Name: ________________________________

Chemistry 122-04 -- General Chemistry II **Spring 2006**

Test #1

1. ***The basics.*** Please answer each of the following questions as tersely as possible. Explanations are only required where explicitly requested. (2 points each unless otherwise noted)

a) Please **draw the structural formula of an organic molecule that bears an oxygen-containing functional group**. Please **indicate the name of the functional group** that appears in the structure you have just drawn.

b) **Indicate the molecular (bond) geometry around a carbon atom that is attached to an oxygen atom** in the structure you have just drawn. If there are multiple carbons attached to oxygens in your structure, please pick one and indicate it with an arrow. (If you can't think of the appropriate term to describe this geometry, you may describe it in words.)

c) Please tell me **how many π bonds and how many σ bonds** are present in your structure.

d) Indicate the kind of **orbital hybridization** you'd expect to find for the valence electrons of the carbon you chose for part (b).

e) Please tell me the **formal charge and oxidation number** of the carbon you chose for part (b).

Question #1, continued...

g) (1 pt each pair) Imagine a bond between each of the following pairs of atoms. For each pair,

- if you think that the bond will be a nonpolar covalent bond, please mark an "X" through the pair
- if you think that the bond will be a polar covalent bond, please circle the atom that will be more negatively charged
- if you think that the bond will be an ionic bond, please put a box around the atom that will form a cation

C and N S and N H and F

h) What **two characteristics** must a **molecule** posses in order to be polar?

i) According to Molecular Orbital theory, what is the **fundamental difference in electron density** between a bonding MO and an antibonding MO? (That is to say, where are the electrons concentrated in each case?)

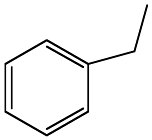
3. **Light and bonds.**

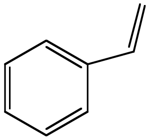
a) Please use the following MO diagrams to illustrate which of the following two molecules should have the **greater bond length**: Carbon monoxide or nitrogen monoxide. Be sure to explain your conclusion. (3 points)

Carbon monoxide		Nitrogen monoxide	
σ_{2p}*	—	σ_{2p}*	—
π_{2p}*	— —	π_{2p}*	— —
σ_{2p}	—	σ_{2p}	—
π_{2p}	— —	π_{2p}	— —
σ_{2s}*	—	σ_{2s}*	—
σ_{2s}	—	σ_{2s}	—

b) In lab last week, you measured the absorbance of light by Koolaid solutions containing the food dye Allura Red (also known as Red Dye #40). In the class session before the lab, I mentioned that the energy difference between the HOMO and the LUMO for this dye is 57 kcal/mol. Please predict the **wavelength** (in nm) **of maximal absorbance** (λ_{max})that should be observed for this molecule. Be sure to show all your calculations. (3 points)

c) Which of the following two molecules would you expect to **absorb light at a longer wavelength**? Please explain your answer briefly but carefully. (3 points)





ANSWERS

1. ***The basics.*** Please answer each of the following questions as tersely as possible. Explanations are only required where explicitly requested. (2 points each unless otherwise noted)

a) Please **draw the structural formula of an organic molecule that bears an oxygen-containing functional group**. Please **indicate the name of the functional group** that appears in the structure you have just drawn.

any alcohol, ether, ester, or carboxylic acid will do.
For example, CH_3OH, methanol, is an alcohol.

b) **Indicate the molecular (bond) geometry around a carbon atom that is attached to an oxygen atom** in the structure you have just drawn. If there are multiple carbons attached to oxygens in your structure, please pick one and indicate it with an arrow. (If you can't think of the appropriate term to describe this geometry, you may describe it in words.)

for methanol, the bond geometry around the carbon is tetrahedral

c) Please tell me **how many π bonds and how many σ bonds** are present in your structure.

methanol has five σ bonds and no π bonds

d) Indicate the kind of **orbital hybridization** you'd expect to find for the valence electrons of the carbon you chose for part (b).

for methanol, the orbital hybridization around the carbon is sp^3

e) Please tell me the **formal charge and oxidation number** of the carbon you chose for part (b).

for the carbon in methanol,
the formal charge is 4 - 4 = 0
the oxidation number is 4 - 6 = -2 (if real electronegativities are used)
[or 4-3 = +1 (if C and H are treated as equally electronegative)]

g) (1 pt each pair) Imagine a bond between each of the following pairs of atoms. For each pair,

- if you think that the bond will be a nonpolar covalent bond, please mark an "X" through the pair
- if you think that the bond will be a polar covalent bond, please circle the atom that will be more negatively charged
- if you think that the bond will be an ionic bond, please put a box around the atom that will form a cation

C and [✓ N]   S ~~and~~ N   H and [✓ F]

h) What **two characteristics** must a **molecule** posses in order to be polar?

It must have at least one polar bond, and it must be asymmetrical.

i) According to Molecular Orbital theory, what is the **fundamental difference in electron density** between a bonding MO and an antibonding MO? (That is to say, where are the electrons concentrated in each case?)

Bonding MOs have high electron density in the region between the nuclei of the atoms, thus bonding them together; Antibonding MOs have nodes -- zero electron density -- between nuclei, thus contributing nothing to the association of the atoms.

3. **Light and bonds.**

a) Please use the following MO diagrams to illustrate which of the following two molecules should have the **greater bond length**: Carbon monoxide or nitrogen monoxide. Be sure to explain your conclusion. (3 points)

Carbon monoxide (10 valence electrons)

σ_{2p}^* __

π_{2p}^* __ __

σ_{2p} _||_

π_{2p} _||_ _||_

σ_{2s}^* _||_

σ_{2s} _||_

Bond order = ½ (8-2) = 3

Nitrogen monoxide (11 valence electrons)

σ_{2p}^* __

π_{2p}^* _|_ __

σ_{2p} _||_

π_{2p} _||_ _||_

σ_{2s}^* _||_

σ_{2s} _||_

Bond order = ½ (8-3) = 2.5

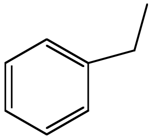
The bond in carbon monoxide is of higher order, so it is stronger and shorter than the bond in nitrogen monoxide. Nitrogen monoxide has the longer bond.

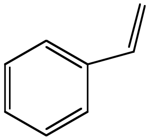
b) In lab last week, you measured the absorbance of light by Koolaid solutions containing the food dye Allura Red (also known as Red Dye #40). In the class session before the lab, I mentioned that the energy difference between the HOMO and the LUMO for this dye is 57 kcal/mol. Please predict the **wavelength** (in nm) **of maximal absorbance** (λ_{max})that should be observed for this molecule. Be sure to show all your calculations. (3 points)

57 kcal is enough energy to excite one mole of Red Dye #40. Converting to Joules and dividing by Avogadro's number shows that 3.96×10^{-19} Joules are required per molecule. This is the energy needed per photon of light.

$E = hc/\lambda$ $\lambda = hc/E = (6.63 \times 10^{-34})(3 \times 10^{8}) / (3.96 \times 10^{-19}) = 5.02 \times 10^{-7}$ m = 502 nm

c) Which of the following two molecules would you expect to **absorb light at a longer wavelength**? Please explain your answer briefly but carefully. (3 points)





The molecule on the right absorbs light of longer wavelength (248 nm) than the molecule on the left (208 nm). This is due to the higher level of conjugation in the right-hand molecule. Higher conjugation leads to greater electron delocalization, which correlates with reduced energy difference between MOs. Thus the molecule with higher conjugation should have a smaller HOMO-LUMO energy gap, and its HOMO electrons will be excited by lower energy light -- light with a longer wavelength.

1. Imagine that atoms of each of the following pairs of elements share electrons to form a bond. Please fill in the table to answer these questions:

i) Do you expect that bond to be an equal or unequal sharing?
ii) If unequal, will it be a polar covalent or an ionic bond?
iii) If unequal, which bonding partner acquires a negative charge and which a positive charge?

Bonding pair	**i -- equal sharing?**	**ii -- ionic/covalent?**	**iii -- which negative?**
C, N			
Ru, Br			
Ca, Se			
P, Cl			
C, H			
H, Cl			

4. Please briefly explain the principle you used in filling out the table in question one. Select a *new* pair of elements to illustrate and inform your argument as you discuss what would lead you to expect a pair of atoms to form an ionic, a polar covalent, and a "pure" covalent interaction.

5. Draw Lewis electron-dot structures to represent molecules with each of the indicated formulas. Then, for each, please fill in the table to indicate:
i) polarity of any one bond (choose and designate one, indicating the more negative atom)
ii) formal charges on all atoms in the structure
iii) oxidation numbers for all atoms in the structure
iv) number of electron domains around the central atom
v) electron domain geometry around the central atom (either a term or a picture will do)
vi) overall molecular geometry (either a term or a picture will do)

molecular formula	**i -- polarity**	**ii -- formal charge**	**iii -- ox #**	**iv -- # e- domains**	**v -- e- domain geometry**	**vi -- molecular geometry**
SeF_2						
SiS_2						
BH_3						
ICl_3						

7. Consider the two molecules methanol (CH_3OH) and methylamine (CH_3NH_2). Would you expect the C-O and C-N bonds, respectively, to be different in terms of polarity? length? Please justify your predictions.

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Answers:

1.

Bonding pair	**i**	**ii**	**iii**
C, N	**unequal**	**polar covalent**	**neg: N**
Ru, Br	**unequal**	**ionic**	**neg: Br**
Ca, Se	**unequal**	**ionic**	**neg: Se**
P, Cl	**unequal**	**polar covalent**	**neg: Cl**
C, H	**equal**		
H, Cl	**unequal**	**polar covalent**	**neg: Cl**

4. Key word: electronegativity.

5.

molecular formula	**i -- polarity**	**ii -- formal charge**	**iii -- ox #**	**iv -- # e- dom**	**v -- e- dom geometry**	**vi -- molecular geometry**
SeF_2	**Se-F bond is polarized towards the F**	**Se:0 F:0**	**Se:+2 F:-1**	**4**	**tetrahedral**	**bent**
SiS_2	**Si-S bond is polarized towards the S**	**Si:0 S:0**	**Si:+4 S:-2**	**2**	**linear**	**linear**
BH_3	**B-H bond is *very* slightly polarized towards the H**	**B:0 H:0**	**B:+3 H:-1**	**3**	**trigonal planar**	**trigonal planar**
ICl_3	**I-Cl bond is polarized towards the Cl**	**I:0 Cl:0**	**I:+3 Cl:-1**	**5**	**trigonal bipyramidal**	**T-shaped**

7. The actual bond lengths are: C-N, 147 pm; C-O, 142 pm.

1. ***Molecular shape.*** For each of the chemical species in the table below, please

- give the Lewis structure, including resonance forms where appropriate
- indicate the electron domain geometry in a word or two
- give a diagram of what you would expect this molecule to look like, given the the electron domain geometry around the central atom

(12 points; 2 points each box)

Molecule or ion	**Lewis structure (incl. resonance)**	**Electron domain geometry**	**Molecular shape**
$\mathbf{CF_2O}$			
$\mathbf{NO_3^-}$			

For ONE of the structures you have drawn above, **please indicate the orbital hybridization and whether you think the molecule will be polar**. (4 points)

Molecule or ion	**Orbital hybridization**	**Polar molecule?**

2. ***Behavior of Gases.***

a) Breathe in. Breathe out. A miracle of chemistry! When you breathe in, muscles in your abdomen expand your chest cavity. Because your lungs are attached to the inside of your chest, this increases the volume of your lungs. When you breathe out, the converse happens. So **why does reducing the volume of your lungs cause air to rush out?** Please explain this phenomenon, BOTH by making reference to the key macroscopic properties of gases that we have been focusing on (P, V, T, n), AND describing what is happening at the molecular level. (8 points)

4. ***Quantitative characterization of gases.*** Suppose that the gas pressure in an aerosol can is 988 torr at 17 degrees C. If the gas in the can behaves ideally and the can is accidentally left near a fire, where its temperature climbs to 500 degrees C, what would you predict to be the pressure in the can, in atmospheres? (5 points)