VUU-_JExMs
2. **A** and **B** are best to draw and work with.
3. But **C/D** make it easier to visualize why it’s called a “chair”: 4 carbons make the seat of the chair, one makes backrest, one a footrest.

Process for Drawing Both Chairs:



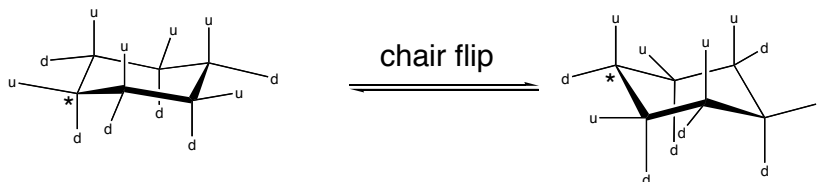
1. Draw a 4-carbon zig-zag. It helps if your left-most carbon is a little lower than your 3rd carbon
2. Add a 5th carbon and 6th carbon, but don't have them exactly underneath the 2nd and 3rd carbons.
3. Connect the 6th carbon to the original 1st carbon
 - For a “left-handed chair”, start up and zig-zag 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)
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
- Online students: (same one as last page) watch <https://www.youtube.com/watch?v=6VUU-JEXMs>

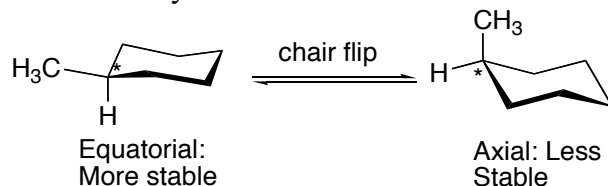


Drawing equatorial and axial bonds:

- 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)

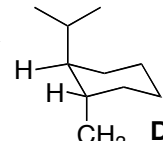
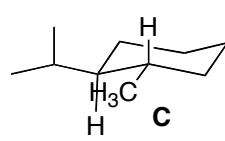
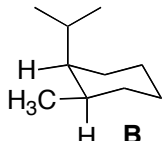
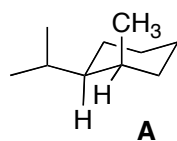
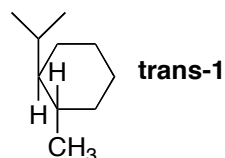
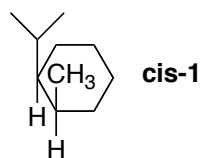
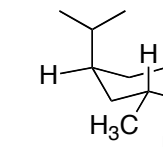
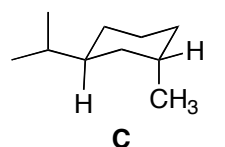
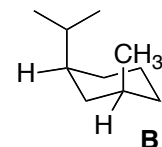
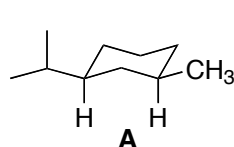
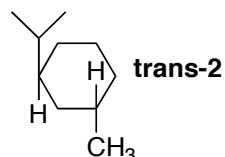
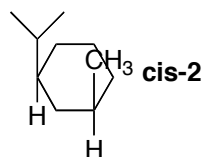
- Always attach the first substituent onto the leftmost carbon (easiest to draw)



- 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
 - Online students, watch: https://www.youtube.com/watch?v=R9VkDTjgd_w&list=PLAhRiX8pHhMKI5fWwZQvZmBpPAv2LMVFQ
 - 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

Cis and Trans Disubstituted CyclohexanesQuestions:

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

1,2-
DiSubbed1,3-
DiSubbed1,4-
DiSubbed