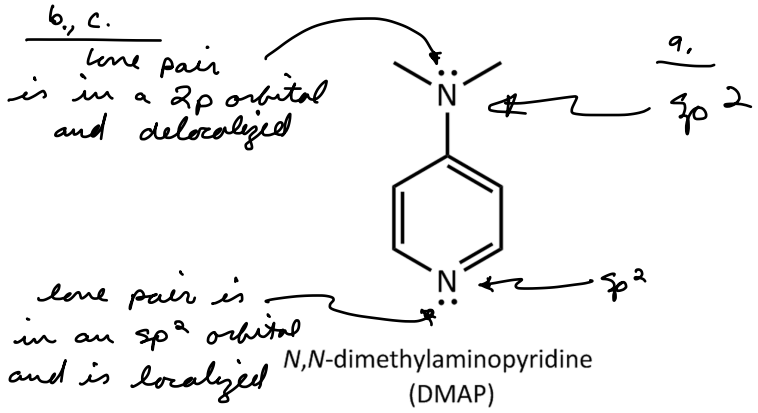
Name Key

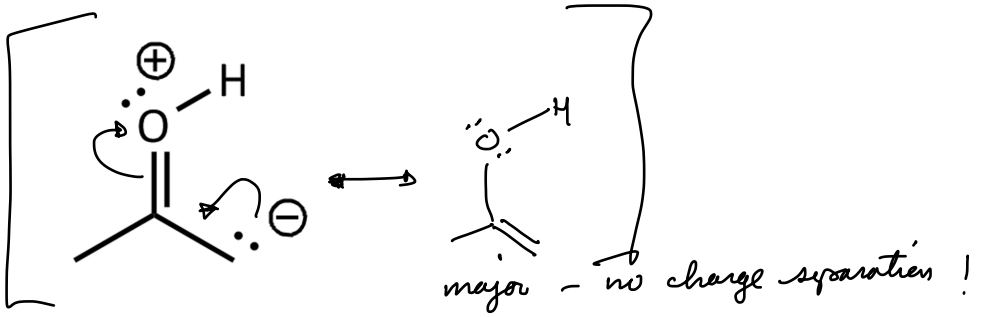
1. The compound called DMAP is shown below.

   a. Indicate the hybridization for each of the nitrogen atoms.
   b. Identify what type of orbital each of the lone pair of electrons is in.
   c. Indicate whether each lone pair of electrons is *localized* or *delocalized*. (15 points)

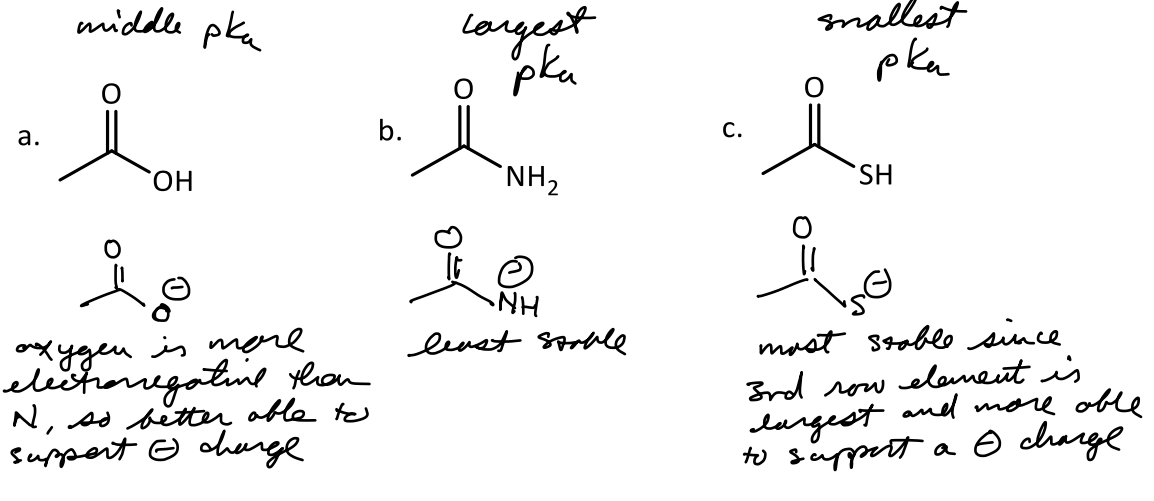


N,*N*-dimethylaminopyridine (DMAP)

2. For the structure shown below, push electrons to show the other resonance form. Circle the *major* resonance form and provide the reason for your choice. (15 points)

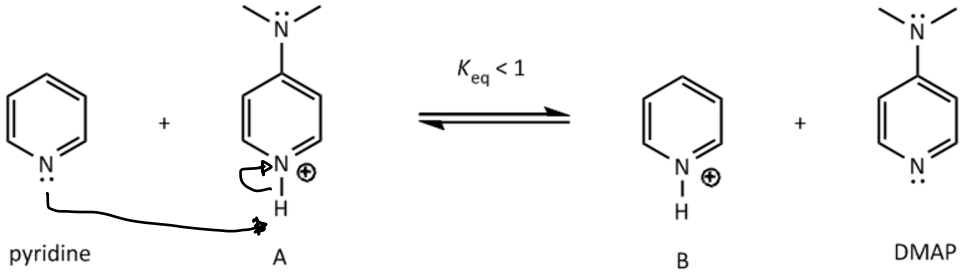


3. Consider the three compounds below. Indicate which compound has the largest pK_a and which has the smallest pK_a. Use ARIO to justify your answers (don't forget about the conj. bases) (20 points)

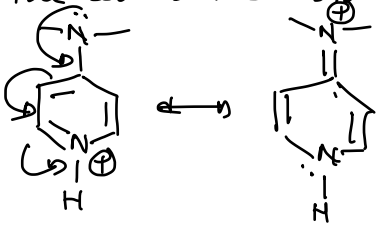


4. Given the information about the equilibrium (K_{eq}), answer the following:

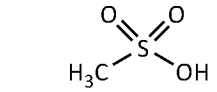
   a. Which ammonium ion, A or B, is the stronger acid? — B
   b. Which amine, pyridine or DMAP, is the stronger base? → DMAP
   c. Suggest a reason for the difference in acidity of A and B.
   d. Use electron pushing to show the proton transfer in the acid/base reaction. (20 points)



c. the enhanced stability of A due to resonance makes DMAP a much stronger base and A a more stable and hence less acidic acid

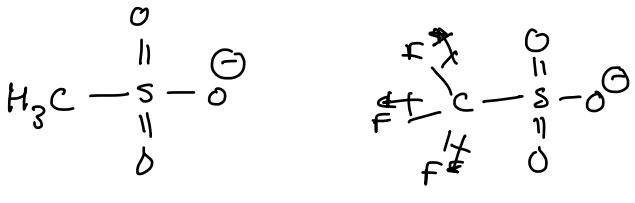


5. Trifluoromethanesulfonic acid (aka *triflic* acid) is one of the strongest known acids. Use ARIO to explain the difference in acidity between methanesulfonic acid and trifluoromethanesulfonic acid (don't forget about the conjugate base). (15 points)



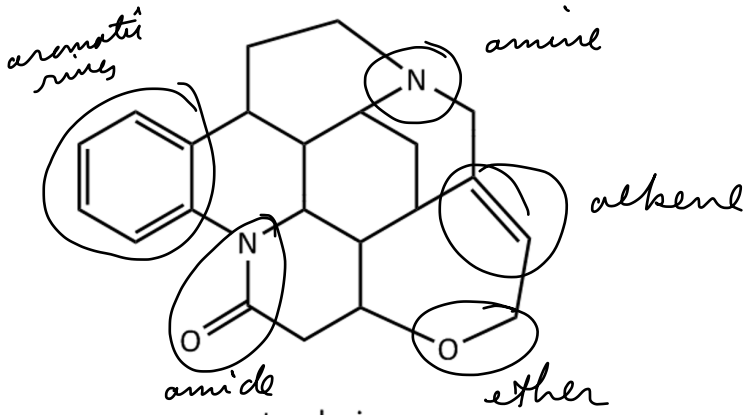
	methane sulfonic acid	trifluoromethane sulfonic acid
pK_a	-2.6	-12

atom effect and resonance effect are the same for both conjugate bases



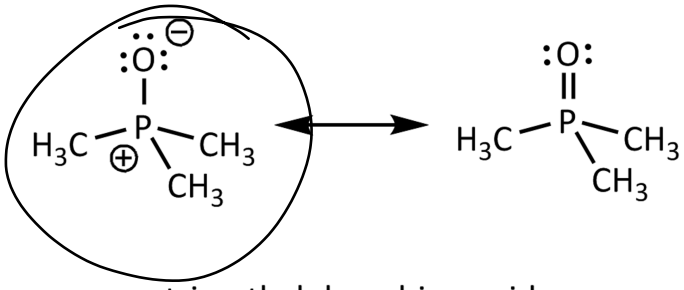
inductive effect of CF_3 group stabilizes this conjugate base, so more stable than from methane sulfonic acid – so the acid is stronger

6. Strychnine is an exceedingly toxic compound – ingesting as little as 20 mg can be fatal. Circle and name as many of the common functional groups as you can. (25 points)



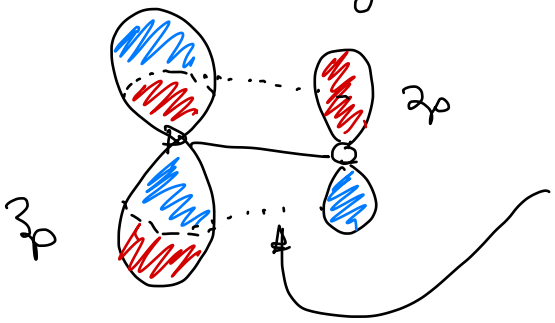
strychnine

7. The two valid resonance structures for trimethylphosphine oxide are shown below. Which one is the major one. Clearly explain the reasoning for your choice. (20 points)



trimethylphosphine oxide

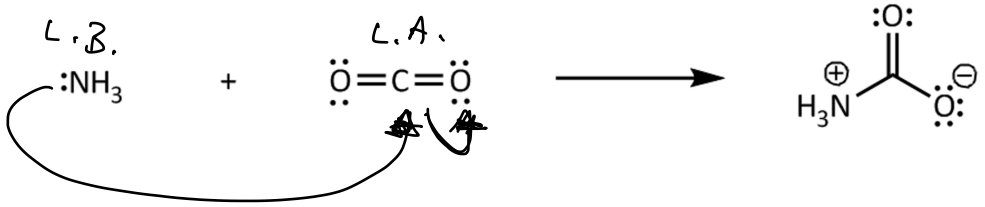
the charge separated structure is best because 3rd row and 2nd row elements do not form stable π bonds, which is shown in the structure on the right.

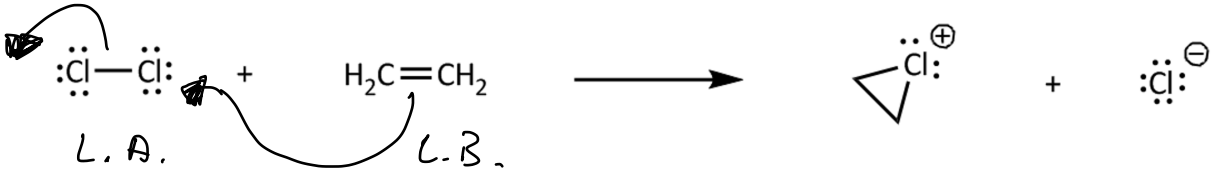


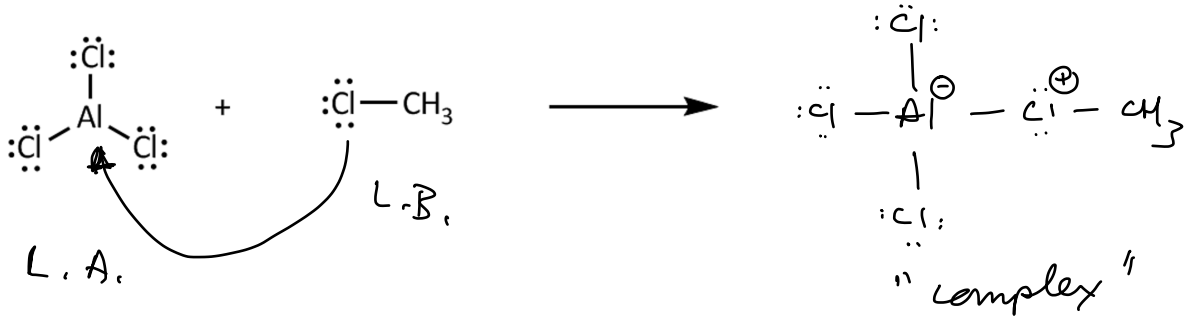
very poor overlap between 2p & 3p orbitals due to the extra orbital node of the 3p orbital.

8. For the following reactions, for the reactants (items on the left), identify the Lewis acid and the Lewis base. Show with electron pushing how the reaction proceeds. For question c., also show what the expected product would be – the Lewis acid/base complex that is formed. (20 points)

Lewis base = L.B. Lewis acid = L.A.

a. 

b. 

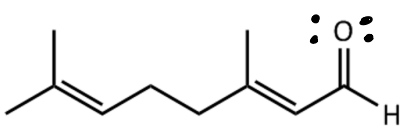
c. 

Name Key

(Lab B)

1. The natural product citral is found in many essential oils, particularly in citrus oils. You might guess what it smells like.

(10 points)



← 2 lone pairs of electrons were not shown originally !

Citral

a. What is the *molecular formula* for citral? $C_{10}H_{16}O$

b. How many valence electrons does citral have? Are they all shown in the structure above? If not, what's missing?

C_{10}	40
H_{16}	16
O	16
	72

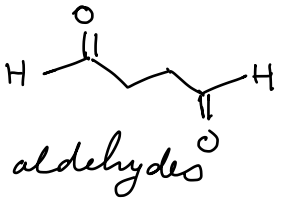
72 valence electrons

– 2 lone pairs on oxygen !

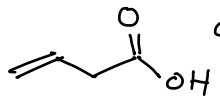
2. Draw a molecule that has the molecular formula $C_4H_6O_2$ that has only the "common" functional groups discussed in Chapter 2 (it could have more than one!).

a. It should be drawn using *bond-line* structures *with any lone pairs of electrons clearly shown*.
b. Label the functional groups

Only draw one molecule! (points will be lost for multiple structures…) (20 points)



aldehydes



carboxylic acid

alkene

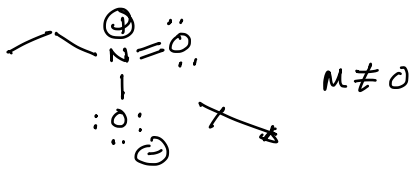
lots of other possibilities

3. For the following molecules,

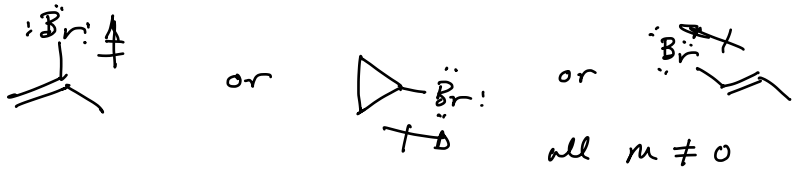
   i. Draw *bond-line* drawings that show the expected *geometry* (use dashes and wedges where necessary).
   ii. In your structures, clearly show any lone pairs of electrons.
   iii. Indicate whether the molecule has a permanent dipole moment ($\mu \neq 0$ D), if it does, then indicate the direction of the overall dipole, or if it doesn't have a permanent dipole moment ($\mu = 0$ D)

   (30 points)

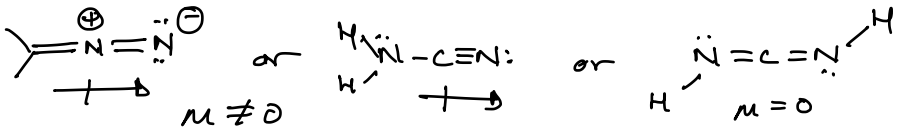
a. **$C_2H_5NO_2$**



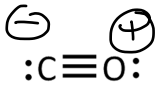
b. **C_3H_5Br**

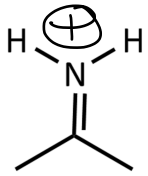


c. **CH_2N_2**

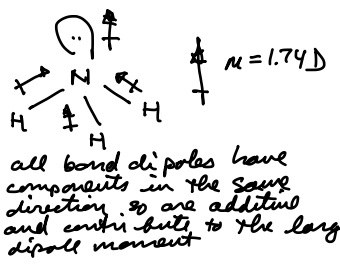


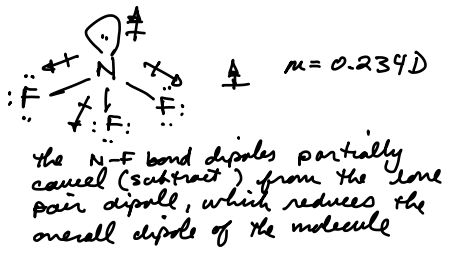
4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

a. 

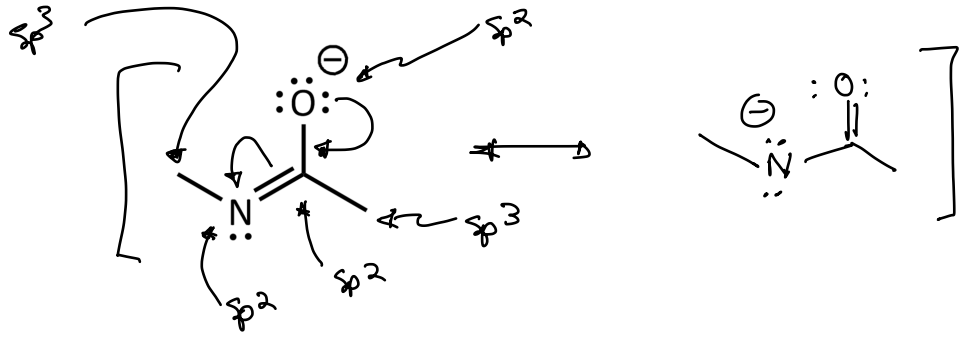
b. 

5. Ammonia (NH_3) has a dipole moment (μ) 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, polarity, and geometry) (15 points)





6. Consider the structure shown below. (20 points)



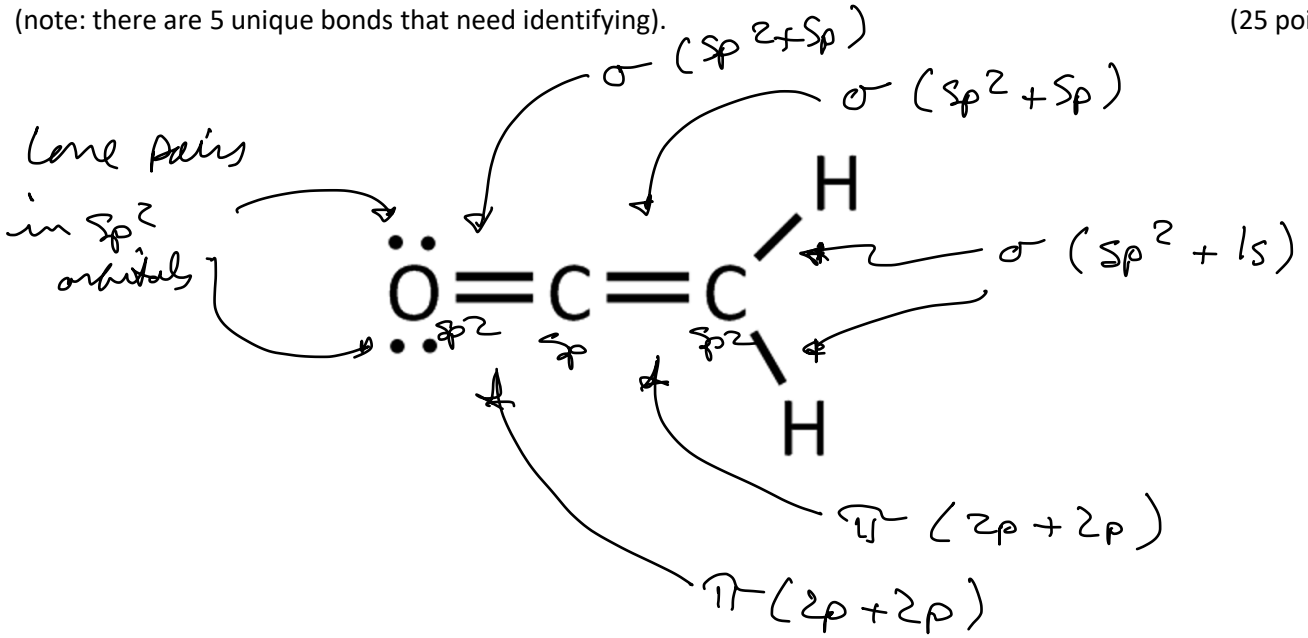
a. Label the hybridization for each of the atoms (except hydrogen).

b. What type of atomic orbital(s) do the three lone pairs on the oxygen occupy? (are they all the same?)

Two lone pairs are in sp^2 orbitals – the third lone pair is in a 2p orbital so that it can be in resonance with the π bond.

c. Show the other resonance form using electron pushing.

7. Ketene, shown below, is a very reactive compound used for preparing esters and amides, and also, derivatives of amino acids. For every bond in the molecule, indicate which *type* of bond it is (π or σ) and what atomic orbitals are used to form them (hybridized orbitals are considered atomic orbitals). Also, what type of orbitals are the *oxygen* lone pairs of electrons in (are they both in the same type?).
(note: there are 5 unique bonds that need identifying). (25 points)

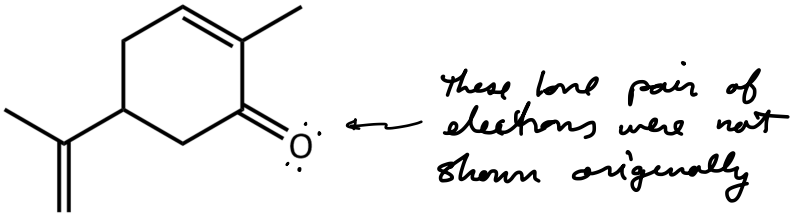


Name Key

(Lab A)

1. The natural product carvone is found in many essential oils, particularly in spearmint oil. You might guess what it smells like.

(10 points)



carvone

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

$C_{10}H_{14}O$

b. How many valence electrons does carvone have? Are they all shown in the structure above? If not, what's missing?

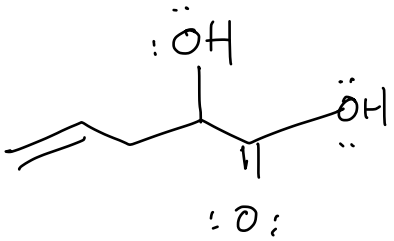
C_{10}	40
H_{14}	14
O	16

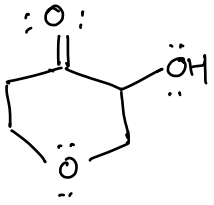
50 valence electrons!

2. Draw a molecule that has the molecular formula $C_5H_8O_3$ that has only the "common" functional groups discussed in Chapter 2 (it could have more than one!).

a. It should be drawn using *bond-line* structures *with any lone pairs of electrons clearly shown*.
b. Label the functional groups.

Only draw one molecule! (points will be lost for multiple structures…) (20 points)





tons of other possibilities

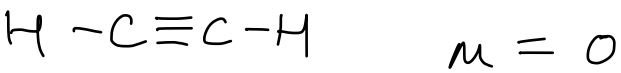
3. For the following molecules,

   i. Draw *bond-line* drawings that show the expected *geometry* (use dashes and wedges where necessary).
   ii. In your structures, clearly show any lone pairs of electrons.
   iii. Indicate whether the molecule has a permanent dipole moment ($\mu \neq 0$ D), if it does, then indicate the direction of the overall dipole, or if it doesn't have a permanent dipole moment ($\mu = 0$ D)

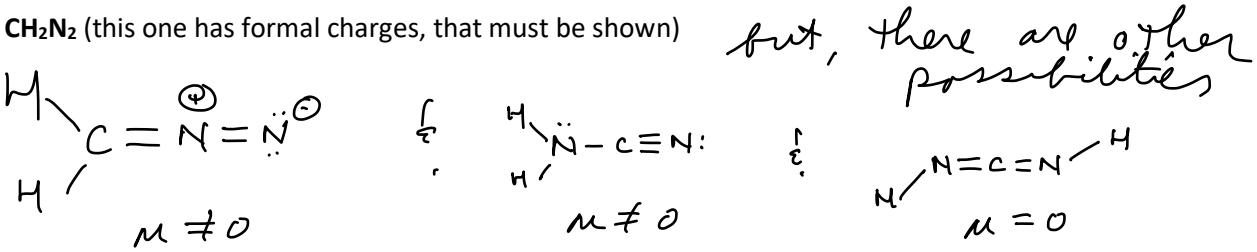
   (30 points)

a. **CO_2**

b. **C_2H_2**



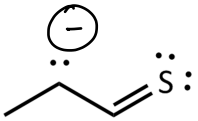
c. **CH_2N_2** (this one has formal charges, that must be shown)



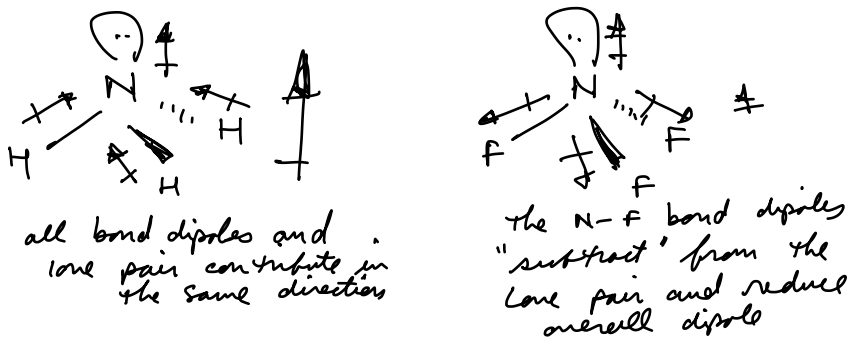
4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

a.

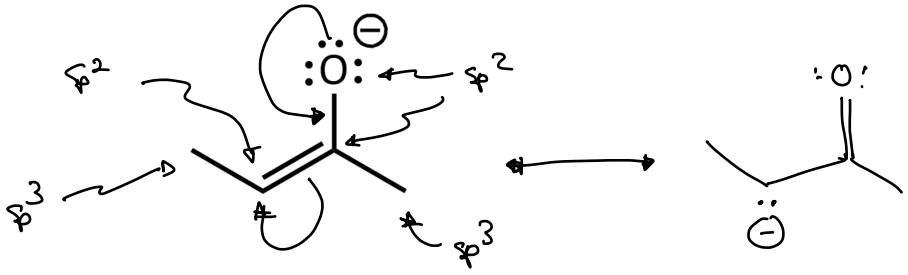
b.



5. Ammonia (NH_3) has a dipole moment (μ) 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, polarity, and geometry) (15 points)



6. Consider the structure shown below. (20 points)



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

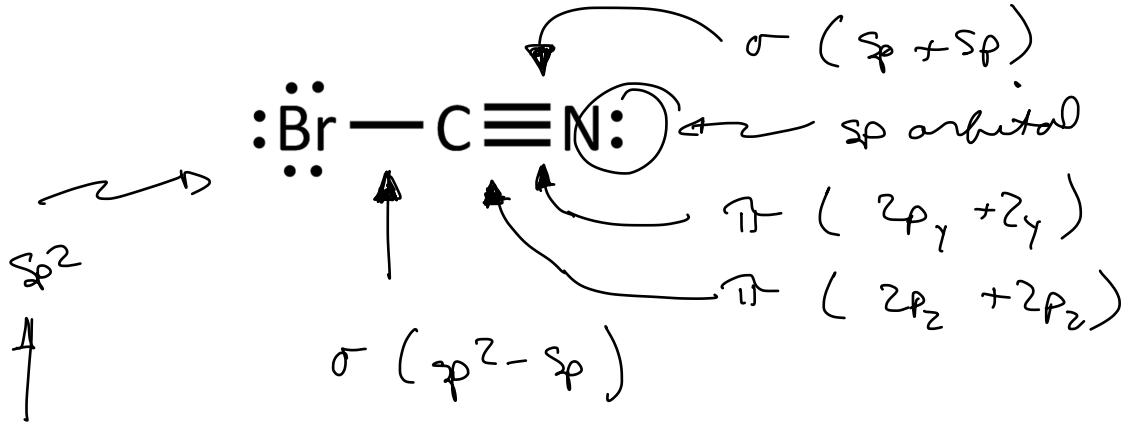
b. What type of atomic orbital(s) do the three lone pairs on the oxygen occupy? (are they all the same?)

two of them are in sp^2 orbitals, one is in a 2p orbital

c. Show the other resonance form using electron pushing.

(major form is on the left)

7. Cyanogen bromide, shown below, is a reagent used for cleaving proteins at specific locations and is useful for protein sequencing. For every bond in the molecule, indicate which *type* of bond it is (π or σ) and what atomic orbitals are used to form them (hybridized orbitals are considered atomic orbitals). Also, what type of orbital is the *nitrogen* lone pair of electrons in. (note: there are 4 unique bonds that need identifying). (25 points)



Note the Br is hybridized sp^2 since it can have resonance with the neighboring triple bond