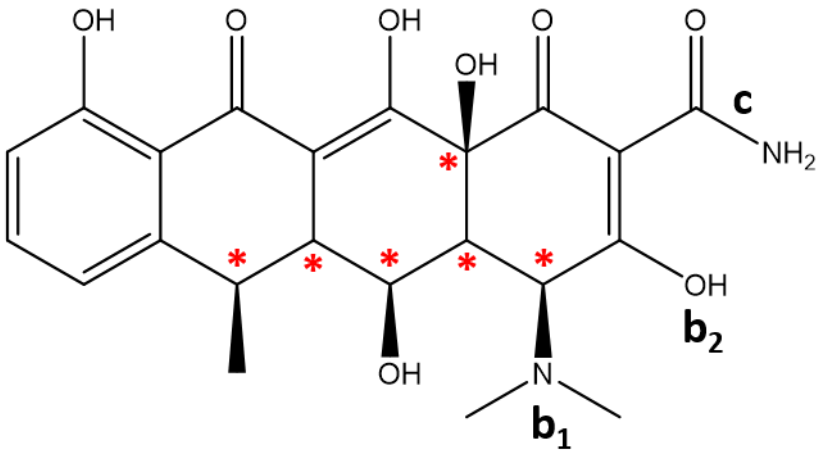
Last Name _____ SID _____

1. **Organic Structure and Identification** (12 pts) Answer the following questions about doxycycline, a broad-spectrum antibiotic used to treat bacterial infections.



a. (3 pts) Besides "alkane" or "alkene" **name three distinct functional groups** present in doxycycline.

Possible answers might be: **amide, amine, alcohol, ketone, phenol**

b. (3 pts) What is the orbital hybridization of the labeled atoms (b_1, b_2)?

b_1: **sp^3** b_2: **sp^2**

c. (4 pts) You find that there is restricted rotation around this bond. Explain why this might be the case.

The amide group is conjugated (lone pair connecting to the carbonyl double bond), creating a pi-system running from the oxygen down to the nitrogen. This conjugation must be broken in order to rotate nitrogen and its substituents, creating an energetic barrier to this action.

d. (2 pts) How many chiral centers are present in doxycycline?

6 chiral centers (marked with asterisks in structure)

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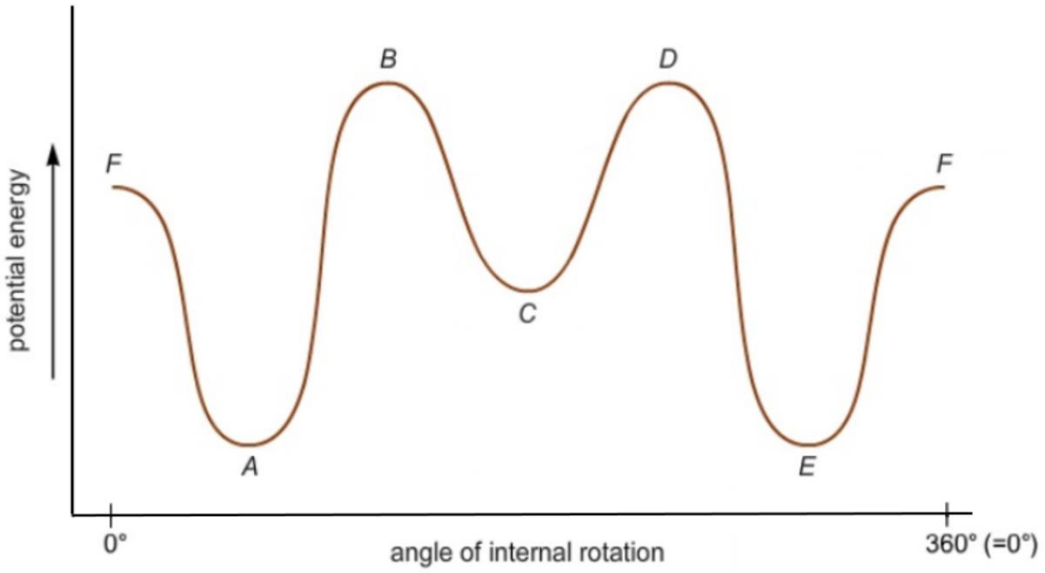
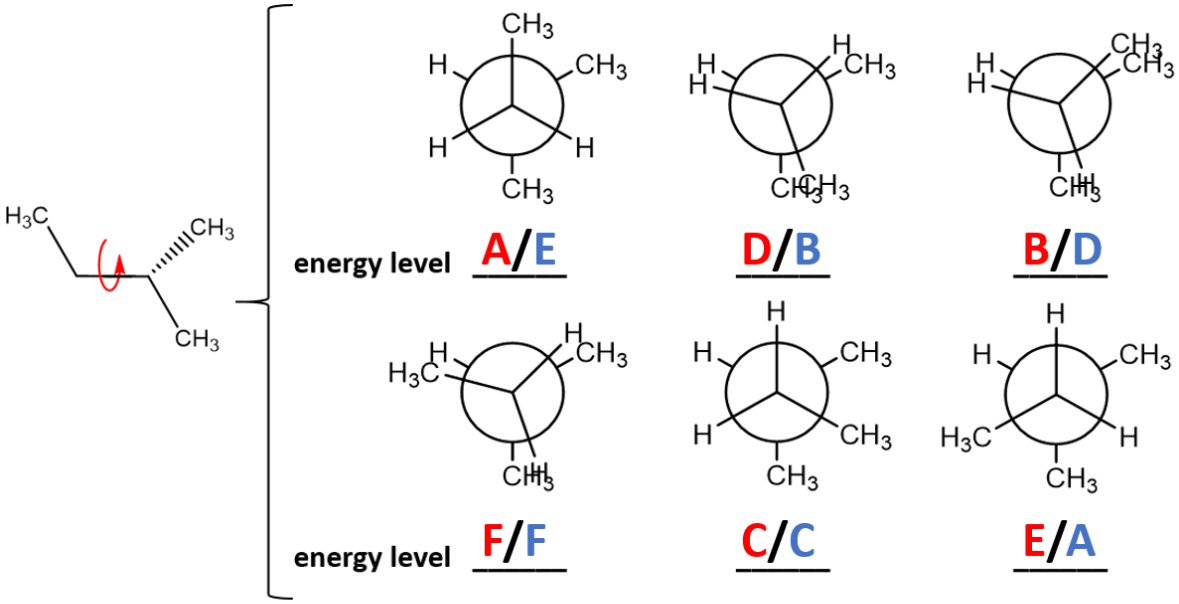
2. **Conformational Isomers** (6 pts) The molecule 2-methylbutane (also known as isopentane) has an allowed rotation between C_2 and C_3. You find the following diagram representing the relative energy levels of the six limiting conformations:



Correspond the following Newman projections to the energy levels above (A-F)



two possible sets of answers, red or blue
representing clockwise or counter-clockwise rotation

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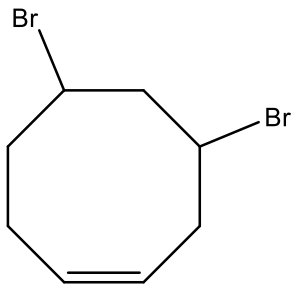
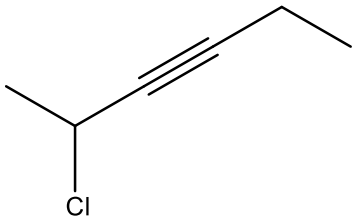
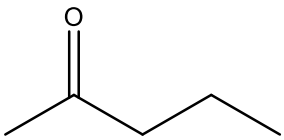
3. **Organic Nomenclature** (8 pts)
   a. (2 pts each) Draw the structures of the following compounds.
      i. 4,6-dibromocyclooct-1-ene



      ii. 2-chlorohex-3-yne

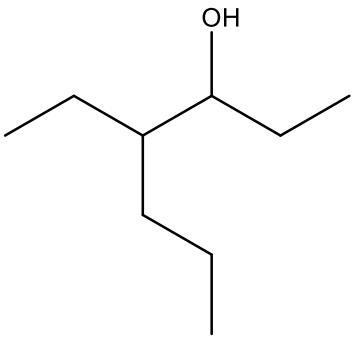


   b. (2 pts each) Write the IUPAC name for each of the following structures.
      i.



pentan-2-one, 2-pentanone

      ii.



4-ethylheptan-3-ol

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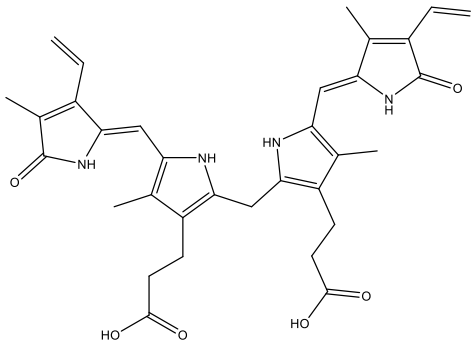
4. **Color and Conjugation** (8 pts) Gilbert's syndrome is a mild disorder in which the liver does not properly process bilirubin. This leads to higher levels of bilirubin in the bloodstream, which may cause discoloration of the eyes under stress (your instructor can directly attest to this particular symptom).



Bilirubin

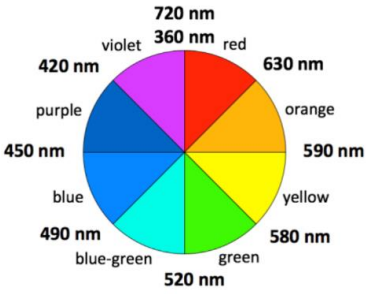
a. (3 pts) Billirubin absorbs light at 450 nm. Which color(s) does bilirubin appear as?

orange/yellow

b. (5 pts) The quantity of bilirubin in a blood sample can be measured with the *van den Bergh* reaction, which converts bilirubin to azobilirubin. Azobilirubin appears violet in color. Knowing what you know about color absorption and conjugation, how did the *van den Bergh* reaction alter the structure of bilirubin, and how did that lead to a color change?

If azobilirubin appears violet, it must absorb green photons (its complementary color). This would be an increase in the wavelength absorbed (450 nm → ~550 nm). A higher wavelength absorbed means a smaller ΔE gap. Therefore, relative to bilirubin, azobilirubin will likely have a more extended conjugated system.

color wheel reference



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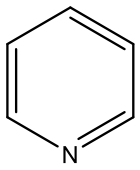
5. **Aromaticity and Stability** (14 pts)
   a. (2 pts each) Identify the following compounds as aromatic, anti-aromatic, or non-aromatic.

i.

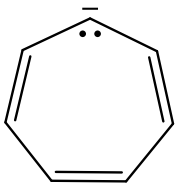
aromatic

ii.



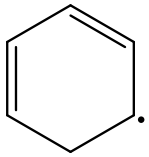
aromatic

iii.



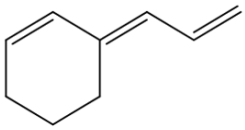
anti-aromatic

iv.

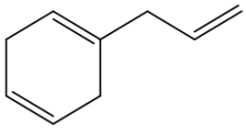


non-aromatic

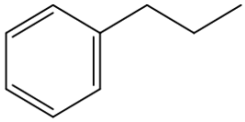
   b. (3 pts) Rank the heats of formation for the following three molecules from greatest to least.



ΔH_{f1}



ΔH_{f2}



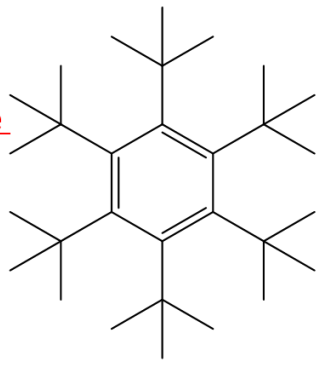
ΔH_{f3}

least stable — more stable

(greatest) **2** > **1** > **3** (least)

   c. (3 pts) Consider the following snowflake-shaped molecule. You find that it fulfills Hückel's Rule but a friend confidently states that it's non-aromatic. Why might this be the case?

The six tert-butyl groups create considerable steric strain, (aka electron repulsion between atoms) and want to get away from each other. This movement starts to distort the planarity of the benzene ring, breaking its conjugated pi-system, and therefore breaking its aromaticity.



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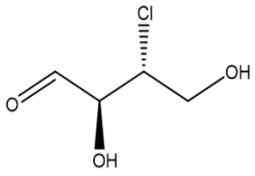
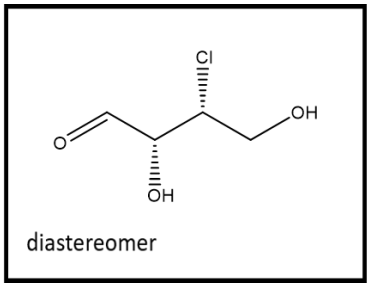
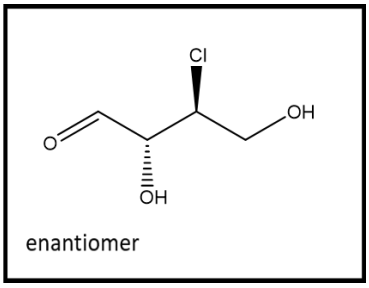
6. **Stereoisomers** (12 pts)
   a. (2 pts) Draw a diastereomer and the enantiomer for the following molecule.

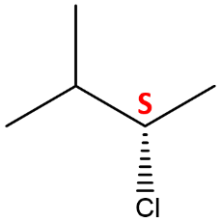




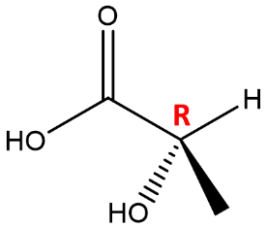


   b. (2 pts each) Assign an R/S designation to the chiral centers of the following molecules.

i.

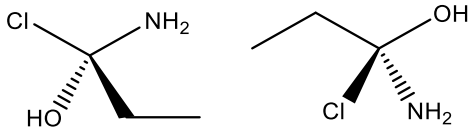


ii.



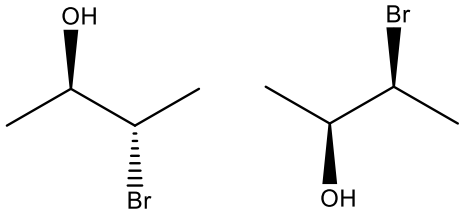
   c. (2 pts each) Indicate whether the following pairs of molecules are: 1) enantiomers, 2) diastereomers, or 3) the same molecule.

i.



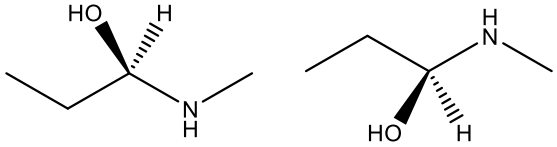
same molecule

ii.



diastereomers

iii.



enantiomers