

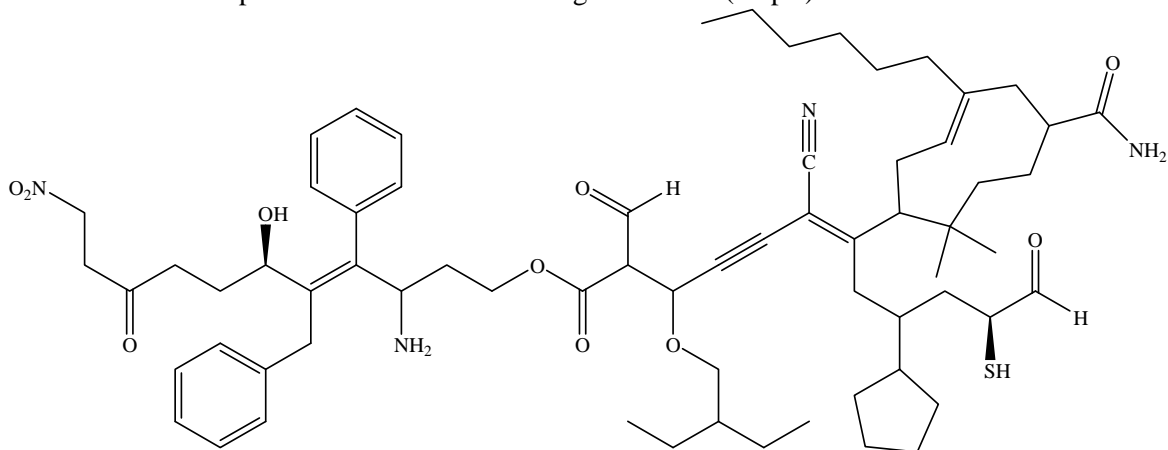
Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Types of Isomers, Degrees of Unsaturation or common nomenclature terms or functional groups or 2D Lewis structure	21	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	30	
4. Newman Projections, Conformational Energies	30	
5. Stereochemical Analysis	30	
6. 3D Structure, Hybridization, Angles, Shapes, Resonance, Formal Charge	30	
7. Types of Isomers, Degrees of Unsaturation or common nomenclature terms or functional groups or 2D Lewis structure	25	
8. Forces of Interaction and Physical Properties	20	
Total	216	

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Write your answers in the space provided. Do your best to show me what you know in the time available.

"You can't go back and change the beginning, but you can start where you are and change the ending."

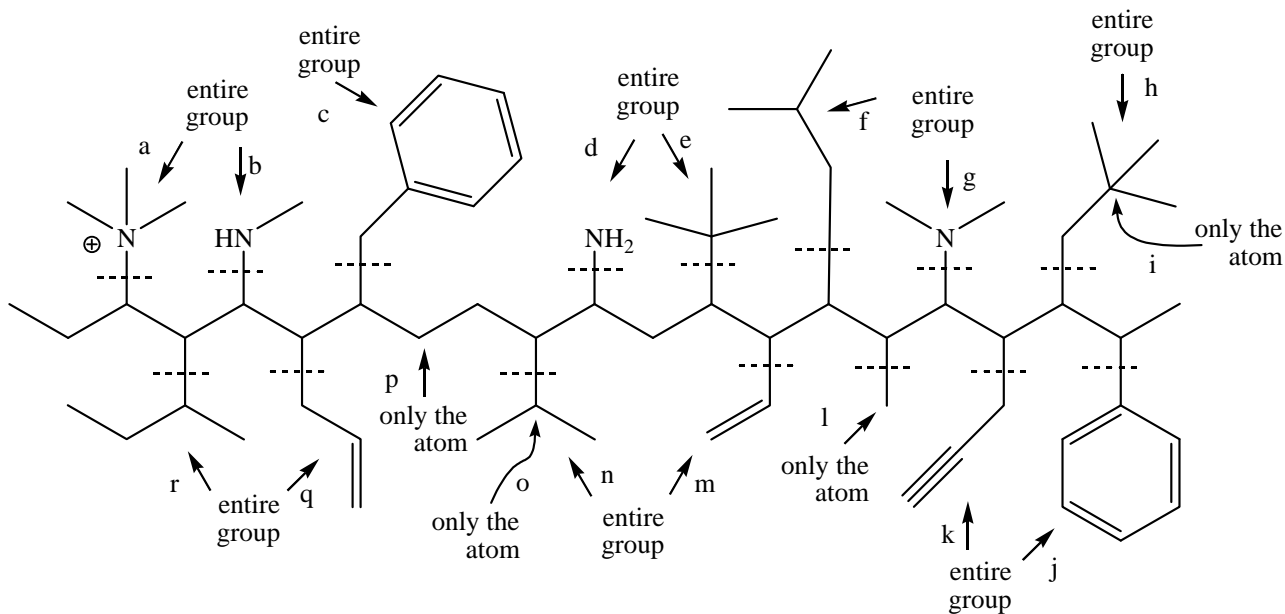
C.S. Lewis

1. Provide an acceptable name for the following molecule. (30 pts)



2. Match the arrows with the terms. Some arrows may be associated with more than one term. (21 pts)

- | | | | |
|--------------------|----------------------------------|-------------------------|---------------------|
| 1. tertiary _____ | 7. quaternary ammonium ion _____ | 12. isobutyl _____ | 18. t-butyl _____ |
| 2. primary _____ | 8. secondary amine _____ | 13. methyl _____ | 19. sec-butyl _____ |
| 3. propargyl _____ | 9. tertiary amine _____ | 14. neopentyl _____ | 20. isopropyl _____ |
| 4. secondary _____ | 10. methylene _____ | 15. phenyl _____ | 21. vinyl _____ |
| 5. methine _____ | 11. quaternary _____ | 16. benzyl _____ | |
| 6. allyl _____ | | 17. primary amine _____ | |

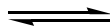


3. Draw all possible chair conformations of cis-1-ethenyl-2- ethynyl cyclohexane. Make C1 the left most carbon and number towards the front. Show **all** axial and equatorial groups in the first chair. If the axial energy of a ethenyl group is 1.7 kcal/mole and 0.5 kcal for a ethynyl group and a ethynyl/ethenyl gauche interaction is 1.0 kcal/mole, which conformation is more stable and what is the energy difference? Draw the more stable conformation first. Provide a reason for your answer. Draw a Newman projection of the more stable conformation using the C₂→C₁ and C₄→C₅ bonds to sight along. Point out any gauche interactions shown in your Newman projection. What are the relative percents of each conformation? Show work. Sketch an energy diagram that shows how the energy changes with the conformational changes. (30 pts)

a.

$$K = 10^{\frac{-\Delta G}{2.3RT}}$$

R = 2 cal/mol-K
T = 300 K



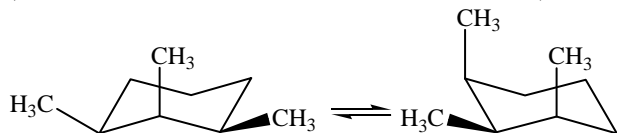
chair 1

chair 2

b. Newman projection – more stable

c. Energy diagram and relative percents

- d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq} . (Assume R = 2 cal/mol-K and T = 300 K.) Use energy values provided in the box. Show your work.



One axial methyl group = +1.7 kcal/mole,
Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
Three axial methyl groups, on the same side = +12.9 kcal/mole and
1,2 gauche methyl groups = 0.8 kcal/mole.

$$\Delta H \approx$$

$$K_{eq} \approx$$

4. Use a Newman projection of the C4→C3 bond of 2-methyl-3-phenylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Using those energy values, calculate ratio of the most stable to the least stable conformations. Show work. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (30 pts)

$$K = 10^{\frac{-\Delta G}{2.3RT}}$$

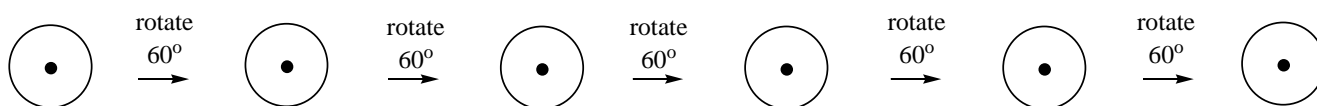
R = 2 cal/mol-K
T = 300 K

2D structure

Approximate Eclipsing Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.7	3.0	2.0
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	3.8	10.0	4.5
i-Pr	1.7	3.0	3.8	7.8	13.0	8.2
t-Bu	3.0	8.5	10.0	13.0	23.0	14.1
Ph	2.0	3.3	4.5	8.2	14.1	8.7

Approximate Gauche Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.3
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.3	3.0	1.6
i-Pr	0.2	1.1	1.3	2.0	3.8	2.3
t-Bu	0.5	2.7	3.0	3.8	8.2	4.1
Ph	0.3	1.4	1.6	2.3	4.1	2.7

most stable conformation
↓



$\Delta H^\circ =$

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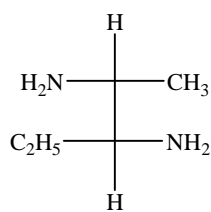
$\Delta H^\circ =$

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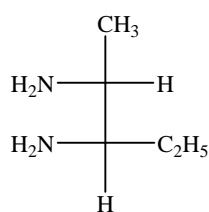
$\Delta H^\circ =$



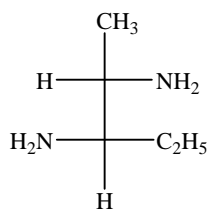
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. (30 pts)



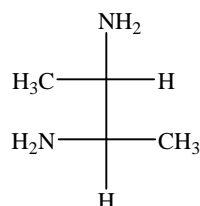
A



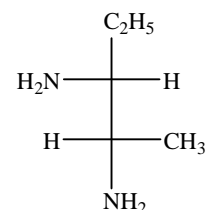
B



C



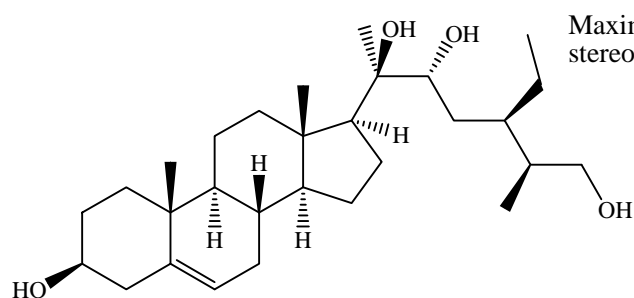
D



E

- a. Which is not an isomer with the others? A B C D E
- b. Which are meso? A B C D E
- c. Which are optically active? A B C D E
- d. Which pairs are identical? AB AC AD AE BC BD BE CD CE DE
- e. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE
- f. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE
- g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BC BD BE CD CE DE
- h. Draw all stereoisomers of pentane-2,3-diamine as Fischer projections. Which is/are not shown above. If there are none, indicate this. Classify all chiral centers as R or S absolute configuration.

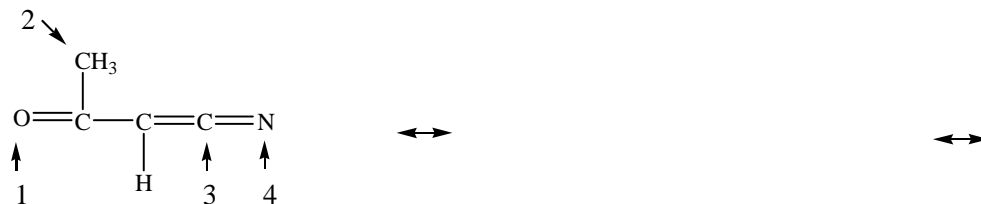
- j. The structure of a steroid, amarasterol was recently isolated from a microorganism, *Cyathula capitata*. Circle all chiral centers. How many stereoisomers are possible from the stereogenic centers shown? (Org. Lett. May 13, 2014, ASAP article)



Maximum possible stereoisomers = _____

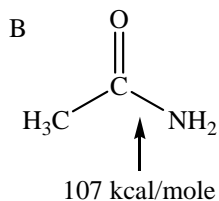
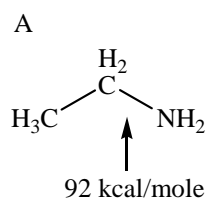
What is the degree of unsaturation? of $\text{C}_{29}\text{H}_{50}\text{BrNO}_4$. Show your work.

6. Fill in any missing lone pairs and formal charge on the first 2D structure. **Assume ALL nonhydrogen atoms have full octets, unless a positive charge is shown.** Draw two additional 2D resonance structures of the given structure using proper resonance curved arrows. Which structure is best (=1), second best, etc. and why? Draw a 3D structure for the given resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms. (30 pts)



Atom	Shape	Hybridization	Bond Angles	# σ bonds	# π bonds	# lone pairs
1						
2						
3						
4						

Explain the different C-N bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of nitrogen in A and B?



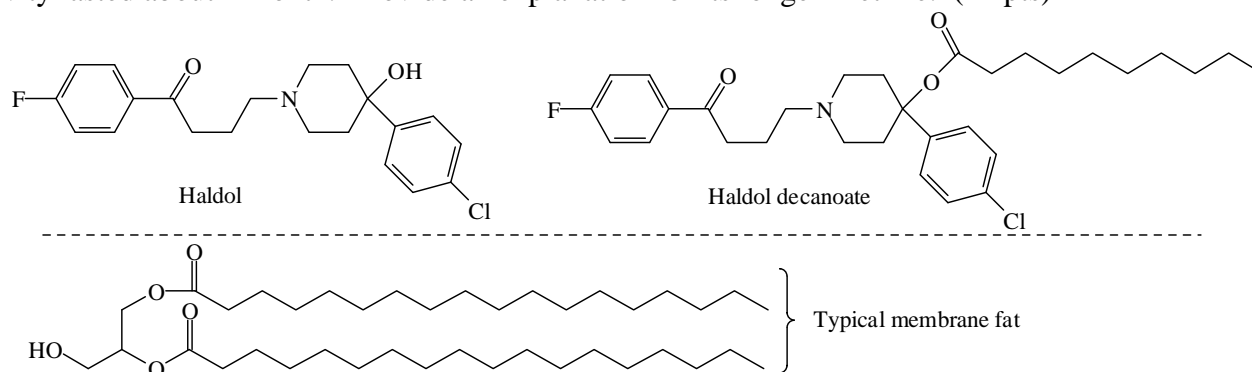
7. Draw a 2D structure that includes the listed functional groups. Write the functional group name by its appearance in your 2D structure. Calculate the degree of unsaturation for the given formula. (25 pts)

alkyne, alkene, 1° amine, ester, alcohol
ether, thiol, ketone, acid, 2° amide, nitrile

degree of unsaturation calculation



8. a. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug was prepared to increase Haldol's lifetime in the body. When injected intramuscularly its anti-psychotic activity lasted about 1 month. Provide an explanation for its longer lifetime. (12 pts)



- b. Provide an explanation for why NaCl is soluble in water, but not soluble in hexane. Use structures. (8 pts)

Very little is needed to make a happy life; it is all within yourself, in your way of thinking. Marcus Aurelius