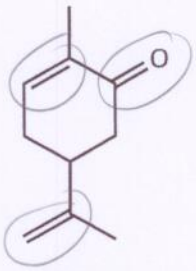
1. Carvone is a natural product found in spearmint and caraway seed. (10 points)



carvone

a. What is the *molecular formula* for carvone?

$C_{10}H_{14}O$ (4)

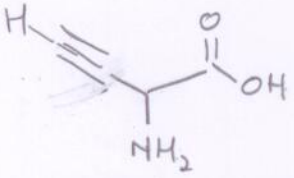
b. Name the *functional groups* found in carvone?

ketone, alkene, (alkane) (6)

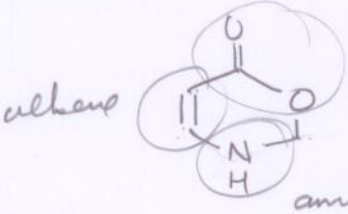
+ the "un-functional" group

2. Draw a molecule that has the molecular formula $C_4H_5NO_2$. The structure must contain only the "common" functional groups discussed in Chapter 2 (it could have more than one!) and should be shown using *bond-line* structures with lone pairs of electrons clearly shown. (10)

Also, name the *functional groups* shown in your structure. (10) (20 points)



alkyne, amine, carboxylic acid

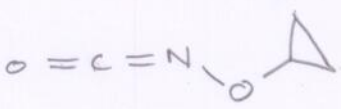


alkene ester amine

Lot's more possibilities!

EXTRA CREDIT - Write a structure for a molecule with the above molecular formula with an "uncommon" functional group – one that you likely can't name, as long as it shows all lone pairs of electrons and that doesn't break any of the rules of bonding. (10 EC points)

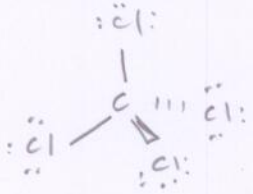
many others!



3. For the following molecules,

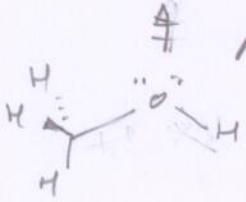
   a. Draw *bond-line* drawings that show the expected *geometry* (use dashes and wedges where necessary).
   b. Show all of the lone pairs of electrons.
   c. Indicate whether the molecule has a permanent dipole moment ($\mu \neq 0$ D), then indicate the direction of the overall dipole, or doesn't have a permanent dipole moment ($\mu = 0$ D) (15 points)

CCl_4



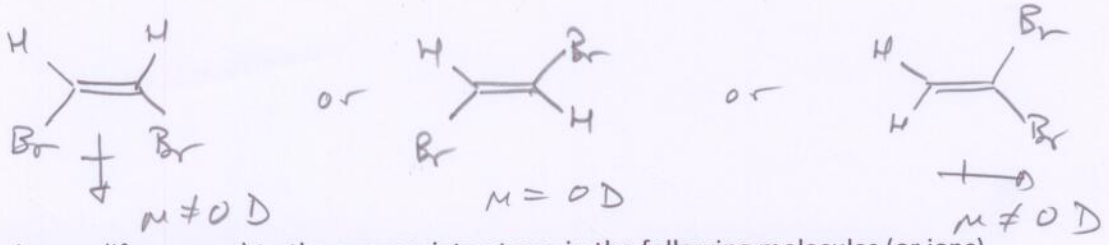
$\mu = 0$ D (5)

CH_3OH



$\mu \neq 0$ D (5)

$C_2H_2Br_2$ (there is more than one answer for this one) (5)



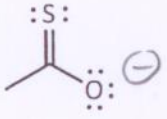
$\mu \neq 0$ D or $\mu = 0$ D or $\mu \neq 0$ D

4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

a.

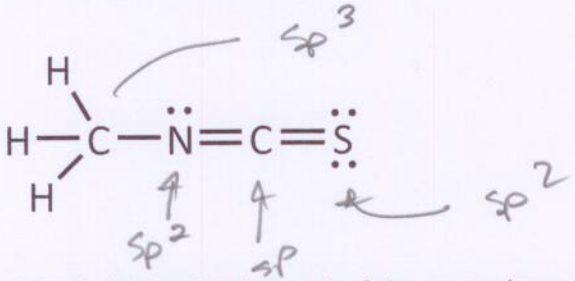
(5)

b.



(5)

5. Consider the structure shown below. (25 points)



a. Label the hybridization for each of the atoms (except hydrogen).

(10)

b. What type of atomic orbital does the lone pair on the nitrogen occupy?

sp^2 (5)

c. What is the approximate bond angle for the C-N-C bond?

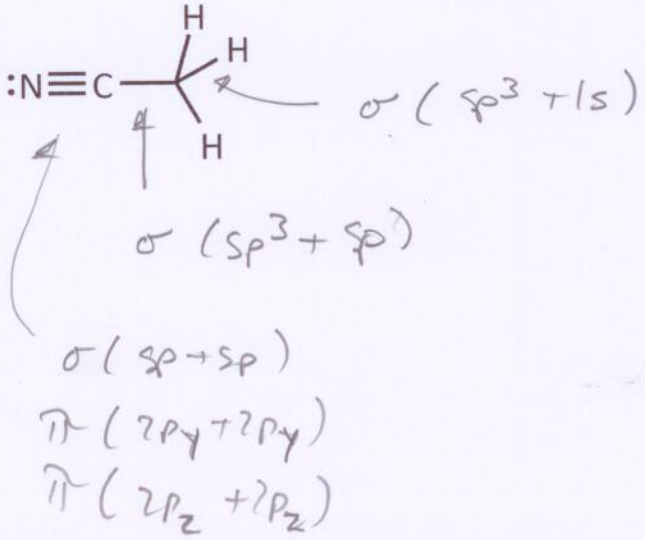
$\sim 120^0$ (5)

d. Which bond is longer, N=C or C=S? Explain.

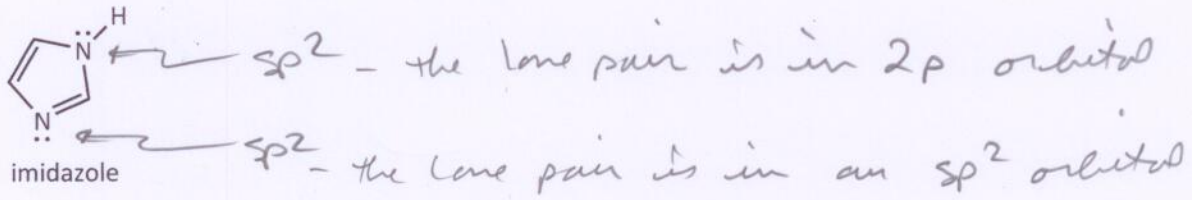
C=S is longer since S is much larger than N

(5)

6. For every bond in the molecule, indicate which *type* of bond it is and what atomic orbitals are used to form them. (15 points)

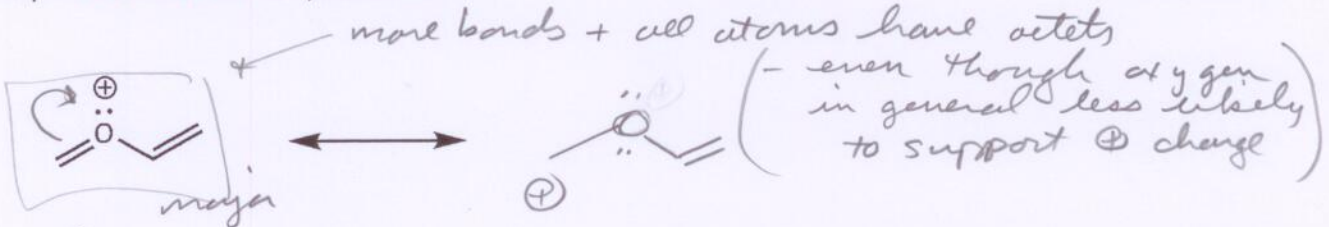


7. Imidazole is shown below. Indicate the hybridization for each of the nitrogen atoms and what type of orbital each the lone pair of electron resides in. (10 points)

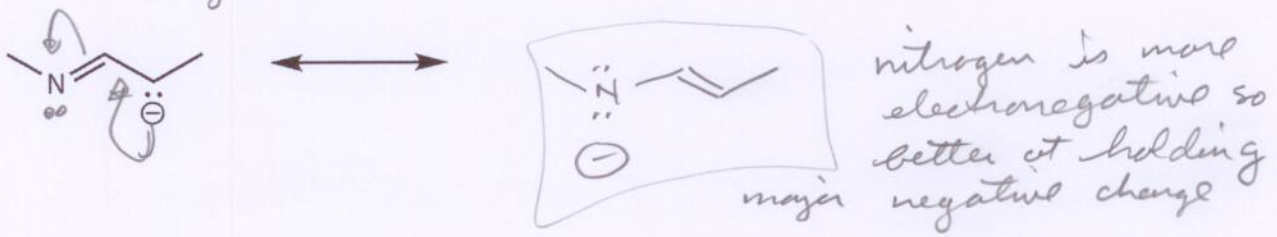


8. By "pushing" electrons, show the other resonance form for the ions shown below. Circle the *major* resonance form and provide the reason for your choice. (20 points)

a.



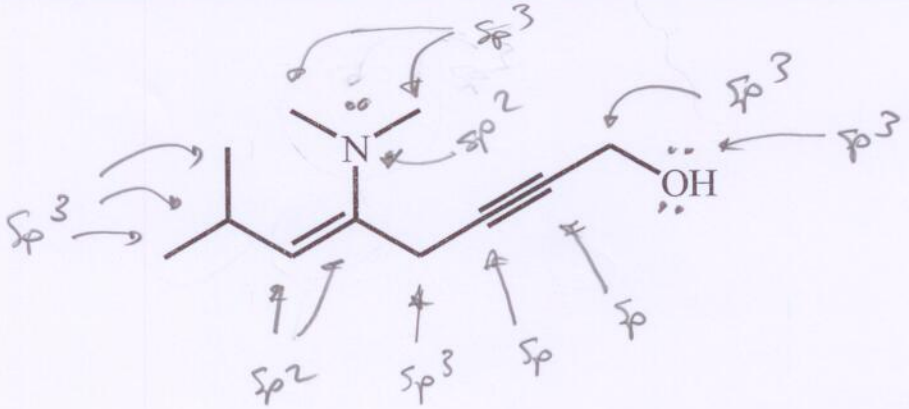
b.



9. Consider the molecule below:

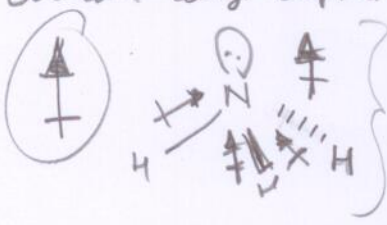
a. Add lone pairs to the structure where appropriate

b. Identify the hybridization of each atom (note there are 13 atoms that are hybridized) (26 points)



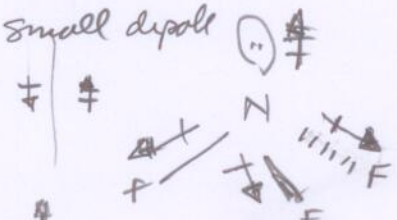
10. Ammonia (NH_3) has a dipole moment (m) of 1.42 D, whereas nitrogen trifluoride (NF_3) has a value of 0.234 D. Suggest a reason for the dramatic difference between these two otherwise similar molecules. (Hint: carefully consider the structure and geometry) (10 points)

overall large dipole



all bond dipole. + the lone pair contributes in the same direction so are additive

small dipole

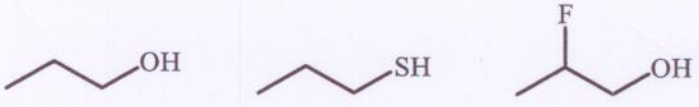


(uncertain which direction)

The three fluorine - nitrogen bond dipole add in a way to partially cancel the dipole of the lone pair

11. The pK_a values for the following compounds are 10.5, 14.4, and 16.0, *irrespectively*.

a. Assign these values to the corresponding compounds.
b. Which compound is the most acidic? (8 points)



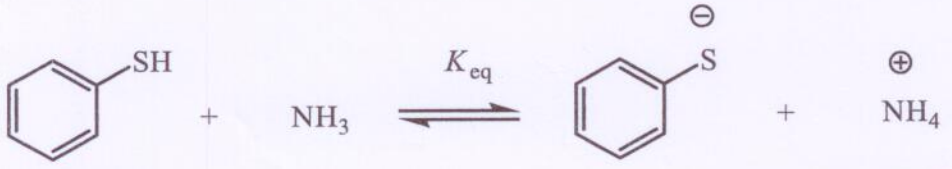
16 10.5 14.4

most acidic

(atom effect)

(inductive effect)

12. Given the pK_a data below, indicate which side of the equilibrium is favored (i.e., right or left). Also, explain why the data indicate this – be clear about this. Calculate the equilibrium constant (K_{eq}) – show your calculation. (15 points)



thiophenol
pK_a = 6.6

stronger acid than $NH_4^{\oplus}$

ammonium ion
pK_a = 9.9

weakest acid!

"Nature" favors the weakest acid

$9.9 - 6.6$

$K_{eq} = 10$

$= 10^{3.3} = 2.0 \times 10^3$

which is greater than 1 so favors the right

13. Taxol is a natural product that was first isolated from the bark of the Pacific yew tree (*Taxus brevifolia*) in 1967. In the late 1970s it was found to be a powerful anticancer agent. Indeed, the molecule is very dense with functional groups! Circle and identify as many of the common functional groups as you can (there are at least 12). (26 points)