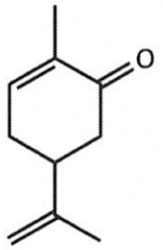
1. Carvone is a natural product found in spearmint and caraway seed. (10 points)



carvone

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

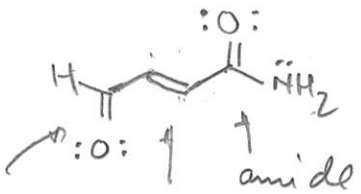
$C_{10}H_{14}O$

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

ketone, alkene

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*.

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

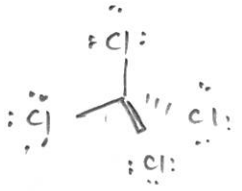


aldehyde alkene

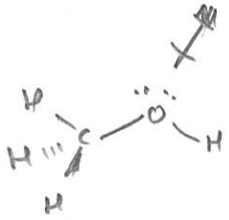
3. For the following molecules,

   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), if it does, then indicate the direction of the overall dipole, or if it doesn't have a permanent dipole moment ($\mu = 0$ D) (15 points)

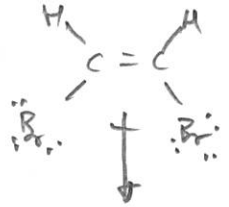
CCl_4



CH_3OH

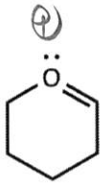


$C_2H_2Br_2$ (there is more than one answer for this one)

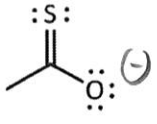


4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

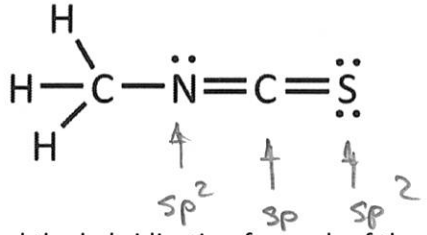
a.



b.



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



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

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

sp^2

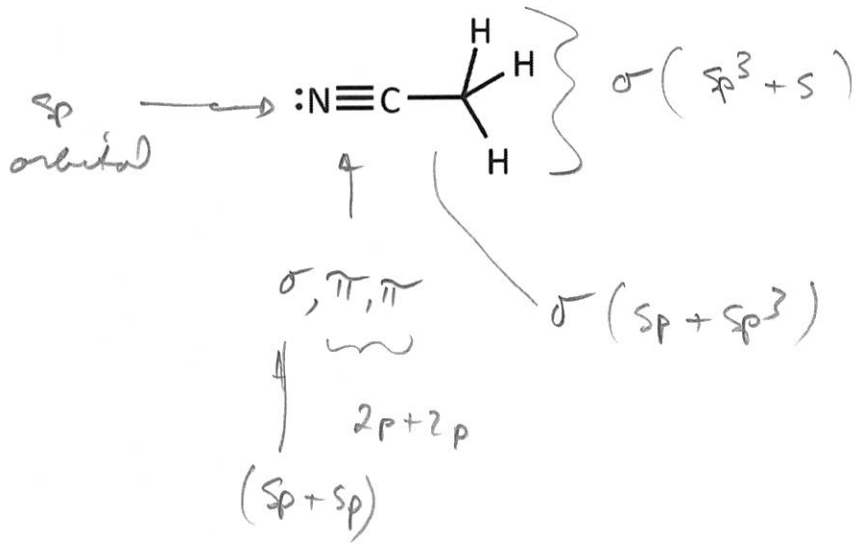
c. What is the approximate bond angle for the C-N-C bond?

≈ 120°

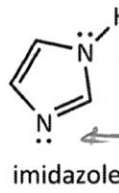
d. Which bond is longer, N=C or C=S? Explain.

C=S sulfur is a much larger atom and is in the 3rd row. Even though atoms generally get smaller going to the right, going down a row is a big size change

6. 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 lone pair of electrons in. (note: there are seven bonds that need identifying). (20 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)



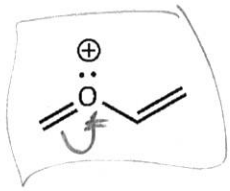
imidazole

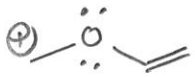
sp^2 – electron pair is in a 2p orbital

sp^2 – electron pair is in an sp^2 orbital

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)

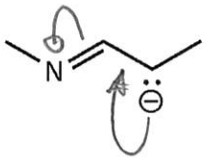
a.

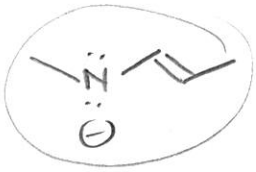




more stable since all atoms have octets, in spite of the positive charge on oxygen

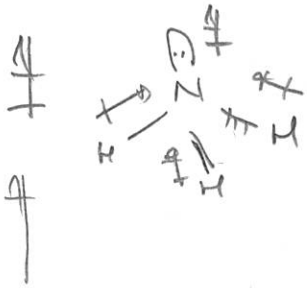
b.





Nitrogen is more electronegative so better able to stabilize the negative charge

9. 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 and geometry) (10 points)



overall $\mu = 1.42D$

all bond dipoles and the lone pair contribute to overall dipole in the same direction

net dipole is small $\mu = 0.234D$ – direction is not obvious!

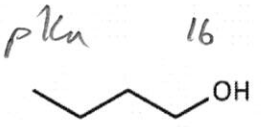
the bond dipoles of the N–F bonds are, in the opposite direction compared to ammonia – the partially cancel the dipole of the lone pair!

10. 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? Which is the least acidic
c. Use ARIO to justify your answers (don't forget about the conj. bases) (20 points)

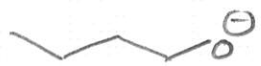
R–S⊖ is more stable than R–O⊖ since it's larger

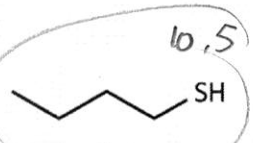
pKa 16 10.5 14.4



A

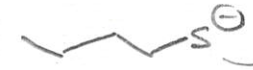
least acidic

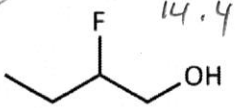




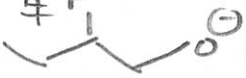
B

most acidic



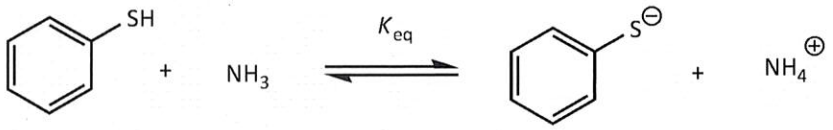


C



inductive withdrawal of F makes this more stable than A

11. 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

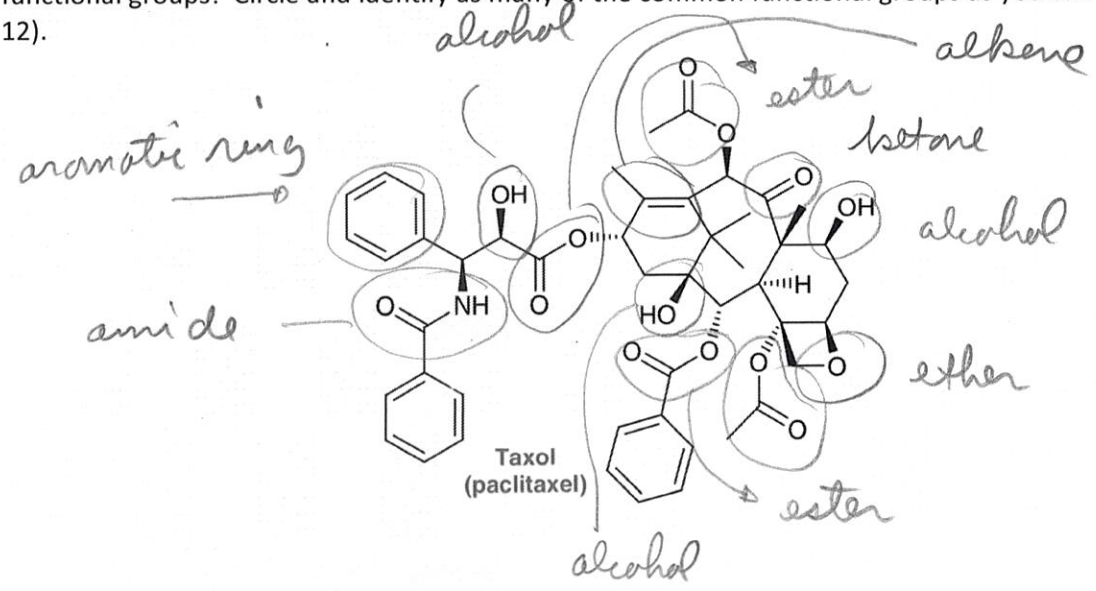
ammonium ion
pK_a = 9.9

nature favors the weakest acid
– higher pka, means less acidic

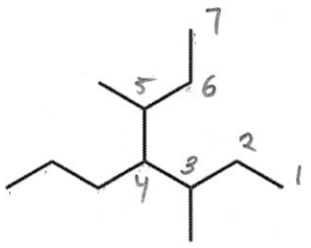
$K_{eq} = 10^{9.9-6.6}$

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

12. 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)



13. Name each of the following compounds using IUPAC (systematic) names. (20 points)

a. 

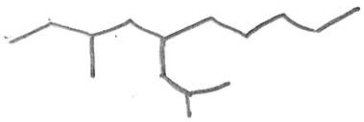
3,5-dimethyl-4-propyl heptane

b. 

1,4-dimethyl bicyclo[2.2.2]octane

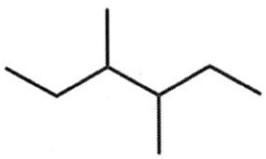
14. Draw structures for the following compounds. (20 points)

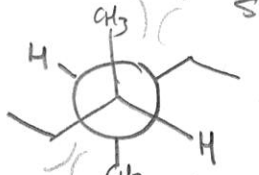
a. 3-methyl-5-(2-methylpropyl)decane



b. *cis*-1,3-diisopropylcycloheptane

15. Consider the molecule below. Using Newman projections, draw the lowest energy and the highest energy conformations around the C3-C4 bond. In each conformation, label it as *staggered* or *eclipsed*, and indicate what type of strain is present – torsional, steric, angle, or some combination of them – be specific about this. (50 points)

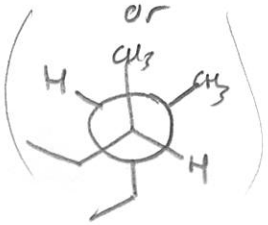


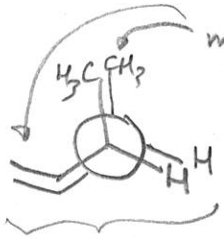


gauche steric strain

staggered

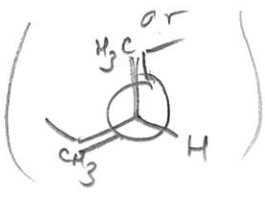
or





torsional & steric strain

or

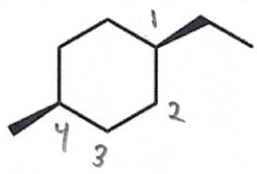


name is wrong!

16. Draw both chair forms of the compound *cis*-1-ethyl-1-methylcyclohexane. Calculate the equilibrium constant (K_{eq}) between the two chairs at 25°C from the least to the most stable chair (least stable chair on left of equilibrium – most stable on the right). Given the following formulas and data

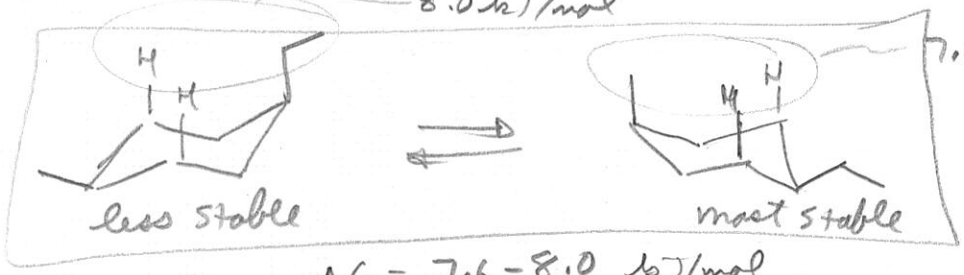
→ cis-1-ethyl-4-methyl-cyclohexane

$K_{eq} = e^{-\Delta G/RT}$
R = 8.314 J/mol · K
K = °C + 273.15



1,3-Diaxial Interactions	
$-CH_3$	7.6 kJ/mol
$-CH_2CH_3$	8.0 kJ/mol

8.0 kJ/mol



7.6 kJ/mol

less stable ⇌ most stable

← both chairs + K_{eq} are the answer

$\Delta G = 7.6 - 8.0$ kJ/mol
$= -0.4$ kJ/mol $= -400$ J/mol

$K_{eq} = e^{-(-400\ J/mol)/(8.314\ J/mol \cdot K)(298.15\ K)}$

$= e^{0.16} = 1.2$

note the two negative signs!

$K_{eq} = 1.2 = \frac{1.2}{1}$

which translate to

45% ⇌ 55%

which barely favors the right side