



# CHEMISTRY 2500

---

Topic #1: Functional Groups and Drawing Organic Molecules

Fall 2014

Dr. Susan Findlay



# Drawing Organic Molecules (Basics)

- Recall the steps for drawing Lewis structures in CHEM 1000:
  1. Determine the **connectivity** (*which atoms are connected*).
  2. Determine the total number of valence electrons.
  3. Use one pair of electrons to make a single bond between each pair of bonded atoms.
  4. Use any remaining electrons as lone pairs around each terminal atom (except H) so that each terminal atom has a complete octet, if possible.
  5. Place any excess electrons around the central atom.
  6. Check the central atom to see if it has a complete octet.
  7. If the central atom has too few electrons, increase the **bond order** of one or more bonds by sharing non-bonded electrons.  
(*In other words, make double or triple bonds as necessary*)
  8. Calculate **formal charge** for all atoms, and indicate any which are not zero.
$$Q_f(X) = e_{\text{valence}} - \left[ e_{\text{nonbonding}} + \frac{1}{2} e_{\text{bonding}} \right]$$
  9. Check the structure when finished to check that you used the correct number of atoms/electrons and did not violate octet rule (unless the atom is an acceptable octet-rule-violator).



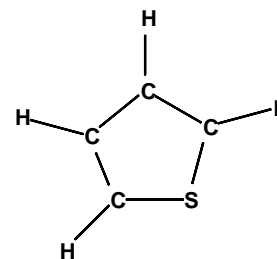
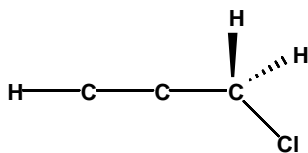
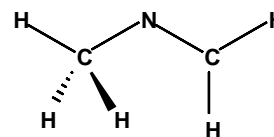
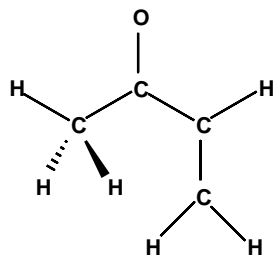
# Drawing Organic Molecules (Basics)

---

- Because we are dealing with organic molecules only, we can add a few more generalizations:
  - Learn how many bonds each type of atom makes when neutral:
    - 4 bonds to C (and Si); 0 lone pairs
    - 3 bonds to N (and P); 1 lone pair
    - 2 bonds to O (and S); 2 lone pairs
    - 1 bond to any halogen; 3 lone pairs
    - 1 bond to hydrogen; 0 lone pairs
  - Minimize formal charge. If there must be charge,
    - No charges larger than +1 or -1 on atoms from periods 1 or 2
    - No charges on carbon if the overall molecule is neutral
    - Don't put like charges on adjacent atoms (no ++ or --)
    - Put negative charges on more electronegative atoms
    - Put positive charges on less electronegative atoms
  - Avoid O-O bonds if possible. Also, avoid halogen-heteroatom bonds (where a **heteroatom** is any atom other than C or H).

# Drawing Organic Molecules (Basics)

- Use the guidelines on the previous two pages to build Lewis structures from the following skeletons (showing connectivity):



*Note that these skeletons show the approximate geometries of the molecules. In this course, it is required that structures show relatively accurate geometries. No right angles! More on this later...*



# Drawing Organic Molecules (Basics)

---

- In many cases the connectivity will be implied by the way in which a molecular formula is written. You won't see formulas like  $C_5H_{12}O$  very often in this course. There is much more information conveyed by either drawing the structure or writing a **condensed structure**. e.g.  $CH_3CH_2CH(OH)CH_2CH_3$
  
- Draw Lewis structures for the following molecules/ions:  
 $CH_3CN$              $CH_2O$              $CF_3CO_2H$              $(H_3CO)_2CH^+$

*In this course, you must always show all lone pairs!*



# Drawing Organic Molecules (Basics)

---

- Recall from CHEM 2000 that there are essentially three different ways to draw organic molecules:
  - Structural formula (essentially the same as Lewis structure)
  - Condensed structure (as shown on the previous page)
  - Line-bond structure (where carbon atoms are not explicitly shown nor are hydrogen atoms attached to them; other hydrogen atoms are still shown as are all heteroatoms).
- Structural formulas and line-bond structures are preferred because they show geometry as well as connectivity. Line-bond structures tend to be used for larger molecules while structural formulas are good for smaller molecules.



# Drawing Organic Molecules (Basics)

---

- There will be times where it is appropriate to combine methods. If we are discussing a reaction of a large molecule, for example, we may draw most of it in line-bond but draw the reacting part as a structural formula so that we can see exactly what is happening to the key atoms.

**Note that, as soon as you explicitly draw a carbon atom, you MUST draw all atoms attached to it!!!!!!!!!!**



# Drawing Organic Molecules (Basics)

---

- Whichever method you choose for drawing an organic molecule, remember to draw it such that you are showing relatively accurate bond angles:

- 180° for linear geometry

NOT

- 120° for trigonal planar geometry

NOT

- 109.5° for tetrahedral geometry (this means showing 3-D!)

NOT

*Marks will be deducted for poorly drawn structures (like those in the "NOT" examples). We will not, however, pull out a protractor to confirm whether an angle is 115° or 120°.*





# Drawing Organic Molecules (Basics)

---

- Drawing a molecule containing tetrahedral atoms:
  - Start by drawing the central atom (usually C) and two substituents in the plane of the page:
  - Next, use a wedge ( $\blacktriangleleft$ ) to represent a substituent which is coming out of the plane of the page toward you and a hashed wedge ( $\text{-----}$ ) to represent an atom or group which is going behind the plane of the page away from you:
  - Keep as many atoms in the plane of the page as possible:



# Drawing Organic Molecules (Basics)

---

- These rules apply to trigonal pyramidal atoms too. It is easiest to have the lone pair in the plane of the page:
  
- If a substituent has tetrahedral atoms within it, it is not necessary to show those in 3D as well since that will usually make the structure difficult to read.

NOT



# Drawing Organic Molecules (Basics)

---

- As you draw organic molecules, you'll notice that certain arrangements of atoms are fairly common. These are typically referred to as the **functional groups**.
- A functional group is a reactive center. It contains:
  - a **heteroatom** (atom other than C or H; usually N, O or S) and/or
  - a **multiple bond** (double or triple)
- So, essentially what we're looking for are:
  - polar bonds
  - lone pairs
  - $\pi$  bonds

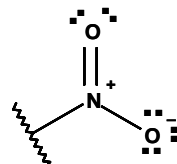
which makes sense since these are the reactive parts of organic molecules. *Note that this makes alkanes "organic compounds without functional groups" since they contain only C-H and C-C single bonds.*

# Functional Groups

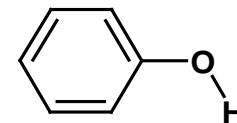
- Functional groups with carbon-carbon multiple bonds:
  - Alkene (contains C=C)
  - Alkyne (contains C≡C)
  - Arene (contains 6 atoms in a ring with 3  $\pi$  bonds):\*



- Functional groups with single bonds to N or O:
  - Amine (contains C–N where C is tetrahedral)
  - Nitro (contains C–NO<sub>2</sub>):



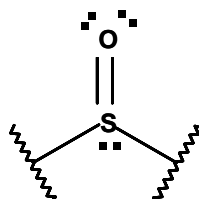
- Ether (contains C–O–C)
- Alcohol (contains C–O–H)
- Phenol (contains C–O–H where C is part of benzene):



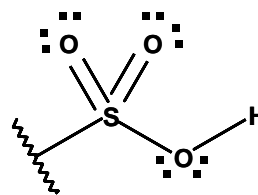
\*This definition expands when we get to the "aromaticity" section.

# Functional Groups

- Functional groups with single bonds to S:
  - Thiol (contains C–S–H)
  - Sulfide (contains C–S–C)
  - Disulfide (contains C–S–S–C)
  
  - Sulfoxide (contains C–S(O)–C)
  - Sulfonic acid (contains C–SO<sub>3</sub>H)



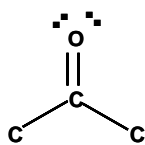
sulfoxide



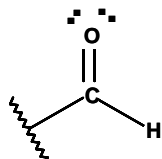
sulfonic acid

# Functional Groups

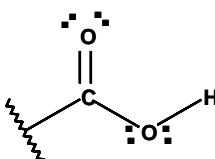
- Functional groups with multiple bonds to N:
  - Nitrile (contains  $C\equiv N$ )
- Functional groups with multiple bonds to O:
  - Ketone (contains  $C=O$  with two C attached)
  - Aldehyde (contains  $C=O$  with H attached)
  - Carboxylic Acid (contains  $C=O$  with OH attached)
  - Ester (contains  $C=O$  with O-C attached)
  - Amide (contains  $C=O$  with N attached)
  - Acid Chloride (contains  $C=O$  with Cl attached)



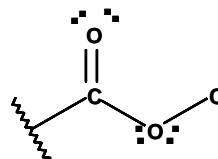
ketone



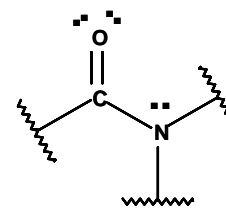
aldehyde



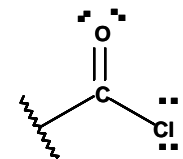
carboxylic acid



ester



amide



acid chloride

- Because it's an important part of so many functional groups,  **$C=O$**  has a special name. It's called a **carbonyl**.



# Drawing Organic Molecules (Resonance)

---

- Recall from CHEM 1000 that it is sometimes possible to draw more than one good structure for a molecule. These alternate structures are referred to as **resonance structures**, and the true molecule exists as a weighted average of the different resonance structures; it *\*does not\** 'bounce back and forth' between them. It is, however, easier for us to draw the different resonance structures rather than attempting to draw **delocalized electrons**.
- We use double-headed arrows to indicate that two structures are resonance structures, and we can use "curly arrows" to show which electrons are delocalized over the two pictures:



# Drawing Organic Molecules (Resonance)

---

- Guidelines for drawing resonance structures:
  - No atoms move! Ever!
  - Only pi electrons can be delocalized, so the only electrons that 'move' between resonance structures will be one pair from a multiple bond and/or lone pairs.
  - Only move electrons to an adjacent position. Options include:
    - Move a lone pair to make a bond to that atom:
    - Move electrons in a pi bond to a lone pair on one of the two bonded atoms:
    - Move electrons in a pi bond to a different pi bond involving one common atom:





# Drawing Organic Molecules (Resonance)

---

- You may move multiple electron pairs at once as long as all guidelines are followed for each:
  
- Resonance structures that look as though the molecule was simply picked up and spun around are referred to as **degenerate**. Since they must be equally good resonance structures, they contribute equally to the averaged overall structure.



# Drawing Organic Molecules (Resonance)

---

- When resonance structures are not degenerate, they do not usually contribute equally to the averaged overall structure. The structure which contributes more will be the better resonance structure (the one which appears more stable). Consider the following factors:
  - Resonance structures in which all second period atoms have complete octets are favoured over those with electron-deficient second period atoms:
  - Resonance structures with fewer formal charges are favoured:
  - If there are the same number of formal charges, resonance structures putting negative charges on more electronegative atoms are favoured:



# Drawing Organic Molecules (Resonance)

---

- How to earn a mark of ZERO on your resonance structure:
  - Have more than eight electrons on a second period atom:
  - Have less than eight electrons on O or N (or a halogen):
  - Have formal charges on more atoms than are necessary (usually means formal charge on more than one atom):
  - Have a second period atom with formal charge greater than +1 or -1:



# Drawing Organic Molecules (Resonance)

---

- Draw all valid resonance structures for each of the following molecules. In cases where they are not degenerate, indicate which is the best resonance structure (contributes most to the overall average molecule or ion).

