Chemistry 3A – Exam #1

Student Name: Pete's Key SID: _____

Point Breakdown

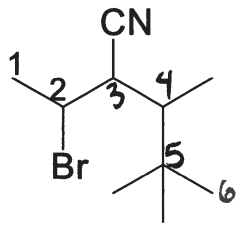
Problem 1	_____	/ 15
Problem 2	_____	/ 20
Problem 3	_____	/ 17
Problem 4	_____	/ 15
Problem 5	_____	/ 21
Problem 6	_____	/ 13
	_____	/ 12
	_____	/ 18
Problem 7	_____	/ 20

Notice: There are 151 possible points. You can earn over 100% on this exam.

Remember: Use your curved arrows to help you. Don't forget about implied hydrogen atoms. Trust yourself and try not to overthink this. And oh yea, Coulomb's Law.

Y'all are friggin' rockstars. ~Pete

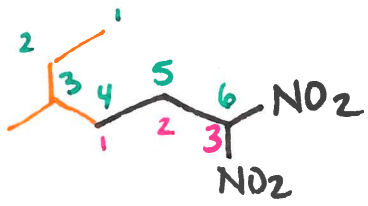
1.A. Provide a systematic name for the following molecule. Use common names where appropriate. Continue numbering the carbons based on the first 2 carbons. (2 pts)



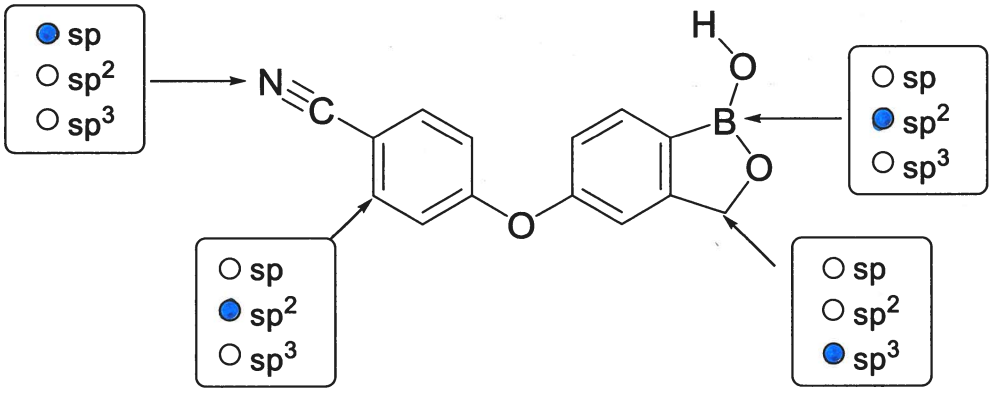
2-bromo-3-cyano-4,5,5-trimethyl hexane

1.B. Draw the molecule according to the incorrect name provided. Then provide a systematic name in the box to the right. (5 points)

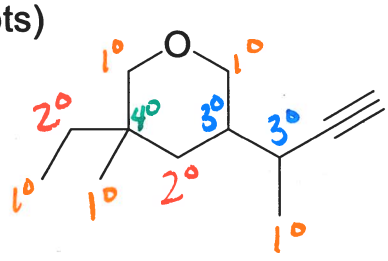
Incorrect name: 1-*sec*Butyl-3,3-dinitropropane

Molecule drawing:	**Correct name:**
	3-methyl-6,6-dinitro-hexane

1.C. What hybridization does each indicated atom have on the molecule below? (4 pts)

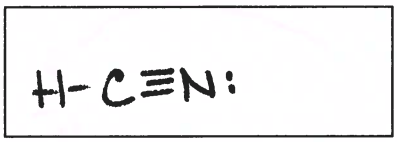


1.D. How many of each type of carbon are there in the structure below? (4 pts)



primary carbons	5
secondary carbons	2
tertiary carbons	2
quaternary carbons	1

2.A. Draw a Lewis Structure for HCN. Be sure to include any lone pairs of electrons. (3 pts)



2.B. Construct a molecular orbital diagram for HCN. Use these guidelines. (12 pts)

i) Count the valence electrons in the molecule.

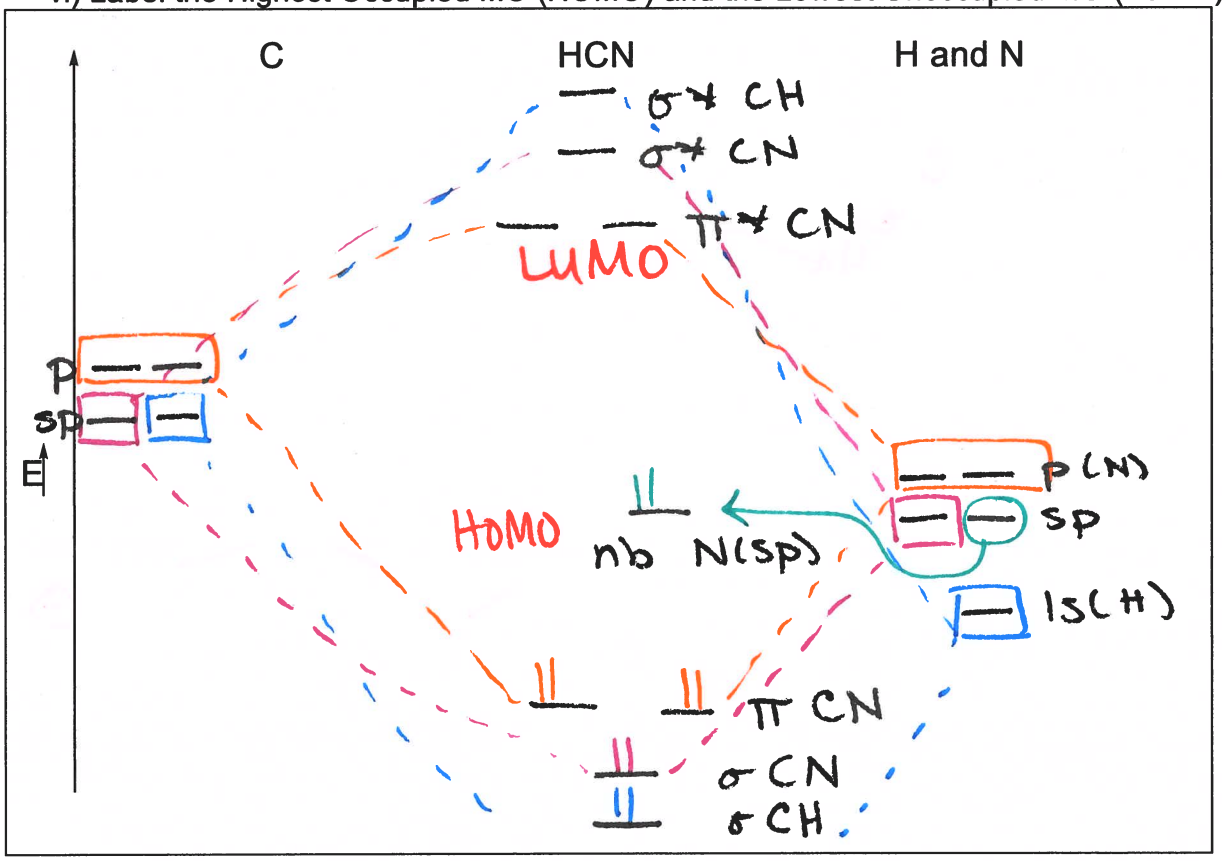
ii) Check if any atoms need to be hybridized.

iii) Construct the MO diagram by mixing atomic orbitals to form the same number of new molecular orbitals. Use your knowledge of EN to determine relative energies of the atoms' valence orbitals.

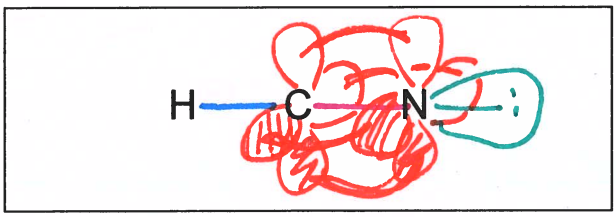
iv) Label all of the MO levels (for example: σCH, πOO, π*FCl, n.b. S(sp^3), etc.)

v) Add all valence electrons to the newly formed MOs

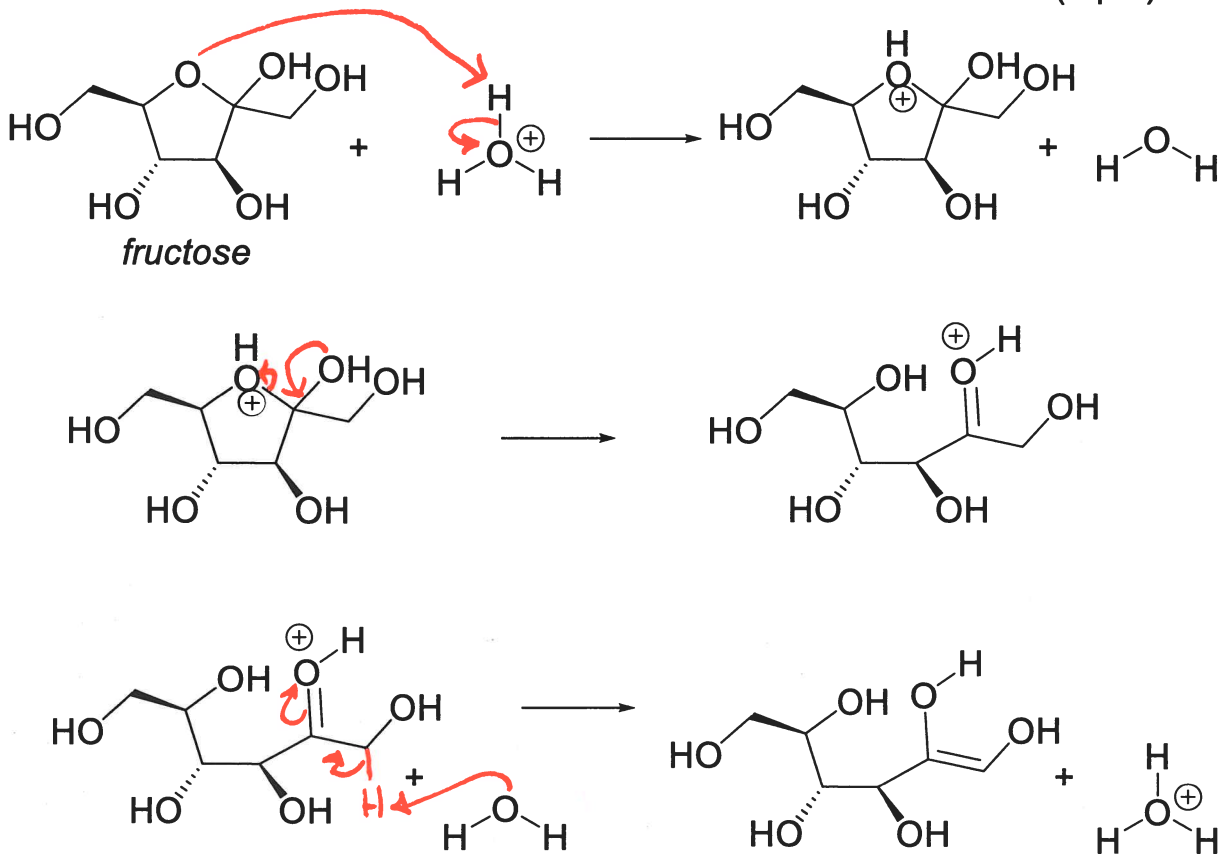
vi) Label the Highest Occupied MO (HOMO) and the Lowest Unoccupied MO (LUMO)



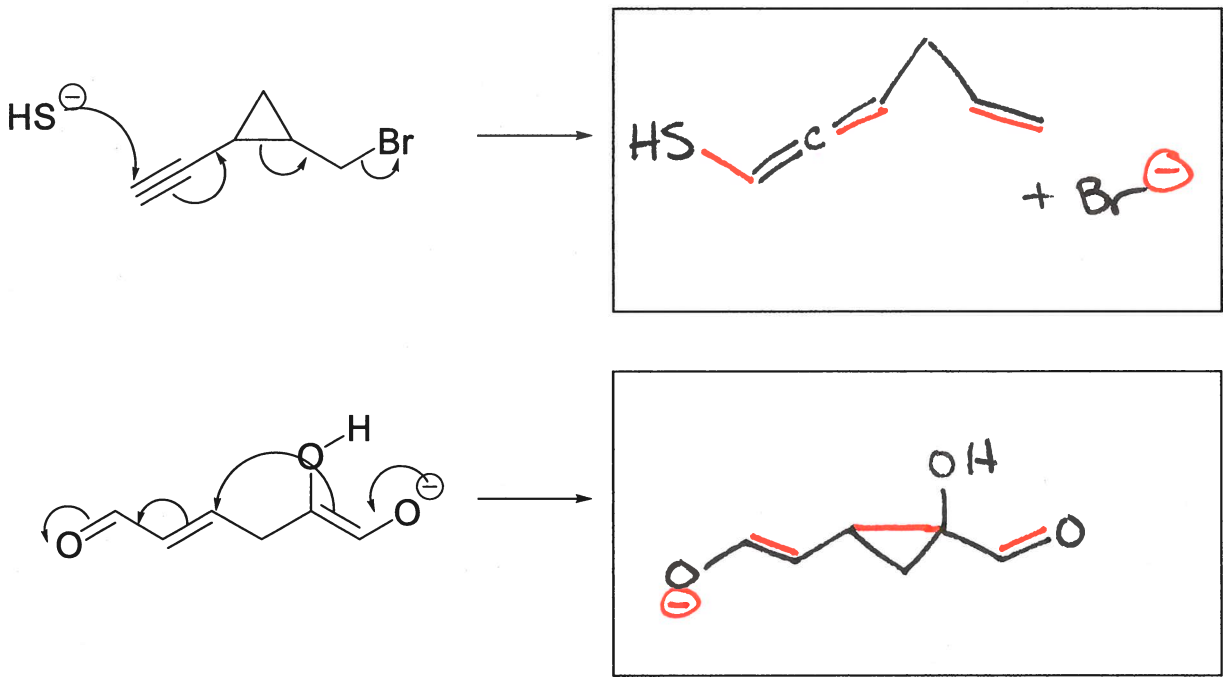
2.C. Draw a 3D picture using our hybrid orbital 3D templates. In particular, specifically show the 3D orientation of the pi-bonds and the lone pairs. (5 pts)

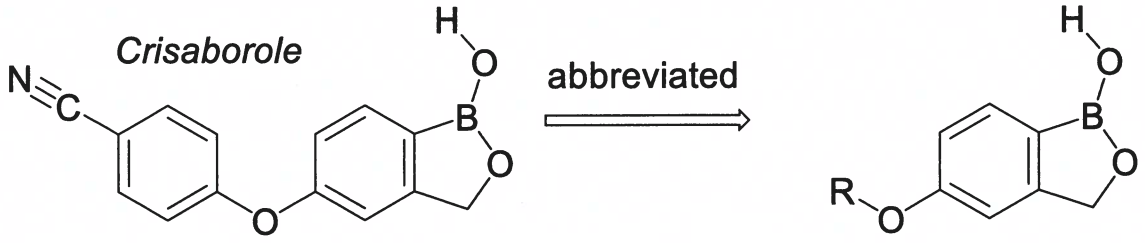


3.A. Add curved arrows to each transformation of fructose below. (9 pts)

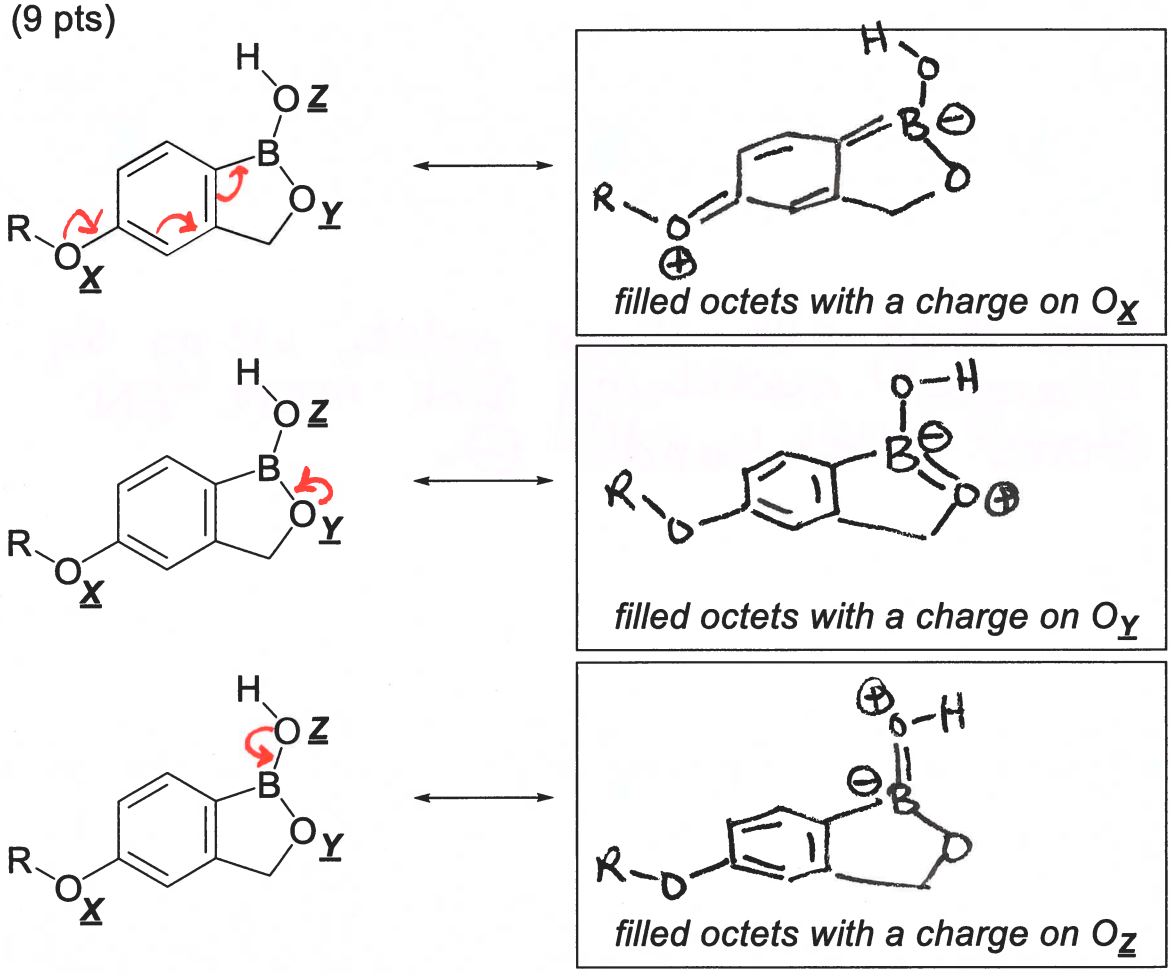


3.B. Show the products of the curved arrows below. (8 pts)





4.A. Crisaborole is a new eczema ointment. Draw the necessary resonance contributors below. **Add curved arrows for each transformation.** (9 pts)

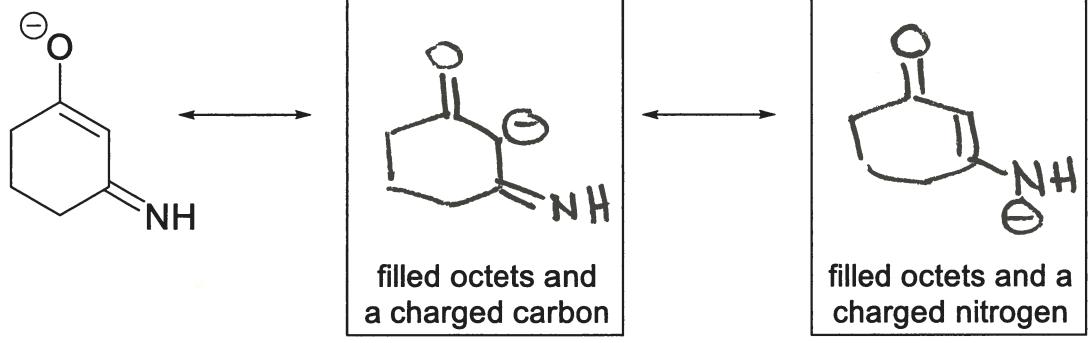


4.B. Which of the resonance contributors that you drew affects the acidity of Crisaborole? Does that increase or decrease its acidity? Why? (6 pts)

The contributor with a charged oxygen ○ X ○ Y ● Z causes the acidity of Crisaborole to ● increase ○ decrease because: ⊕ on oxygen repels the acid OR e⁻ density flows away from the acid, ↑ $S_{\oplus}$.

15 words or fewer

5.A. Show two more resonance contributors for the compound below. (6 pts)



rank 1 rank 3 rank 2

5.B. Rank the contributors above from best (1) to worst (3). Explain your ranking in 15 words or fewer. (6 pts)

Since they all have octets, we go by charges matching EN. more EN atoms better handle ⊖.

5.C. Solely based on the amount of relative partial negative charge on the atoms due to resonance, which atom would be LEAST basic? (2 pts)

○ oxygen ● carbon ○ nitrogen

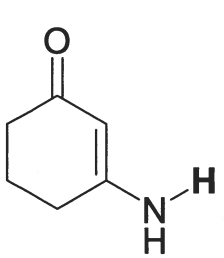
5.D. Based on the inductive effect, which atom should be LEAST basic? (2 pts)

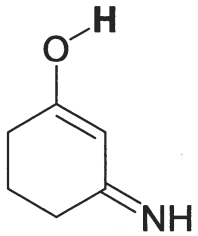
○ oxygen ● carbon ○ nitrogen

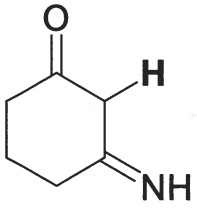
5.E. Based on the inherent electronegativity of the atom, which atom should be LEAST basic? (2 pts)

● oxygen ○ carbon ○ nitrogen

5.F. Based on the relative pKas of the bolded hydrogen atoms below, which atom of the anion from 5.A. is LEAST basic? (3 pts)


pKa = 15


pKa = 9

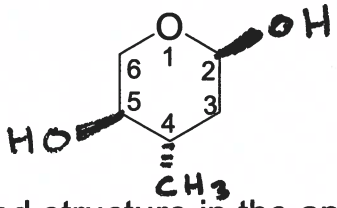

pKa = 18

Least basic atom from the anion in 5.A.

● oxygen
● carbon
○ nitrogen

lowest pKa = strongest Acid ⇒ came from weakest conjugate base.

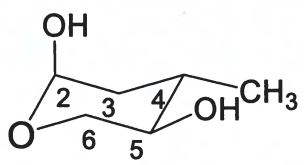
6.A. Draw the flat-ring representation of the "Chair" molecule depicted in the box under 6.D. below. Please use the provided template and use wedges and dashes. (3 pts)



6.B. Draw the chair-flipped structure in the appropriate box below. (3 pts)

6.C. Using the data provided below, calculate the ΔG for the chair flip and write the answer in the appropriate box. Show your work. (5 pts)

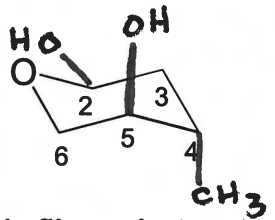
6.D. Based on your ΔG, draw in the equilibrium arrow for this chair-flip in the appropriate box. (2 pts)



Chair

ΔG = +0.2

equilibrium arrow



Chair-flipped structure

Show work:

OH(2) ax → eq −1.0
CH3(4) eq → ax +1.7
OH(5) eq → ax +1.0
+1.7

Chair: Gauche MeOH +1.5
Chairflip: None.
1.5 → 0
ΔG = −1.5 ⇒ ΔG = +0.2

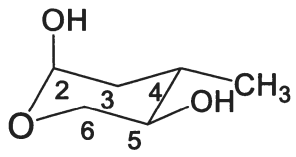
The energies reported are from flipping the chair conformer with the indicated substituent equatorial to the conformer with that substituent axial.	
Substituent	ΔG° (kcal/mol)
Me	1.70
OH	1.0

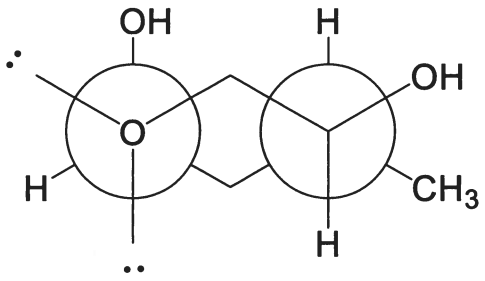
Every substituent-substituent **gauche** interaction is 1.5 kcal.

Every substituent-substituent **diaxial** interaction is 1.0 kcal.

6.E. The double-barrel Newman Projection of the "Chair" molecule has been provided below. The eyes are looking from O→2 and from 5→4. State if there are any intramolecular H-bonding interactions, and if so, which specific groups are participating. (3 pts)

Chair





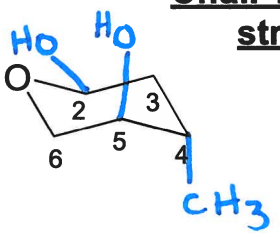
Newman O→2 and 5→4

6.E. Possible intramolecular H-bonding

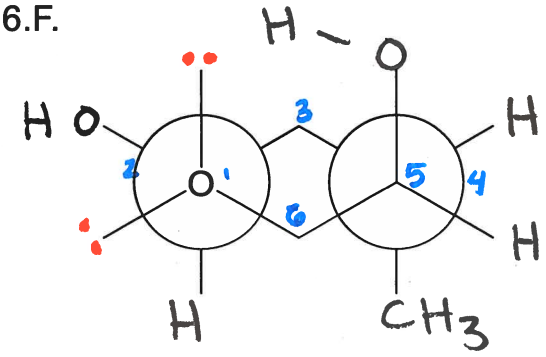
NONE

6.F.

Chair-flipped structure



6.F.



Newman O→2 and 5→4

6.G. Possible intramolecular H-bonding

OC1) and OH(5) create a 5 memb ring.

6.F. Redraw the chair-flipped structure you drew on the last page in the box above. Fill in the double-barrel Newman projection for the chair-flipped confomer along the O→2 and 5→4 bonds. (3 pts)

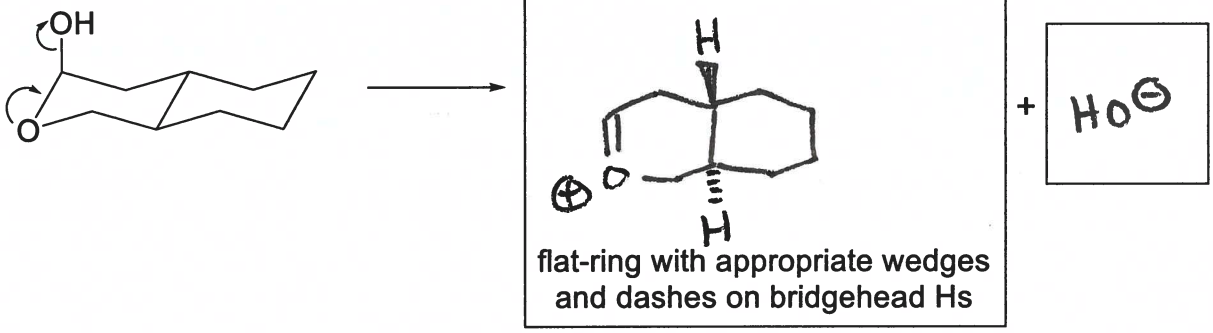
6.G. State if there are any intramolecular H-bonding interactions in the chair-flipped confomer, and if so, which specific groups are participating. (3pt)

6.H. What effect will intramolecular hydrogen bonding have on the ΔG of going from the "chair" confomer to the "chair-flipped" confomer? (3 pts)

Solely due to intramolecular hydrogen bonding, ○ "Chair" ● "Chair-flipped" is favored.

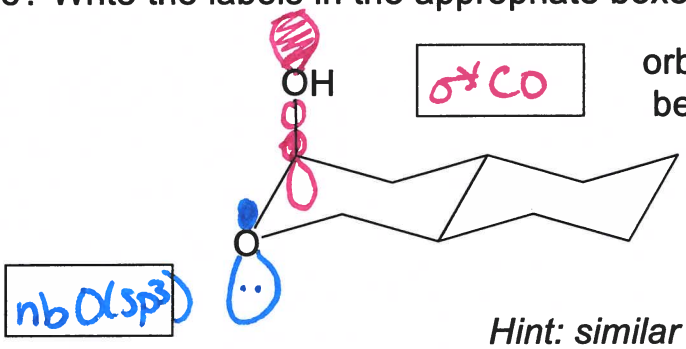
This causes the ΔG to become ○ more ● less positive.

6.I. Show the products of the curved arrows below using a flat-ring for any cyclic products. Don't forget about formal charges. Clearly add the Hs on the bridgehead atoms. Add all necessary wedges and dashes. (5 pts)



flat-ring with appropriate wedges and dashes on bridgehead Hs

6.J. Which orbitals are overlapping on the molecule for the reaction to take place? Write the labels in the appropriate boxes. (4 pts)



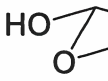
orbital electrons are being donated into

orbital originating on the oxygen in the ring

Hint: similar orbital overlap as seen in hyperconjugation.

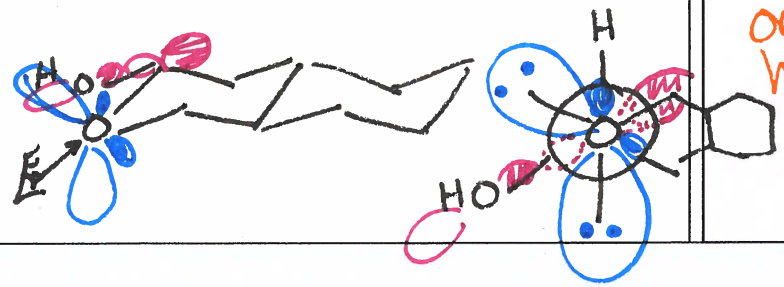
6.K. On the structure above, draw a 3D represtenation of those overlapping orbitals with proper shading to show a constructive overlap. (4 pts)

6.L. Can the isomer below undergo the same reaction shown in 6.I.? Explain your choice in 20 words or fewer and at least one image. (5 pts)



This isomer ○ can ● cannot undergo the same reaction.

image

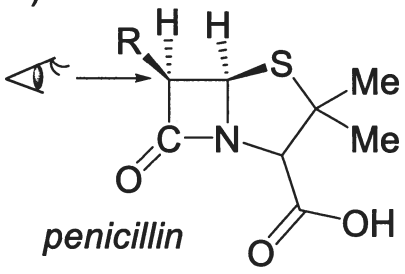


explanation

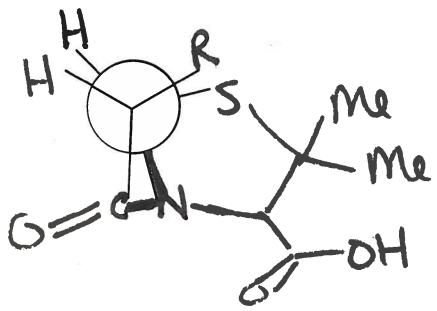
orbitals do not have correct geometry to overlap.

20 words or fewer

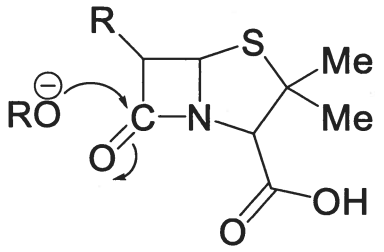
7.A. Draw a Newman Projection along the indicated bond of penicillin. (4 pts)

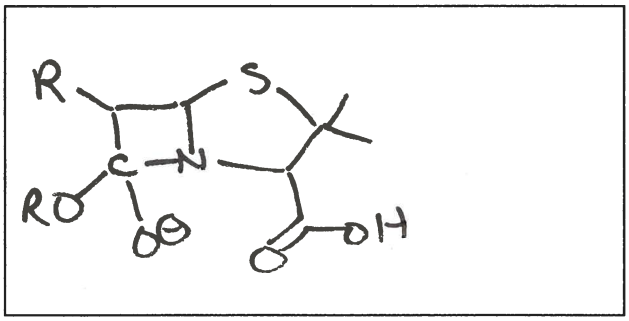


penicillin



7.B. Draw the product of the shown nucleophile attacking the electrophilic carbonyl of the amide functional group in penicillin. (3 pts)





C hybridization ○ sp ● sp^2 ○ sp^3

C hybridization ○ sp ○ sp^2 ● sp^3

7.C. What is the difference in hybridization of the attacked carbon atom in the two structures above? Fill in the appropriate bubbles. (4 pts)

7.D. Which compound would have higher ring strain? Explain in 10 words or fewer. (4 pts)

The ● reactant ○ product will have higher ring strain because:

observed angle is 90°, sp^2 desires 120° vs 109° for sp^3.

7.E. Finish the statement below. (5 pts)

The carbon atom of the amide functional group in penicillin is much more electrophilic than the carbon of a normal amide because:

reaction leads to a favorable decrease in ring strain.

You're all done! Hugs and love, y'all.