NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
1st Midterm
September 22, 2022

Please print the first three letters of your last name in the three boxes

Please Note: Please take your time. We are giving you three hours to take this exam even though it is really a one hour exam. The idea is to give you enough time to show us what you know, not how fast you can draw structures. Please take all the time you need to draw the best possible structures that you can! Do not be surprised if you are comfortable leaving the exam long before 9 PM. That is to be expected!

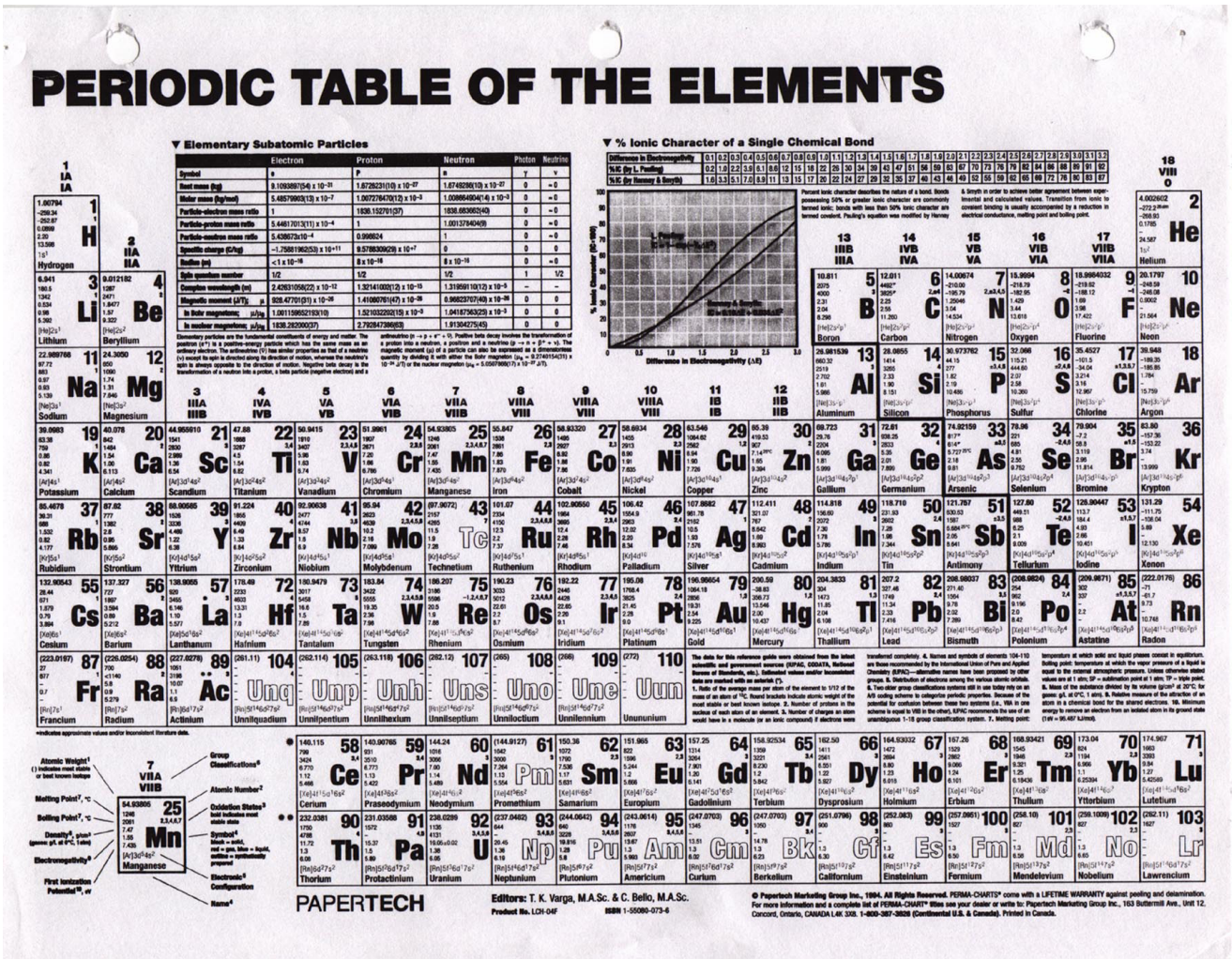
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Student Honor Code

“As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity.”

_____

(Your signature)

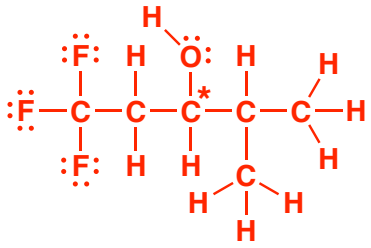


1. (4 points) What is the most important question in Organic Chemistry?

Where are the electrons?

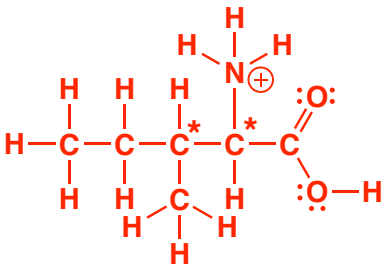
2. (8 pts each) For the following molecular formula, draw complete Lewis line structures in which all atoms (even H atoms) are drawn, lines are used as bonds, all lone pairs are drawn AND ALL FORMAL CHARGES ARE INDICATED. Note you must infer the formal charges as we do not indicate them on the chemical formulas given. You only have to draw one important contributing structure if that is relevant.

1) $CF_3CH_2CHOHCH(CH_3)_2$



How many different stereoisomers are possible for the above molecule? 2

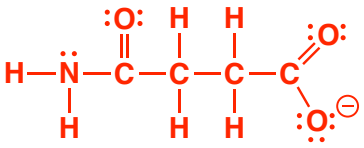
2) $CH_3CH_2CH(CH_3)CHNH_3CO_2H$



This is the amino acid isoleucine (Ile), the only amino acid with two chiral centers

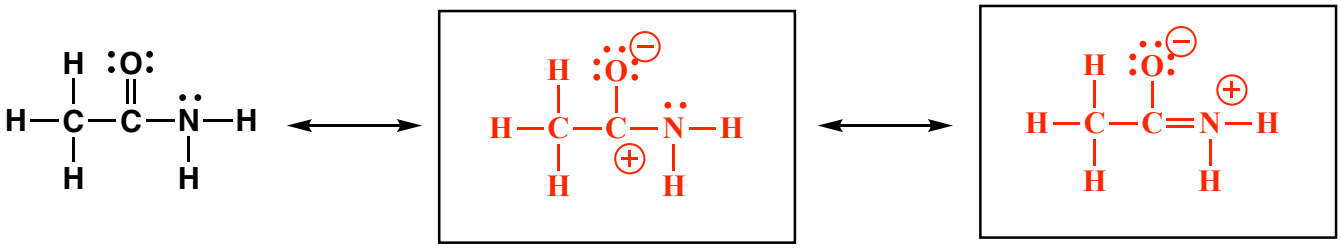
How many different stereoisomers are possible for the above molecule? 4

3) $H_2NCOCH_2CH_2CO_2$ **Hint: this one has a 1- overall charge**



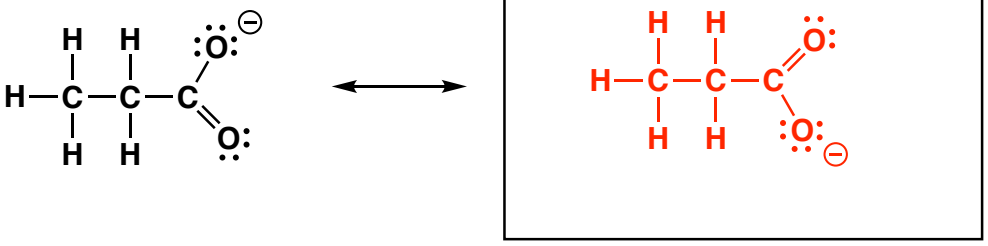
How many different stereoisomers are possible for the above molecule? 1

3. (6 pts) I told you this would be here. The following amide molecule is best represented as the hybrid of three contributing structures. **Draw the second and third important contributing structures** in the spaces provided, including all lone pairs and formal charges.

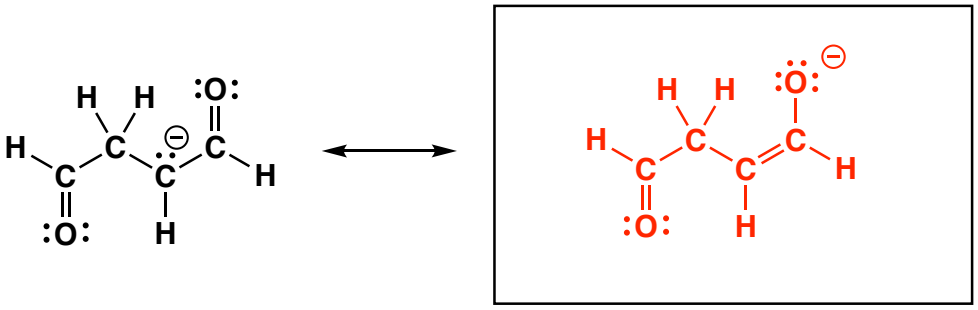


4. (6 pts) The following molecules are best represented as the hybrid of contributing structures. **Draw the second important contributing structure** in the space provided, including all lone pairs and formal charges.

A.

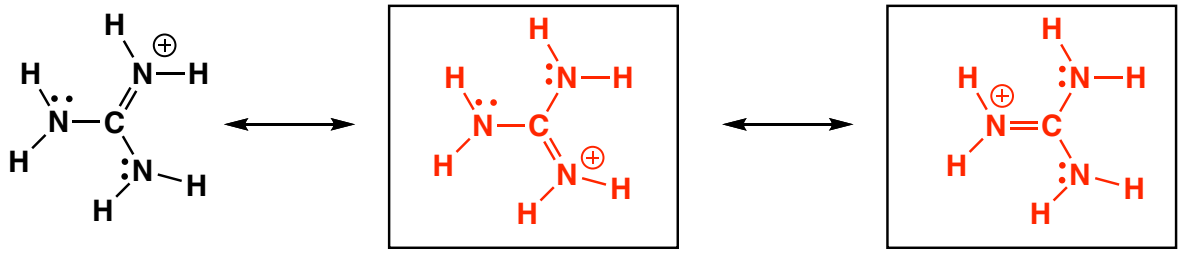


B.

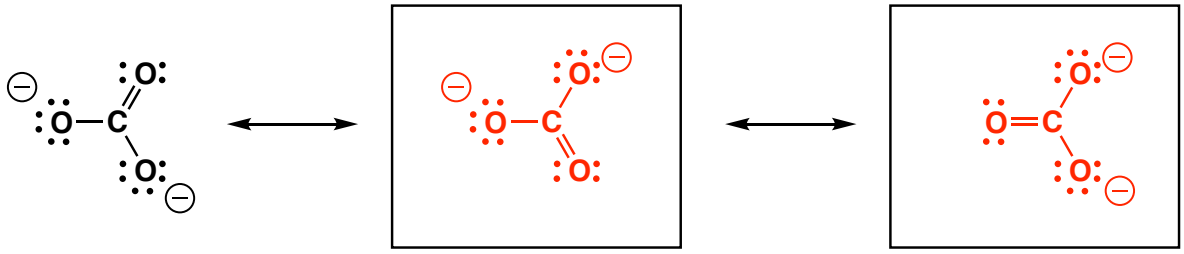


5. (12 pts) The following molecules are best represented as the hybrid of three contributing structures. **Draw the second and third important contributing structures** in the spaces provided, including all lone pairs and formal charges.

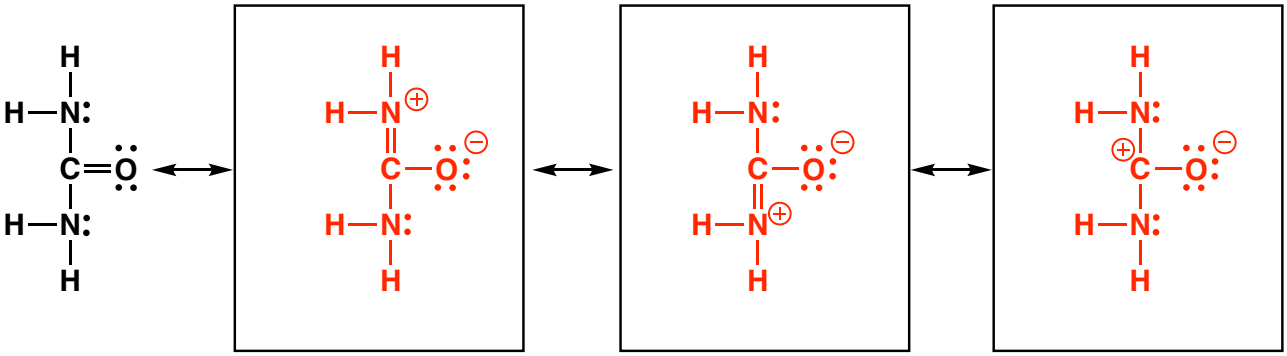
A.



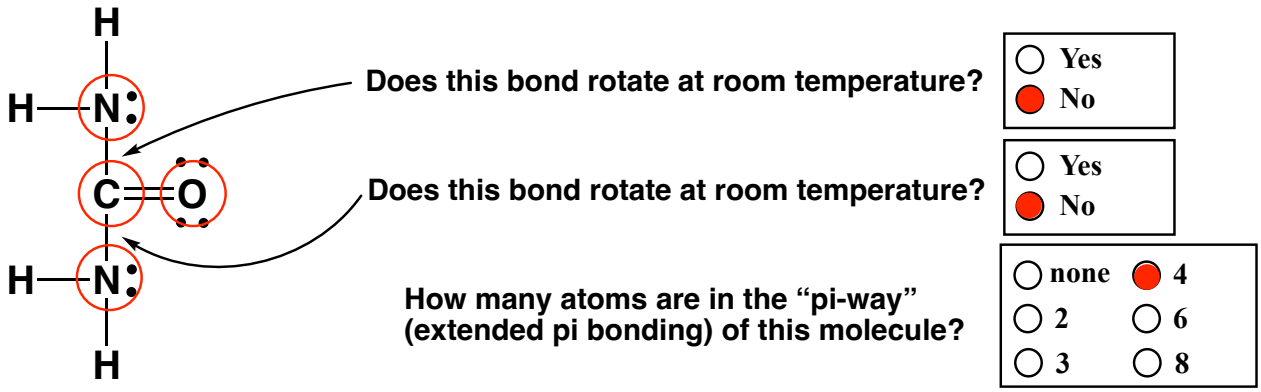
B.



6. (9 pts) The following molecule is called urea and is best represented as the hybrid of four contributing structures. **Draw the second, third and fourth important contributing structures** in the spaces provided, including all lone pairs and formal charges.



7. (10 pts) On the following molecule, circle all the atoms that are sp^2 hybridized and answer the three questions in the boxes provided by filling in the circles next to the correct answers.



8. (1 pt each) Fill in each blank with the word or words that best completes the sentences.

For organic chemistry, it is best to think of electrons as ___waves___.

The electron density in molecules can be described mathematically by adding the ___wave___ functions of all the atomic orbitals for all the atoms in the entire molecule, an approach refered to as ___molecular___ ___orbital___ theory.

The wave functions for the ___valence___ atomic orbitals on each atom can be added together first, a process referred to as ___hybridization___, before looking for overlap with orbitals from other atoms. This aproach is called ___valence___ ___bond___ theory.

You need to be able to think about all ___sigma___ bonding in molecules as being derived from the overlap of ___hybridized___ orbitals and all pi bonding as being derived from overlap of unhybridized ___2p___ orbitals.

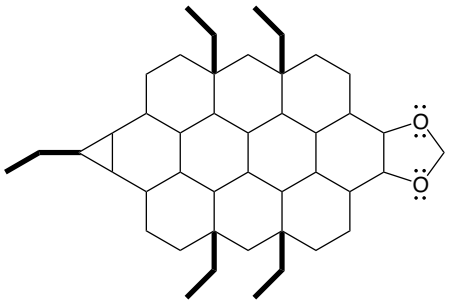
Especially for charged molecules, it is stabilizing to have ___pi___ electron density as well as charges delocalized over more than two atoms. This concept is usually referred to as "stabilization due to ___delocalization___" or simply "resonance stabilization".

For pi bonding and therefore pi delocalization to occur over more than ___two___ atoms (i.e. pi-ways), parallel ___2p___ orbitals are needed on ALL of the adjacent atoms involved, explaining why ALL of these atoms must be ___sp^2___(or ___sp___) hybridized and why these sytems are planar.

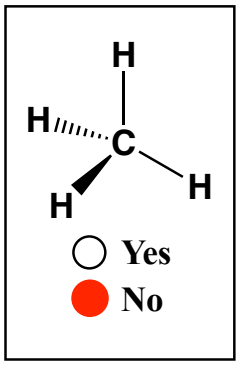
NEWS FLASH: A new species of turtle was just discovered in the turtle pond:

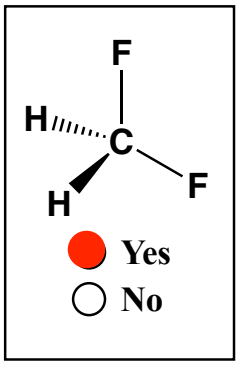
According to IUPAC, its official name is:

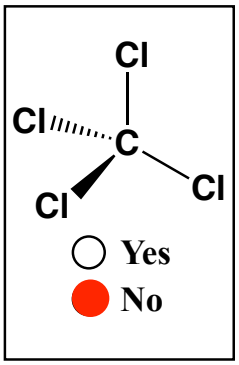
(7a*R*,8a*S*,11*r*,13a*R*,14a*S*)-7a,8a,11,13a,14a-pentaethyldotriacontahydro-1*H*-cyclopropa[10,11]ovaleno[3,4-*d*][1,3]dioxole

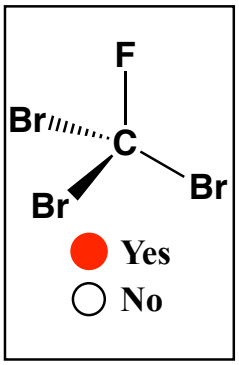


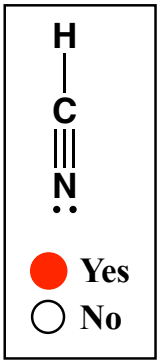
9. (18 pts) Indicate which of the following molecules have an overall molecular dipole moment. You do not need to indicate the direction of the dipole moment, or any of the individual bond dipoles. Fill in the circle next to "Yes" if the molecule has an overall molecular dipole, or "No" if the molecule does not have an overall molecular dipole moment.

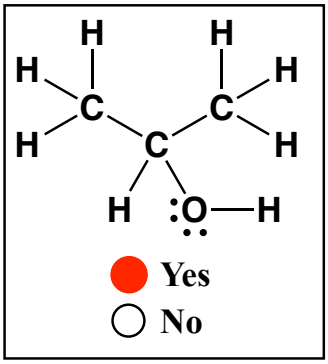


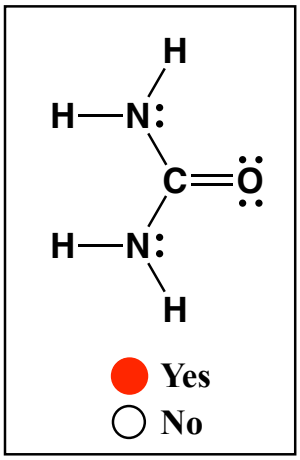


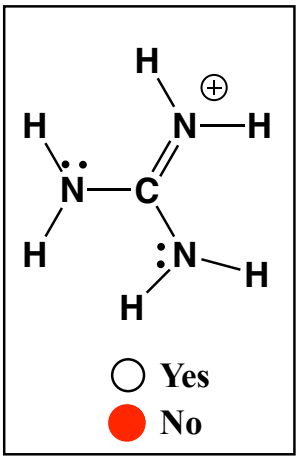


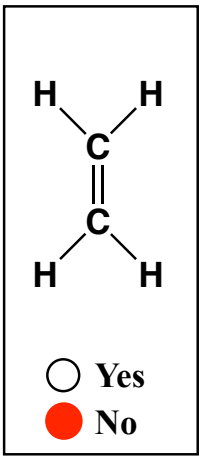




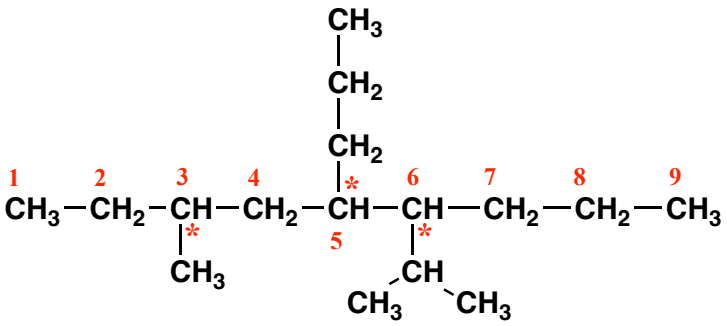








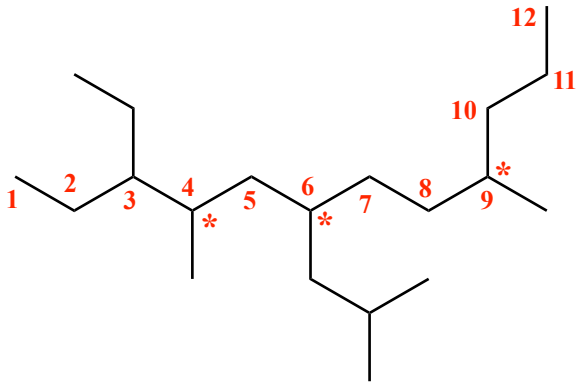
10. (7 pts) Provide an acceptable IUPAC name for the following molecule. Do not designate R or S for this.



6-isopropyl-3-methyl-5-propylnonane
or 3-methyl-6-(1-methylethyl)-5-propylnonane

Although stereochemistry is not indicated on the above structure, how many stereoisomers are possible? $2^3 = 8$

11. (7 pts) Provide an acceptable IUPAC name for the following molecule. Do not designate R or S for this.

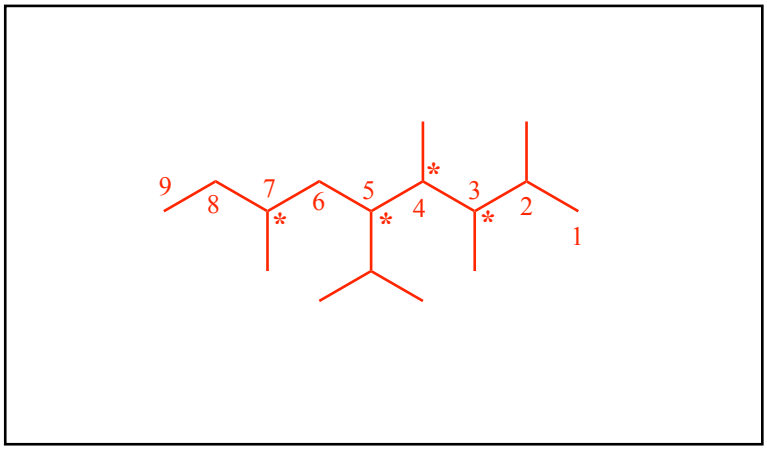


3-ethyl-6-isobutyl-4,9-dimethyldodecane
or 3-ethyl-4,9-dimethyl-6-(2-methylpropyl)dodecane

Although stereochemistry is not indicated on the above structure, how many stereoisomers are possible? $2^3 = 8$

12. (10 pts each) For the following IUPAC name, draw the appropriate line angle drawing. You can ignore R and S for this one.

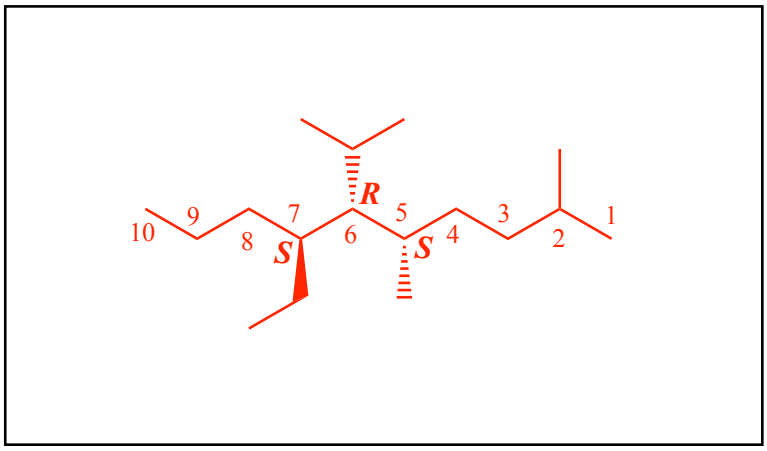
5-isopropyl-2,3,4,7-tetramethylnonane



Although stereochemistry is not indicated in the above name or your structure, how many stereoisomers are possible? $2^4 = 16$

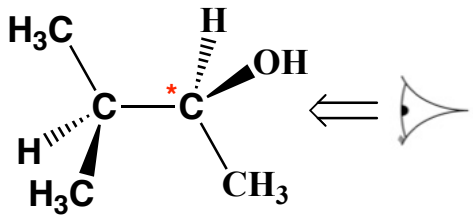
13. (10 pts each) For the following IUPAC name, draw the appropriate line angle drawing. For this one, you need to use wedges and dashes to indicate the appropriate stereochemistry at all chiral centers.

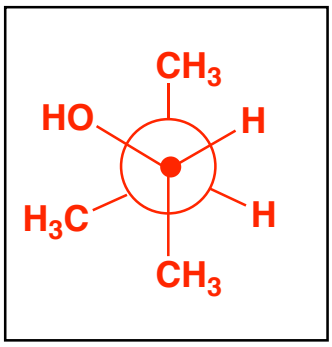
(5*S*,6*R*,7*S*)-7-ethyl-6-isopropyl-2,5-dimethyldecane



14. (5 pts) Draw the Newman projection for the conformation of 3-methyl-3-butanol as shown.

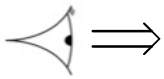
A)

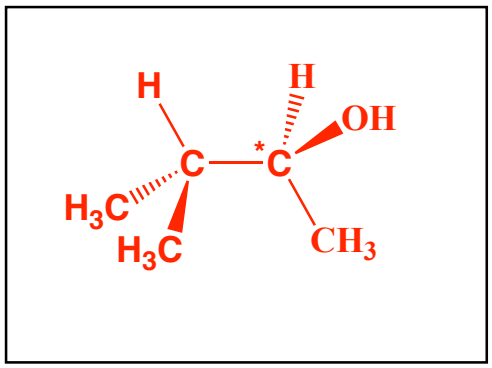


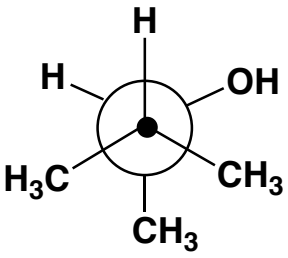


(7 pts) In the empty box draw the conformation of 3-methyl-3-butanol indicated by the Newman projection shown.

B)



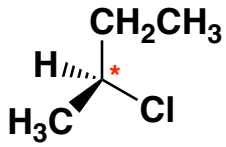




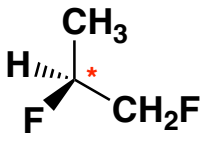
NOTICE THIS

The same molecule was used in both parts of this problem. It is chiral, is it R or S? *S*

15. (2 pts each) Examine the following structures. For each molecule with a chiral center, assign the stereochemistry then write "R" or "S" as appropriate in the box provided below each structure. For all molecules that have no chiral centers, do not put anything in the box.

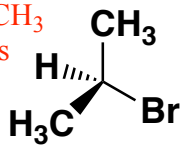


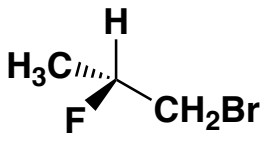
S



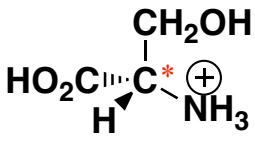
S

two -CH_3 groups

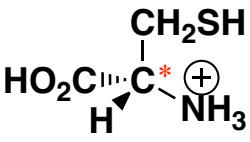




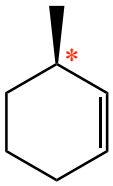
R



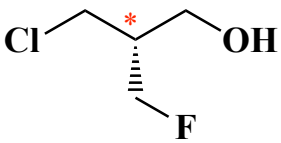
S



R

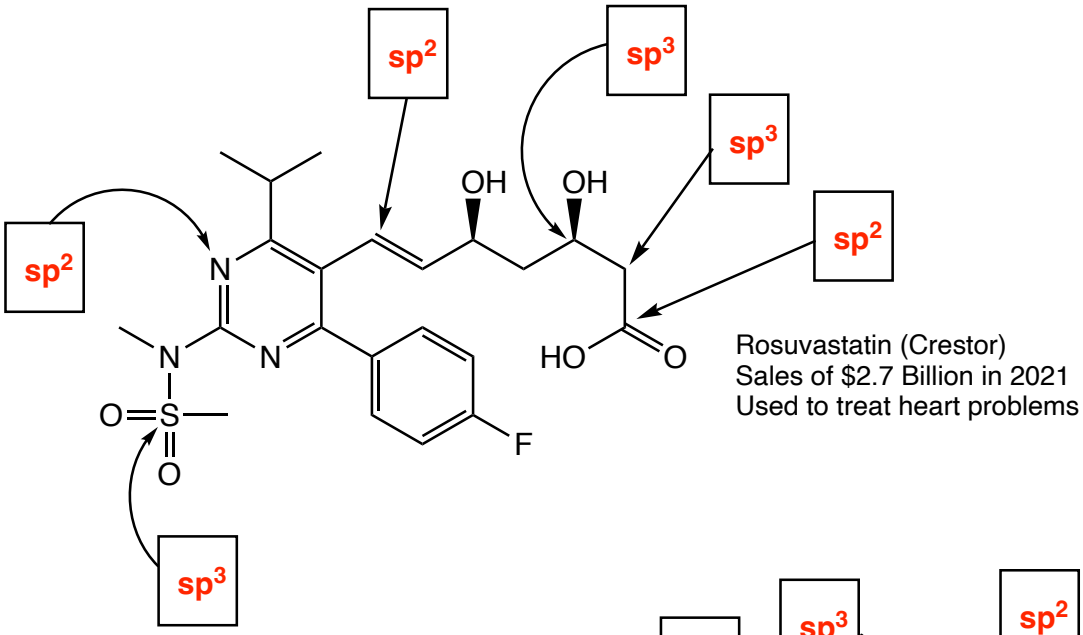


R

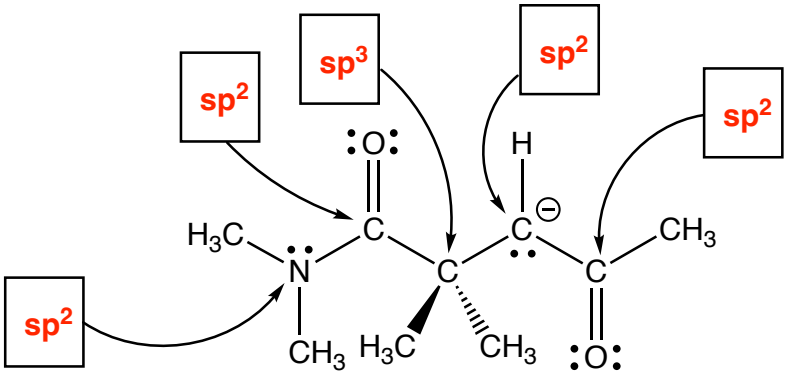


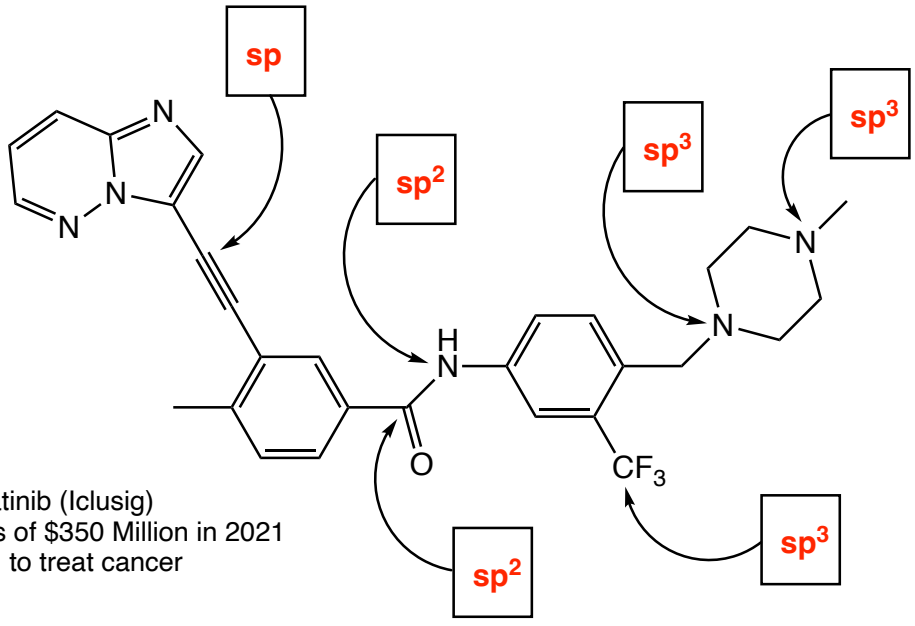
R

16. (1 pt each) In the boxes provided, write the hybridization state of the atoms indicated by the arrow.



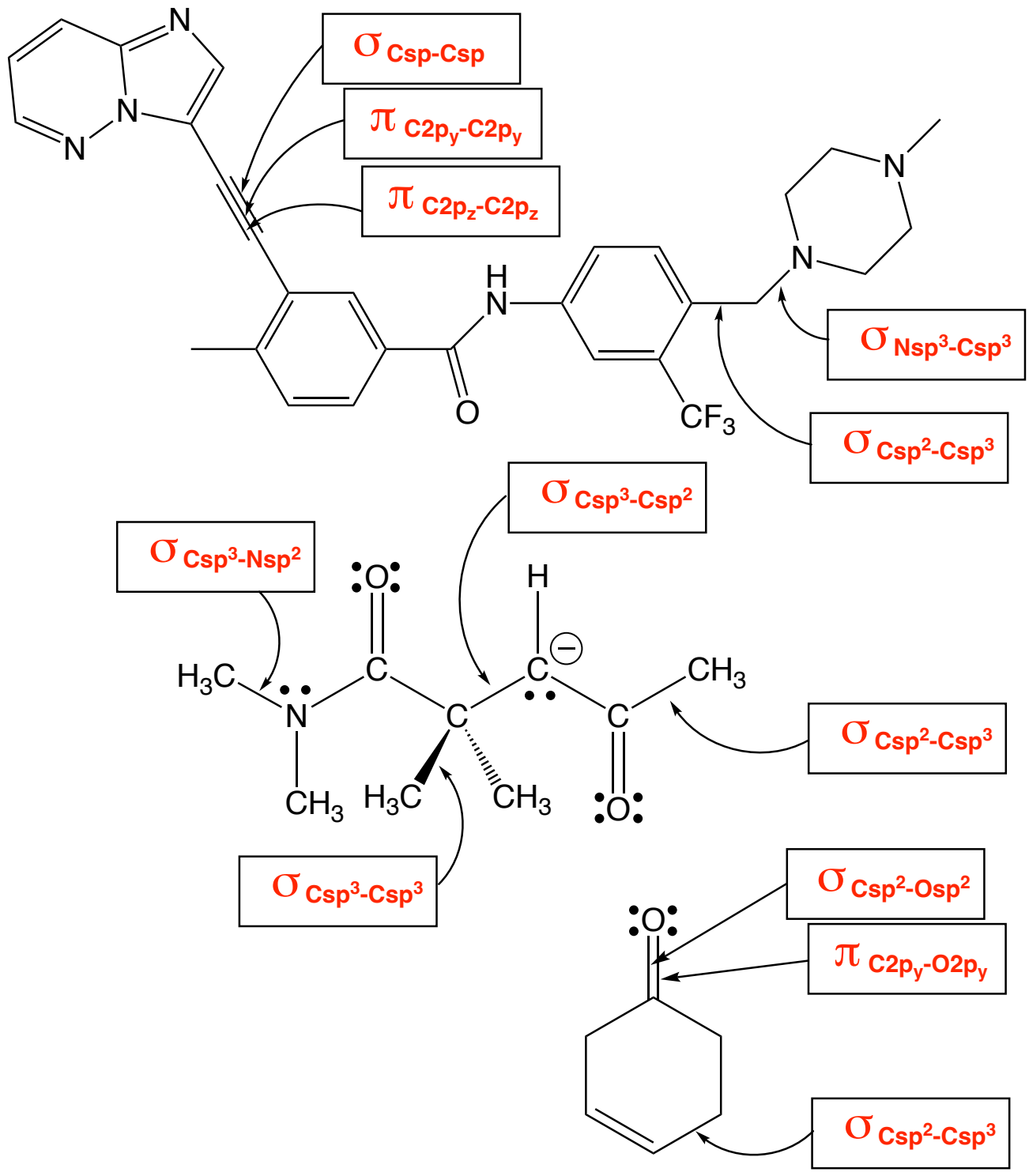
Rosuvastatin (Crestor)
Sales of $2.7 Billion in 2021
Used to treat heart problems



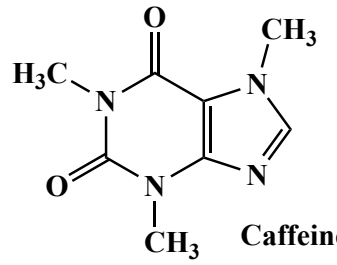


Ponatinib (Iclusig)
Sales of $350 Million in 2021
Used to treat cancer

17. (2 pts each) Describe each bond indicated with an arrow as the overlap of orbitals. For example, an answer might be $\sigma_{Csp^3\text{-}Csp^3}$

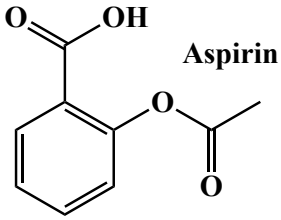


18. (22 pts) **Fill in the appropriate circle to indicate whether the molecule is chiral or not chiral. Then answer the three questions at the bottom of the page.**



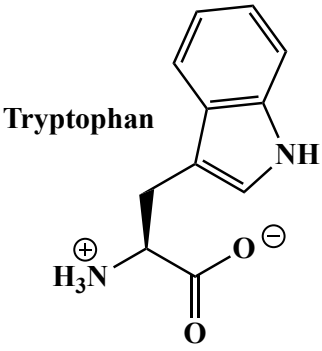
Caffeine

○ Chiral ● Not Chiral



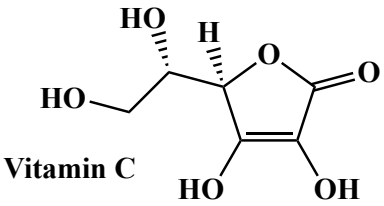
Aspirin

○ Chiral ● Not Chiral



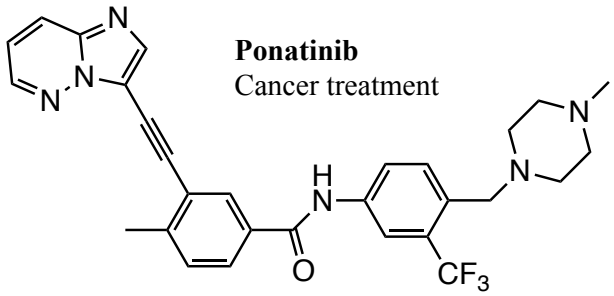
Tryptophan

● Chiral ○ Not Chiral



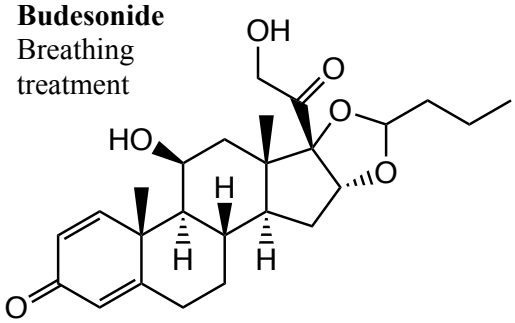
Vitamin C

● Chiral ○ Not Chiral



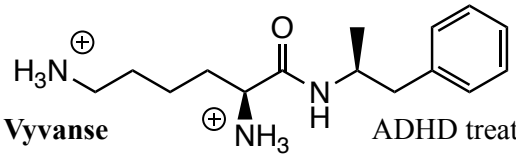
Ponatinib
Cancer treatment

○ Chiral ● Not Chiral



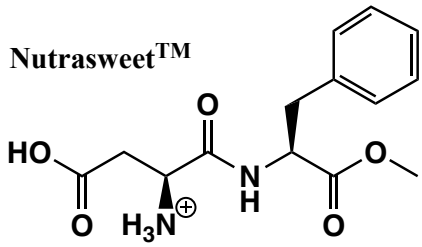
Budesonide
Breathing treatment

● Chiral ○ Not Chiral



Vyvanse — ADHD treatment

● Chiral ○ Not Chiral



Nutrasweet™

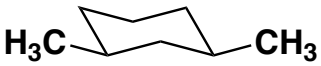
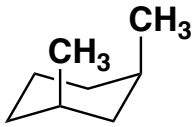
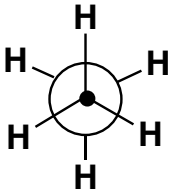
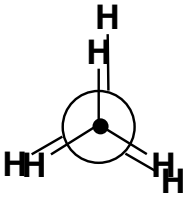
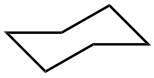
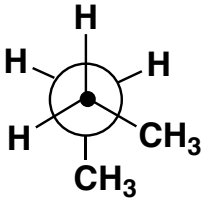
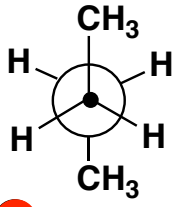
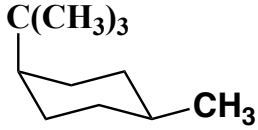
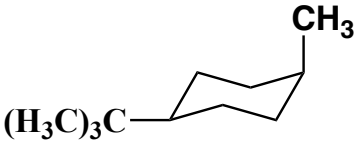
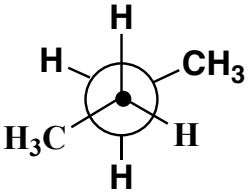
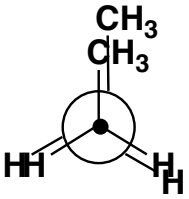
● Chiral ○ Not Chiral

How many stereoisomers of Tryptophan are possible? **2**

How many stereoisomers of aspirin are possible? **1**

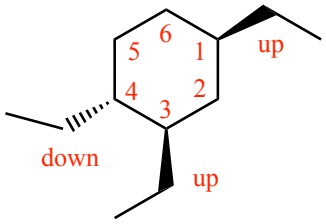
How many stereoisomers of Nutrasweet™ are possible? **4**

19. (4 pts each) For each pair of molecules, fill in the circle under the one that is more stable of the two, then put an "X" in the box under all the types of strain that explain(s) your answer:

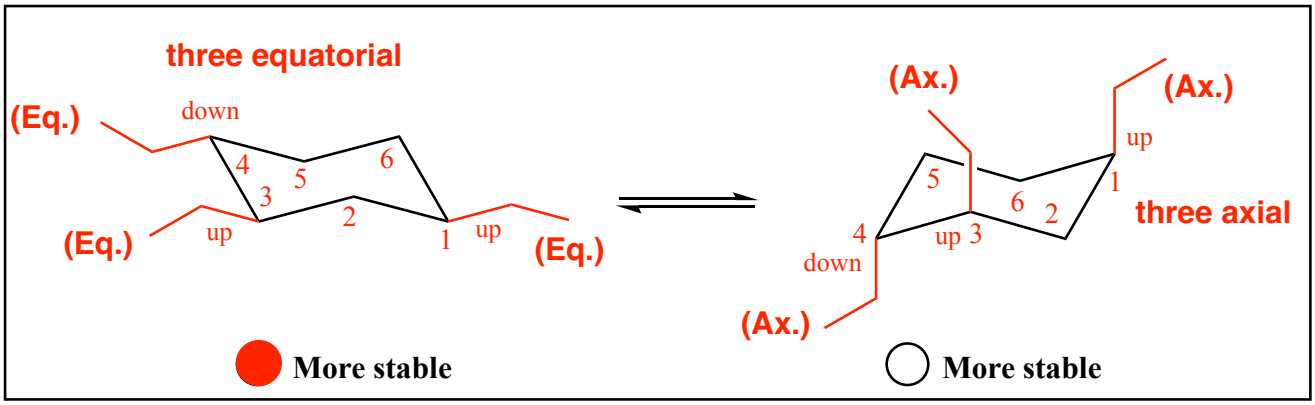
		Angle strain	Torsional strain	Steric strain
 ● More stable	vs.  ○ More stable	☐	☐	X
 ● More stable	vs.  ○ More stable	☐	X	☐
 ● More stable	vs.  ○ More stable	X	X	☐
 ○ More stable	vs.  ● More stable	☐	☐	X
 ○ More stable	vs.  ● More stable	☐	☐	X
 ● More stable	vs.  ○ More stable	☐	X	X

20. (20 pts) For the following cyclohexane derivatives, draw the two alternative chair conformations. IF there is a difference in stability, fill in the circle that says "More stable". If there is not any difference in stability, do not fill in any circle.

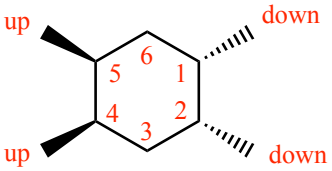
A)



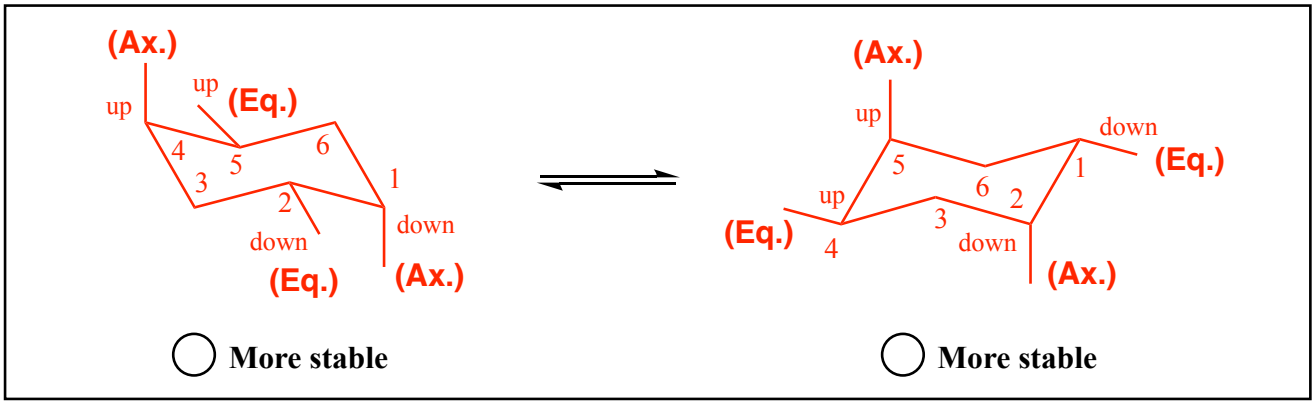
It is critical that you number in the same direction on all structures, I numbered clockwise here



B)

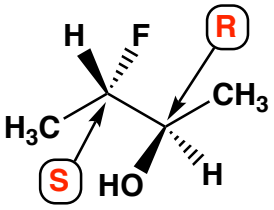


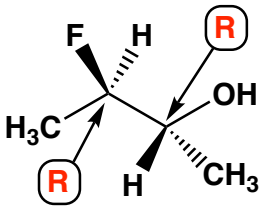
It is critical that you number in the same direction on all structures, I numbered clockwise here



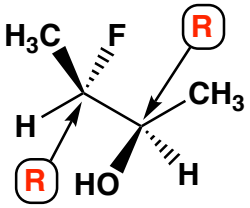
23. (38 pts) For each pair of molecules, on the line provided state the relationship between the two structures. Possible answers could be **enantiomers**, **diastereomers, consitutional isomers**, or **same molecule. Fill in the circle to indicate the correct relationship between the molecules shown. In the boxes provided next to each chiral center, write "R" or "S" to indicate the absolute stereochemistry present.**

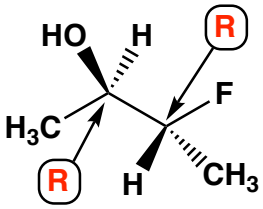
Relationship:



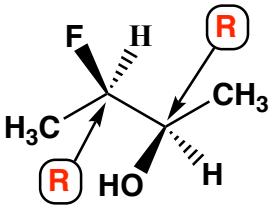


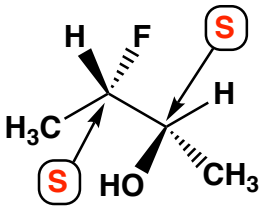
- ○ enantiomers
- ● diastereomers
- ○ constitutional isomers
- ○ same molecule



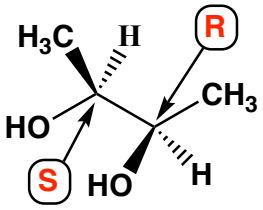


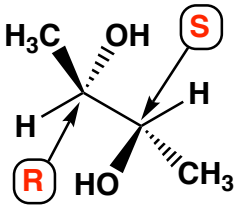
- ○ enantiomers
- ○ diastereomers
- ○ constitutional isomers
- ● same molecule





- ● enantiomers
- ○ diastereomers
- ○ constitutional isomers
- ○ same molecule

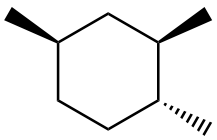


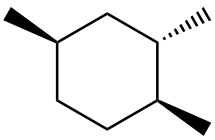


Both are meso!

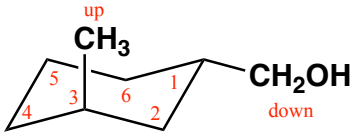
- ○ enantiomers
- ○ diastereomers
- ○ constitutional isomers
- ● same molecule

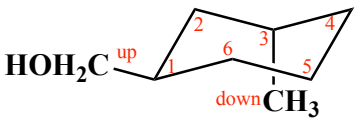
You do not need to label the chiral centers with "R" or "S" on these last three.





- ○ enantiomers
- ● diastereomers
- ○ constitutional isomers
- ○ same molecule

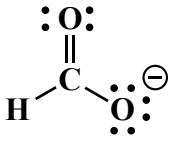




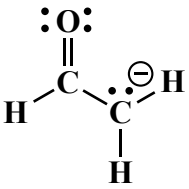
- ● enantiomers
- ○ diastereomers
- ○ constitutional isomers
- ○ same molecule

22. (22 points total). Here is an "apply what you know" problem in the form of an MCAT style passage.

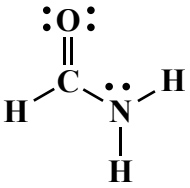
We have seen a number of molecules that contains a three-atom, delocalized pi bond (a "pi-way"). In partcular, we have seen a carboxylate ion, enolate ion, and of course, amides. Each of the three atoms donates a 2p orbital that overlap.



Carboxylate Ion

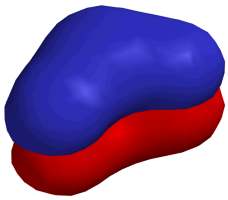


Enolate Ion

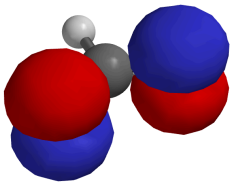


Amide

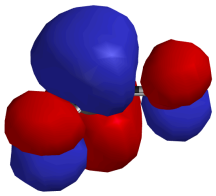
When the three 2p orbitals overlap, there are three pi molecular orbitals formed that extend over all three atoms. You have seen these before, and they are shown below:



Orbital A



Orbital B



Orbital C

1. (4 pts) From the following choices, fill in the circle for the answer that accurately **lists the three molecular orbitals in order from lowest to highest energy**:

- ● Orbital A Orbital B Orbital C
- ○ Orbital B Orbital C Orbital A
- ○ Orbital A Orbital C Orbital B
- ○ Orbital C Orbital B Orbital A

One of the more difficult parts of the analysis of delocalized pi bonding concerns how many electrons are involved in the pi molecular orbitals. Each of the ions shown above, the carboxylate ion, the enolate ion, and the amide, have the same number of pi electrons in the pi molecular orbitals.

22 (cont).

2. (4 pts) Fill in the circle for the answer that **lists how many electrons reside in these pi molecular orbitals in the carboxylate ion, the enolate ion and the amide**?

- ◯ 2 pi electrons total
- ◯ 3 pi electrons total
- ● 4 pi electrons total
- ◯ 6 pi electrons total

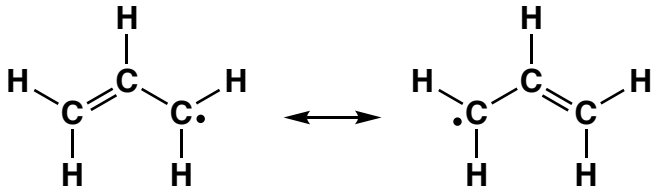
3. (4 pts) Fill in the circle for the answer that lists **which of the orbitals are filled by the electrons you listed in part two above**.

- ◯ Orbitals A, B and C
- ● Orbitals A and B
- ◯ Orbital A only
- ◯ Orbitals A and C

Your answer to part 3. explains the properties of the carboxylate ion, the enolate ion and the amide.

For example, let's consider the carboxylate ion. By understanding which of these orbitals are filled, it explains why there is partial double bond chacacter over all three atoms (O-C-O) and why the negative charge is located on only the two oxygen atoms.

Later this semester you will learn that there are some highly reactive intermediates that have an unpaired electron in their valence shell, and these are called "radicals". One example is shown below, it is called the "allyl radical" and it is best described as the resonance hybrid of two contributing structures. Note that radicals have no formal charge!



The allyl radical

It turns out that all of the carbon atoms of the allyl radical are sp^2 hybridized and the three 2p orbitals overlap to create the same three pi molecular orbitals shown above in this problem.

22 (cont).

4. (4 pts) Fill in the circle for the answer that lists **how many electrons reside in these pi molecular orbitals in the allyl radical?**

- ◯ 2 pi electrons total
- ● 3 pi electrons total
- ◯ 4 pi electrons total
- ◯ 6 pi electrons total

One of the pi molecular orbitals of the allyl radical is only half-filled, containing the electron density for only a single electron, not a pair of electrons! That is why radicals are so reactive, they react to make bonds that fully fill their valence shell.

5. (4 pts) Given everything you know about delocalized pi molecular orbitals, fill in the circle for the answer that correctly lists **the pi molecular orbital that is half-filled in the allyl radical**.

- ◯ Orbital A
- ● Orbital B
- ◯ Orbital C
- ◯ Yay, only one more 2pt question and you finished the exam!

6. (2 pts) Examine the contributing structures for the allyl radical above, does the orbital you selected in part 5. make sense to you?

- ◯ No, there is no correlation between the molecular orbitals and contributing structures
- ● Yes, the orbital I chose and the contributing structures place the unpaired electron density on the same atoms.

A good way to get ready for a 5K race is to remember that avoiding a running injury means being patient and increasing your distance slowly. Start by running as far as you can comfortably. Do not push it at the beginning. Let's say you can run 1 mile before feeling too out of breath. Run that 1 mile 2-3 times a week at first, making sure you have no foot or leg pain. If you do have foot/leg issues, try new running shoes fit by a professional (The Loop or Rogue Running are great running stores for this). After you are comfortable running 1 mile for a week, try 1.25 miles for 2-3 times the next week. Then run to 1.5 miles, then 2.0 miles, then 2.5 miles each 2-3 times for a week. It will then be time for the race and you will make it!!!