

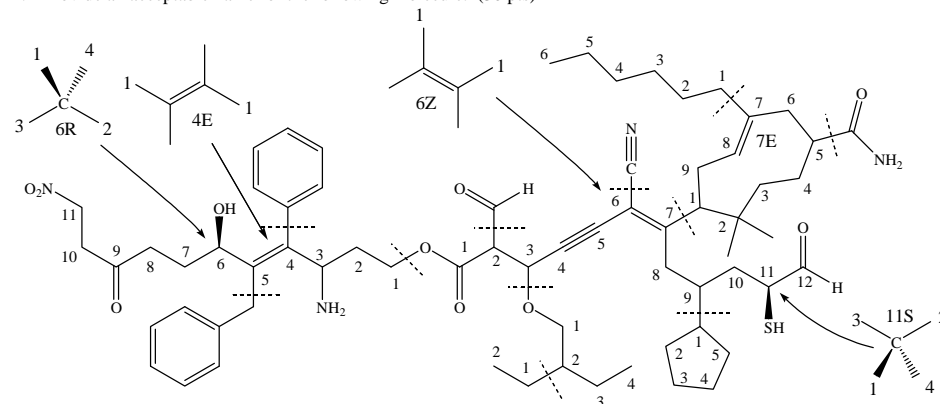
Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Types of Isomers, Degrees of Unsaturation or common nomenclature terms or functional groups or 2D Lewis structure	21	
3. Cyclohexane Conformations, 2 substituents, Newman Projections	30	
4. Newman Projections, Conformational Energies	30	
5. Stereochemical Analysis	30	
6. 3D Structure, Hybridization, Angles, Shapes	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

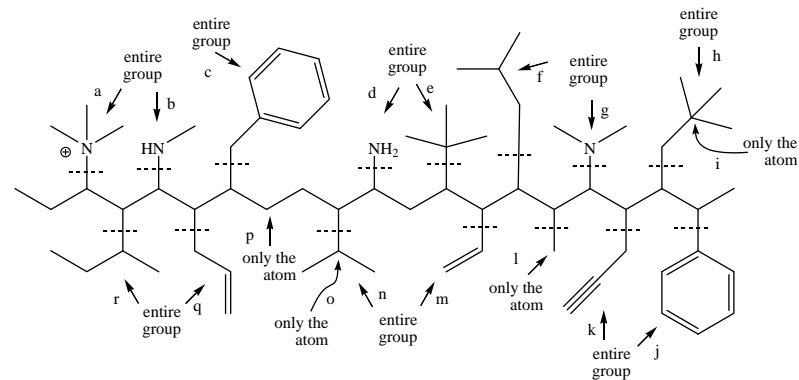
1. Provide an acceptable name for the following molecule. (30 pts)



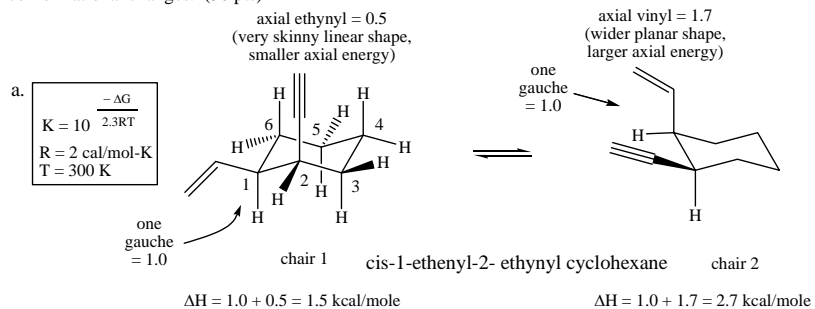
3-amino-4-phenyl-5-benzyl-6R-hydroxy-9-oxo-11-nitroundec-4E-enyl 2-formyl-3-(2-ethylbutoxy)-6-cyano-7-(7-hexyl-5-amido-2,2-dimethylcyclohex-7E-enyl)-9-cyclopentyl-11S-mercapto-12-oxododec-6Z-en-4-ynoate -11S-sulfanyl-

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

- | | | | |
|-----------------------|-------------------------------------|----------------------------|------------------------|
| 1. tertiary <u>o</u> | 7. quaternary ammonium ion <u>a</u> | 12. isobutyl <u>f</u> | 18. t-butyl <u>e</u> |
| 2. primary <u>l</u> | 8. secondary amine <u>b</u> | 13. methyl <u>l</u> | 19. sec-butyl <u>r</u> |
| 3. propargyl <u>k</u> | 9. tertiary amine <u>g</u> | 14. neopentyl <u>h</u> | 20. isopropyl <u>n</u> |
| 4. secondary <u>p</u> | 10. methylene <u>p</u> | 15. phenyl <u>j</u> | 21. vinyl <u>m</u> |
| 5. methine <u>o</u> | 11. quaternary <u>i</u> | 16. benzyl <u>c</u> | |
| 6. allyl <u>q</u> | | 17. primary amine <u>d</u> | |

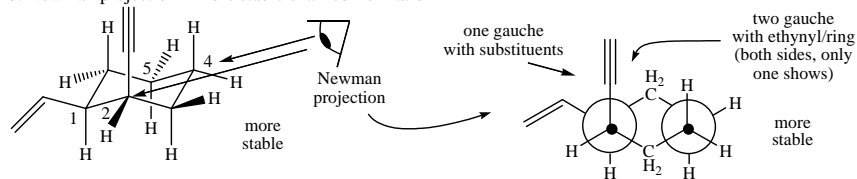


3. Draw all possible chair conformations of cis-1-ethenyl-2- ethynyl cyclohexane. Make C1 the left most carbon and number towards the front. Show **all** axial and equatorial groups in the first chair. If the axial energy of a ethenyl group is 1.7 kcal/mole and 0.5 kcal for a ethynyl group and a ethynyl/ethenyl 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? Sketch an energy diagram that shows how the energy changes with the conformational changes. (30 pts)

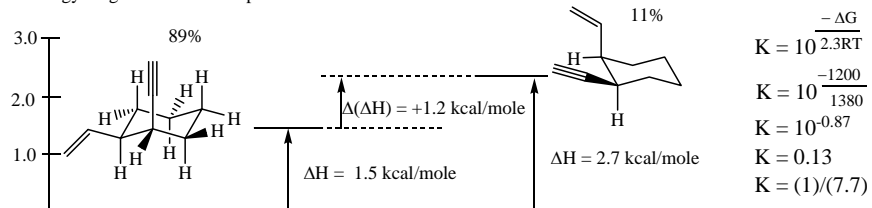


larger group (higher axial energy) is axial in right structure so ΔG is positive and $K_{eq} < 1$.

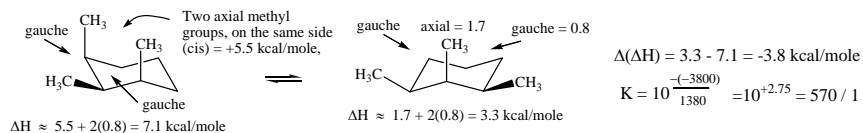
- b. Newman projection – more stable chair conformation



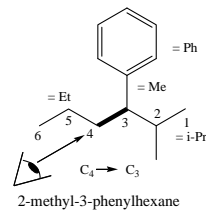
- c. Energy diagram and relative percents



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



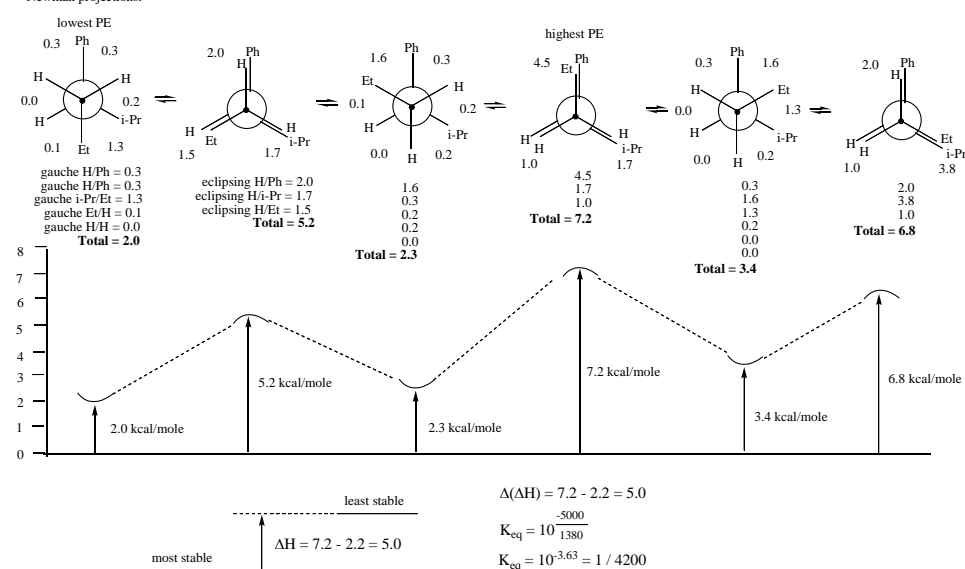
4. Use a Newman projection of the C₄→C₃ bond of 2-methyl-3-phenylhexane to show the most stable conformation first. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot 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)



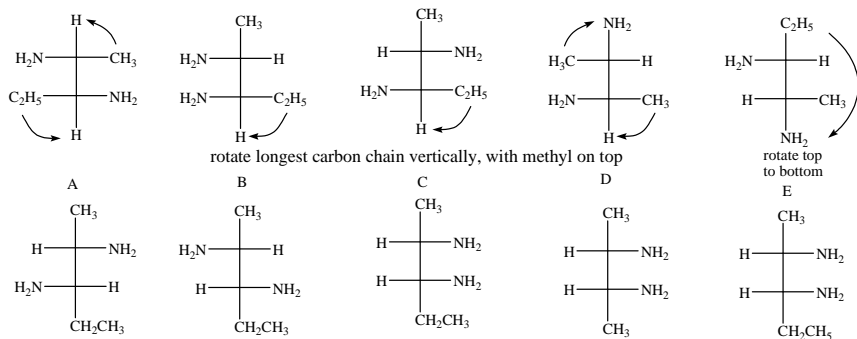
Approximate Eclipsing Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.7	3.0	2.0
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	3.8	10.0	4.5
i-Pr	1.7	3.0	3.8	7.8	13.0	8.2
t-Bu	3.0	8.5	10.0	13.0	23.0	14.1
Ph	2.0	3.3	4.5	8.2	14.1	8.7

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

Newman projections:



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. Which is not an isomer with the others?

A B C D E
 A B C D E

This is a methyl, not an ethyl.

b. Which are meso?

A B C D E

D is NOT an isomer.

c. Which are optically active?

AB AC AD ~~AE~~ BC ~~BD~~ BE ~~CD~~ CE ~~DE~~

d. Which pairs are identical?

AB AC AD ~~AE~~ BC ~~BD~~ BE ~~CD~~ CE ~~DE~~

e. Which pairs are enantiomers?

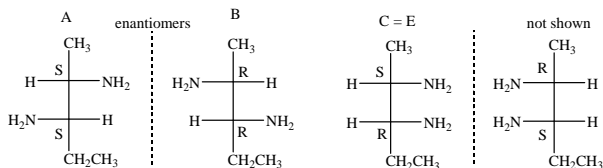
AB AC AD AE BC BD BE CD CE ~~DE~~

f. Which pairs are diastereomers?

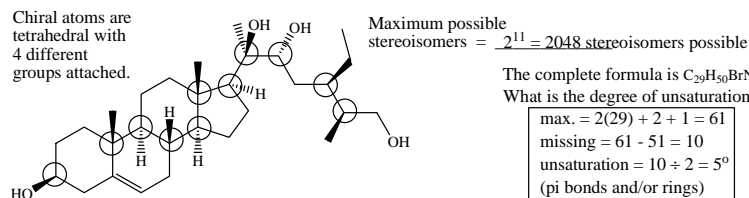
AB AC AD AE BC ~~BD~~ BE ~~CD~~ CE ~~DE~~

g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?

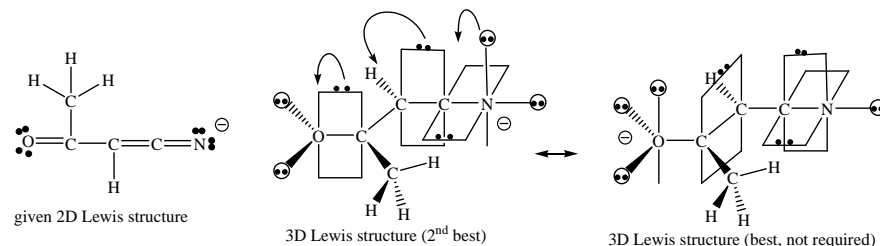
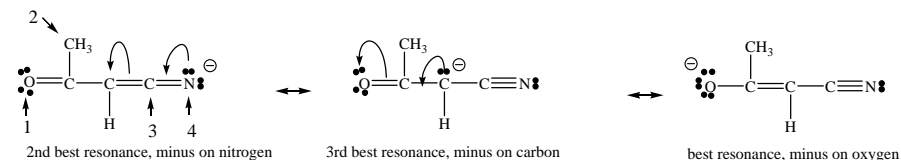
h. Draw all stereoisomers of pentane-2,3-diamine as Fischer projections. Which is/are not shown above. If there are none, indicate this. Classify all chiral centers as R or S absolute configuration.



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)

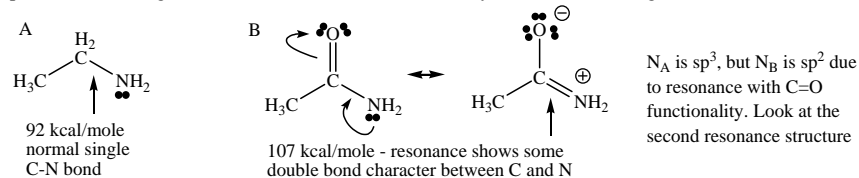


6. Fill in any missing lone pairs and formal charge on the first 2D structure. Assume ALL nonhydrogen atoms have full octets, unless a positive charge is shown. Draw two additional 2D resonance structures of the given structure using proper resonance curved arrows. Which structure is best (=1), second 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)



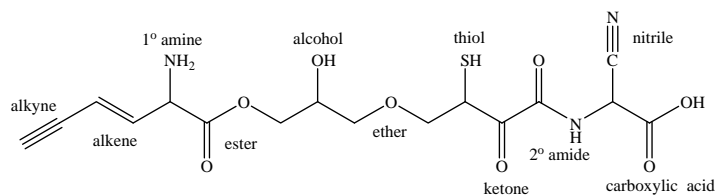
Atom	Shape	Hybridization	Bond Angles	#σ bonds	# π bonds	# lone pairs
1 oxygen	trigonal planar	sp ²	120°	1	1	2
2 carbon	tetrahedral	sp ³	109°	4	0	0
3 carbon	linear	sp	180°	2	2	0
4 nitrogen	linear	sp	180°	1	1	2

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



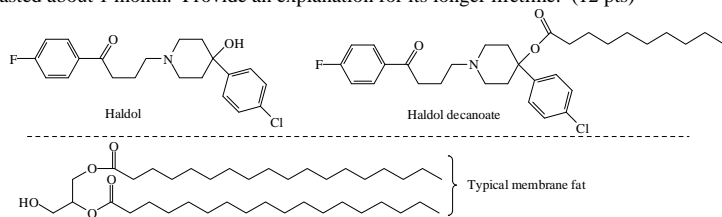
$$\begin{aligned} \text{maximum bonding} &= 2n + 2 + \#N \\ &= 2(17) + 2 + 3 = 39 \end{aligned}$$

$$\begin{aligned} \text{actual number of single bond groups} &= H + \text{halogens} \\ &= 21 + 4 = 25 \end{aligned}$$

$$\text{number of missing single bonding groups} = 39 - 25 = 14$$

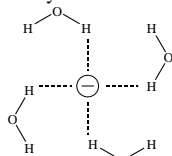
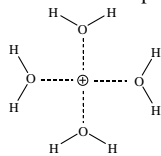
$$\text{degrees of unsaturation} = 14 \div 2 = 7^\circ \text{ (pi bonds and/or rings)}$$

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)

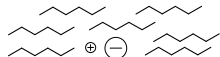


The alcohol of Haldol makes it too water (blood) soluble and it is degraded as the blood passes through the liver by oxidizing enzymes, so it is excreted in the urine and/or feces. When the alcohol is esterified it is much less water (blood) soluble and gets stored in fatty tissue, where it is slowly released to the blood over a much longer time. Probably the ester is slowly hydrolyzed making it become more water soluble again as the alcohol.

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



Water has the ability to interact with positive or negative charge and compensate for loss of the ion-ion interactions of the NaCl salt. Nonpolar hexane cannot do this, so the ions stay surrounded by opposite charge in the lattice structure and sink to the bottom because they are more dense.



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