**CHE 2060: Homework set 2**

Use hex or graph paper for HW assignments. Do not answer problems on these pages.

When drawing structures, be sure to show all lone pairs.

*Note: In questions involving drawing resonance contributors, assume that all second-row*

*atoms should have a complete octet in all structures with the exception of positively charged*

*carbons.*

**2.1: Covalent bonding in organic molecules**

**1.** Rank the bonds a-f below according to increasing bond length.



**2.** For each of the bonds indicated by arrows b-f in the figures below, describe the bonding picture. An example is given for bond 'a'.

Note that for a double bond (bond 'c'), you will need to describe two bonds.

Note: you are being asked to describe the bonding picture for one specific resonance contributor.

*bond a: "this is a π bond formed by the overlap of an sp3 orbital on one carbon and an sp2*

*orbital on another carbon."*



**3.** Below is the structure of the cholesterol-lowering drug Lovastatin. For bonds a, b, c, ad d: (1) Describe hybridization of the atoms in the bond; and (2) predict the trend in bond length.



**4.** Draw a 3D-accurate picture showing the orbitals involved in bonding for dimethyl ether (CH3OCH3).

* Draw all bonds, both σ and π, as overlapping orbitals.
* Indicate whether each orbital is s, p, sp, sp2, or sp3, and indicate (with words or a color scheme) orbitals that are pointed into or out of the plane of the page.
* Locate all lone pairs in their appropriate orbitals.

An example is provided for ethene, CH2CH2:



**5.** For the bonds labeled a-f below, describe the orbitals involved in the bonds indicated by the arrows.



**2.2: Molecular orbital theory**

**6.** Identify any isolated alkene groups in the PAC-1 structure, and in the genipin structure.



**7.** Imagine that you hear a description of the bonding in water as being derived directly from the atomic orbital theory, without use of the hybrid orbital concept. In other words, the two bonds would be formed by the overlap of the half-filled 2py and 2pz orbitals of oxygen with the 1s orbitals of hydrogen, while the two lone pairs on oxygen would occupy the 2s and 2px orbitals. What is wrong with this picture? How would the bonding geometry differ from what is actually observed for water?

**8.** Draw a picture showing the geometry of the overlapping orbitals that form the bonding network in allene, H2CCCH2. Then, draw a Lewis structure for the molecule, using the solid/dash wedge bond convention as necessary to indicate the correct geometry of the π bonds.

**9.** Below is the structure of ropinerol, a drug made by GlaxoSmithKline for the treatment of Parkinson's disease. Is the five-membered ring part of the aromatic system?

Explain your answer.



**10.** Classify each of the molecules/ions below as aromatic or not aromatic. Explain your reasoning.



**2.3: Resonance**

**11.** Resonance contributors:

(a) Draw curved arrows showing how each of the resonance contributors on the left could be converted to the one on the right.

(b) Label contributors as major, minor, or approximately equivalent to each other.



**12.** Neither of the pairs of structures below are pairs of resonance contributors.

(a) Explain why not.

(b) What in fact is the relationship between them?



**13.** Below is the structure of Rimonabant, a drug candidate which is being tested as a possible treatment for alcohol/tobacco dependence and obesity (see Chemical and Engineering News, October 15, 2006, p. 24). Draw minor resonance contributors in which:

(a) there is a separation of charge between the nitrogen indicated by the arrow and the oxygen.

(b) there is a separation of charge between a chlorine (positive) and one of the three nitrogens.



**14.** For the molecules below, draw minor resonance contributors in which formal charges are placed on the atoms indicated by arrows. Use curved arrows to show how you are rearranging electrons between resonance contributors.



**15.** The human brain contains naturally occurring cannabinoid compounds which are related in structure to Δ9-tetrahydrocannabinol, the active compound in cannabis. Cannabinoids are thought to exert an antidepressant effect. Researchers at the University of California, Irvine are studying synthetic compounds, such as the one shown below, which inhibit the degradation of natural cannabinoids in the brain. This compound has been shown to have antidepressant-like effects in rats and mice. (Chemical and Engineering News, December 19, 2005, p. 47; Proc. Natl. Acad. Sci. USA 2005, 102, 18620.)



Several minor resonance contributors can be drawn in which the oxygen atom indicated by an arrow bears a positive formal charge. Indicate atoms where a corresponding negative formal charge could be located in these contributors.

**16.** For each of the compounds below, several minor resonance contributors can be drawn in which the atom indicated by an arrow bears a positive formal charge. Circle all atoms which could bear the corresponding negative formal charge.



**2.4: Non-covalent interactions**

**17.** Intermolecular forces: For a-c below, you may want to review amino acid/protein structure basics in section 1.3D and Table 5 at the end of the book. Use abbreviations as appropriate to focus the viewer's attention on the interaction in question.

(a) Which of the 20 natural amino acids have side chains capable of forming hydrogen bonds with water?

(b) Draw a picture of a hydrogen bond in a protein between an alanine main chain nitrogen and a glutamate side chain.

(c) Draw a picture of a hydrogen bond in a protein between a tyrosine main chain (acting as donor) and a threonine side chain (acting as acceptor).

(d) Draw a picture of a charge-charge (ionic) interaction in a protein between an aspartate and a lysine.

**18.** In properly folded protein structures, main chain nitrogens often participate in hydrogen bonding interactions in the role of donor, but rarely as acceptor. Speculate as to why this might be so, using what you have learned in this chapter.

**2.5: Physical properties of organic compounds**

**19.** In problem **1.10**, you were asked to draw four different amides with molecular formula C3H7NO. One of these constitutional isomers is significantly less soluble in water than the other three. Which one, and why?

**20.** For each pair of molecules below, choose the one that is more water-soluble, and explain your choice.



**21.** Give the expected trend (lowest to highest) in boiling points for the following series of compounds.

