

Chemistry S-20: Introduction

Course Content

This course introduces students to the chemistry of carbon-containing compounds. Organic chemistry is at the heart of biology and medicine: proteins, carbohydrates, fats, and DNA are all organic compounds. Plastics, detergents, cosmetics, and pharmaceuticals are also organic compounds.

Course Organization

Lectures give overview of each topic, conceptual background, and demonstrations

Textbook provides much more detail and explains how to solve problems

Laboratory gives hands-on experience and reinforces chemical concepts

Discussion Sections show how to solve problems and give you practice

Review Lectures (Fri. at 3:00pm) give extra help in problem solving

Practice problems give you practice in problem-solving

Practice examinations give you more practice in solving problems

Examinations evaluate your ability to solve organic chemistry problems

Course Philosophy

The Chemistry Team:

Our Coaching Staff:

Background

We expect that you have taken a one-year course in General Chemistry and that you remember (or can quickly review) most of what you learned in that course.

The Periodic Table of the Elements

1 H Hydrogen 1.00794															2 He Helium 4.003		
3 Li Lithium 6.941	4 Be Beryllium 9.012182																
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050																
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 131.29	54 Xe Xenon 132.90447
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113 (277)	114 (277)				
58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967				
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)				

The Organic Chemist's Periodic Table

1 H Hydrogen 1.00794															
3 Li Lithium 6.941	4 Be Beryllium 9.012182														
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050														
5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032											
13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527											
				35 Br Bromine 79.904											
				53 I Iodine 126.90447											

- As of Thursday, June 5 2014: chemists have identified **88 million** organic and inorganic substances, of which **65 million** are available commercially!
- “Learning organic chemistry is hard work. The amount of information out there is as **close to infinite** as makes no difference... The best solution is to make sure that we understand what we learn... **develop a feel for the way molecules behave.**”

—A.J. Kirby, Cambridge UK

The Hydrogen Atom

- The hydrogen atom is the simplest atom. What is the structure of the hydrogen atom?
- It turns out that, contrary to our expectations, the electron in a hydrogen atom can have only certain allowed energies, and it can make transitions between these energy levels only in discrete amounts. We say that the energy levels of an electron in a hydrogen atom are *quantized*.
- Erwin Schrödinger realized that an electron confined to an atom might behave like a wave confined to a string. He was able to derive the *wavefunction* that describes the behavior of an electron in an atom. Each possible solution of his famous equation corresponds to a *standing wave*, and is referred to as an *orbital*. An *orbital* is a three-dimensional region of space which defines where an electron can be found.
- The Schrödinger Equation requires three quantum numbers. What are these quantum numbers, what are the valid integer values they can take, and what do they represent?

n

Name:

Possible Values:

Represents:

l

Name:

Possible Values:

"The Chemist's Code":

Represents:

ml

Name:

Possible Values:

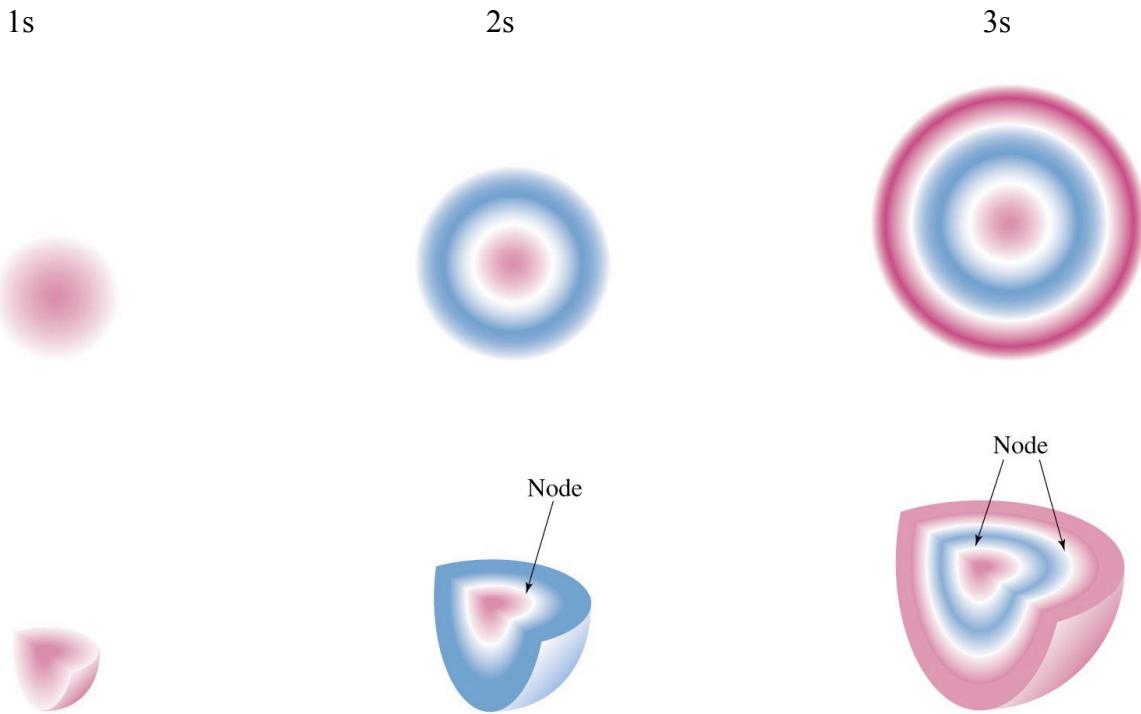
Represents:

Reading: Section 1.6

The *s* orbitals and Radial Nodes

The *s* orbitals are spherical in shape. (*s* = spherical)

How can we imagine the distribution of electrons in an *s* orbital?



What do the nodes signify?

What do the two colors (shades of gray?) signify?

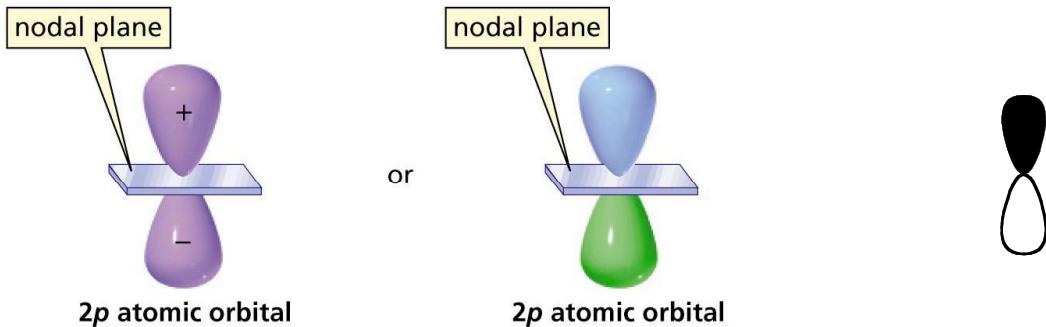
What is the relationship between energy, principal quantum number n , and the nodes?

Reading: Section 1.6

The p orbitals and Angular Nodes

The p orbitals are shaped somewhat like a peanut (?) (p = peanut?)

How many p orbitals are there for a given principal quantum number n ?



A $2p$ orbital should have one node. Is it a radial node?

Why might we call this an *angular* node?

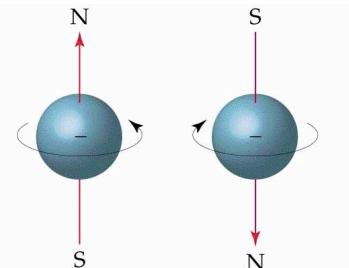
What is the significance of the colors (shading)? How is the shading related to the nodes?

What is the relationship between the quantum number l and the number of angular nodes?

Reading: Section 1.6

Electrons in Orbitals

- The **Pauli Exclusion Principle** states that no two electrons can have identical sets of quantum numbers.
- Each orbital can contain up to two electrons.**
There is another quantum number m_s for **electron spin**. What do we mean by electron spin? How does this allow two electrons per orbital?



Let's fill in the electrons for the elements H, He, Li, Be, and B:

	1s	2s	2p	Configuration
H:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
He:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
Li:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
Be:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
B:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	

Now where does the next electron go for C? **Hund's Rule:** Don't crowd the electrons!

	1s	2s	2p	Configuration
C:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
N:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
O:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
F:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	
Ne:	<input type="text"/>	<input type="text"/>	<input type="text"/> <input type="text"/> <input type="text"/>	

Reading: Section 1.7

Lewis Structures: Rules

These rules are helpful guidelines. Practice using them until they become second-nature.

1. **Count** the total number of valence electrons that must appear in the structure.

- Be sure to account for the extra or fewer electrons in a polyatomic ion!

2. **Arrange** the atoms in the correct arrangement for the molecule or ion.

- A few guidelines:

- Molecules are often written in the order that the atoms are connected.
- The least electronegative atom is usually the central atom.
- Hydrogen and fluorine are always terminal atoms.

- In oxyacids (H_2SO_4 , HNO_3 , etc.), the oxygen atoms are bonded to the central atom, and the hydrogen atoms are bonded to the oxygens.

3. **Connect** each pair of adjacent atoms with a single bond. (Use lines for bonds.)

4. **Complete** the octets of terminal atoms by filling in lone pairs of electrons. (Use dots!)

- Remember that hydrogen should only have two electrons.

5. **Add leftover electrons** to the central atom (even if that gives it more than an octet).

6. **Try multiple bonds** if the central atom lacks an octet.

- As a guide for where to place multiple bonds in order to minimize formal charges, the total number of bonds to any **uncharged** atom is usually given by its position on the periodic table. This is a guideline, not a hard-and-fast rule!

Group #:	1A	2A	3A	4A	5A	6A	7A
Example:	H	Be	B	C	N	O	F
# of bonds:	1	2	3	4	3	2	1

6. **Check** formal charges on each atom, and write in any non-zero formal charges.

- Formal charge = (# of valence e^- in free atom) – (# of dots and lines around atom)
- The sum of the formal charges on all atoms will equal zero for a neutral molecule, and will equal the charge on the ion for a polyatomic ion.
- Lewis structures should be drawn to minimize formal charges.
- In general, negative formal charge should go on the most electronegative atoms.

7. **Check** for resonance, and indicate it if necessary.

8. **Check** your Lewis structure.

- Have you drawn the correct number of valence electrons?
- Do all atoms have octets? (Except for examples of reduced or expanded octets.)
- Have you minimized formal charges?

Reading: Sections 1.2 – 1.4

Lewis Structures

- Using the rules for Lewis structures, provide Lewis structures for each of the following. Be sure to include any non-zero formal charges, and resonance (if appropriate).

NH_3 (ammonia)

$(\text{CH}_3)_3\text{C}^+$ (the tert-butyl carbocation)

H_2CO (formaldehyde)

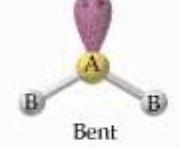
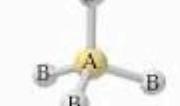
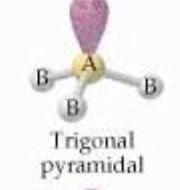
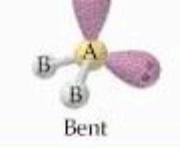
CH_3CO_2^- (the acetate ion)

CH_3NC (methyl isonitrile)

Reading: Sections 1.2 – 1.4

Molecular Shapes: The VSEPR Model

TABLE 9.2 Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains About the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2 domains		2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3 domains		3	0	 Trigonal planar	$\begin{array}{c} \vdots \text{F} \cdot \\ \vdots \text{F} \cdot \text{B} \cdot \text{F} \cdot \end{array}$
		2	1	 Bent	$\left[\begin{array}{c} \vdots \text{O} \cdot \\ \vdots \text{N} = \text{O} \cdot \end{array} \right]^-$
4 domains		4	0	 Tetrahedral	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$
		3	1	 Trigonal pyramidal	$\begin{array}{c} \text{H} \cdot \text{H} \cdot \text{N} \cdot \text{H} \\ \\ \text{H} \end{array}$
		2	2	 Bent	$\begin{array}{c} \text{H} \cdot \text{H} \cdot \ddot{\text{O}} \cdot \\ \\ \text{H} \end{array}$

- Note the “wedge and dash” notation that chemists use to represent three-dimensional structures on a flat page.

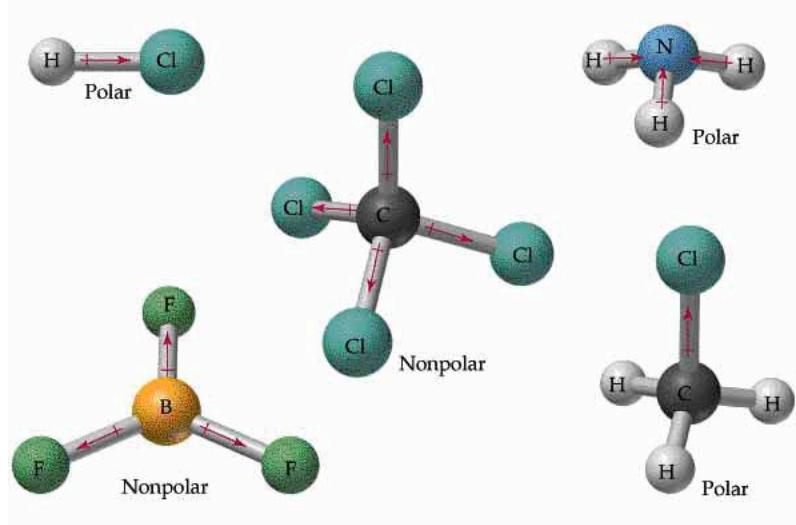
Reading: Section 1.3

Electronegativity and Polarity

- Linus Pauling invented the tremendously useful concept of *electronegativity* to describe the distribution of electron density in covalent compounds. The electronegativity of an atom is a measure of its tendency to attract electron density in covalent bonds. Here are the electronegativities of the main-group elements:

H 2.2		He
Li 0.98	Be 1.57	
Na 0.93	Mg 1.31	
K 0.82	Ca 1.00	
Rb 0.82	Sr 0.95	
Cs 0.79	Ba 0.89	
B 2.04	C 2.55	N 3.04
Al 1.61	Si 1.90	P 2.19
Ga 1.81	Ge 2.01	As 2.18
In 1.78	Sn 1.96	Sb 2.05
Tl 2.04	Pb 2.33	Bi 2.02
O 3.44	F 3.98	Cl 3.16
Se 2.55	Br 2.96	Kr 2.9
Te 2.1	I 2.66	Xe 2.6
Po 2.0	At 2.2	Rn

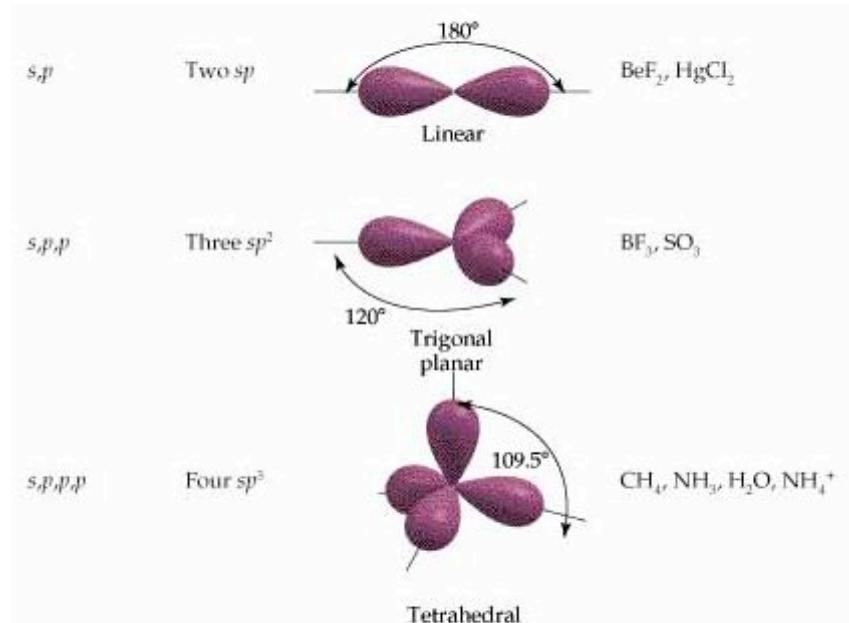
- A bond can be *polar* if there is a difference in electronegativity between the atoms in the bond. However, even if a molecule contains polar bonds, it is possible for the entire molecule to be *nonpolar*. Let's look at some examples:



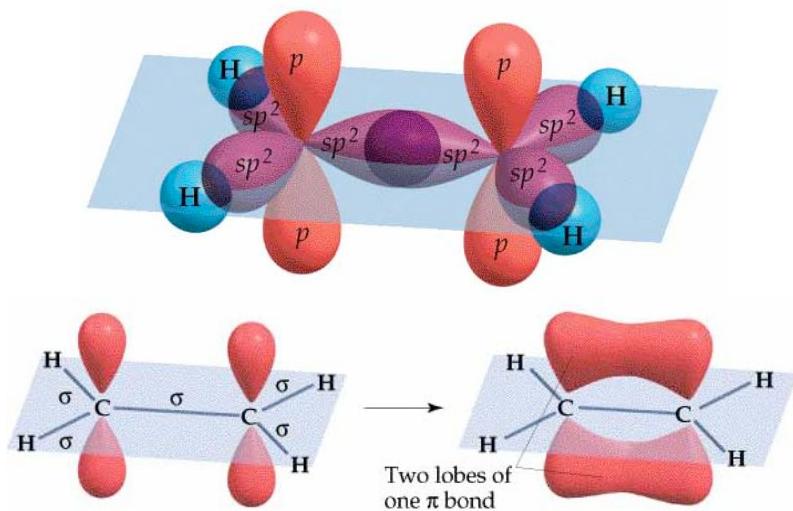
Reading: Section 1.2

Hybridization and Multiple Bonds

- A dirty secret:*
Hybridization is simply a code for electron domain geometry. Let's take a look:



- Consider ethylene (also called ethene): C_2H_4 . Draw a Lewis structure, and use it to determine the geometry and hybridization of each of the carbon atoms. How can we describe a double bond in terms of the overlap of orbitals?



Reading: Section 1.9

The Master Table of Bonding and Hybridization

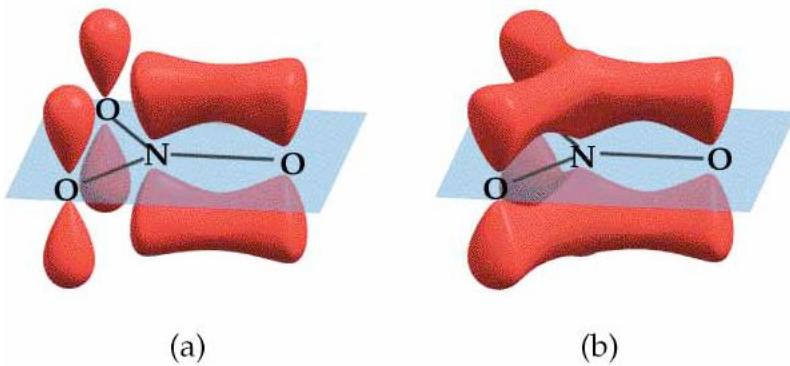
- Let's fill out the following table of bonding and hybridization:

Number of Electron Domains	Electron Domain Geometry	Hybridization	Number of Hybridized Orbitals	Number of “Leftover” p-orbitals

- Now let's use this table to describe the bonding in acetonitrile (CH_3CN):

Delocalized π Bonding

- Draw the Lewis structure for the nitrate ion, NO_3^- .
- Using the "Master Table", how can we describe the bonding in nitrate? Remember: the actual molecule must somehow be an "average" of the resonance structures.
- Nitrate is a classic example of delocalized π -bonding. How do the pictures below represent localized and delocalized π -bonding?



- What is the hybridization of each oxygen atom in nitrate?

Now go back to page 8 and do VSEPR and hybridization for those Lewis structures!

Reading: Section 15.6 (really; that's not a typo!)

Resonance and Hybridization: The Wrong View

- *Note: From here on, the material is new; we are finished with our review of topics from general chemistry!*
- Draw the Lewis structure of formamide, HCONH₂.

- What is the hybridization of the nitrogen atom?

- The bond angles around the nitrogen atom in formamide are 120°. Is this consistent with the hybridization that you determined?

Resonance and Hybridization: The Right View

- Draw all the *reasonable* resonance structures of formamide, HCONH₂.
- What is the hybridization of the nitrogen atom in each of these resonance structures?
- Why *must* the hybridization of an atom be the same in *all* resonance structures?
- How can we resolve this question of hybridization?

Introduction to Organic Chemistry: Alkanes

- Because there are so many different organic compounds, we must group them into classes based on their structure. The simplest class of organic compounds is the *alkanes*:

An *alkane* is a compound that contains only C and H atoms, and contains only single bonds.

- What are some examples of alkanes? Where do alkanes come from? What are the uses of alkanes?

- What is the general molecular formula of an alkane?
- How many **constitutional isomers** have the molecular formula C₅H₁₂?

Reading: Sections 2.1 and 2.2

Conformations of Ethane

- Consider the molecule *ethane*, C₂H₆. This molecule can exist in different **conformations**. How can we represent these conformations?
- What are the relative *energies* of these conformations?

Reading: Section 2.3

Conformations of Butane

- Consider rotations around the central C—C bond in the molecule *n*-butane (the straight-chain C₄H₁₀ alkane). What are the conformations that result from rotations around this central bond?
- What are the relative *energies* of these conformations?

Reading: Section 2.3

Nomenclature of Alkanes

- How can we assign names to alkanes?

Straight-Chain Alkanes

Branched Alkanes

Reading: Section 2.4

Skeletal Structures

- One of the most useful skills in organic chemistry is the ability to write and understand *skeletal structures*. Let's take a look at some skeletal structures for several alkanes:

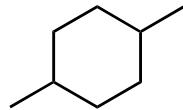
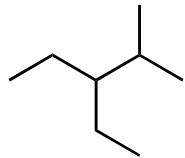
heptane

2,2-dimethylpentane

cyclooctane

tert-butylcyclohexane

- For each of the following skeletal structures, *count* the number of carbon and hydrogen atoms in the structure, and provide a systematic name for the alkane:



Reading: Section 2.5

Functional Groups

- One way to bring some order to the vast diversity of organic molecules is by classifying them based on the **functional groups** they contain. A functional group is a group of atoms bonded together in a particular way. Molecules that contain the same functional group tend to react in similar ways. Here are examples of some common functional groups:

Carboxylic Acid

Alcohol

Alkene

Alkyl Halide

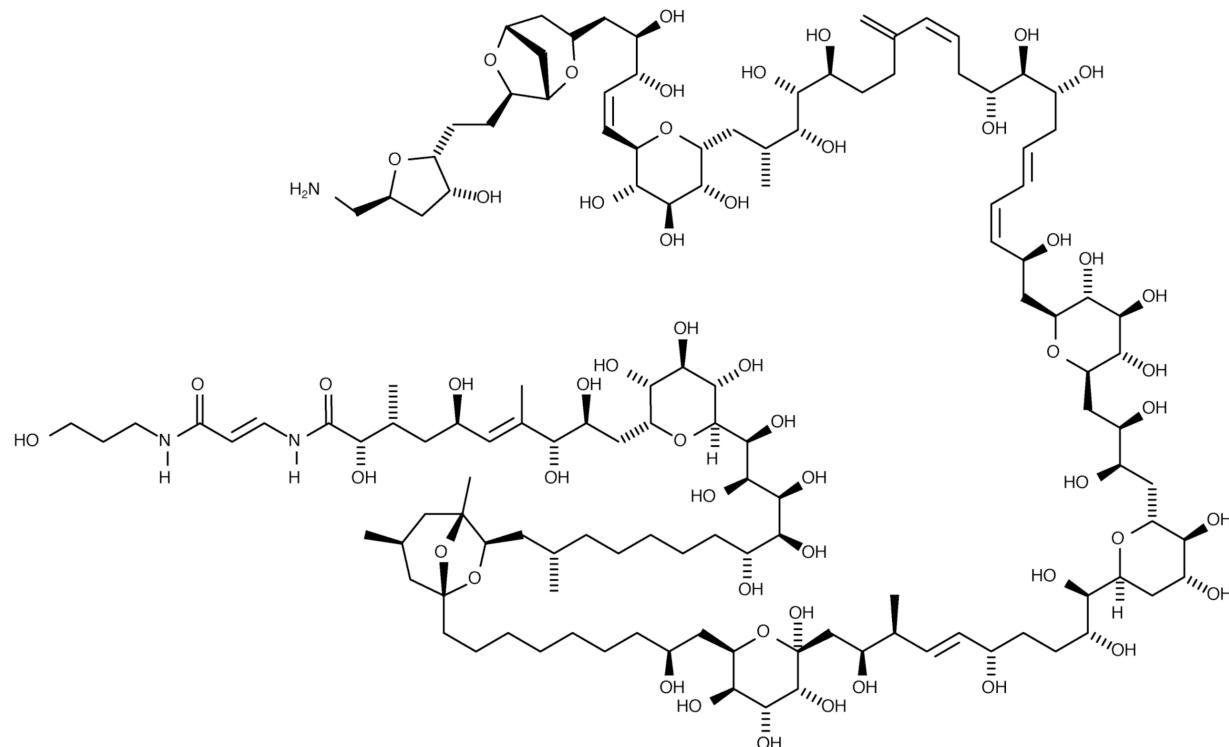
- In what other ways do functional groups play a role in classifying molecules?

Reading: Section 2.9

Functional Groups, Skeletal Structures, and Organic Reactivity

- One of the properties of alkanes is that they are generally not very reactive; conversely, any portion of a molecule that is *not* an alkane is likely to be reactive. How do skeletal structures help us to understand organic reactivity?

- Here is the skeletal structure of *palytoxin*, one of the most poisonous compounds known. It is isolated from marine coral. Palytoxin was synthesized in 1994 by a group of researchers led by Professor Yoshito Kishi here at Harvard. It is probably the most complicated organic molecule that has ever been synthesized.



Do you recognize any functional groups in palytoxin?

Can you find any portions of the structure of palytoxin that will be *unreactive*?