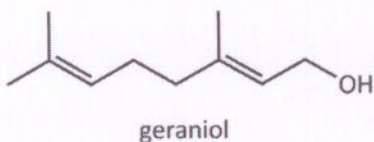
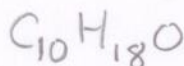


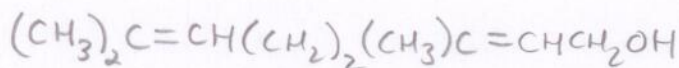
1. Geraniol is a natural product found in many essential oils, most notably in rose oil. (15 points)



- a. What is the molecular formula for geraniol?  
b. What are the functional groups found in geraniol?  
c. Write a condensed formula for the structure.



alkene, alcohol  
(alkane)

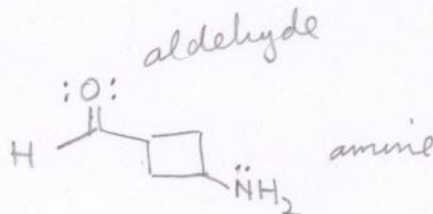
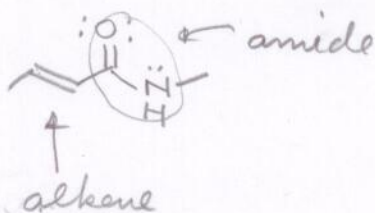


other variations possible

2. Draw a molecule that has the molecular formula  $C_5H_9NO$ . 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.

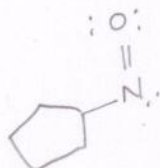
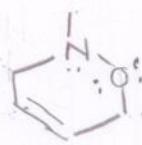
Also, name the functional groups shown in your structure.

(20 points)



+ many other 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)

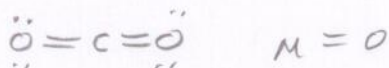


+ many other possibilities

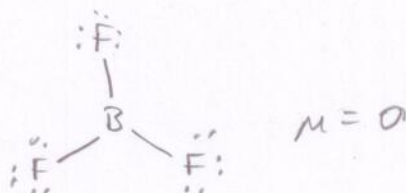
3. For the following molecules,

- Draw *bond-line* drawings that show the expected *geometry* (use dashes and wedges where necessary).
- Show all of the lone pairs of electrons.
- 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)

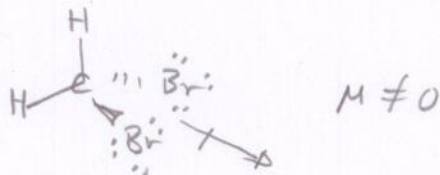
CO<sub>2</sub>



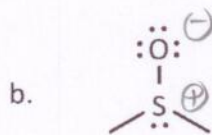
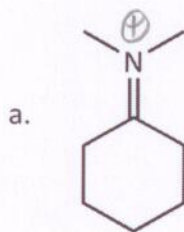
BF<sub>3</sub>



CH<sub>2</sub>Br<sub>2</sub>

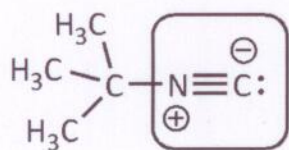


4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

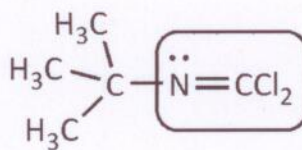


5. Consider the structures shown below.

(25 points)



A



B

a. For A, label the hybridization for each of the atoms inside the box?



b. For A, what type of atomic orbital does the lone pair of electrons occupy?



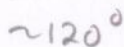
c. For B, label the hybridization of just the nitrogen atom?



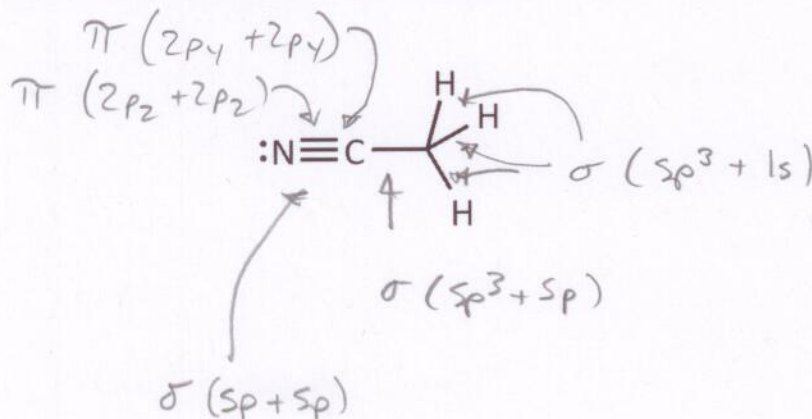
d. For B, what type of atomic orbital does the lone pair of electrons occupy?



e. For B, what is the approximate bond angle for the N-C-Cl bonds?

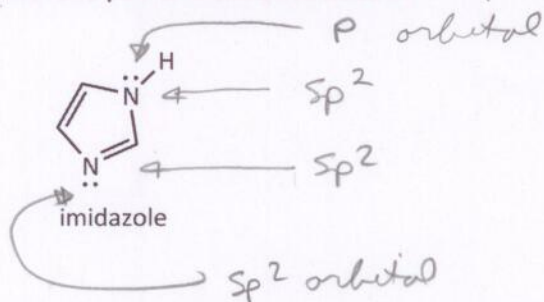


6. For every bond in the molecule, indicate which *type* of bond it is and what atomic orbitals are used to form them. (Hint: this is the valence bond theory of bonding) (15 points)

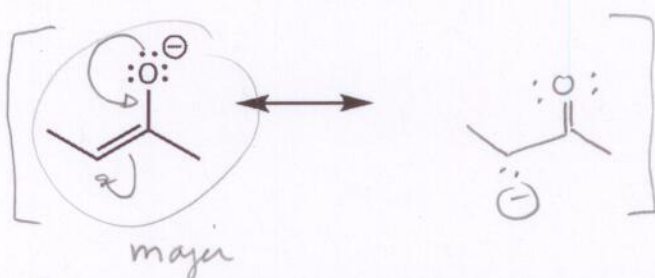




7. Imidazole is shown below. Indicate the hybridization for each of the nitrogen atoms and what type of orbital each the lone pair of electron resides in. (10 points)



8. By "pushing" electrons, show the other resonance form for the ion shown below. Circle the *major* resonance form and provide the reason for your choice. (10 points)



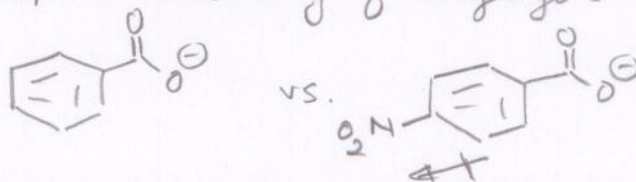
9. The  $pK_a$  values for benzoic acid ( $C_6H_5CO_2H$ ), phenol ( $C_6H_5OH$ ), and the respective *para*-nitro derivatives are given below. (20 points)

Compound	$pK_a$
benzoic acid	4.2
<i>para</i> -nitrobenzoic acid	3.3
phenol	10
<i>para</i> -nitrophenol	7.2

omitted -  
 used as extra  
 credit

- a. Explain why the *para*-nitro derivative of benzoic acid is more acidic than unsubstituted benzoic acid.

compare stability of conjugate bases



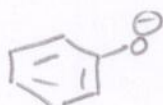
This causes inductive stabilization of the carboxylate, so the nitro acid is more stable.

by resonance, the  $NO_2$  group pulls  $e^-$ s from the aromatic ring and makes it electron-poor

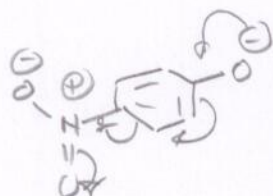


- b. Note that substituting phenol in the *para*- position with the nitro group results in a greater increase in acidity than does substituting benzoic acid with the nitro group in the *para* position. Explain why the acidity of phenol is greater enhanced by the presence of the nitro group than is a benzoic acid.

*consider the conjugate bases.*



*has resonance stability*

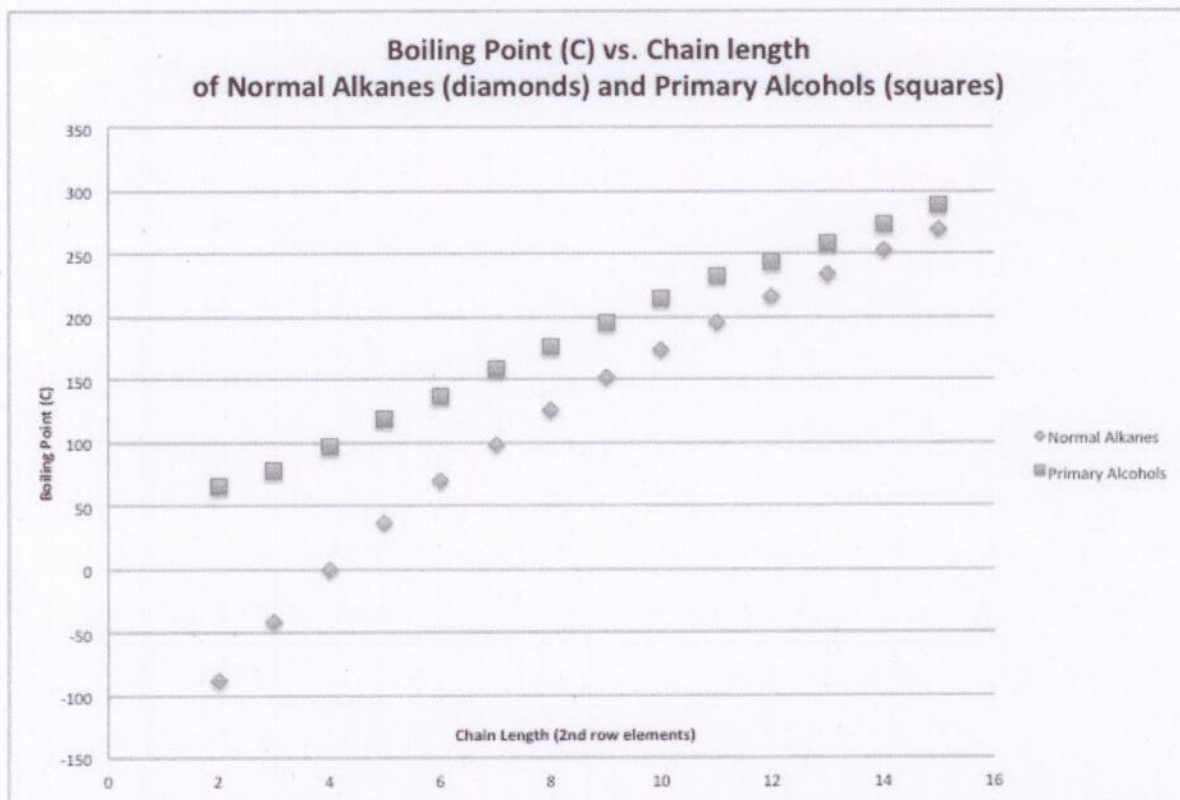


*has more resonance stability*

*resonance stability is larger effect on stability of conjugate base than inductive so the difference in acidity is 1000 fold rather than 10 fold*

10. In general, primary alcohols (R-OH) have higher boiling points than alkanes of the same size (R-H). However, considering alcohols and alkanes that have roughly the same chain length (total number of 2<sup>nd</sup> row elements) and molar mass (only off by 2 g/mol), the following trend is observed (see table and chart): The boiling points "approach" the same value as the chain length gets longer. (10 points)

Chain Length	Alkane	BP (C)	Alcohol	BP (C)
2	Ethane	-89	methanol	65
3	Propane	-42	ethanol	78
4	Butane	-1	1-propanol	97
5	Pentane	36	1-butanol	118
6	Hexane	69	1-pentanol	137
7	Heptane	98	1-hexanol	158
8	Octane	126	1-heptanol	176
9	Nonane	151	1-octanol	195
10	Decane	174	1-nonanol	214
11	Undecane	196	1-decanol	232
12	Dodecane	216	1-undecanol	243
13	tridecane	234	1-dodecanol	259
14	tetradecane	253	1-tridecanol	274
15	pentadecane	270	1-tetradecanol	289



- a. What is the fundamental reason for the higher boiling points of the smaller alcohols compared to the similarly sized alkanes? (e.g., pentane, bp 37°C vs. 1-butanol, bp 118°C)

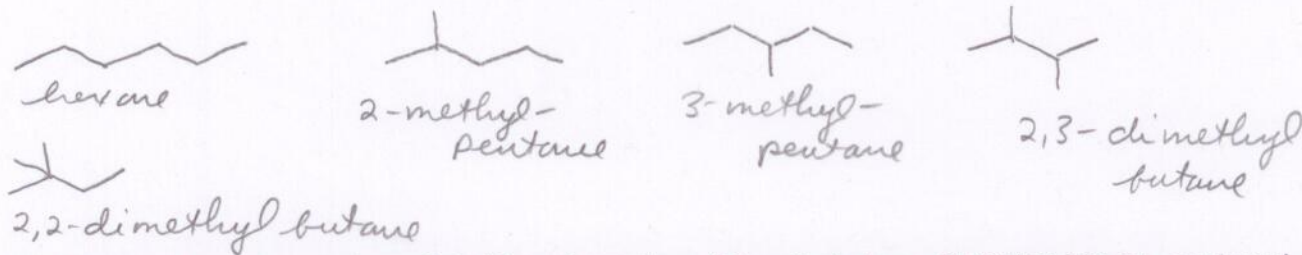
*Hydrogen-bonding is a stronger effect than London dispersion forces*

- b. Why do the boiling points "approach" the same value as the chain length gets longer? (Consider the intermolecular forces at work)

*as the chain length gets longer the cumulative effect of the London dispersion forces becomes the dominant effect that affects the bp. The polar -OH becomes less significant relative to the non-polar alkyl side chain.*



11. Draw and name all of the constitutional isomers of the alkanes with molecular formula  $C_6H_{14}$ . (25 points)

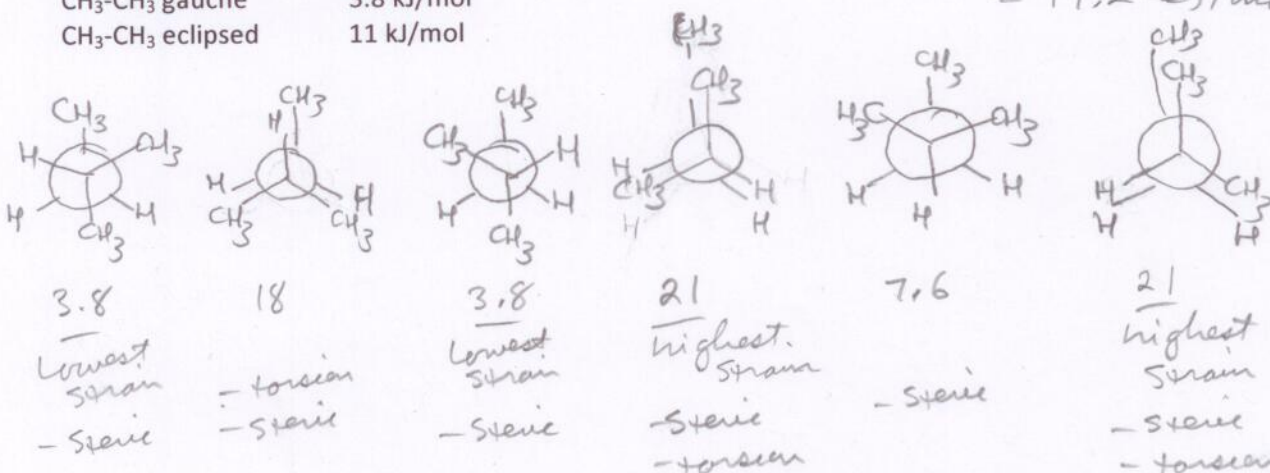


12. Using Newman projections, show all six (6) conformations of 2-methylbutane,  $CH_3CH(CH_3)CH_2CH_3$ , as viewed down the C2-C3 bond. (15 points)

- For each conformation, indicate what type of strain is present - torsional, steric, or angle strain.
- Indicate the least stable and the most stable conformations. If any of the conformations have the same energy then show which ones do.
- Use the data below to estimate the barrier to rotation about the C2-C3 bond.

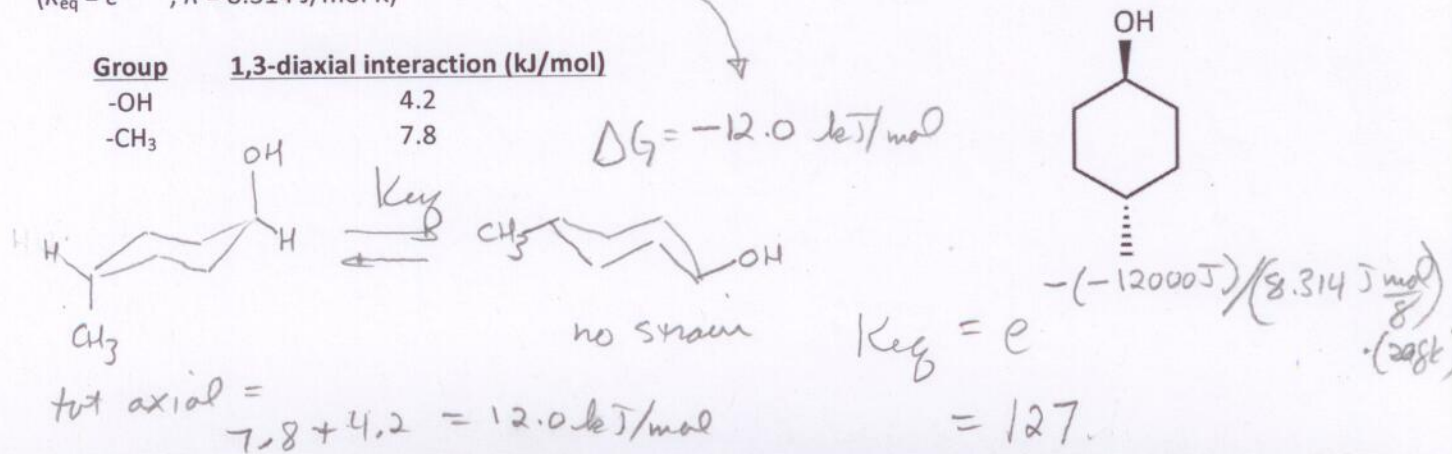
H-H eclipsed	4 kJ/mol
H-CH <sub>3</sub> eclipsed	6 kJ/mol
CH <sub>3</sub> -CH <sub>3</sub> gauche	3.8 kJ/mol
CH <sub>3</sub> -CH <sub>3</sub> eclipsed	11 kJ/mol

Barrier = highest - lowest  
 = 21 - 3.8 kJ/mol  
 = 17.2 kJ/mol



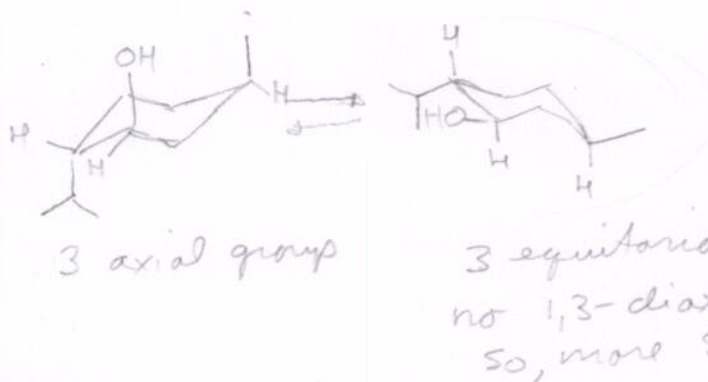
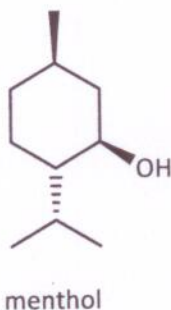
13. Given the data below, calculate the equilibrium constant ( $K_{eq}$ ) between the two chair forms of *trans*-4-methylcyclohexanol from highest to lowest energy chairs at 25°C (298K). (Remember, you get points for well-drawn chairs) (20 points)

$(K_{eq} = e^{-\Delta G/RT}, R = 8.314 \text{ J/mol K})$

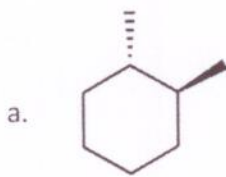




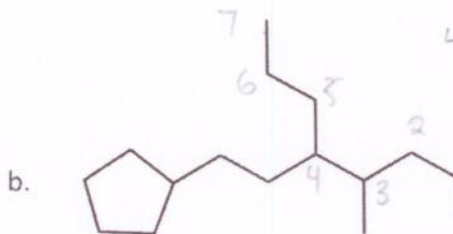
13. Menthol, isolated from various mint oils, is shown below. Draw both chairs of menthol and indicate which one is more stable. (Remember, you get points for well-drawn chairs) (10 points)



14. Name the following compounds. (20 points)



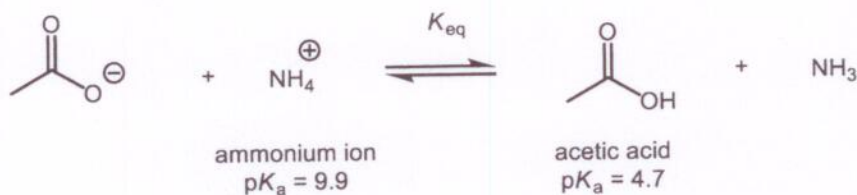
*trans-1,2-dimethylcyclohexane*



*4-(2-cyclopentylethyl)-3-methylheptane*

~~1-cyclopentyl-4-methyl-3-propylhexane~~

15. 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)



*nature favors the weakest acid, which is the ammonium ion*

$$\begin{aligned}
 K_{eq} &= 10^{4.7-9.9} \\
 &= 10^{-5.2} \\
 &= 6.3 \times 10^{-6}
 \end{aligned}$$

*which is  $< 1$  and implies that reactants are favored in the acid/base equilibrium*