Chemistry 3A – Exam #1

Student Name: ________________________ Key

Student ID Number: ________________________

TA or Section: ________________________

Point Breakdown

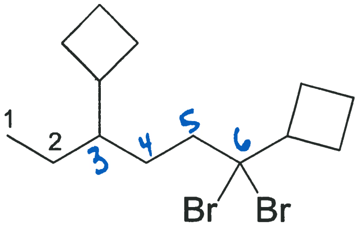
Problem 1	________	/ ~~18~~ 21
Problem 2	________	/ 16
Problem 3	________	/ 29
Problem 4	________	/ 15
	________	/ 24
	________	/ ~~18~~ 15
Problem 5	________	/ 13
	________	/ 17
Total	________	/ 150

Check that you have 9 pages.

You will have 120 minutes for this exam.

REMEMBER: Opposites attract, formal charges are required, and the octet rule is super important

1. A. Provide systematic names for the following molecules. Use common names where appropriate. Continue numbering the carbons based on the first 2 carbons. (4 pts)

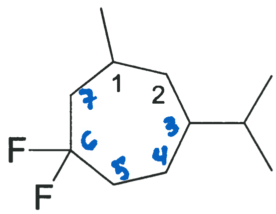


~~3,4~~ 3,6-dicyclobutyl-6,6-dibromo hexane

or

6,6-diBromo-3,6-dicyclobutyl hexane

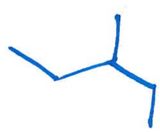
1pt root, 1pt subs



1-methyl-3-isopropyl-6,6-difluoro cycloheptane

1pt root
1pt subs

1. B. The following names are incorrect. Draw the molecule according to the name written. Write the correct name in the provided box. (8 pts)

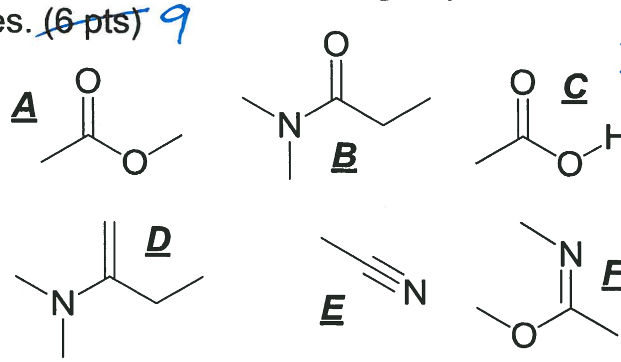
Incorrect name: *sec*Butylethane	
Molecule drawing: 	**Correct name:** 3-methyl pentane
Incorrect name: tetraMethylmethane	
Molecule drawing:  or 	**Correct name:** 2,2-dimethyl propane

2pt for drawing
2pt for accurate name of drawing

1. C. Match the names with the structures by placing the letter for the structure next to the name based on the functional group. There are more structures than names. ~~(6 pts)~~ 9

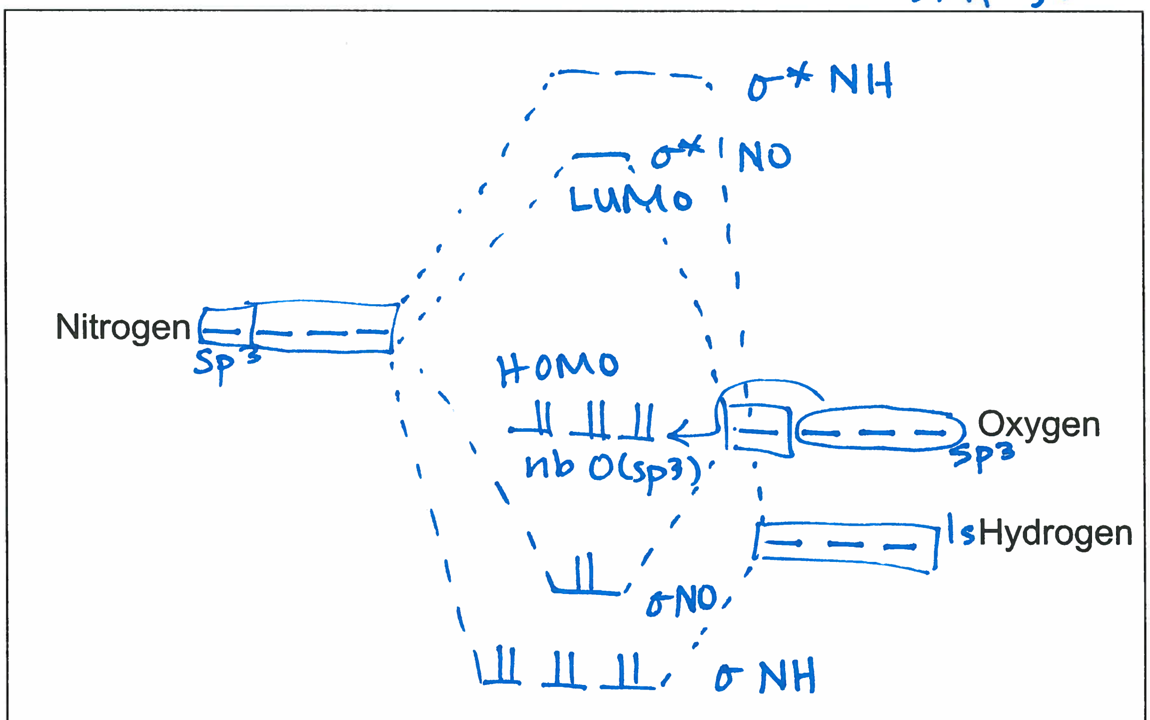
3pts each

a methyl ester	A
a dimethyl amide	B
acetonitrile	E



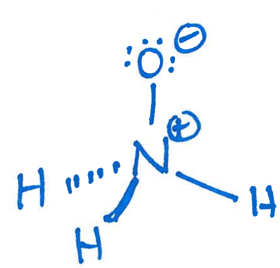
2. Construct the molecular orbital diagram for the molecule H_3NO, using the following guidelines and labeling schemes. The nitrogen is the central atom. Please be sure to include everything asked for below. (16 pts)
   a. Assume the nitrogen and oxygen atoms are both **sp^3** hybrized
   b. Indicate the relative energy levels of any atomic and hybrid orbitals on both the left and right of the diagram
   c. Clearly indicate which orbitals are being combined to make MOs
   d. Fill in all of the electrons
   e. Label all of the levels (σ, π, π*, non-bonding, etc.)
   f. Label the HOMO and LUMO

N=5, O=6, 3×H=3 } 14e⁻

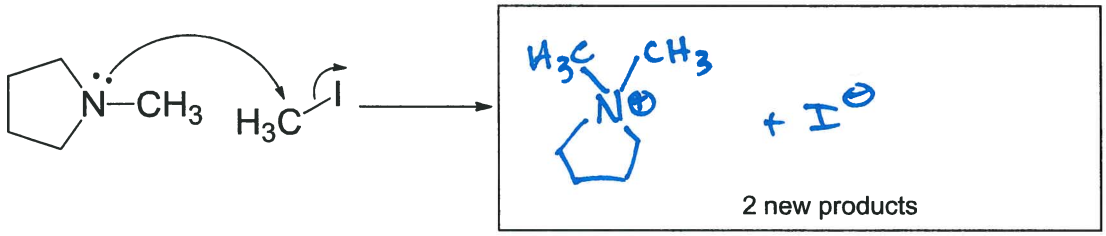


Molecular Orbital Diagram for H_3NO

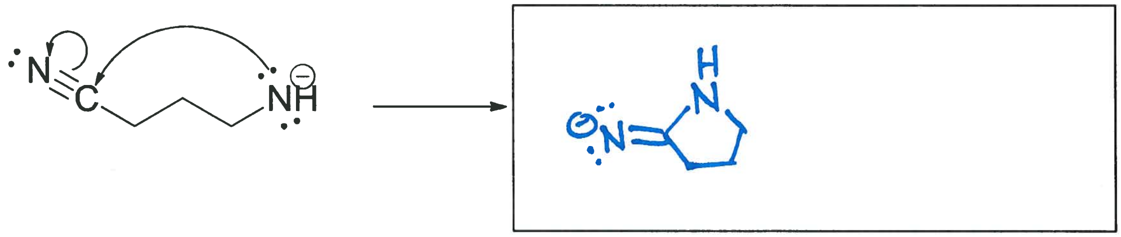
   g. Draw the 3D representation of H_3NO below. You do not need to show the location of lone pairs on oxygen. Feel free to use our template from class. You must clearly show all formal charges.

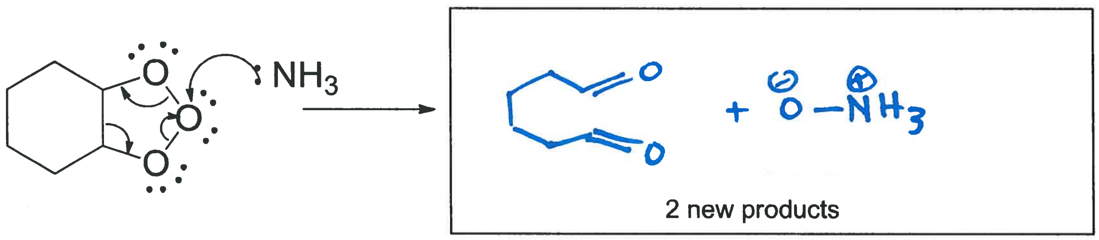


3. A. Provide the products following the electron-pushing arrows shown. Remember to pay attention to formal charges. (15 points)

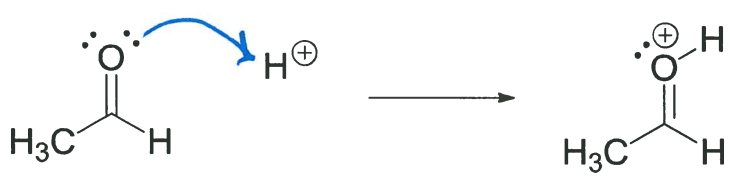


3 pts each product.

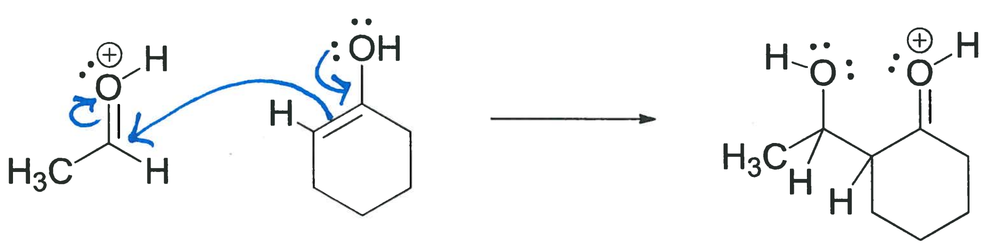


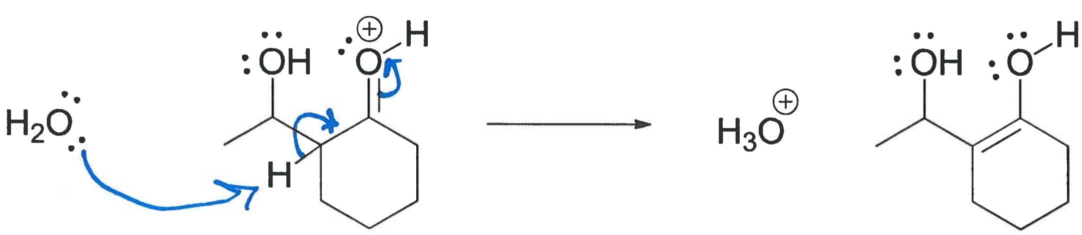


3. B. Add appropriate electron-pushing arrows for the following reactions. (14 points)

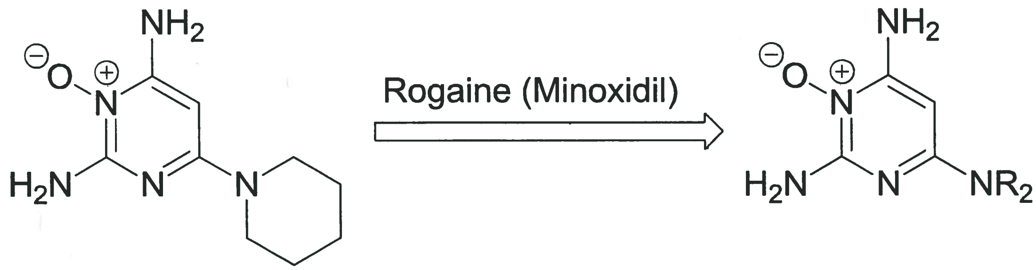


2 pt per arrow.



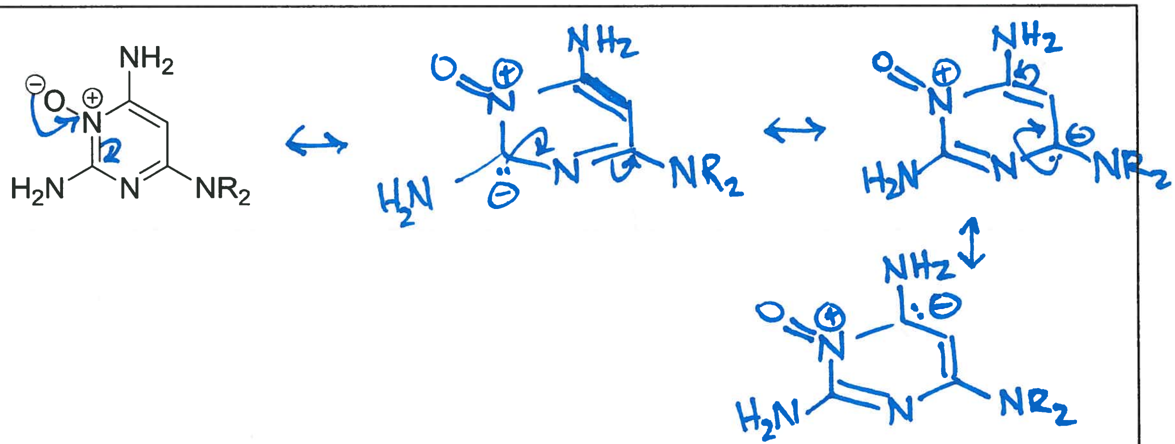


4. Minoxidil is a vasodilator medication. It's also known as Rogaine©.



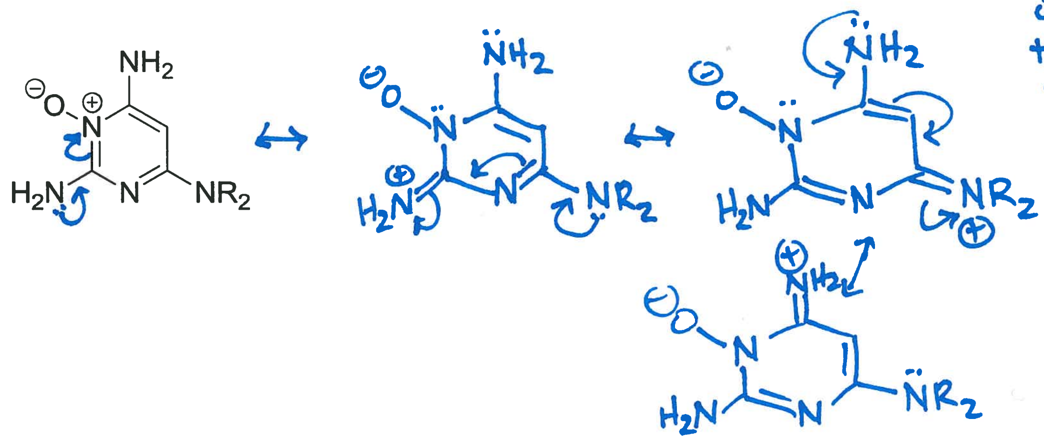
4. A. Provide resonance contributors where all atoms have filled octets for the structures below. Pay special attention to the specifications in each box. (15 pts).

3 pt each



Three more contributors, each with a **NEUTRAL oxygen** atom and a **NEGATIVE carbon** atom.

Any 2 of the 3 shown

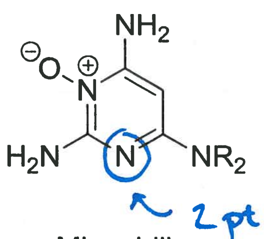


Two more contributors where all **atoms inside the shown ring** are **neutral**

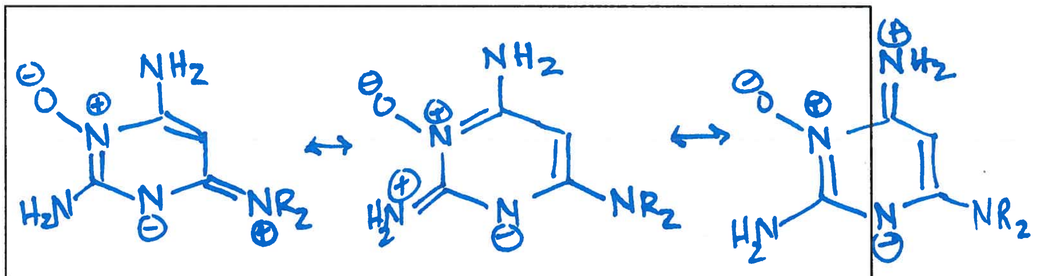
4. B. Match the four terms on the left with the four definitions on the right. Place the letter of the definition in the box next to the appropriate term. (6 pts) 1.5 pt each

Bronsted Acid	C	**A**	Molecule with a lone pair of electrons on an atom with a partial negative charge
Electrophile	B	**B**	Molecule with a partial positive charge
Bronsted Base	D	**C**	Molecule that will donate a proton
Nucleophile	A	**D**	Molecule with a lone pair of electrons that can accept a proton

4. C. Circle the Nitrogen atom on Minoxidil that is the most basic. (2 pts)



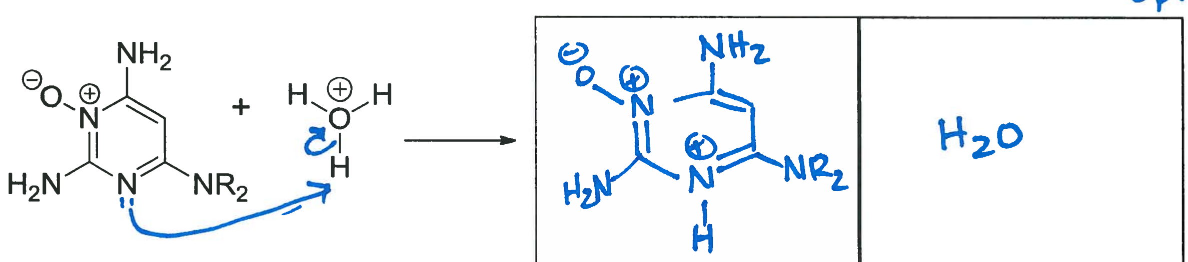
Minoxidil



Two resonance contributors for question 4.D.

4. D. Draw two resonance contributors in the space above to prove your choice in 4.C. They must have filled octets. (6 pts) any 2 of the 3 shown

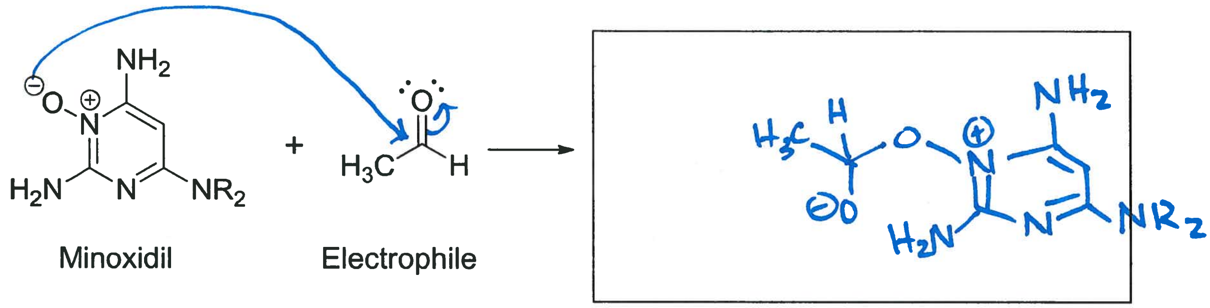
4. E. Draw the products of the reaction between the most basic nitrogen on Minoxidil and hydronium below. Make sure the formal charges are correct and that the products are in the appropriate boxes. (6 pts) 3pt per strxr



Minoxidil Hydronium Conjugate Acid Conjugate Base

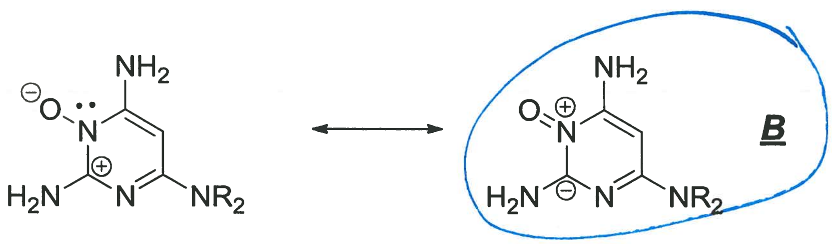
4. F. Add electron-pushing arrows to the reactants above that lead to the products drawn. (4 pts) 2 pt per arrow

4. G. Show the product of the reaction between the nucleophilic oxygen atom on Minoxidil and the electrophilic carbon on the electrophile. (3 pts)



4. H. Add appropriate electron-pushing arrows to the reactants to show the formation of the product you drew in 4.G. (4 pts)

4. I. Circle the more important resonance contributor below. (3 pts)



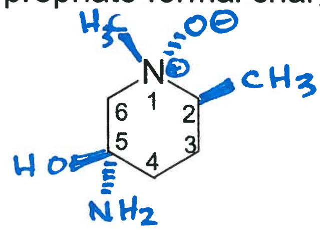
4. J. Explain your answer to 4.I. in the box below. **You may use 1 sentence and no more than 10 words.** (3 pts)

B has filled octets

4. K. Based on your answer to 4.I., do you think the carbon atoms on Minoxidil are more likely to act as electrophiles or nucleophiles? Explain. (2 pts)

nucleophiles b/c partial neg charge.

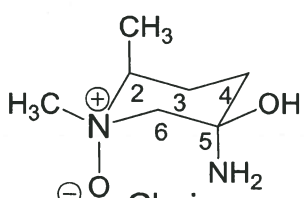
5. A. Draw the flat-ring representation of the "Chair" molecule depicted in the box below. Please use the provided template and use wedges and dashes. Add the appropriate formal charges. (3 pts)



5. B. Draw the chair-flipped structure in the box on the right. (3 pts)

5. 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)

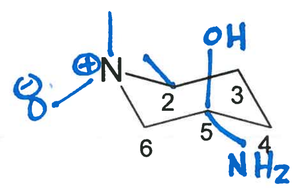
5. D. Based on your ΔG, draw in the equilibrium arrow for this chair-flip in the appropriate box. (2 pts)



Chair

ΔG = −2.5

equilibrium arrow



Chair-flipped structure

Show work:

Me eq→ax = +1.7
Me ax→eq = −1.7
O⊖ ax→eq = −2.0
HO eq→ax = +1.0
NH2 ax→eq = −1.5

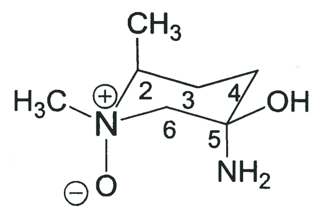
} −2.5 Kcal/mol

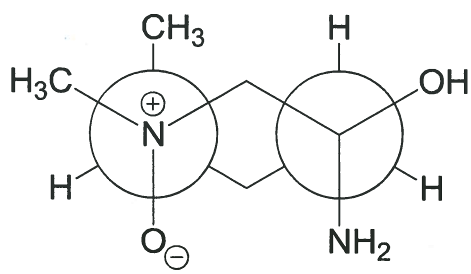
The energies reported are from flipping the piperidine chair conformer with the indicated substituent **equatorial to the conformer with the substituent axial**.

Substituent	ΔG° (kcal/mol)	Substituent	ΔG° (kcal/mol)
$O^{\ominus}$	2.0	NH_2	1.5
Me	1.70	OH	1.0

5. E. The double-barrel Newman Projection of the "Chair" molecule has been provided below. The eyes are looking from N→2 and from 5→4. Catalog all of the SUBSTITUENT-SUBSTITUENT steric interactions. Label them as either Gauche or 1,3-diaxial. (4 pts)

Chair





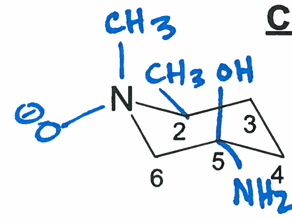
Newman N→2 and 5→4

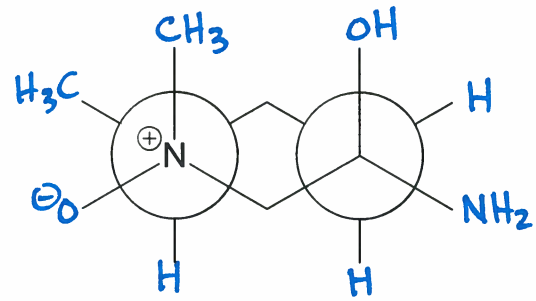
Substituent-Substituent steric interactions

Gauche: MeMe

1,3 diaxial: $O^{\ominus}$, NH_2

Chair-flipped structure





Newman N→2 and 5→4

Substituent-Substituent steric interactions

Gauche: MeMe , Me, $O^{\ominus}$

1,3 diaxial: MeOH

5. F. Redraw the substituents on the Chair-flipped structure above. Fill in the substituents on the double-barrel Newman Projection looking down the N→2 and 5→4 bonds. (3 pts)

5. G. Catalog all of the SUBSTITUENT-SUBSTITUENT steric interactions present in the Chair-flipped structure. Label them as either Gauche or 1,3-diaxial. (4 pts)

5. H. The negatively charged oxygen is less basic than expected. Explain this using the inductive effect. Use 1 sentence. (3 pts)

oxygen is bound to Nitrogen$^{\oplus}$, which pulls some e^- density toward it.

5. I. The negatively charged oxygen is even less basic in the "chair" than in the "chair-flipped" conformation. Explain. (3 pts)

lone pair on $O^{\ominus}$ can H-bond w/ NH_2 proton when 1,3 diaxial interaction is present.