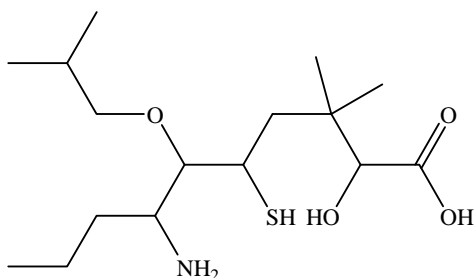


Chem 201 Sample Midterm
Beauchamp

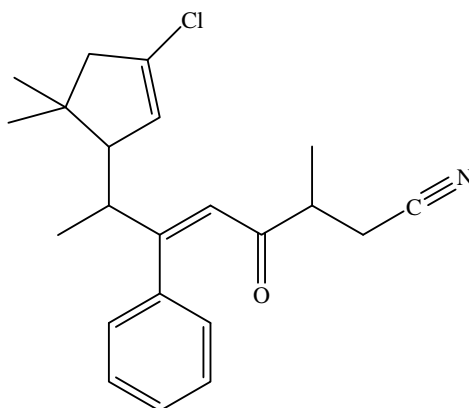
Exams are designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate.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

1. Provide an acceptable names for the following molecules.

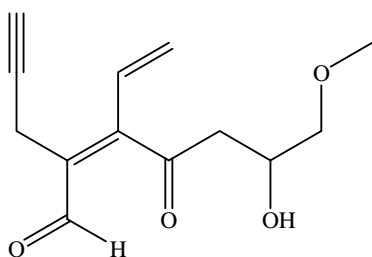
1



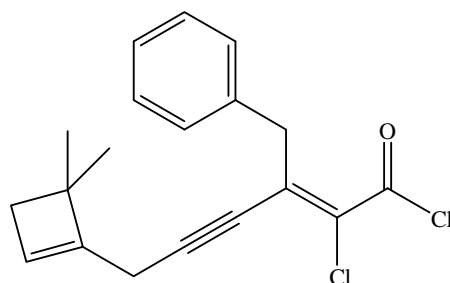
2



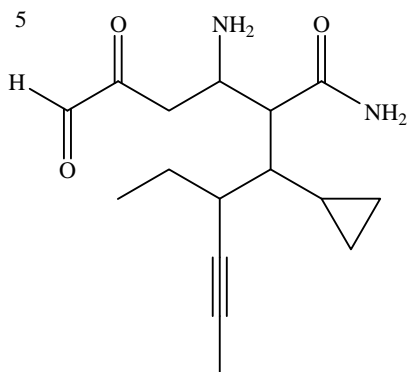
3



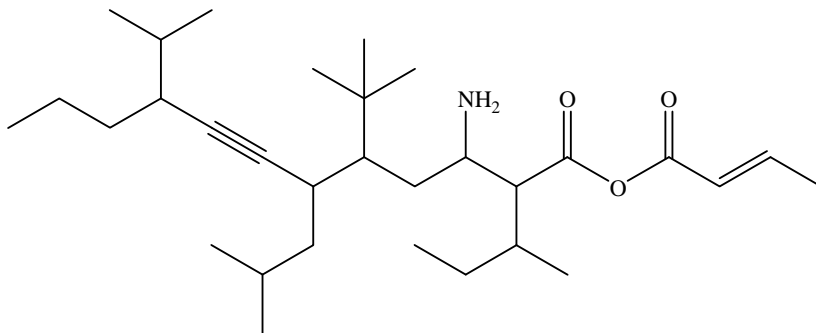
4



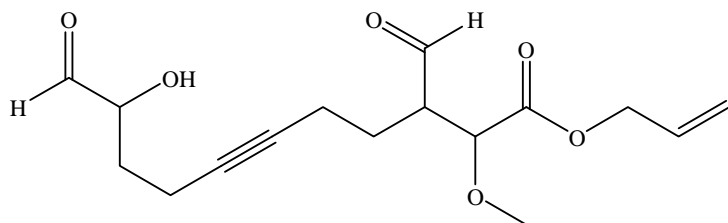
5

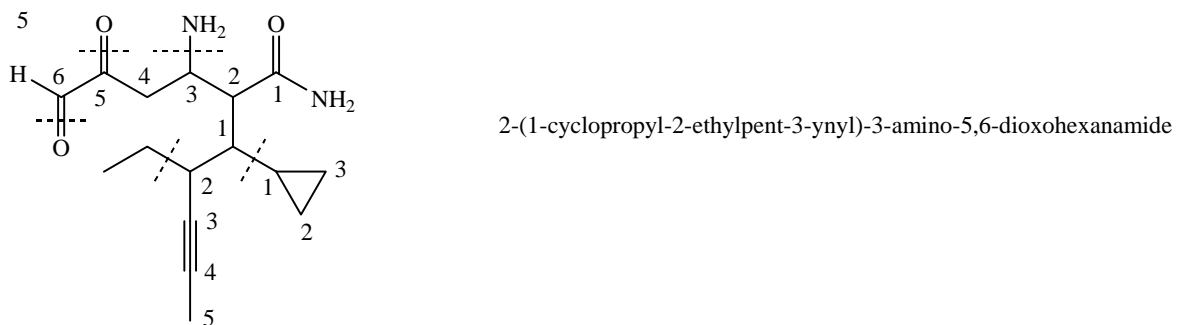
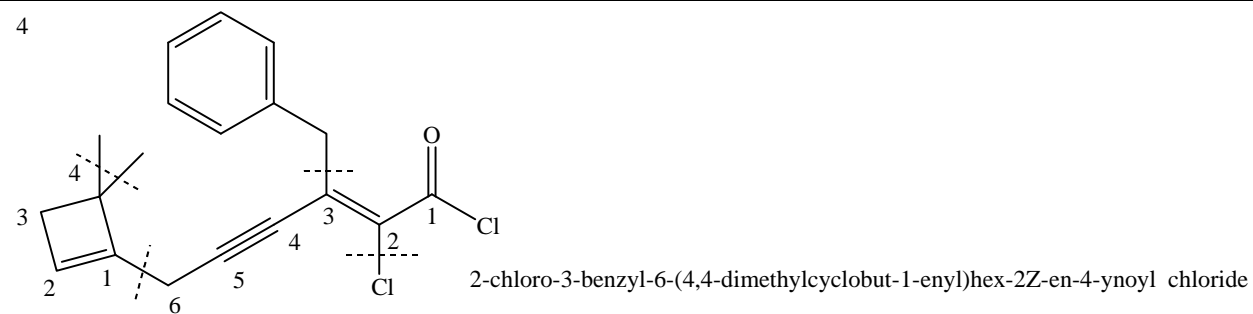
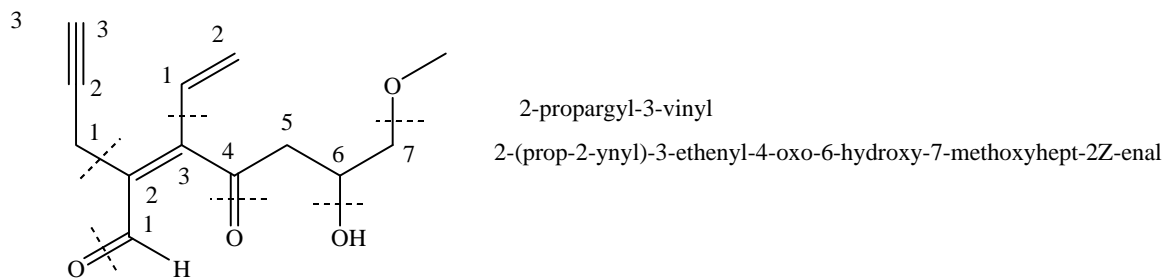
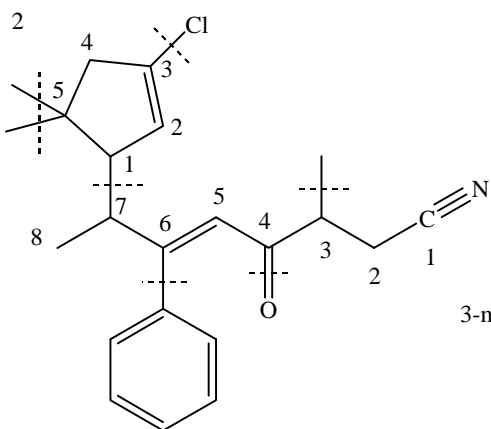
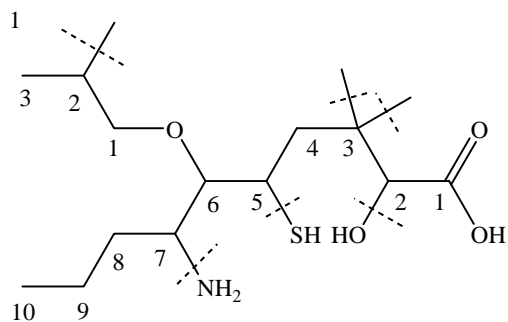


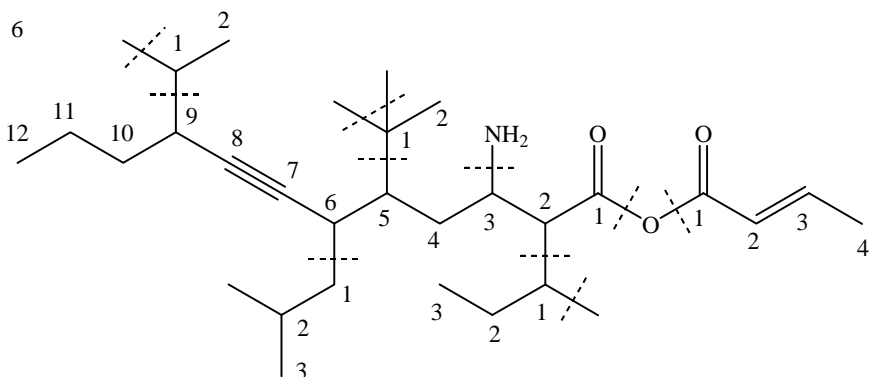
6



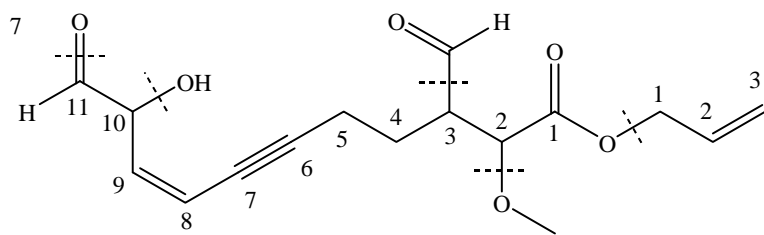
7







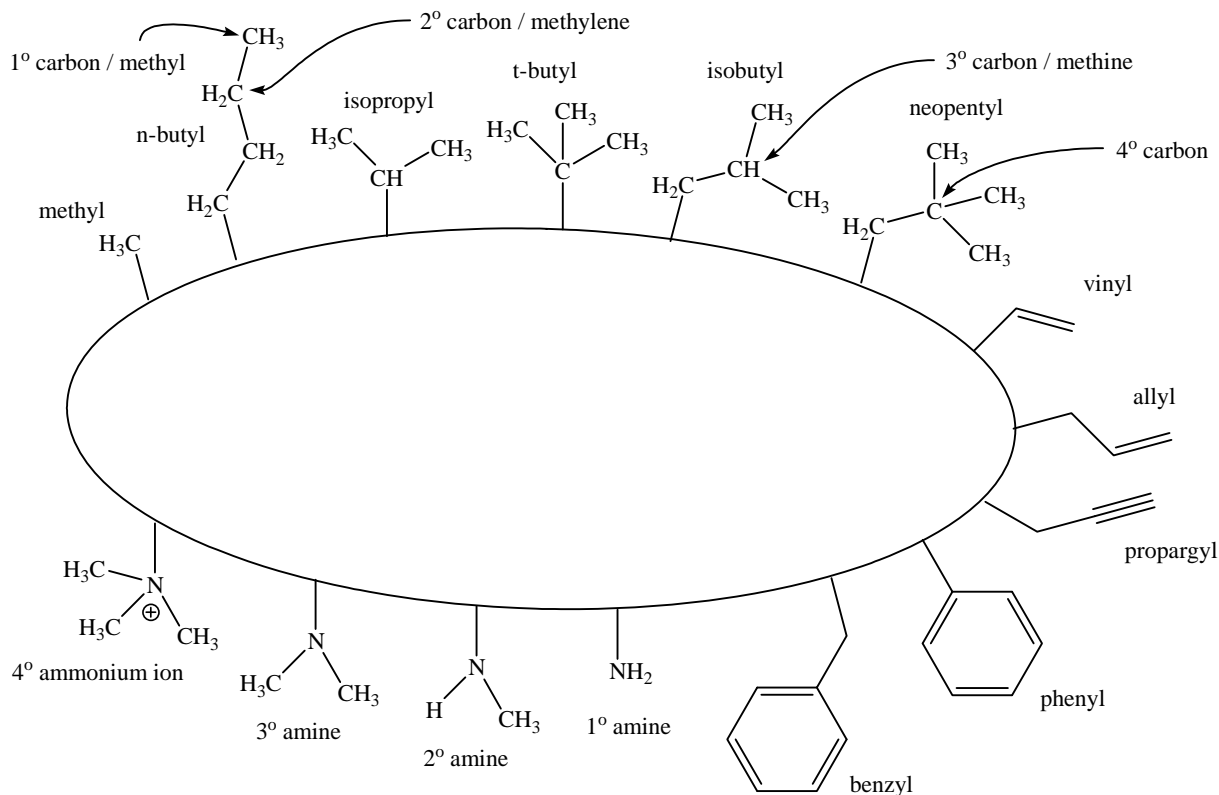
but-2E-enoic 2-(1-methylpropyl)-3-amino-5-(1,1-dimethylethyl)-6-(2-methylpropyl)-9-(1-methylethyl)dodec-7-ynoic anhydride
 2-sec-butyl 5-t-butyl 6-isobutyl 9-isopropyl



allyl
 prop-2-enyl 2-methoxy-3-formyl-10-hydroxy-11-oxoundec-8Z-en-6-ynoate

2. Draw an example of each of the following.

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



3. Use the given formula to calculate the degree of unsaturation. Draw an example molecule that has the indicated functional groups.

a. $C_{22}H_{24}ClNO_7$, functional groups: acid, ester, alcohol, ether, nitrile, alkene, ring, chloro, aromatic

b. $C_{17}H_{22}ClN_2S_2O_6$, functional groups: amide, amine, anhydride, alkyne, aldehyde, sulfide, thiol, acid chloride

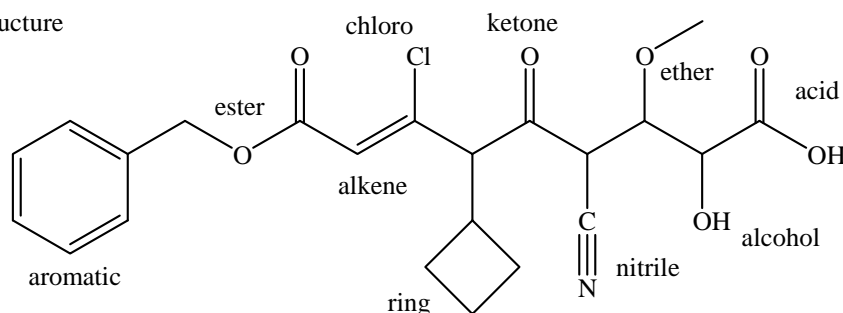
a. formula = $C_{22}H_{24}ClNO_7$

complete saturation = $2(22) + 2 + 1 = 47$

total single bonding groups = -25 (H + Cl)

missing single bonding groups ($\div 2$) = $22 \div 2 = 11$ degrees of unsaturation

Possible structure



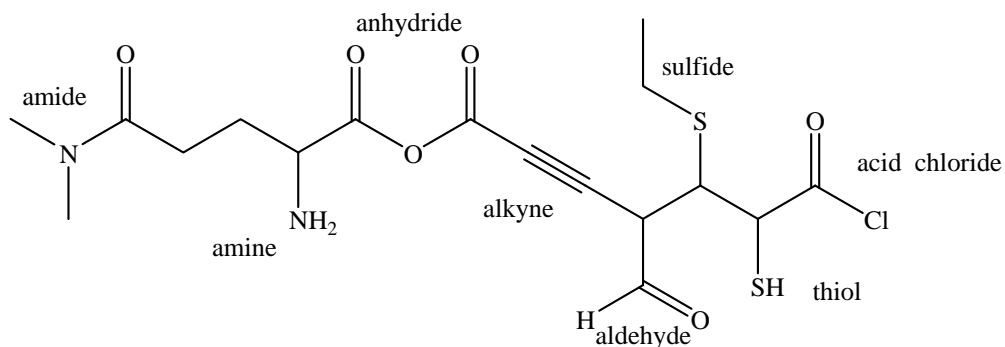
b. formula = $C_{17}H_{23}ClN_2O_6S_2$

complete saturation = $2(17) + 2 + 2 = 38$

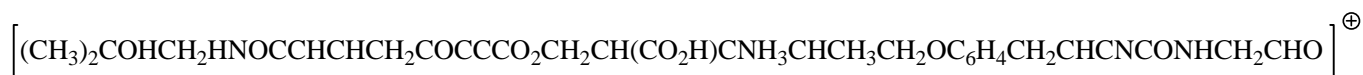
total single bonding groups = -24 (H + Cl)

missing single bonding groups ($\div 2$) = $14 \div 2 = 7$ degrees of unsaturation

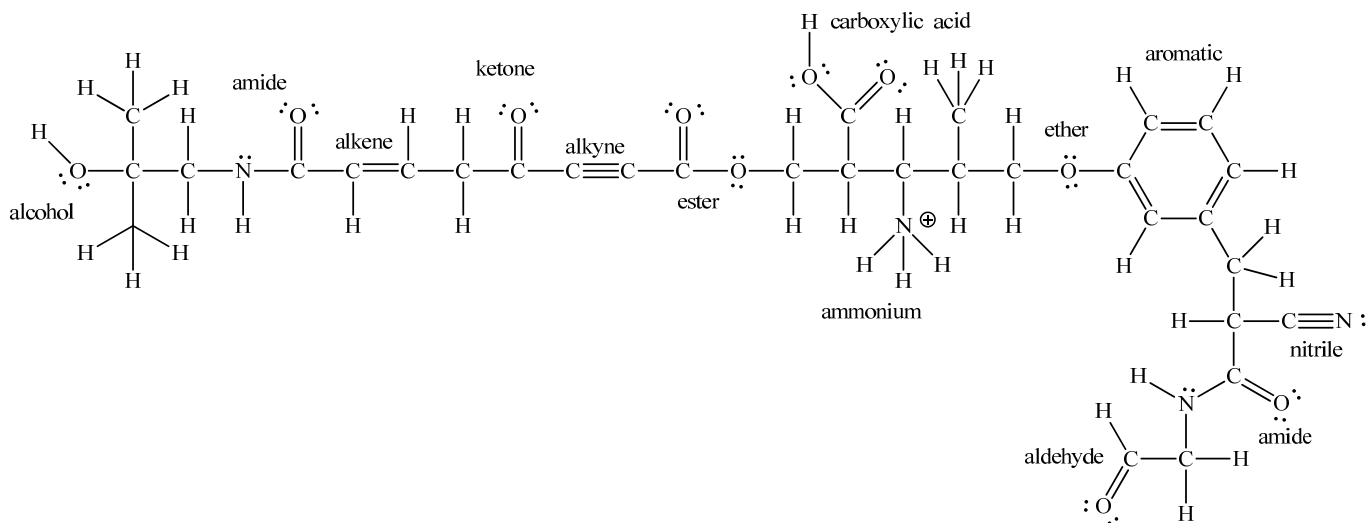
Possible structure



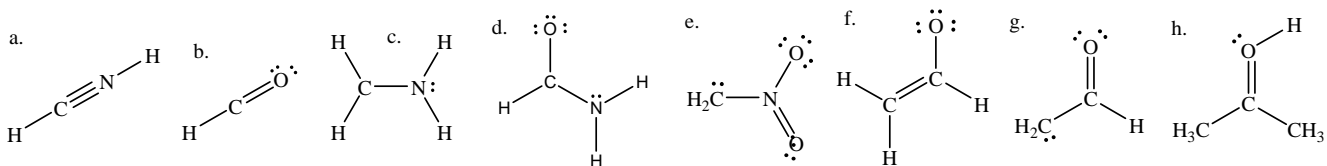
4. Draw an acceptable Lewis structure (2D) for each of the following. Show all single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atom where present. Identify any functional groups by name (i.e. ketone, amide, etc.)



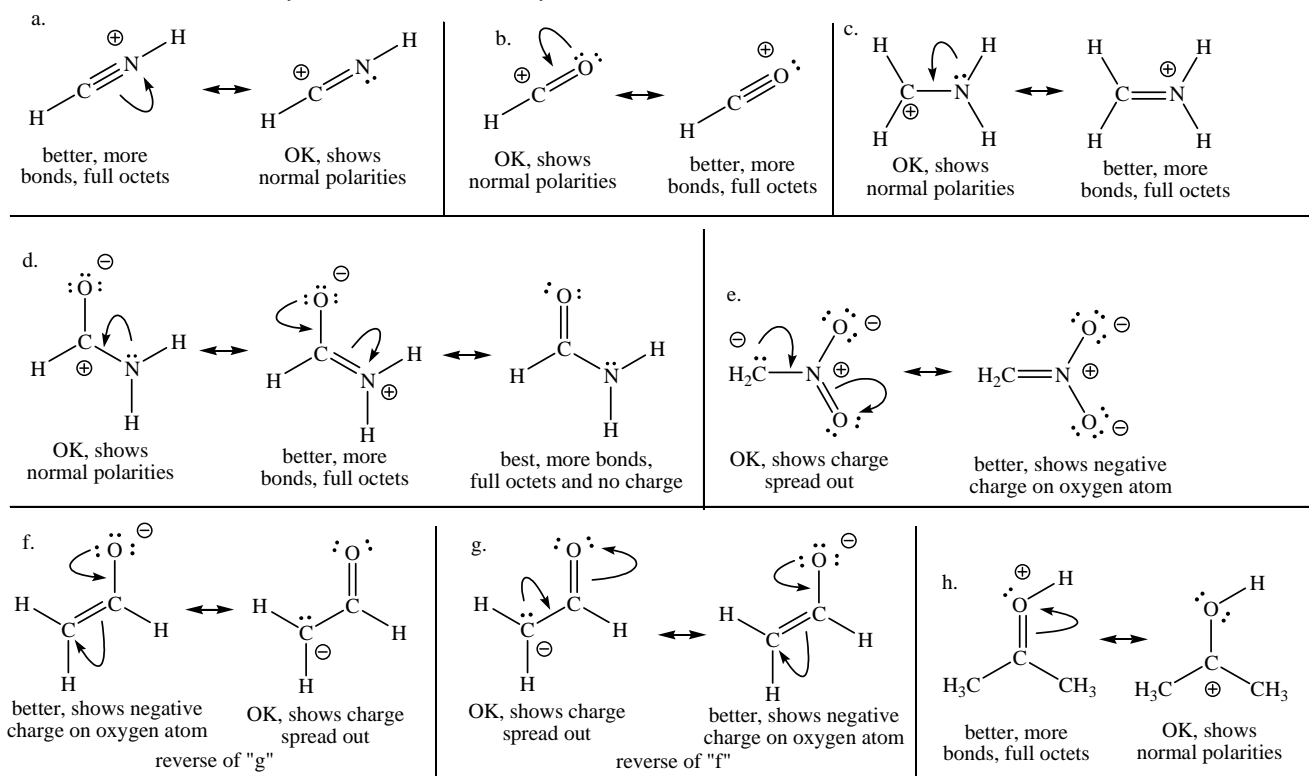
Break up string of atoms into recognizable pieces



5. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw one additional resonance structure using the proper arrow conventions.

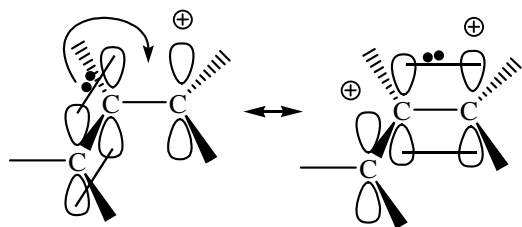


You should be able to draw any of these three dimensionally.

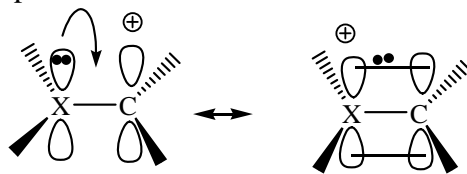


These are the most common resonance possibilities.

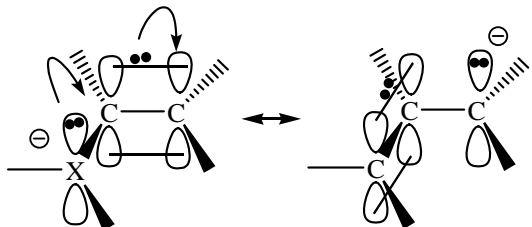
1. Push electrons from lone pairs or pi bonds (alkenes, alkynes or aromatics). All in 2p orbitals.
2. Accept electrons into empty 2p orbitals or pi bonds. All in 2p orbitals.



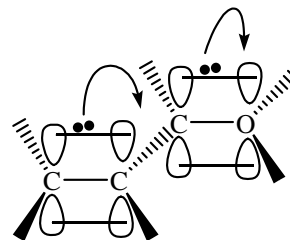
donor = pi bond (alkenes, alkynes or aromatics)
acceptor = empty 2p orbital (usually C)



donor = lone pair of electrons (usually N or O)
many possibilities (neutral or anion)
acceptor = empty 2p orbital (usually C)

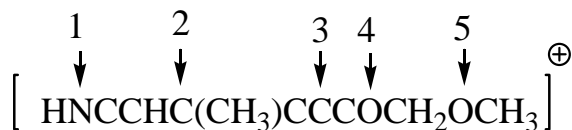


donor = lone pair of electrons (usually N or O)
many possibilities (neutral or anion)
acceptor = pi bond (better when O > N > C)

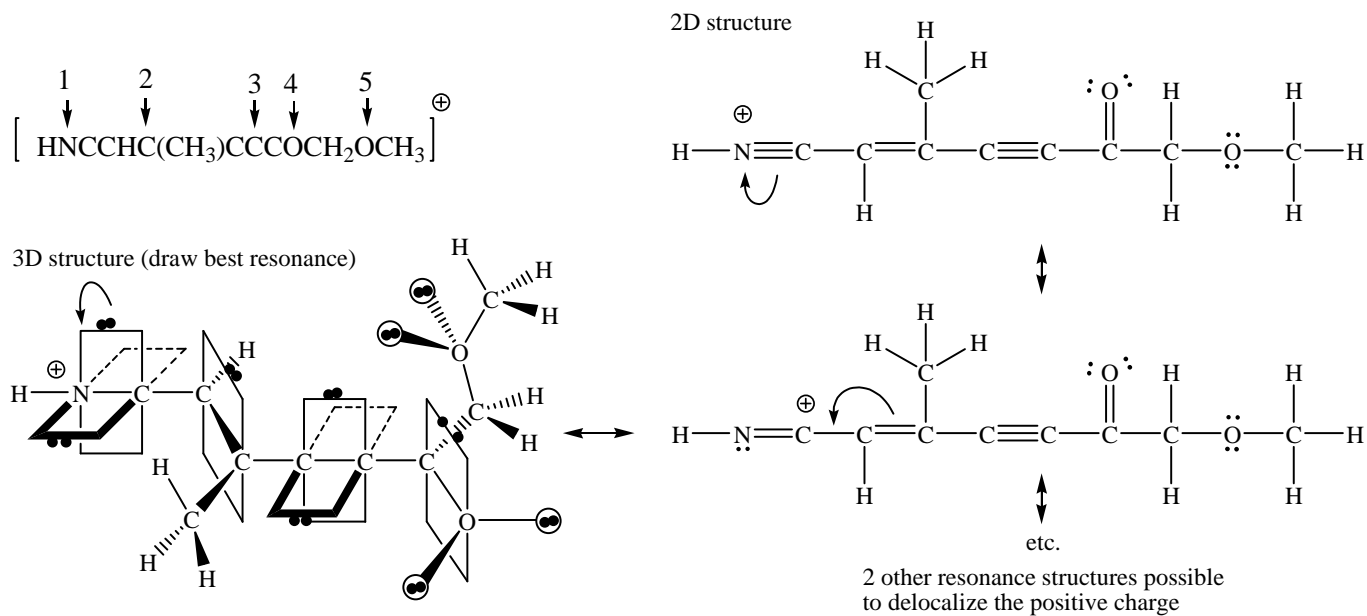


donor = pi bond (alkenes, alkynes or aromatics)
acceptor = pi bond (better when O > N > C)

6. Draw a 3-D structure for the following molecule. 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.



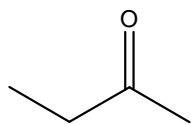
Atom	Shape	Hybridization	Bond Angles	# σ bonds	# π bonds	# lone pairs
1						
2						
3						
4						
5						



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

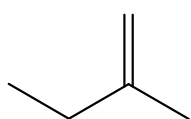
The following problems come from Topic 1 (polarity) and answers can be found in the Topic 1 Key. They are just randomly picked examples. You should be able to work any sort of problem found in topic 1.

7. Match the given boiling points with the structures below and give a short reason for your answers.
 (-7°C, +31°C, +80°C, +141°C, 1420°C)



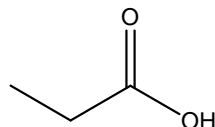
2-butanone

MW = 72 g/mol



2-methyl-1-butene

MW = 70 g/mol



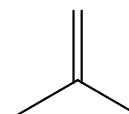
propanoic acid

MW = 74 g/mol

KCl

potassium chloride

MW = 74.5 g/mol



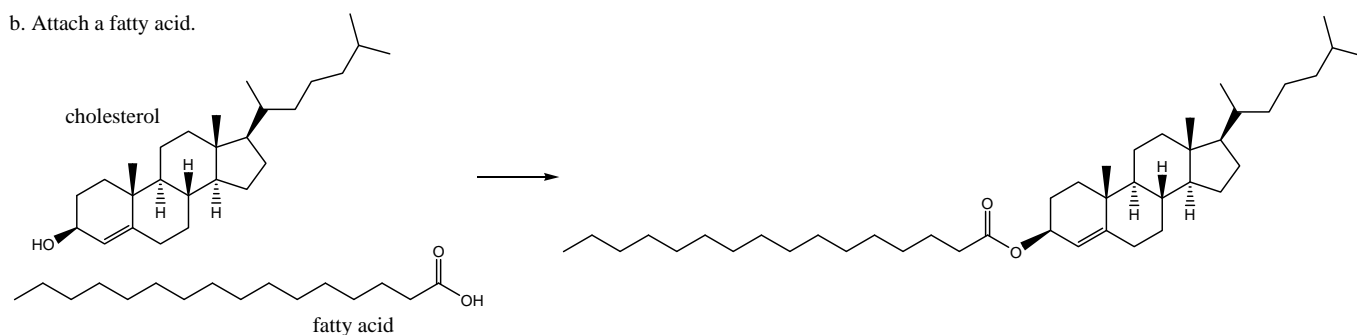
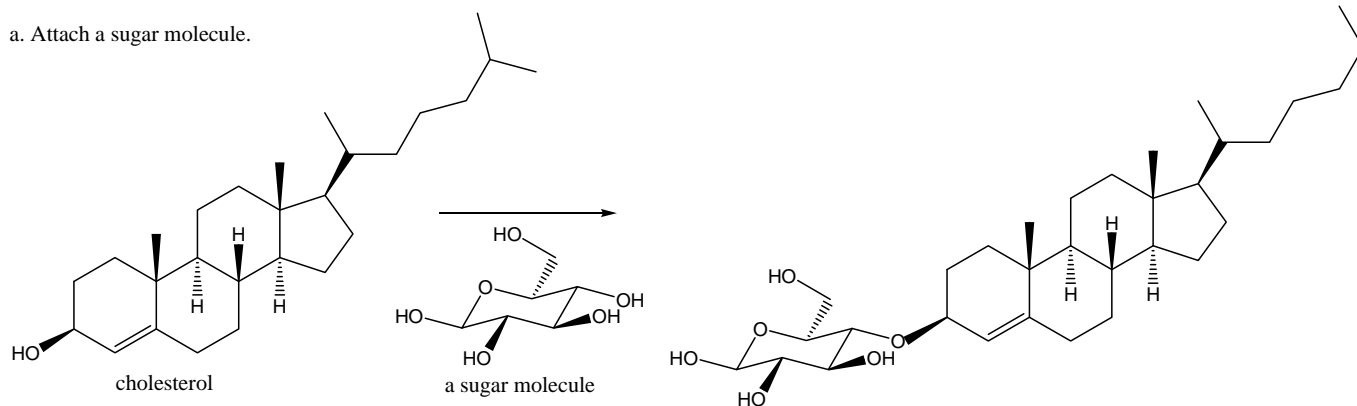
2-methylpropene

MW = 56 g/mol

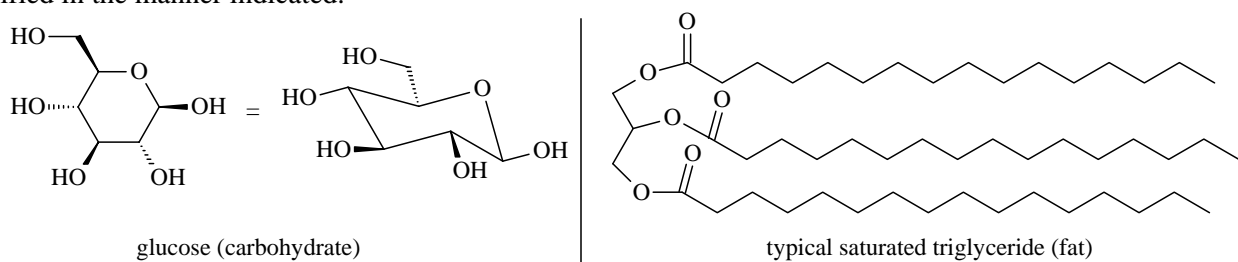
8. a. Hexane (density = 0.65 g/ml) and water (density = 1.0 g/ml) do not mix. Which layer is on top? Why don't they mix?
 b. Carbon tetrachloride (density = 1.59 g/ml) and water (density = 1.0 g/ml) do not mix. Which layer is on top?
9. The melting point of NaCl is very high ($\approx 800^\circ\text{C}$) and the boiling point is even higher ($> 1400^\circ\text{C}$). Does this imply strong, moderate or weak forces of attraction between the ions? Considering your answer, is it surprising that NaCl

dissolves so easily in water? Why does this occur? Consider another chloride salt, AgCl. How does your analysis work here? What changed?

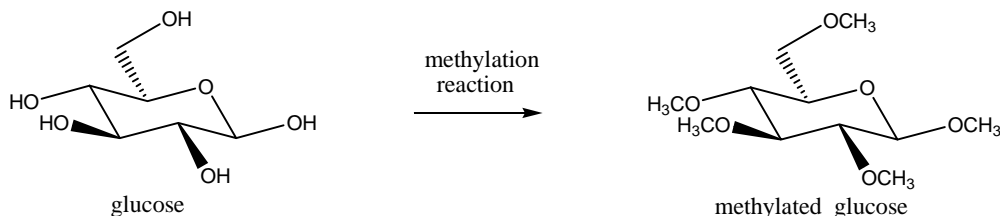
10. a. Which solvent do you suspect would dissolve NaCl better, DMSO or hexane? Explain your choice?
 b. Which solvent do you suspect would dissolve NaCl better, methanol or benzene? Explain your choice?
11. Different groups can be connected to the “O-H” substituent of cholesterol. What effect on water solubility do you expect for each of the following changes. Why?



12. a. Carbohydrates are very water soluble and fats do not mix well with water. Below, glucose is shown below as a typical hydrophilic carbohydrate, and a triglyceride is used as a typical hydrophobic fat. Point out why each is classified in the manner indicated.



- b. All of the “OH” groups in glucose can be methylated. What do you think this will do to the solubility of glucose? Why? One of these structures is soluble in carbon tetrachloride the other one is not. Which one is it and why?



13. a. Draw all possible chair conformations of trans-1-t-butyl-3-ethylcyclohexane. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw Newman projections of both conformations using the $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ bonds to sight along. Point out any gauche interactions shown in your Newman projections. Assume any gauche interaction of side chain groups is 0.8 kcal/mole, combined with any axial energy values (see table) to determine the relative percents of each conformation. Sketch an energy diagram that shows how the energy changes with the conformational changes.

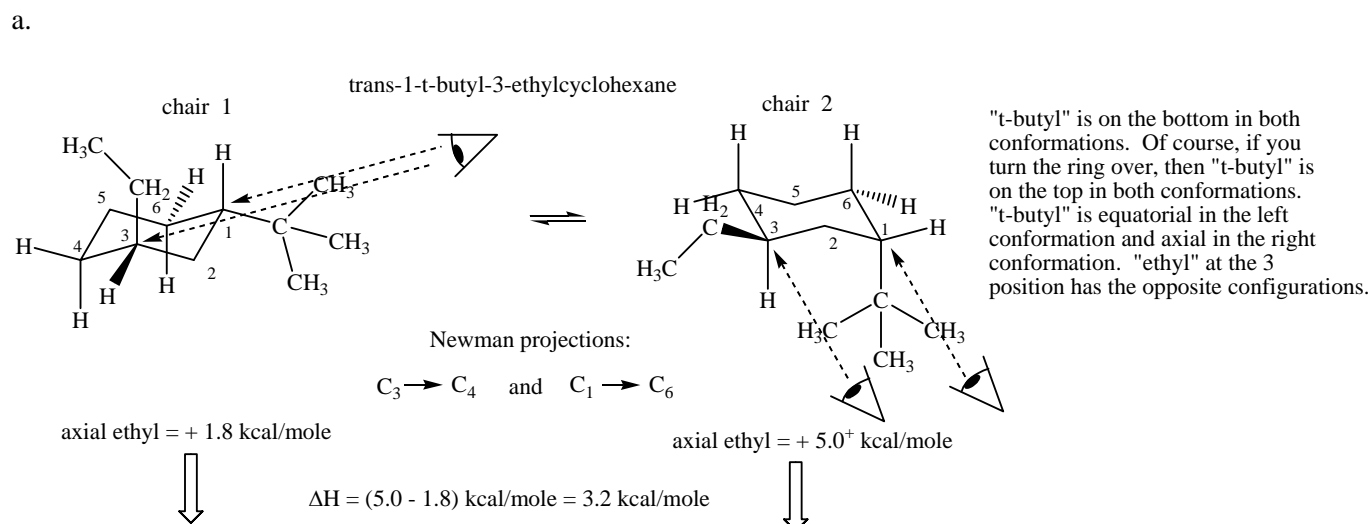
b. Draw all possible chair conformations of cis-1-isopropyl-2-hydroxycyclohexane. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw Newman projections of both conformations using the $C_1 \rightarrow C_2$ and $C_5 \rightarrow C_4$ bonds to sight along. Point out any gauche interactions shown in your Newman projections. Assume any gauche interaction of side chain groups is 0.8 kcal/mole, combined with any axial energy values (see table) to determine the relative percents of each conformation. Sketch an energy diagram that shows how the energy changes with the conformational changes.

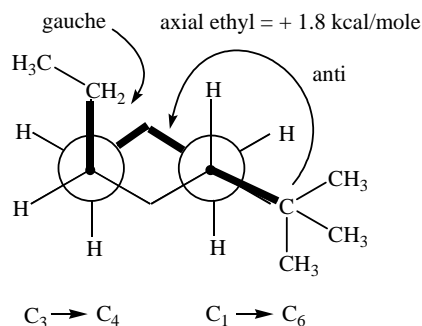
Substituent	ΔG° (A value)	Substituent	ΔG° (A value)
-H	0.0	-CH ₂ OH	1.8
-CH ₃	1.7	-CH ₂ Br	1.8
-CH ₂ CH ₃	1.8	-CF ₃	2.4
-CH(CH ₃) ₂	2.1	-O ₂ CCH ₂ CH ₃	1.1
-C(CH ₃) ₃	> 5.0	-OH	0.9
-F	0.3	-OCH ₃	0.6
-Cl	0.5	-SH	1.2
-Br	0.5	-SCH ₃	1.0
-I	0.5	-SC ₅ H ₆	1.1
-CH=CH ₂	1.7	-SOCH ₃	1.2
-CH=C=CH ₂	1.5	-SO ₂ CH ₃	2.5
-CCH	0.5	-SeC ₅ H ₆	1.0
-CN	0.2	-TeC ₅ H ₆	0.9
-C ₅ H ₆ (phenyl)	2.9	-NH ₂	1.2(C ₆ H ₅ CH ₃), 1.7(H ₂ O)
-CH ₂ C ₅ H ₆ (benzyl)	1.7	-N(CH ₃) ₂	1.5 (C ₆ H ₅ CH ₃), 2.1(H ₂ O)
-CO ₂ H	0.6	-NO ₂	1.1
-CO ₂ [⊖]	2.0	-HgBr	0.0
-CHO	0.7	-HgCl	-0.2
		-MgBr	0.8

chair 1 \rightleftharpoons chair 2

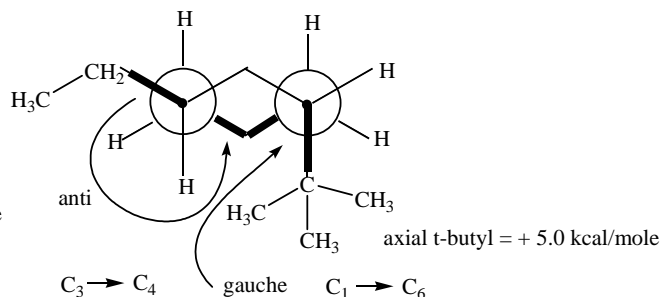
$$K = \frac{\text{chair 2}}{\text{chair 1}} = 10^{\frac{-\Delta G}{2.3RT}}$$

R = 2 cal/(mole-K)
T \approx 300 K





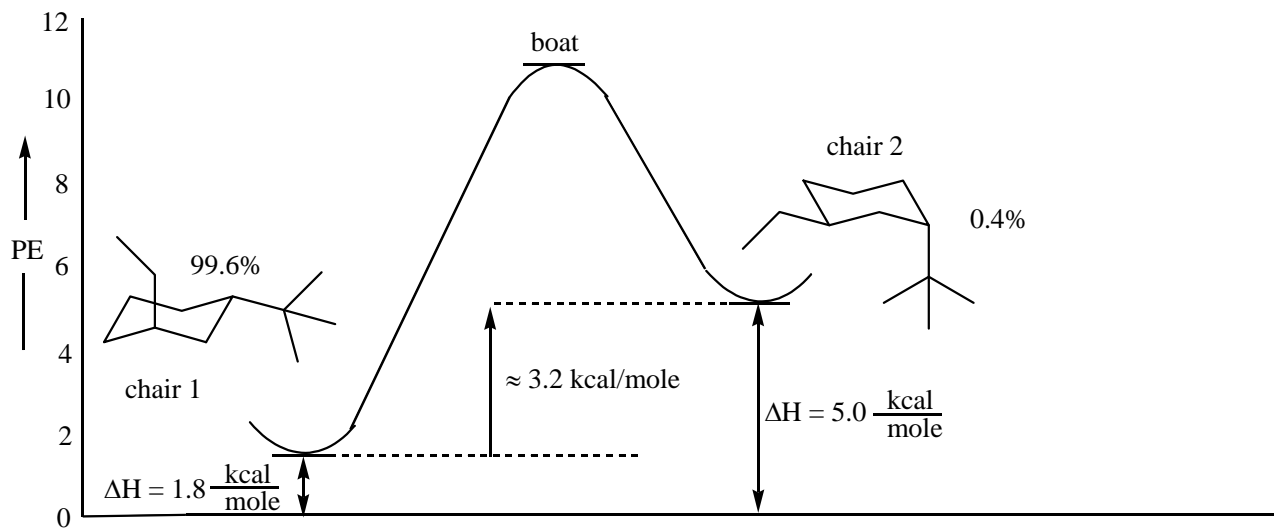
$$\Delta H = (5.0 - 1.8) \text{ kcal/mole} = 3.2 \text{ kcal/mole}$$



Equatorial "t-butyl" is anti to the ring on two sides. Only one shows in this Newman projection. This is the best conformation. The axial "ethyl" group is the preferred conformation because it's sterically smaller.

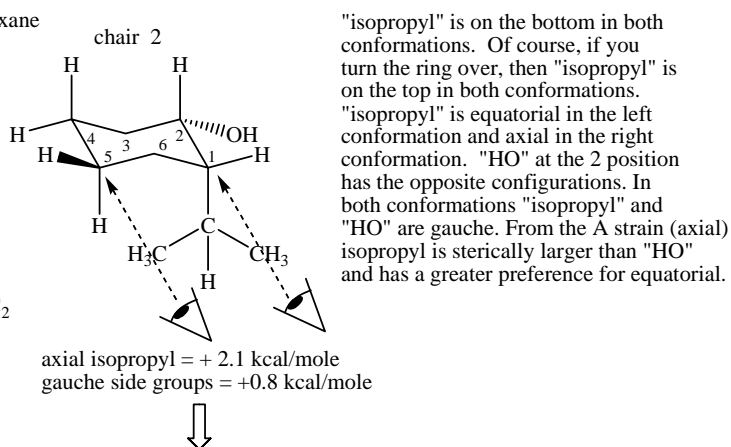
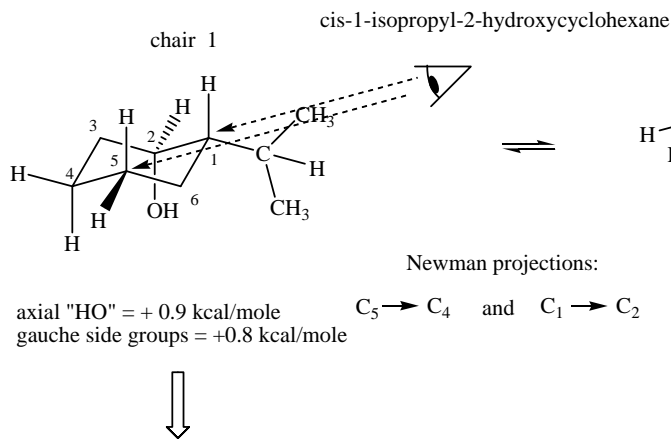
Axial "t-butyl" is gauche to the ring on two sides. Only one shows in this Newman projection. It avoids this conformation at all cost. The t-butyl group is the sterically largest group in our table.

$$K = \frac{\text{chair 2}}{\text{chair 1}} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-(3200 \text{ cal/mole})}{(2.3)(2 \text{ cal/mol-K})(298 \text{ K})}} = 10^{-2.31} = 0.0049 = \frac{1}{204} = \frac{0.4\%}{99.6\%} = \frac{\text{axial t-butyl}}{\text{axial ethyl}}$$

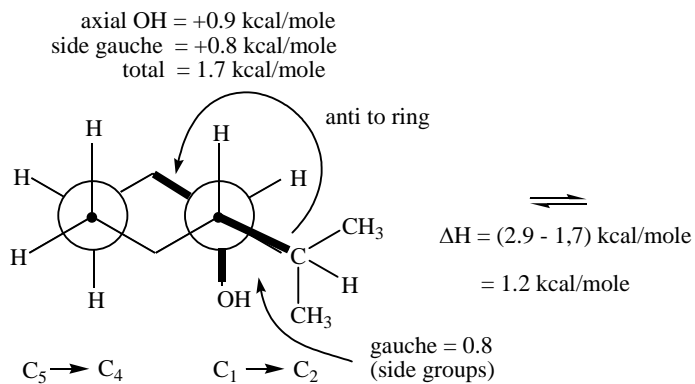


Energy changes of trans-1-t-butyl-3-ethylcyclohexane conformations.

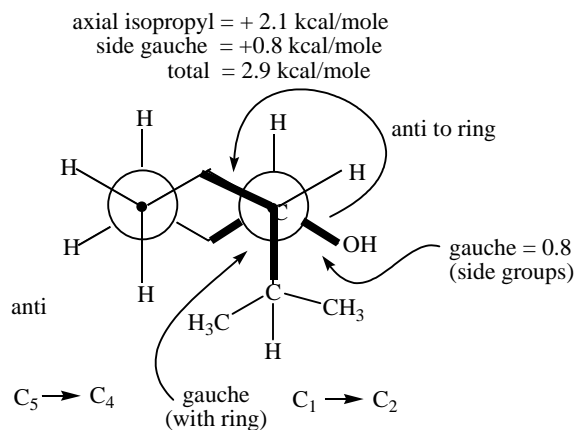
b.



"isopropyl" is on the bottom in both conformations. Of course, if you turn the ring over, then "isopropyl" is on the top in both conformations. "isopropyl" is equatorial in the left conformation and axial in the right conformation. "HO" at the 2 position has the opposite configurations. In both conformations "isopropyl" and "HO" are gauche. From the A strain (axial) isopropyl is sterically larger than "HO" and has a greater preference for equatorial.

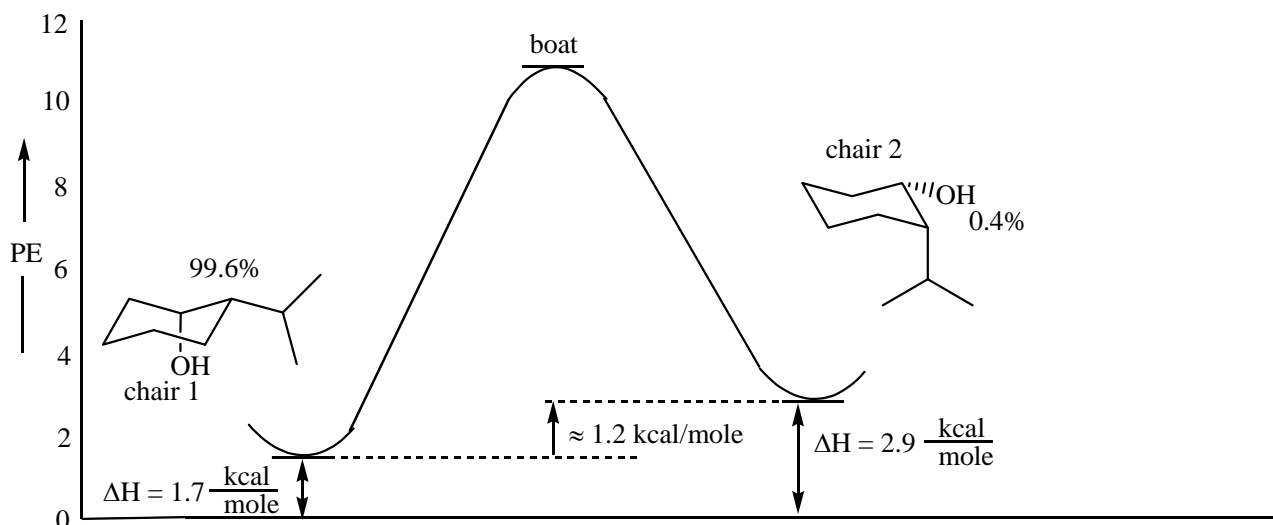


Equatorial "t-butyl" is anti to the ring on two sides. Only one shows in this Newman projection. This is the best conformation. The axial "ethyl" group is the preferred conformation because it's smaller than the t-butyl group.



Axial "t-butyl" is gauche to the ring on two sides. Only one shows in this Newman projection. It avoids this conformation at all cost.

$$K = \frac{\text{chair 2}}{\text{chair 1}} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-(1200 \text{ cal/mole})}{(2.3)(2 \text{ cal/mol-K})(298 \text{ K})}} = 10^{-0.87} = 0.13 = \frac{1}{7.7} = \frac{11\%}{89\%} = \frac{\text{axial isopropyl}}{\text{axial OH}}$$



Energy changes of trans-1-isopropyl-2-hydroxycyclohexane conformations.

14. Use a Newman projection of the C3→C4 bond of 3-methyl-4-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. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (This is the way your question will read on the final exam. On the midterm exam you will only have to draw the highest energy conformation and the lowest energy conformation.)

2D structure

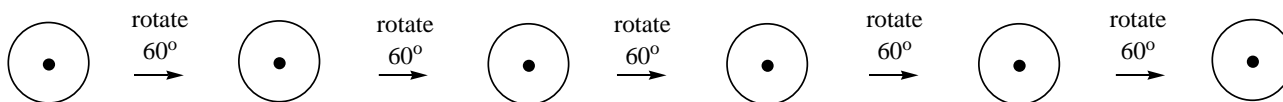
Approximate Eclipsing Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.6	3.0	1.7
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	4.5	10.0	3.8
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5
Ph	1.7	3.3	3.8	8.1	13.5	8.3

$$\Delta G \approx \Delta H$$

$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

Approximate Gauche Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.2
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.6	3.0	1.5
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9
Ph	0.2	1.4	1.5	2.1	3.9	2.3

most stable conformation
↓



$\Delta H^\circ =$

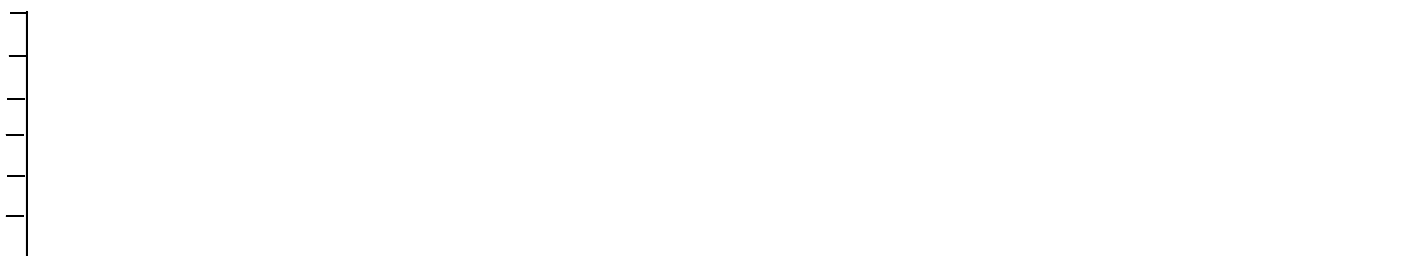
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

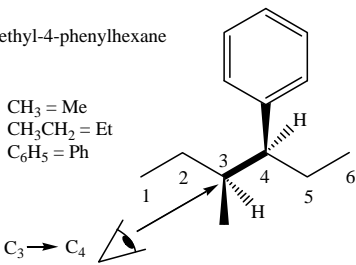
$\Delta H^\circ =$

$\Delta H^\circ =$



3-methyl-4-phenylhexane

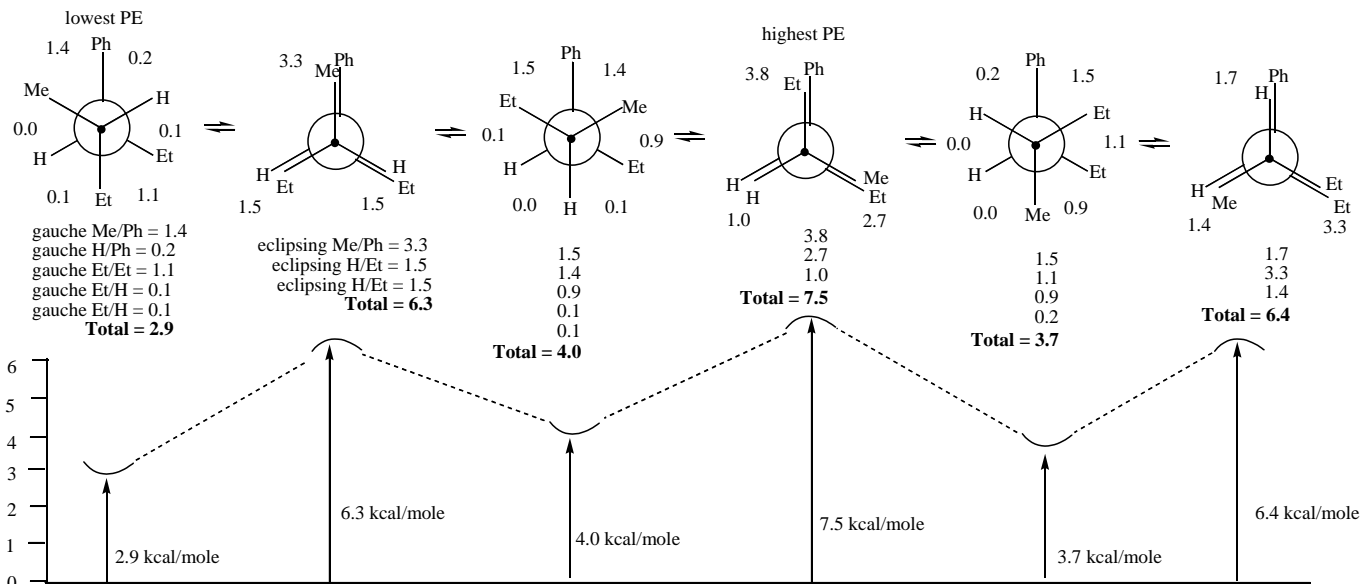
CH₃ = Me
CH₃CH₂ = Et
C₆H₅ = Ph



This problem actually has two answers because there are two chiral centers and diastereomers are possible. The structure drawn is (3S,4S) which gives the same result as its enantiomer (3R,4R). However, (3R,4S) and (3S,4R) give a different result. This can be shown by switching the ethyl and methyl groups on the front carbon (the dot) and recalculating the energy values of the different conformations.

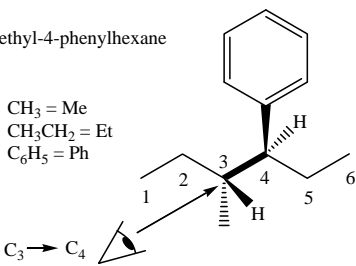
Newman projections:

(3S,4S)



3-methyl-4-phenylhexane

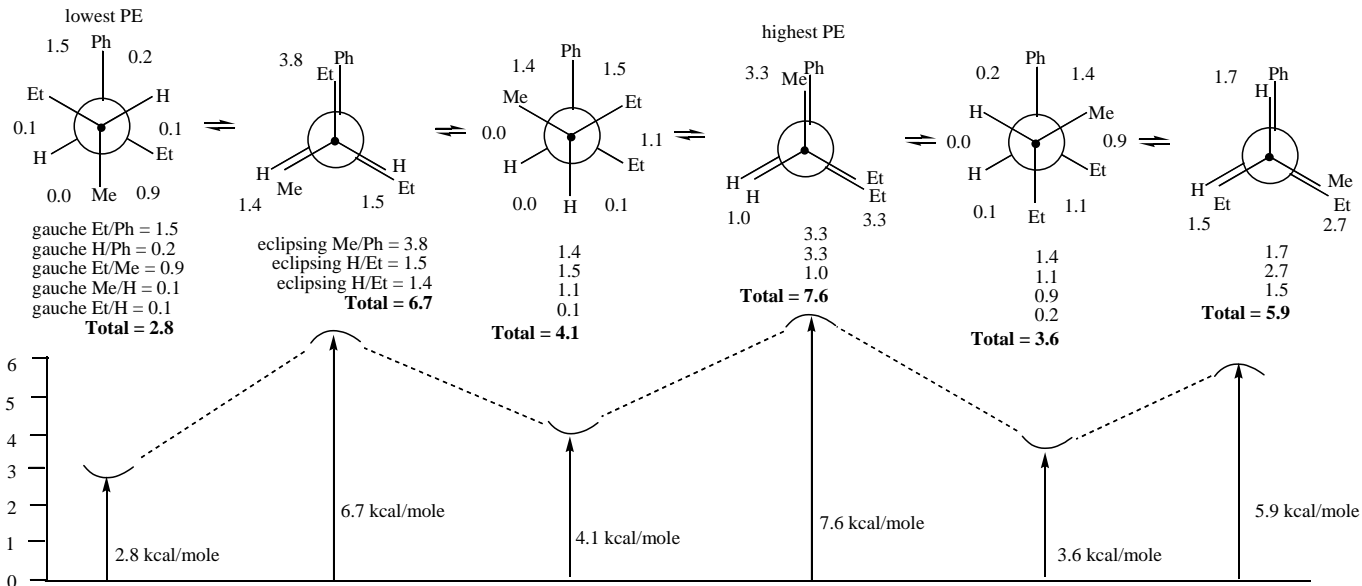
CH₃ = Me
CH₃CH₂ = Et
C₆H₅ = Ph



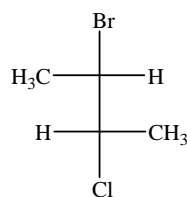
This molecule (3R,4S) is a diastereomer of the above molecule (3S,4S). As diastereomers, they could have completely different properties, including different conformational energies.

Newman projections:

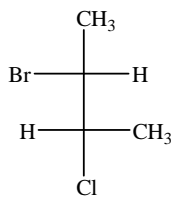
(3R,4S)



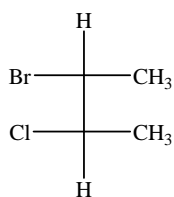
15. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration and write an acceptable name for that isomer.



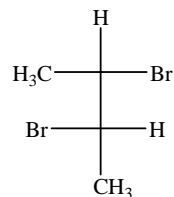
A



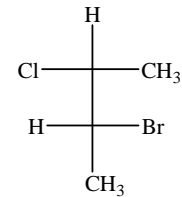
B



C



D

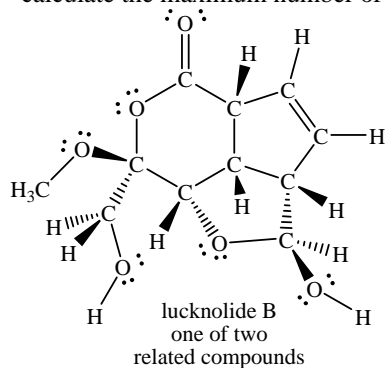


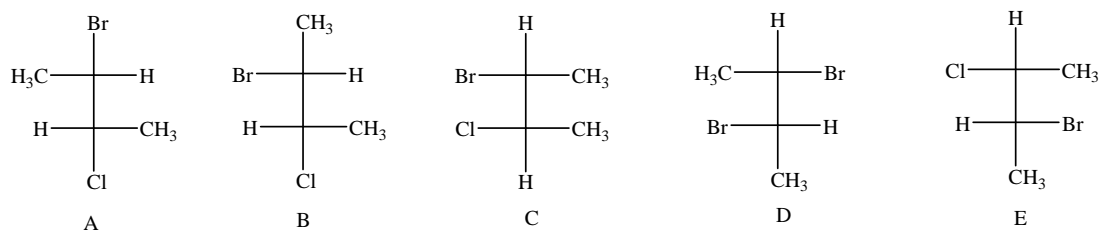
E

- a. Which are optically active? A B C D E
- b. Which are meso? A B C D E
- c. Which is not an isomer with the others? A B C D E
- d. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE
- e. Which pairs are identical? 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 any stereoisomers of 2-bromo-3-chlorobutane as Fischer projections, which are not shown above. If there are none, indicate this.

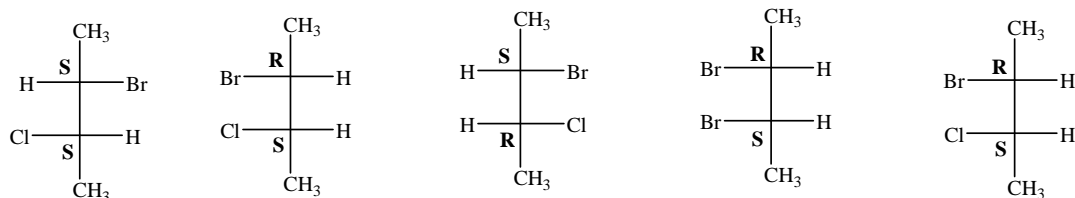
- i. Would anything change if, in compound D, the Br was replaced with a Cl group? How about compound A?

- j. The structure of lucknolide B was recently determined (and the absolute configuration of all chiral centers!). It was isolated from the terrestrial bacteria, *Streptomyces* sp. ANK-289, in screenings for new medicinal lead compounds (Org. Lett. p.3800, 2010). Circle all chiral centers and any other stereochemical features, and calculate the maximum number of stereoisomers possible.





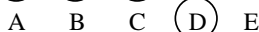
Top and/or bottom carbon rotated to make longest carbon chain vertical and "E" was twisted 180° to get Br on the top.



a. Which are optically active?



b. Which are meso?



c. Which is not an isomer with the others?



d. Which pairs are enantiomers?



e. Which pairs are identical?



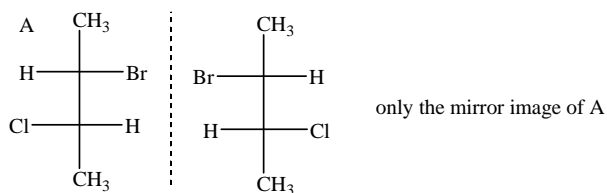
f. Which pairs are diastereomers?



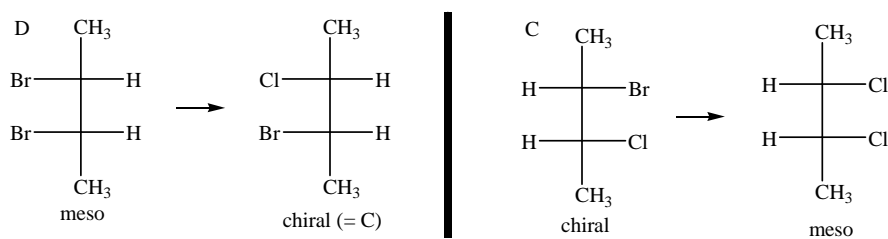
g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?



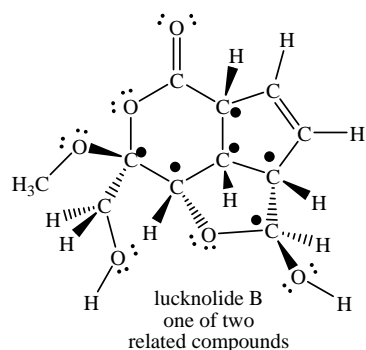
h. Draw any stereoisomers of 2-bromo-3-chlorobutane as Fischer projections, which are not shown above. If there are none, indicate this.



i. Would anything change if, in compound D, the top Br was replaced with a Cl group? How about compound C?



j. The structure of lucknolide B was recently determined (and the absolute configuration of all chiral centers!). It was isolated from the terrestrial bacteria, *Streptomyces* sp. ANK-289, in screenings for new medicinal lead compounds (Org. Lett. p.3800, 2010). Circle all chiral centers and any other stereochemical features, and calculate the maximum number of stereoisomers possible.



• = chiral center

6 chiral centers

$2^6 = 64$ possible stereoisomers