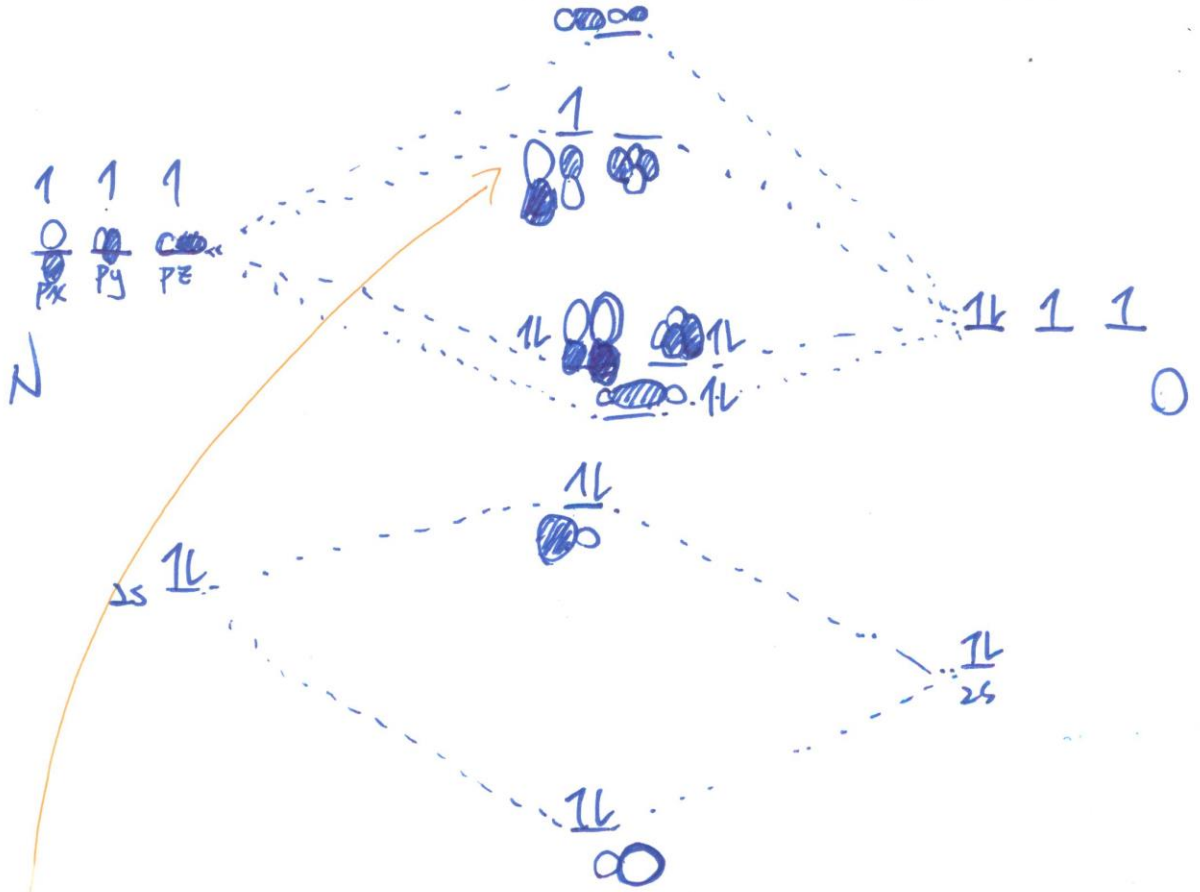
Problem 1.

a. Draw the Lewis dot structure of nitric oxide (NO).

b. Draw the molecular orbital diagram of nitric oxide (NO). Assume nitrogen and oxygen have similar size atomic orbitals before mixing; be sure to show the relative energy of orbitals.

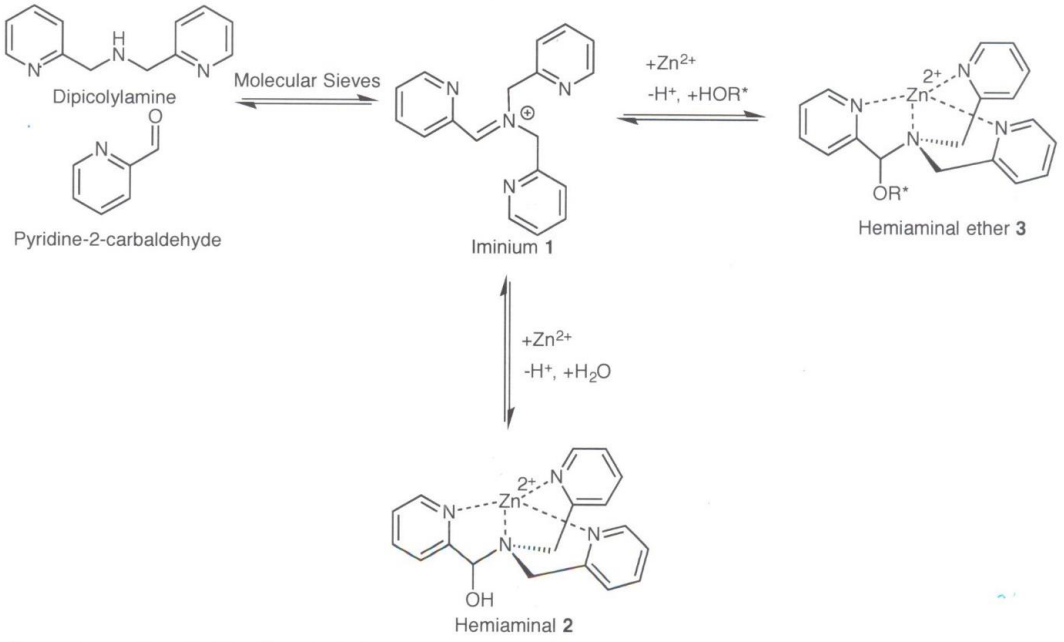


c. With the constructed molecular orbitals above, explain where the radical electron primarily resides on NO. Use pictures and arrows, do not write more than 5 sentences.

The radical electron resides in the π^* orbital, which has a larger lobe on the nitrogen atom.

Problem 2.

Below is a proposed route for the formation of a zinc centered dynamic assembly. Pyridine-2-carbaldehyde and dipicolylamine condense to form iminium **1**. In the presence of Zinc(II) and water, the tris-pyridyl ligand coordinates to yield hemiaminal **2**. With the introduction of an alcohol species, the alcohol gets incorporated into the assembly to form a hemiaminal ether **3**.



Questions are on the next page!

Circle the correct answer.

a. What is the facial stereochemical topicity on the iminium **1**?

Homotopic **enantiotopic** **diastereotopic**

b. Without any alcohol, how many stereoisomer(s) of hemiaminal **2** species would be generated?

1 **2** **3** **4**

c. What is the stereochemical relationship of these hemiaminal **2** species?

Not Applicable **enantiomers** **diastereomers** **enantiomers and diastereomers**

d. With the addition of only (S)-2-butanol, what is the stereochemical relationship of the hemiaminal ether **3** isomer(s) generated?

Not Applicable **enantiomers** **diastereomers** **enantiomers and diastereomers**

e. With the addition of only (S)-2-butanol, would you expect to observe exact 1:1 ratio of the hemiaminal ether **3** isomers or something else? Circle the most plausible answer.

Not Applicable (only one generated) **1:1** **1:2** **1:1:1** **1:1:1:1**

f. Based on your answer from e. With the addition of only (R)-2-butanol, would you expect to observe exact 1:1 ratio of the hemiaminal ether **3** isomers or something else? Circle the most plausible answer.

Not Applicable (only one generated) **1:1** **1:2** **1:1:1** **1:1:1:1**

g. With addition of racemic 2-butanol, what is the stereochemical relationship of the hemiaminal ether **3** isomer(s) generated?

Not Applicable **enantiomers** **diastereomers** **enantiomers and diastereomers**

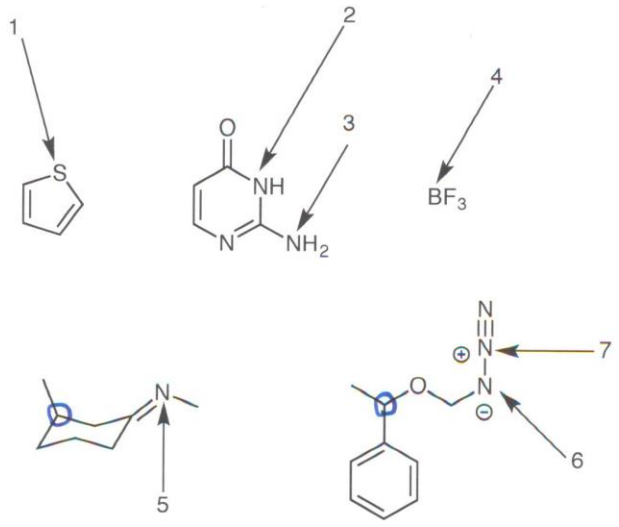
h. Is the formation of hemiaminal **2** stereospecific or stereoselective?

Stereospecific **Stereoselective** **Both** **Neither**

Problem 3.
Fill in the blanks

	Hybridization of the atom	Orbital(s) of the lone pair(s), or not applicable
1	sp^2	sp^2 , p
2	sp^2	p
3	sp^2	p
4	sp^2	n/a
5	sp^2	sp^2
6	sp^2	p
7	sp	n/a

If you see a stereocenter in the molecules below, put a ring on it.



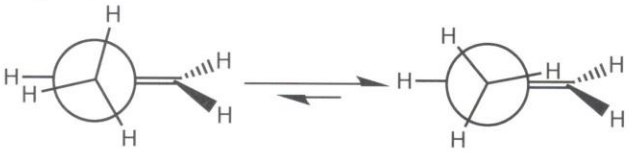
Problem 4

The staggered conformation for butane is preferred by 4 kcal/mol when compared to the eclipsed conformation. Eclipsed is, of course, a transition state while the staggered is in an energy well.

Preferred ($\Delta G° = 4$ kcal/mol)

The same trend is not observed for propene and 1-butene. The eclipsed conformer of the methyl group is in a well, while eclipsing of the methyl with a hydrogen is a transition state.

Propene



a transition state

($\Delta G° = -2$ kcal/mol)
in an energy well

1-Butene

a transition state

($\Delta G° = -0.8$ kcal/mol)
in an energy well

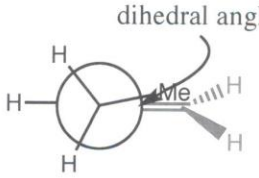
a. Rationalize why eclipsing with the CH2 group in propene and 1-butene is in a well while eclipsing with the H-is a transition state.

Better hyperconjugation, unfavorable overlap of σ and π

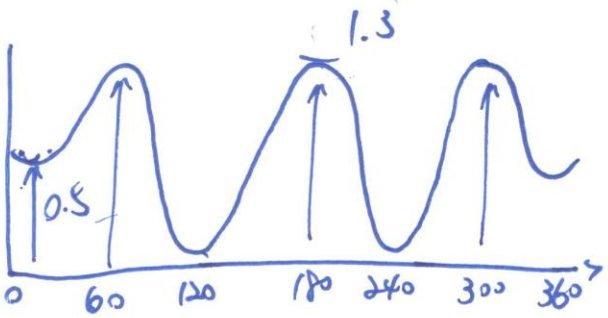
b. Why is methyl eclipsing C=CH2 bond in 1-butene less preferred than in propene? Explain.

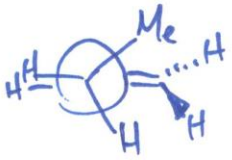
1,2-allylic strain

c. Draw the torsional energy plot for 1-butene. Start with the methyl group eclipsing the C=CH2 bond (see below). Draw Newman projections.



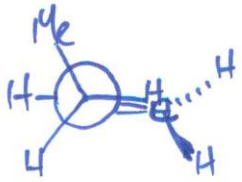
$1.3 - 0.8 = 0.5$



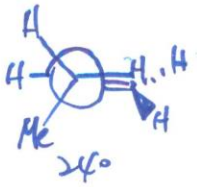


60

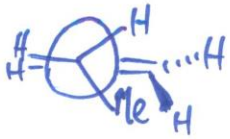
180



120



240



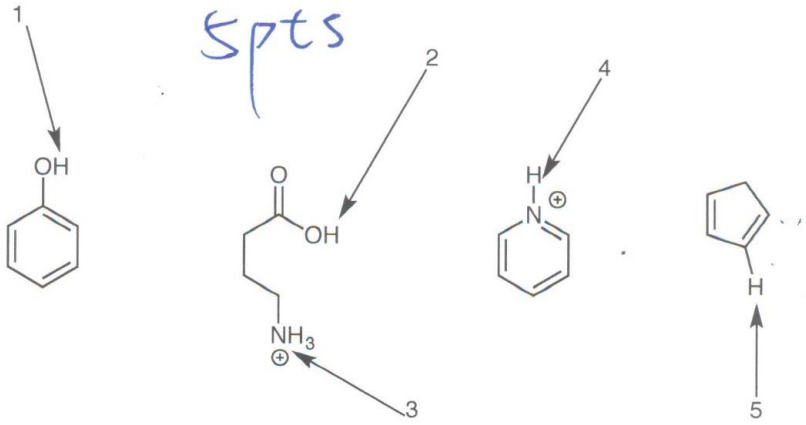
300

Problem 5

Please provide the pKa of the following molecules.

	PKa
1	10
2	4
3	9-10
4	4-5
5	40-45

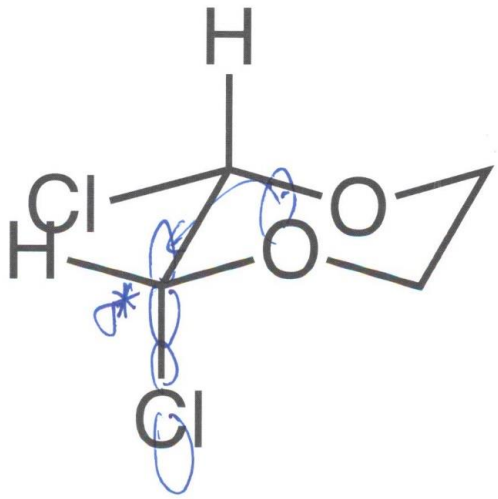
5pts



Problem 6

The structure has two C-Cl bonds. Identify the longer one, then rationalize why one C-Cl bond is longer than the other one. Please use pictures, and no more than 5 sentences (including run-on clauses).

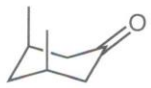
3pts



Problem 7

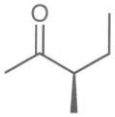
Write the answer of the following questions for each of the molecule in the boxes provided.

A. Label the face of carbonyl shown as Re or Si. Otherwise, write n/a.
B. Would you expect the reaction to be stereoselective? Write yes or no.
C. Would you expect the reaction to be stereospecific? Write yes or no.

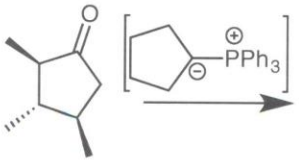


A	B	C
n/a	y	n

4 total



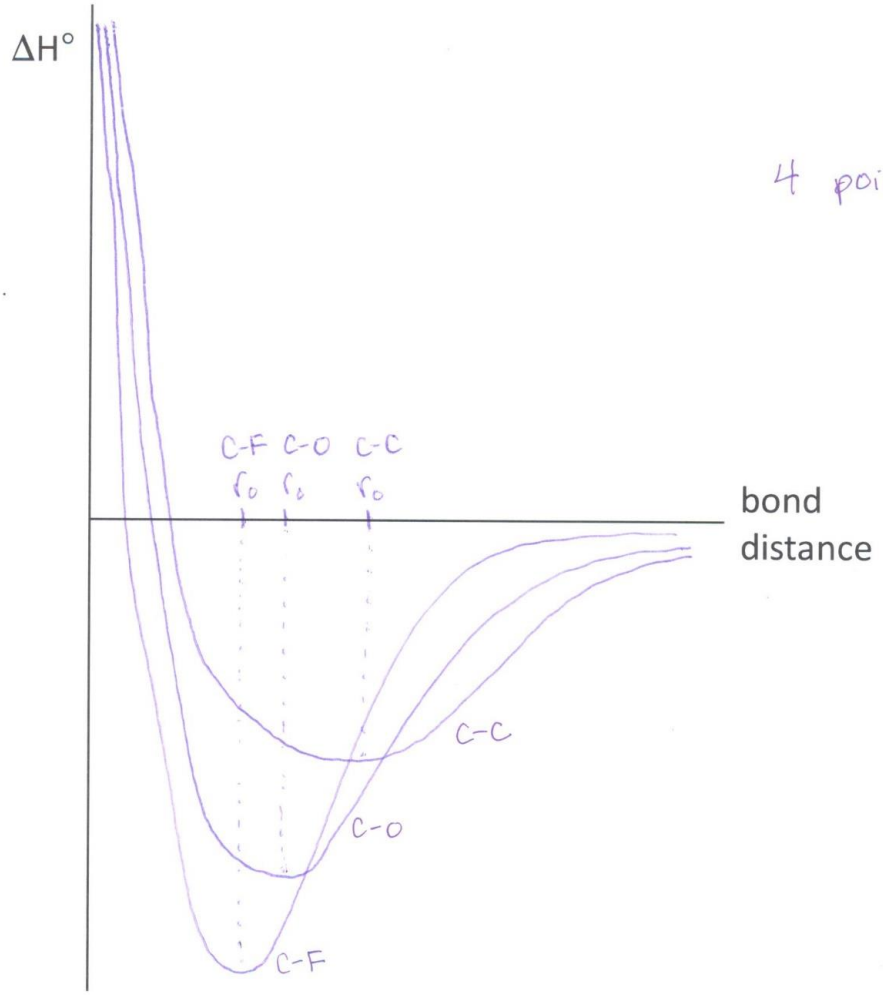
A	B	C
Re	y	y



A	B	C
Si	n or y	n or y

Problem 8

a) On the same plot, draw the Morse potential for a C-C, C-O, and C-F bond. Indicate relative energies and shapes, and label r_0 for each bond on your diagram.



4 points

b) Assign each of the following IR frequencies to a C-C, C-O, or C-F bond.

1400 cm^{-1}: C-F

1300 cm^{-1}: C-O

3 points

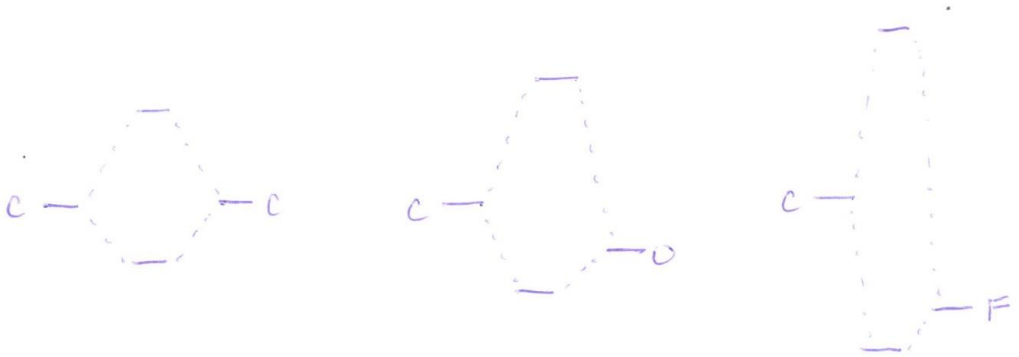
1200 cm^{-1}: C-C

c) Predict the order of the bond dissociation energies (BDEs).

C-F > C-O > C-C

1 point

d) Explain your answer to (c).



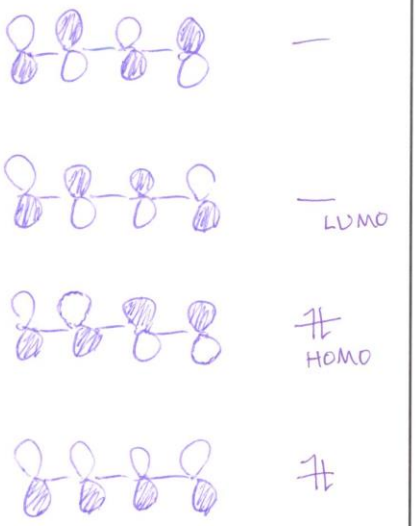
More polar bonds are more stabilized by mixing.

2 points

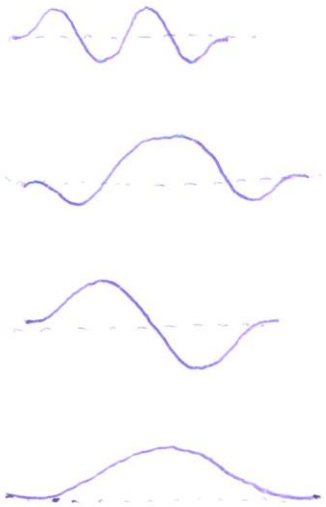
Problem 9

a) Draw the four MOs for the π system of butadiene. Fill in electrons appropriately and label the HOMO and LUMO. Then draw the waves that are analogous to the kinetic energy of the orbitals.

MOs

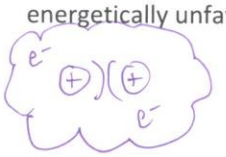


Kinetic energy/waves



4 points

b) Explain in pictures and/or words why one might think that bond formation would be energetically unfavorable.



Atoms repel one another due to electrostatics and the potential energy increases.

2 points

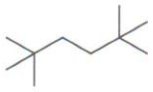
c) Explain in pictures and/or words why bond formation is actually energetically favorable.

The kinetic energy of the wavefunctions decreases upon bond formation.

2 points

Problem 10. Calculate ΔH_f° using Benson group increments for the following molecules. Show your work. (It's okay to *only* show your work and not waste time adding it up to a final number; just show all the parts!)

a)



$\Delta H_f^\circ = 2(C-(C)_4) + 6(C-(H)_3(C)) + 2(C-(H)_2(C)_2)$

$= 2(0.5) + 6(-10.20) + 2(-4.93)$

$= -70.06$ kcal/mol

2 points

b)

$\Delta H_f^\circ = 2(C-(H)_3(C)) + 8(C-(H)_2(C)_2)$

$= 2(-10.20) + 8(-4.93)$

$= -59.84$ kcal/mol

2 points

c) Which compound is more stable? What specific group(s) contribute(s) to this stability?

The compound in part (a) is more stable than the compound in part (b) due to the methyl groups.

2 points

d) Why do/does the specific group(s) mentioned in (c) impart stability?

ΔH_f° is all about bond strengths. The methyl groups are stabilizing because their C-H bonds are stronger than the C-H bonds in a methylene group.

3 points

Problem 11. Consider cyclopropane and cyclopropene.

a) Give an argument for why cyclopropane might be more strained.

The molecule is forced to be planar, so all of the hydrogens are eclipsed. 2 points

b) Give an argument for why cyclopropene might be more strained.

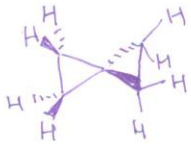
The bond angles are even further from ideal on an sp^2 carbon (ideal angle 120° versus actual angle 60°) than an sp^3 carbon (ideal 109.5° versus 60°). 2 points

c) Which molecule actually has the greater strain energy? Explain how you chose between your arguments in (a) and (b).

Cyclopropene has the greater strain energy because the deviation from the ideal angle adds more strain energy than eclipsing hydrogens. 2 points

Problem 12. Explain why the strain energy of spiro[2.2] pentane is more than simply double the strain energy of cyclopropane.

spiro[2.2]pentane



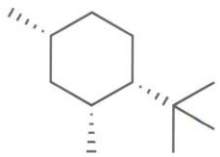
This spiro ring has the same eclipsing problem as cyclopropane, but now H eclipses a CH_2 group instead of another H. This increases the negative steric effect explained in part (a). 3 points

Also accepted an argument about bond angles, with two 60° bond angles at the central carbon.

Just for fun:

Problem 13.

a) Use A values to draw the following structure in its most stable chair conformation.



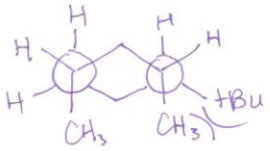
2 points

b) List the types of strain present in the chair conformation above.

g^+, g^- (or 1,3-diaxial)

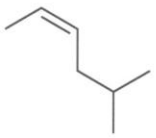
gem-dimethyl

gauche:



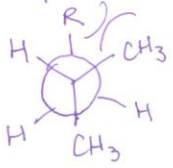
3 points

c) List the types of strain present in the following molecule.



gem-dimethyl

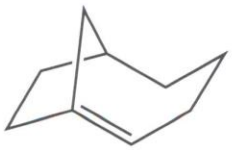
gauche:



A-strain

3 points

d) List the types of strain present in the following molecule.



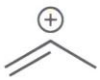
anti-Bredt (trans double bond in a ring)

transannular

gauche

3 points

Problem 14. Consider the following two molecules and their hydride ion affinities (in kcal/mol, in the gas phase).



HIA	246	258

a) Explain how the definition of hydride ion affinity tells you which carbocation is more stable.

HIA is the energy required to remove a hydride anion, so a higher value of HIA means the resulting carbocation is less stable. ⊕ has a smaller HIA, so it is more stable.

2 points

b) Rationalize your choice above: why is that carbocation more stable?

⊕ has a neighboring sp^2 carbon which is more electronegative than an sp^3 carbon. Thus, it is withdrawing electron density from an already positively charged carbon, which is destabilizing. ⊕ is stabilized because it has two methyl groups (instead of one) that can hyperconjugate.

2 points

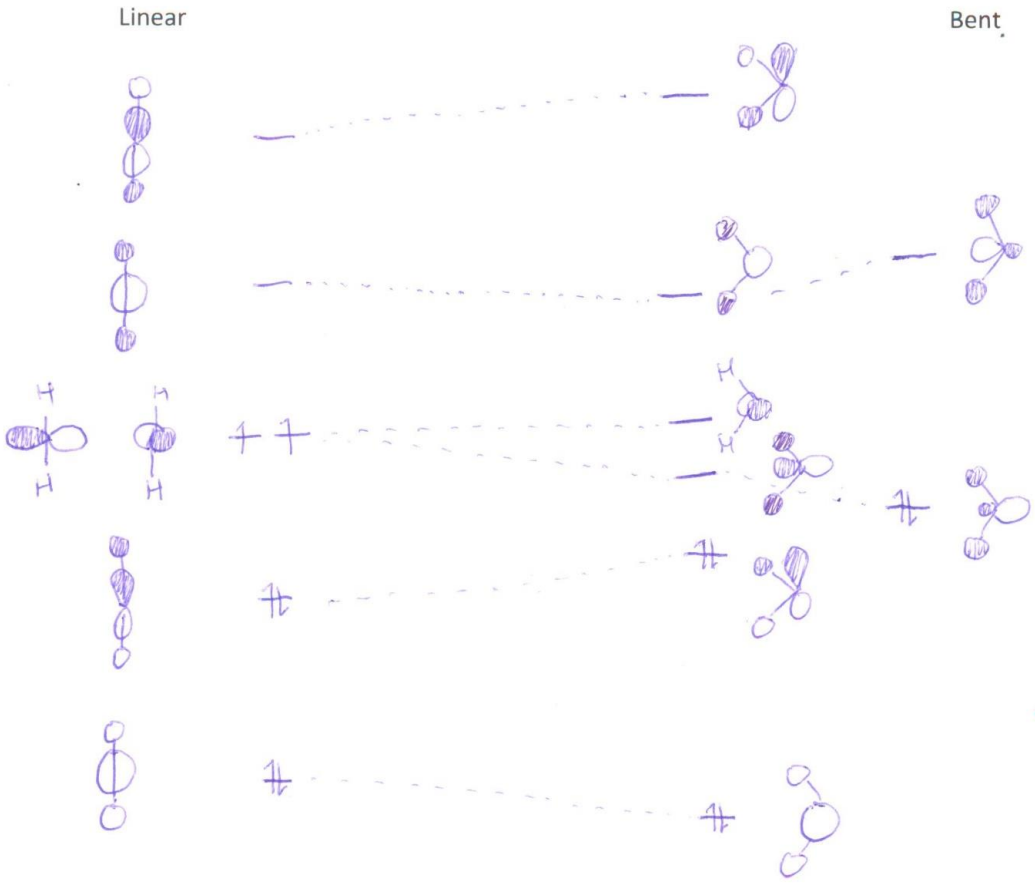
Problem 15. Explain how the H-C-H bond angles change in H_3C-X as X becomes more electronegative. Why does this occur?

As X becomes more electronegative, the C-X bond becomes more polar. More electron density is on the X. C then "rehybridizes" to put its shared electrons into an orbital with more p character. The remaining orbitals that make C-H bonds then have more s character, so the ideal bond angles increase, ie. H-C-H angle is bigger.

3 points

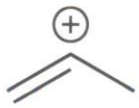
Problem 16. This is the last question!!

a) Draw the Walsh diagram for a **linear** CH_2 group on the left side of the page. Then show how the group orbitals become a **bent** CH_2 group on the right side of the page. Draw **all** orbitals and fill in electrons as appropriate for neutral CH_2 (carbene).



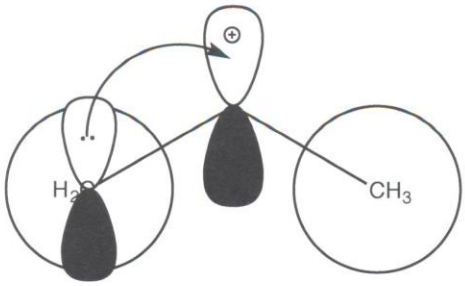
6 points

b) Below is 2-propenyl cation as it is normally drawn in introductory organic classes. Using VSEPR, predict the C-C-C bond angle as well as the hybridization of the central carbon.

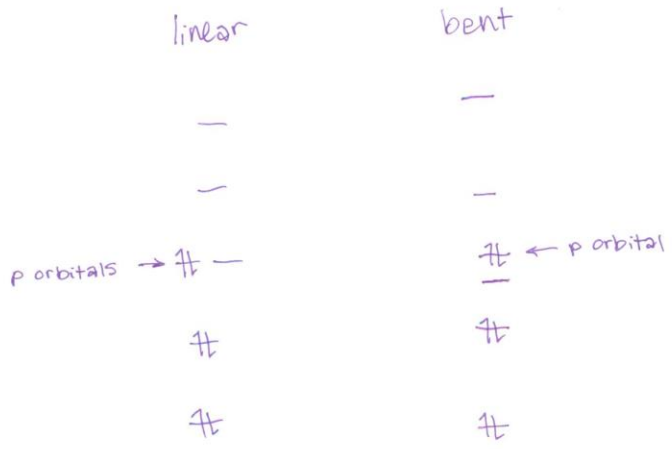


180° (linear) sp 2 points

c) Now consider the simplified version of the 2-propenyl cation below; you may treat it as you would the CH_2 group in your Walsh diagram in part (a).



Each σ bond to the central carbon contributes two electrons but the CH_2 group donates an additional pair of electrons to the p orbital of the central carbon. Given this information, populate the linear and bent forms of the CH_2 group with electrons in a simplified version of the Walsh diagram. (Simplified = don't draw all the orbitals again. Simply draw horizontal lines with appropriate relative energy to represent the orbitals for linear and bent.) Recognize that in BOTH the linear and bent forms in your diagram, the central carbon's p orbital should be occupied and you will not generate any triplet states.



6 points

d) In each form of 2-propenyl cation, linear and bent, what is the lowest-energy orbital that is empty?

linear: p orbital
bent: σ(out)

2 points

e) The experimental C-C-C bond angle is 178°. What does this mean for the energy level changes of the orbitals upon going from linear to bent in part (a)?

The occupied p orbital does not change in energy between the linear and bent forms, so the difference must be in the other two occupied orbitals, $\sigma(CH_2)$ and $\pi(CH_2)$. Thus, upon bending, $\pi(CH_2)$ must increase in energy more than $\sigma(CH_2)$ decreases in energy.

3 points

f) Compare the following bends. Which one do you expect to be lower frequency vibration (a "looser" bend)? Explain.

The highest occupied orbital, the p orbital, does not change in energy in the cation, so the cation is more free to bend (lower frequency) than the alkyne.

4 points