Bonding and Structure of Organic Molecules

Suggested Reading
- Review general chemistry textbook as needed
- Brown and Foote (5th edition), Chapter 1: Sections 1–3 and 5
- Klein (2nd edition), Chapter 1: Sections 5 and 6

Lecture Supplement Handouts *From lecture; also available at course web site*
Bonding and Structure of Organic Molecules

Optional Web Site Reading
More on Lewis Structures (www.towson.edu/~ladon/lewis.html)

Suggested Text Exercises
- Brown and Foote (5th edition), Chapter 1: 1–12, 14, 20–37, 41–50, and 64–66
- Klein (2nd edition), Chapter 1: 33–68

Related Tutorials (web.chem.ucla.edu/~harding/tutorials/tutorials.html)
- Drawing Lewis Dot Structures
- Formal Charge
- Curved Arrows
- Molecular Model Kit

Common Questions About Organic Chemistry Problems

I don't have time to do all these problems! There are many problems available to enhance your understanding of organic chemistry, including the Concept Focus Questions (CFQ; in this Thinkbook), the Practice Problems (PP; also in this Thinkbook), as well as suggested problems from the text and other sources. Working all these problems can be time-consuming, *but this task is essential to your understanding of the course material*. **Rarely do students who skimp on problem solving get good grades.** Most students who study a topic for the first time really do need to work all the problems. Problem solving is an excellent way to reinforce the concepts in your mind. If you can honestly say to yourself that you have a firm grasp on the concept, then feel free to skip the problem. On the other hand if you are not 100% sure, then work the problem. Even students who have a firm conceptual grasp should work a few "obvious" problems every now and then to stay sharp.

Which problems are most important? Here is a suggested order of priority:

1. CFQ: Always read these *before* lecture, and then again when you study the textbook. They outline the fundamental concepts presented in lecture, and are the most important problems in this course.

2. OWLS and PP: Written by the same person who writes the exams. OWLS problems are designed to stimulate discussion during discussion section meetings.

3. All other problems, including the optional ones: Different students get the most out of different problem sources, although most students seem to get more out of the textbook problems than from the other sources. *Organic Chemistry as a Second Language* and the course web site tutorials focus on specific topics, and should be examined if you are having trouble with these specific topics.

Wikipedia: Another Good Organic Chemistry Learning Tool

The Wikipedia (www.wikipedia.org) is a huge online encyclopedia of knowledge created and updated by thousands of people all over the world (including college students). It does contain a few errors here and there, and shouldn't be used as the only source of information for a research paper, but it is a great place to start learning about a topic.

Concept Focus Questions

1. Provide precise yet concise definitions for the following terms:
   (a) δ^- (d) Electronegativity (g) Lone pair
   (b) δ^+ (e) Formal charge (h) Orbital
   (c) Covalent bond (f) Functional group (i) Polar covalent bond

2. Draw the Lewis dot structure for CH_3OH.

3. How does electronegativity influence electron distribution within bonds? Illustrate with CH_3OH as an example.

4. Why are functional groups important to a systematic study of organic chemistry?

5. Prepare a functional group list that includes the name and basic structure of each functional group, as well as an example molecule that contains exactly six carbons. Include all lone pairs and formal charges. *Try to avoid using the same example molecules as given in the lecture supplement*.

Concept Focus Questions Solutions

1. Illustrated definitions can be found at the Illustrated Glossary of Organic Chemistry available at the course web site.

   (a) δ^-: An atom that bears this symbol has a slight electron excess, but not enough to give it a full negative formal charge.

   (b) δ^+: An atom that bears this symbol has a slight electron deficiency, but not enough to give it a full positive formal charge.

   (c) Covalent bond: A chemical bond formed between two atoms by orbital overlap and sharing of an electron pair.

(d) Electronegativity: The measure of an atom's attraction for electrons in a chemical bond.

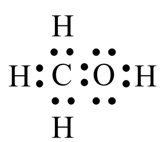
(e) Formal charge: The charge on an atom in a Lewis structure if the bonding was perfectly covalent and the atom has exactly a half-share of the bonding electrons.

(f) Functional group: A group of atoms whose bonding is the same from molecule to molecules.

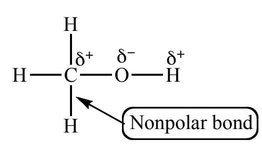
(g) Lone pair: A pair of electrons assigned to just one atom. Also called a nonbonded pair.

(h) Orbital: The mathematical description of a volume of space in which there is a certain probability of finding an electron of a certain energy.

(i) Polar covalent bond: A covalent bond between two atoms of different electronegativity, resulting in an uneven sharing of the bonding electron pair.

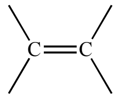
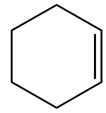
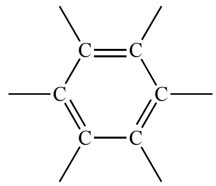
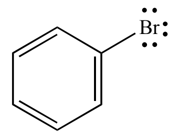
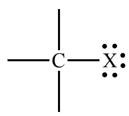
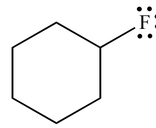
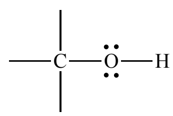
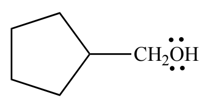
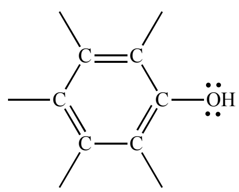
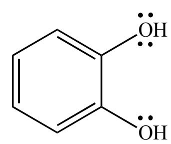
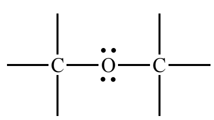
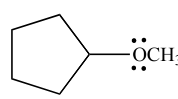
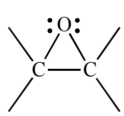
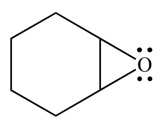
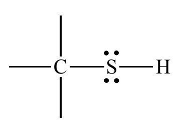
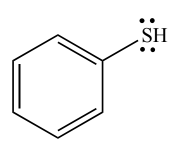
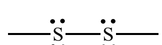
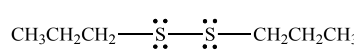
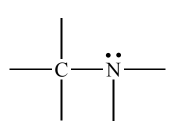
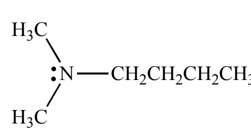
2. 

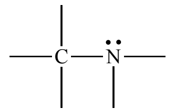
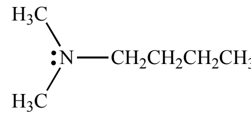
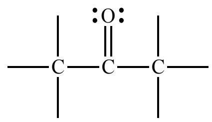
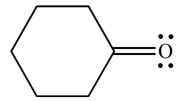
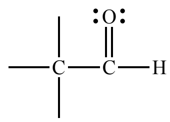
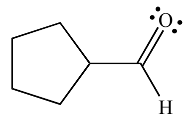
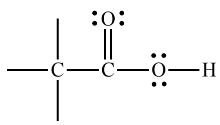
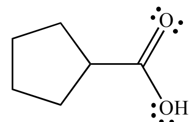
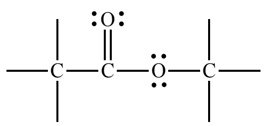
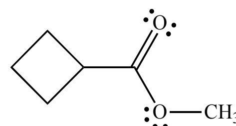
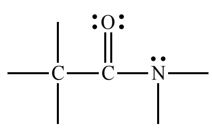
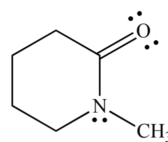
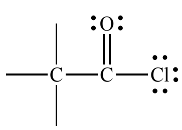
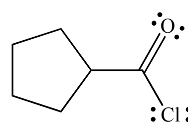
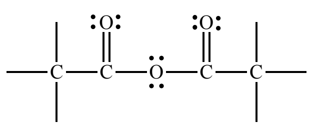
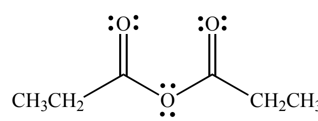
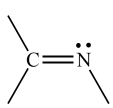
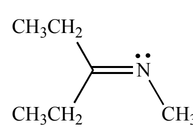
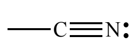
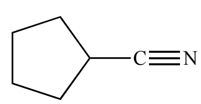
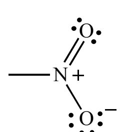
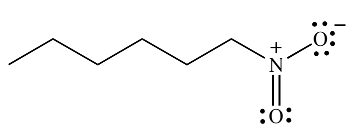
3. The distribution of bonding electron density is influenced by the electronegativity of the atoms that comprise the bond. A more electronegative atom attracts more electron density toward itself. Thus, end of the bond with the more electronegative atom will have a small negative charge (δ^-). The less electronegative atom loses electron density, as so has a small positive charge (δ^+). In the C–O bond, carbon is less electronegative than oxygen, so the carbon has a δ^+ charge and the oxygen atom has a δ^- charge. The reasoning applies to the O–H and C–H bonds. The combination of short bond length and low electronegativity difference causes C–H bonds to be nonpolar.



4. A functional group is a set of atoms, bonded together, that gives a molecule particular chemical and physical properties. Because chemical reactions involve changes in electron distribution and bonds, functional groups with similar electronic structures will react in similar ways. This is just one reason why the study of functional groups is so critical to a systematic study of organic chemistry.

5.

Name	Generic Structure	Example
Alkene		
Alkyne	$—C\equiv C—$	$CH_3CH_2CH_2—C\equiv C—CH_3$
Benzene ring		
Alkyl halide	 X = F, Cl, Br, or I	
Alcohol		
Phenol		
Ether		
Epoxide		
Thiol		
Disulfide		
Amine		

Name	Generic Structure	Example
Amine		
Ketone		
Aldehyde		
Carboxylic acid		
Ester		
Amide		
Acid chloride		
Acid anhydride		
Imine		
Nitrile		
Nitro		

Be prepared to name or draw functional groups, but you do not memorize specific examples of molecule that contain functional groups.

OWLS Problems

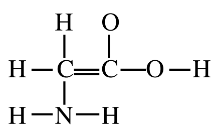
Solutions to OWLS problem sets are posted on the course web site approximately one week after the material is covered in lecture.

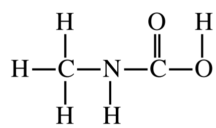
In this problem set you will explore the structure of glycine, the simplest amino acid. Amino acids are the small molecules that are the basic building blocks of proteins. In aqueous solution neutral amino acids exist in equilibrium with their zwitterionic isomers. An incomplete representation of this equilibrium is shown.

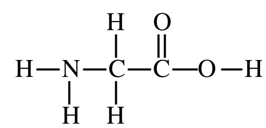
$$H_2NCH_2COOH \rightleftharpoons H_3NCH_2CO_2$$

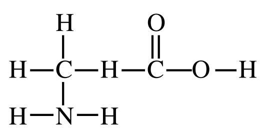
Neutral form — Zwitterionic form

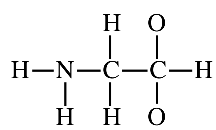
1. Select the structure for glycine. Explain why the others were eliminated.

(a) 

(c) 

(e) 

(b) 

(d) 

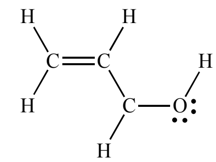
2. Complete the bond-line structure selected in the previous question by including all lone pairs. Assume all of atoms carry a formal charge of zero.

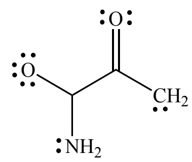
3. “Zwitterion” means “hybrid ion.” Verify the ionic nature of zwitterionic glycine by drawing its bond-line structure (it will be very similar to your answer to question 1), adding lone pairs, and calculating all formal charges.

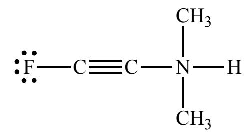
4. Functional groups are the centers of reactivity in organic molecules. Their systematic study essentially eliminates the need for extensive memorization of organic reactions. Therefore it is critical that you learn to rapidly identify and draw functional groups.
   (a) Using the best structure selected in problem 1, label the functional groups of glycine.
   (b) Draw an isomer of glycine containing two functional groups not mentioned in problem 4(a). Label these functional groups.

Practice Problems

1. Complete the following drawings by adding correct formal charges.

(a) 

(b) 

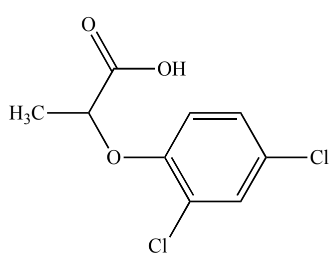
(c) 

2. For the molecules in question 1, add or subtract hydrogens so that each atom has a formal charge of zero. Do change any atoms other than hydrogen.

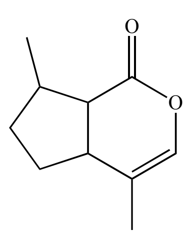
3. For each structure in question 1, rank the atoms in order of decreasing electronegativity. Include the electronegativity values.

4. Sulfuric acid (H_2SO_4) is a common reactant in organic chemical reactions. Draw a Lewis structure for sulfuric acid. Briefly describe how the polarity of a chemical bond is estimated by using only the Lewis structure of a molecule. Illustrate your answer with the S–O bond in sulfuric acid.

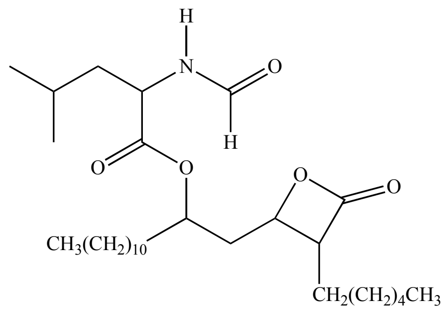
5. For each of the following molecules:
   (a) Write the chemical formula (i.e., $C_6H_{12}O_6$).
   (b) Label the most polar bond (i.e., largest δ^- and δ^+ charges).
   (c) Label all functional groups.



2,4-DP, a herbicide (a chemical used to kill plants).



Nepetalactone, the active component of catnip.

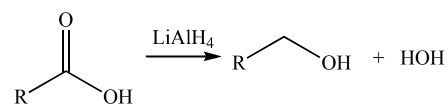


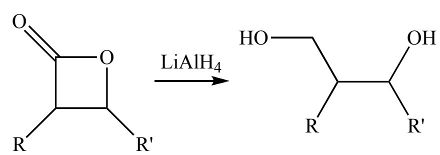
Xenical (orlistat), a weight loss drug that work by irreversibly blocking stomach and intestinal enzymes involved in fat metabolism.

6. Draw a single molecule that contains the listed functional groups. Do not use any abbreviations such as R or X, and do not include any functional groups not listed. Label the functional groups in your example molecules. Include all lone pairs.
   (a) Ester, amide, and alcohol
   (b) Carboxylic acid, alkene, benzene ring, and ether
   (c) Alkyl chloride, nitrile, ketone, and aldehyde

7. Why do we expect many similarities in chemical and physical properties of alcohols and water?

8. A carboxylic acid reacts with $LiAlH_4$ to form a primary alcohol. We can therefore conclude that the four-membered ring of Xenical (question 5), which contains a functional group called a lactone, reacts in a similar manner. Briefly explain why we can make this conclusion.

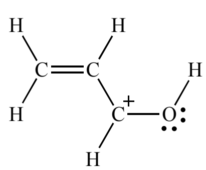
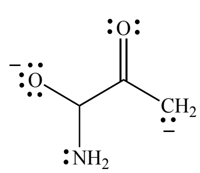
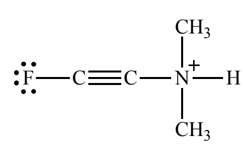
Carboxylic acid reaction: 

Lactone reaction: 

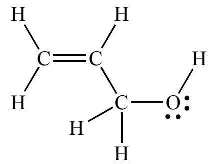
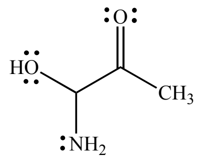
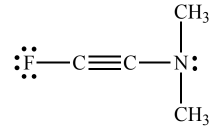
9. Which two of the following three functional groups has the most similar chemistry: ester, amide, and alcohol? Briefly explain.

Practice Problems Solutions

1. Formal charges of zero are usually not written.

(a)  (b)  (c) 

If this problem was not easy, you should review the formal charge tutorial available in the Tutorials section of the course web site.

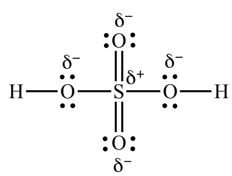
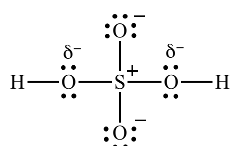
2. (a)  (b)  (c) 

3. (a) O (EN 3.5) > C (EN 2.5) > H (EN 2.1)

   (b) O (EN 3.5) > N (EN 3.0) > C (EN 2.5) > H (EN 2.1)

   (c) F (EN 4.0) > N (EN 3.0) > C (EN 2.5) > H (EN 2.1)

4. Any legitimate Lewis structure for sulfuric acid is acceptable in this case. Formal charges are considered a part of any Lewis structure, and must be included as well. Bond polarity is a result of uneven distribution of the electron density within a covalent bond. This is analyzed by considering the electronegativities of the bonded atoms. Oxygen (EN 3.5) is more electronegative than sulfur (EN 2.5), so the bonding electron density is shifted a bit toward the oxygen. The slight negative charge that results on oxygen is designated with the δ^- symbol. Sulfur is on the losing end of the unequal sulfur-oxygen bond electron sharing, so sulfur is a bit electron deficient. This slight positive charge on sulfur is indicated by the δ^+ symbol.

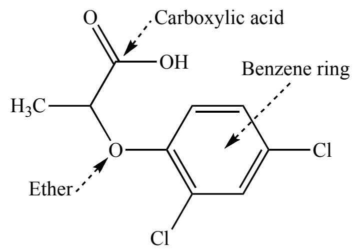
    or 

   When the atom already has a formal charge, it is not necessary to show δ^+ or δ^- charges on that atom. This is illustrated in the second Lewis structure shown above.

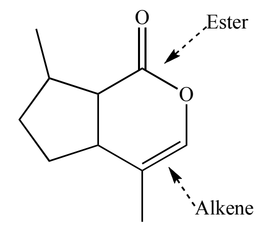
5. In the chemical formula of an organic molecule, we write the number of carbons, the number hydrogens, and then the numbers of all remaining elements in alphabetical order.

   The most polar bond has the largest electronegativity difference between its atoms.

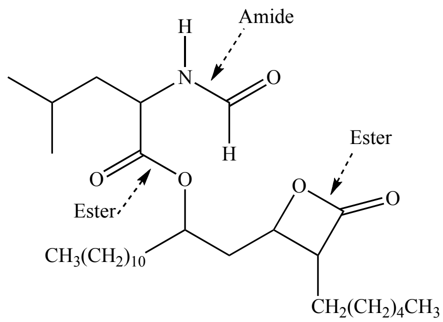
   Remember that we do not say that a more complex functional group contains a simpler functional group. For example a benzene ring does not contain an alkene, an ester does not contain an ether, and a carboxylic acid does not contain an alcohol.



2,4-DP
Formula: $C_9H_8Cl_2O_3$
Most polar bond: O–H



Nepetalactone
Formula: $C_{10}H_{14}O_2$
Most polar bond: C–O (C=O is shorter and therefore predicted to be less polar than C–O.)

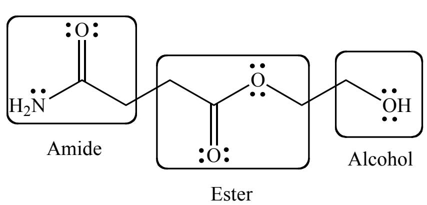


Xenical
Formula: $C_{29}H_{53}NO_5$
Most polar bond: C–O

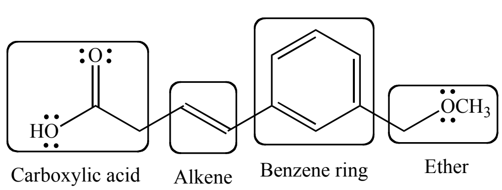
6. There are an infinite number of acceptable answers, as long as they contain the required functional groups and no extraneous functional groups.

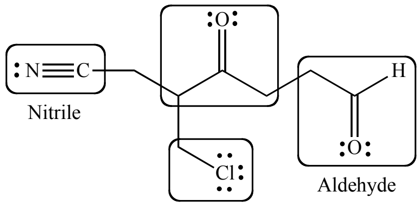
   Students often ask if functional groups can share atoms. They can in some circumstances and not in others. The exact rules are a bit complex for Chem 30A, so when in doubt, avoid this conundrum by inserting one or more non-functional group carbons between the functional groups in question.

(a)



(b)



(c) 

7. Bond properties (strength, polarity, etc.) are the basis of physical and chemical properties. Water (H–O–H) and alcohols (C–O–H) both have O–H bonds, so we expect their chemical and physical properties that arise from O–H bonds to be somewhat similar. There will be some differences as well, because (among other things) water lacks the C–O bond present in alcohols.

   In general, similar functional groups impart similar properties.

8. The carboxylic acid and lactone functional groups both have a carbonyl group attached to an oxygen atom, so they are similar (but not identical) functional groups. Because bonding arrangements in functional groups control chemical reactions (such as reduction with $LiAlH_4$ shown in this problem), similar functional groups react in similar ways. Thus, because the carboxylic acid and lactone functional groups are similar in structure we expect them to undergo similar reactions.

9. Chemical reactions are controlled by the electronic and atomic structure of the functional groups. Therefore functional groups with similar electronic and atomic structure are expected to react in a similar fashion. The functional group that is most similar to an ester in this case is the amide.