Problems	Points	Credit
1. Functional Group Nomenclature	25	
2. Degrees of Unsaturation & Functional Groups or Various Nomenclature Terms	15	
3. 2D structure, Functional Groups	20	
4. 2D / 3D Resonance Structures, Formal Charge	25	
5. Simple 2D Resonance Structures, Formal Charge	12	
6. Physical Properties, Forces of Interaction	15	
7. Cyclohexane Conformations, Substituents, Energy, K_{eq}.	25	
8. Newman Projections, Open Chain Structure, Relative Energies, K_{eq}.	20	
9. Stereochemical Analysis	25	
Total	182	

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. Do your best to show me what you know in the time available.

In the middle of every difficulty lies opportunity.   Albert Einstein

1. Provide an acceptable name for the following molecule. Same as your midterm, except I added in a double bond to the cyclopentane ring, which also changes the numbering direction in the ring.

N

O

OH
10
H 11

C
4
5
6
7
8
9
NH₂

O
3

O
2
1

O

1
2
3
could also be
called allyl

O
2
1

1
5
2
4 3

2 1
4 3

1 2
3 4
5 6
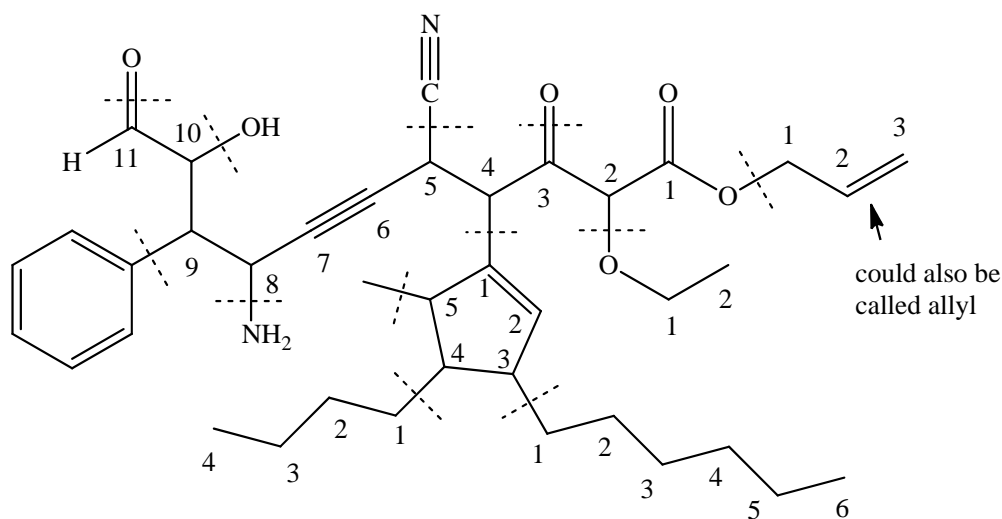
prop-2-enyl 2-ethoxy-3,11-dioxo-4-(5-methyl-4-butyl-3-hexylcyclopent-1-enyl)-

5-cyano-8-amino-9-phenyl-10-hydroxyundec-6-ynoate

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

$C_{25}H_{27}BrClNO_7S_2$, functional groups: carboxylic acid, anhydride, thiol, sulfide, amide, alkyne, ring, bromo, aromatic, acid chloride
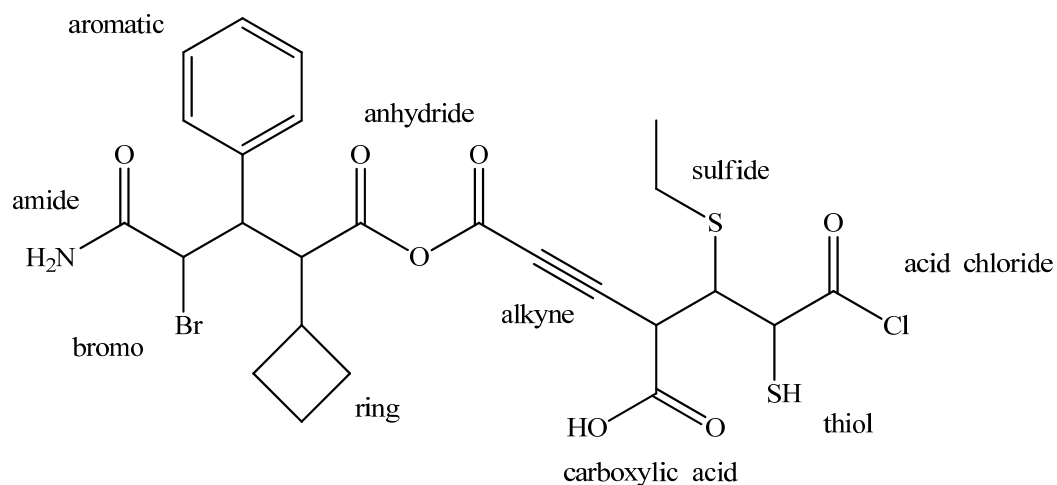
formula = $C_{25}H_{27}BrClNO_7S_2$

There are probably millions of ways to draw possible structures. This is just one of them.

complete saturation = 2(25) + 2 + 2 = 53
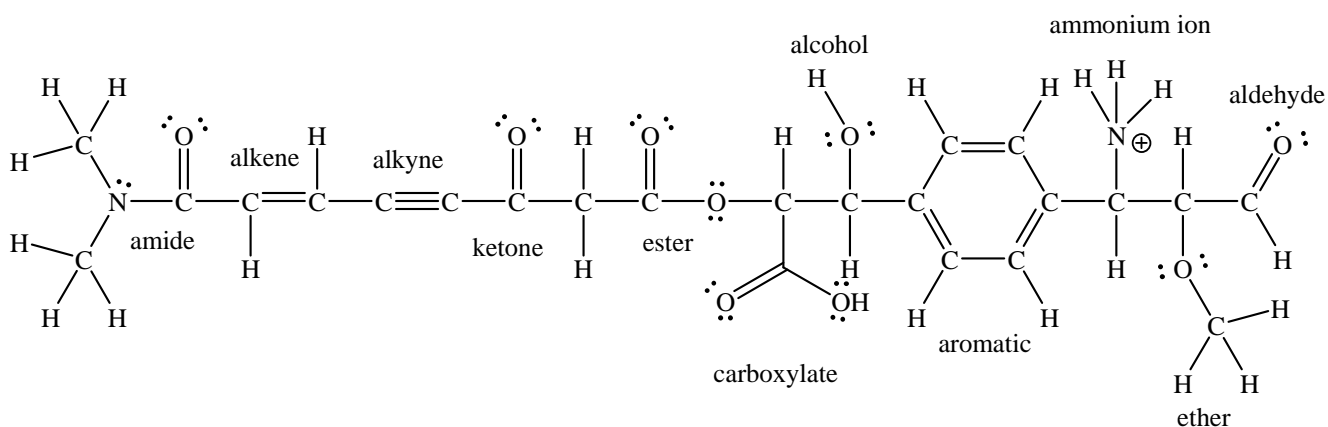total single bonding groups   = -29 (H + Cl)
missing single bonding groups (÷ 2) = 24 ÷ 2 = 12 degrees of unsaturation
Possible structure

aromatic

anhydride

sulfide

amide

H₂N

Br
bromo

O

O O

O

S

O

alkyne

SH

acid chloride

Cl

ring

HO   O

thiol

carboxylic acid

3. Draw an acceptable Lewis structure (2D) for the following formula. Show <u>all</u> 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.)

$$\left[(CH_3)_2NOCCHCHCCCOCH_2CO_2CH(CO_2H)CHOHC_6H_4CHNH_3CH(OCH_3)CHO \right]^{\oplus}$$

$$\left[(CH_3)_2NOCCHCHCCCOCH_2CO_2CH(CO_2H)CHOHC_6H_4CHNH_3CHOCH_3CHO \right]^{\oplus}$$
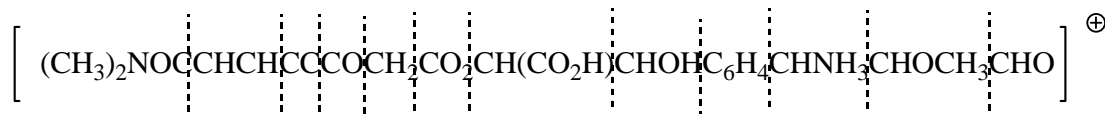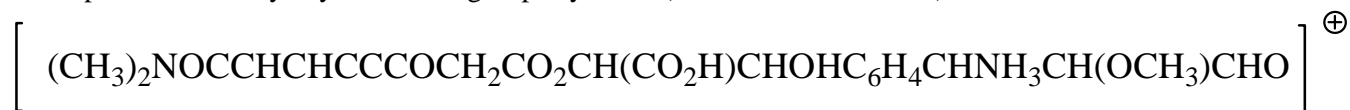

4. First draw a 2D Lewis structure and one additional resonance structure of the following molecule (there are 4 total, include the best). Draw one correct 3D structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbital representations for pi bonds and lone pairs along with their electrons. Fill in the informational table at the bottom for the numbered atoms. (25 pts)
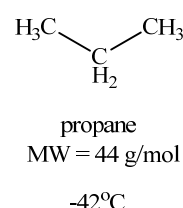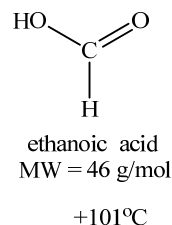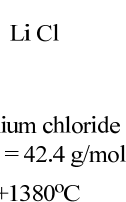

2 more resonance structures are possible
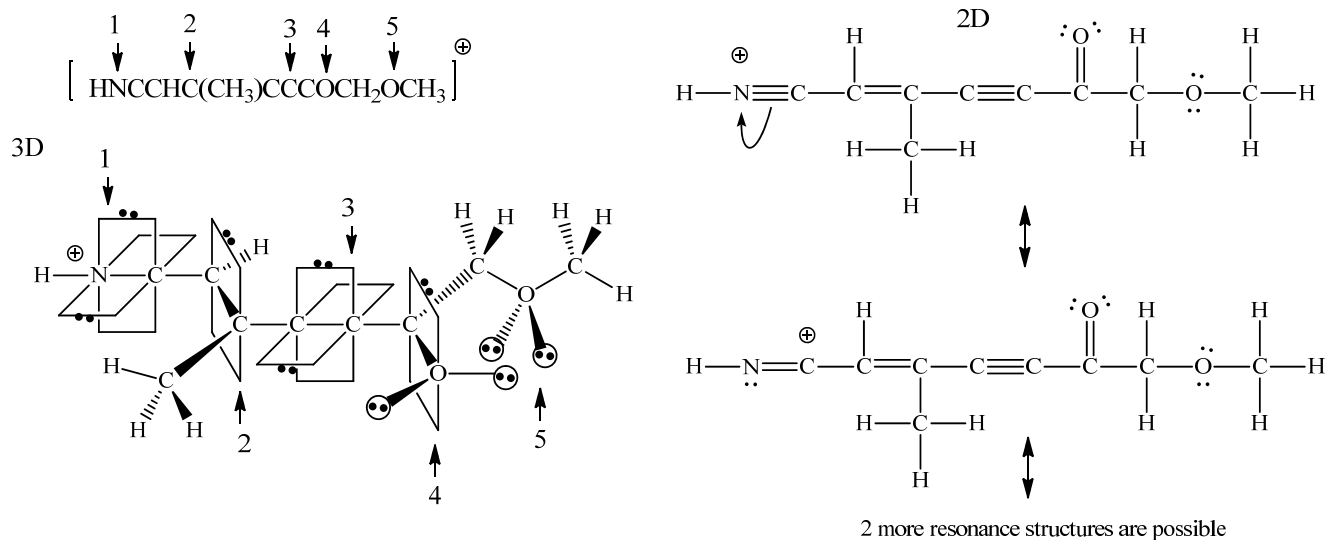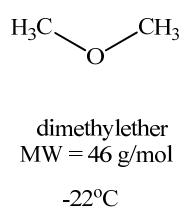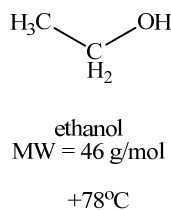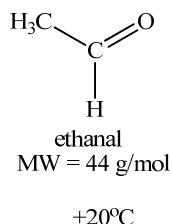
Atom	Shape	Hybridization	Bond Angles	#σ bonds	#π bonds	# lone pairs
1	linear	sp	180°	2	2	0
2	trigonal planar	sp²	120°	3	1	0
3	linear	sp	180°	2	2	0
4	trigonal planar	sp²	120°	1	1	2
5	tetrahedral	sp³	109°	2	0	2

4. Draw all 2D resonance structures for the following structures. Assume full octets for all nonhydrogen atoms unless there is a positive charge written. Use correct arrows, formal charge and include lone pairs. (6 pts each)

    a. $HCCCH_2^{\oplus}$

    b. CH_2CHO
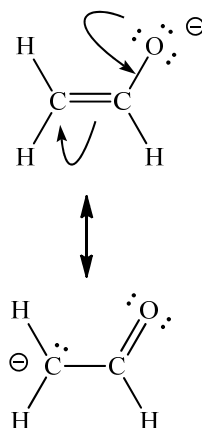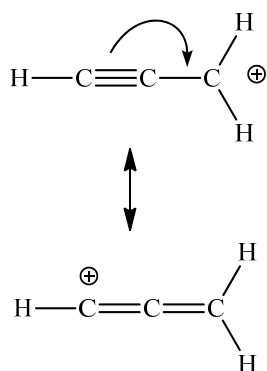
The problem says assume full octets unless there is a positive charge written, so the oxygen atom must have 3 lone pairs, or you could draw the resonance structure with negative charge on the carbon first.

5. Match the given boiling points with the structures below and give a short reason for your answers. (-42°C, -22°C, +20 °C, +78 °C, +101°C, 1380°C) (15 pts)

ethanal	ethanol	dimethyl ether	lithium chloride	ethanoic acid	propane
MW = 44 g/mol	MW = 46 g/mol	MW = 46 g/mol	MW = 42.4 g/mol	MW = 46 g/mol	MW = 44 g/mol
+20°C	+78°C	-22°C	+1380°C	+101°C	-42°C

Ionic forces are clearly the strongest and usually require very high temperatures to melt a salt. The carboxylic acid is next where strong polarity reinforced by resonance is combined with hydrogen bonding (OH). The alcohol is next with strong hydrogen bonding. The aldehyde is next with the strongly polar carbonyl, reinforced by resonance. The ether has slight polarity, but no hydrogen bonding and last is the alkane with only weak dispersion forces.

7. Draw all possible chair conformations of trans-1-phenyl-2-chlorocyclohexane. 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. Assume a single boat transition state, TS (you do not have to draw the boat) (25 pts)
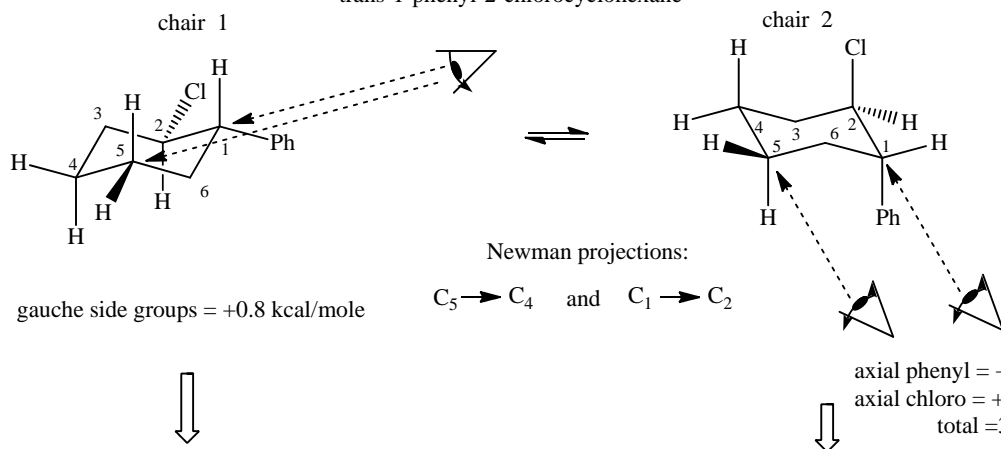
Given Information

Substituent	ΔG^o (A value)	Substituent	ΔG^o (A value)
-H	0.0	-F	0.3
-CH_3	1.7	-Cl	0.5
-CH_2CH_3	1.8	-Br	0.5
-CH(CH_3)_2	2.1	-I	0.5
-C(CH_3)_3	> 5.0	-C_6H_5 (phenyl)	2.9

chair 1 ⇌ chair 2

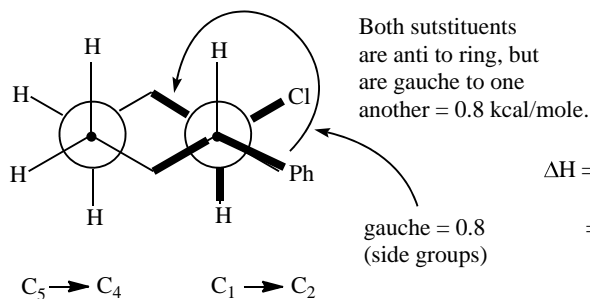$$K = \frac{chair\ 2}{chair\ 1} = 10^{\frac{-\Delta G}{2.3RT}}$$

R = 2 cal/(mole-K)
T ≈ 300 K

trans-1-phenyl-2-chlorocyclohexane
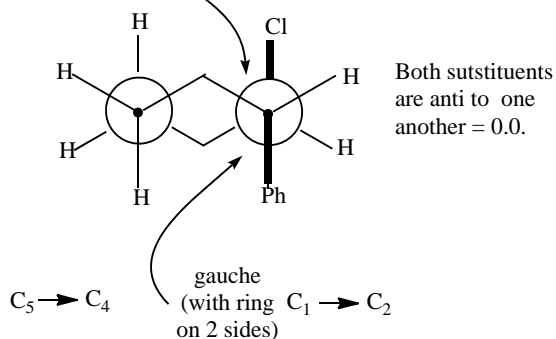
chair 1

chair 2

"phenyl" is on the bottom in both conformations. Of course, if you turn the ring over, then "phenyl" is on the top in both conformations. "chloro" is on the top (equatorial) in the left conformation and top axial in the right conformation. In the first structure Cl and Ph are gauche and the cost listed is 0.8 kcal/mole. In the second conformation the A strain (axial) phenyl is 2.9 and the A strain for the chloro is 0.5, combined = 3.4. The difference between the two conformation is (3.4 - 0.8) = 2.6.

Newman projections:

$C_5 \rightarrow C_4$ and $C_1 \rightarrow C_2$

gauche side groups = +0.8 kcal/mole

axial phenyl = + 2.9 kcal/mole
axial chloro = +0.5 kcal/mole
total = 3.4 kcal/mole

---

side gauche = +0.8 kcal/mole
total = 0.8 kcal/mole

gauche (with ring on 2 sides)

axial phenyl = + 2.9 kcal/mole
axial chloro = +0.5 kcal/mole
total = 3.4 kcal/mole

Both sutstituents are anti to ring, but are gauche to one another = 0.8 kcal/mole.

Both sutstituents are anti to one another = 0.0.

$\Delta H = (2.9 + 0.5) - (0.8)$ kcal/mole

= 2.6 kcal/mole

gauche = 0.8 (side groups)

$C_5 \rightarrow C_4$ $C_1 \rightarrow C_2$

gauche (with ring on 2 sides)

$C_5 \rightarrow C_4$ $C_1 \rightarrow C_2$

$$K = \frac{chair\ 2}{chair\ 1} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-(2600\ cal/mole)}{(2.3)(2\ cal/mol-K)(298\ K)}} = 10^{-1.88} = 0.013 = \frac{1}{76} = \frac{1.3\%}{98.7\%} = \frac{axial\ isopropyl}{axial\ OH}$$

boat

chair 2

0.1.3%

chair 1

98.7%

PE

≈ 2.6 kcal/mole

$\Delta H = 3.4 \dfrac{kcal}{mole}$

$\Delta H = 0.8 \dfrac{kcal}{mole}$
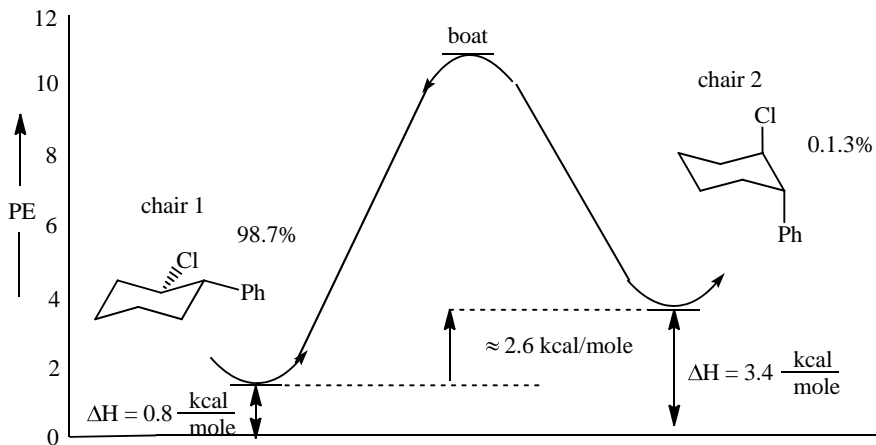
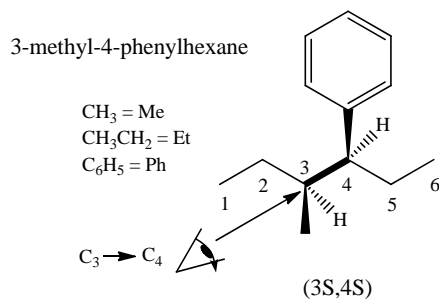Energy changes of trans-1-isopropyl-2-hyroxycyclohexane conformations.

8. 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.) (20 pts)

2D structure

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

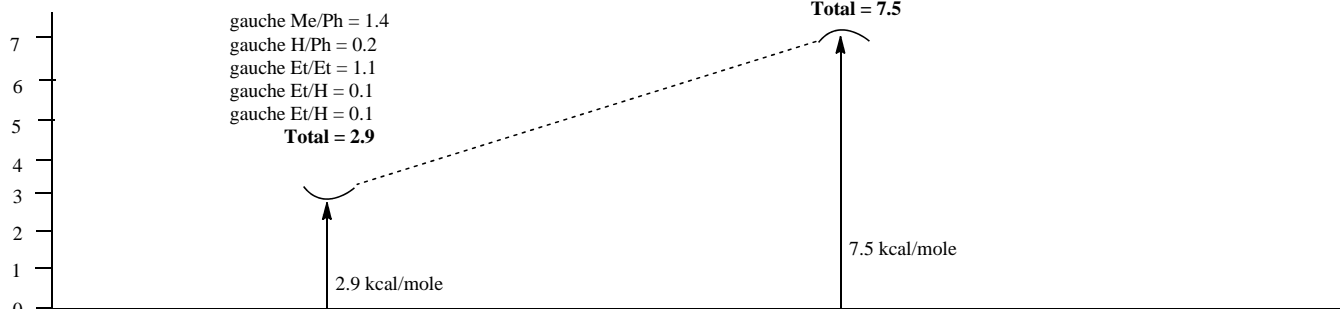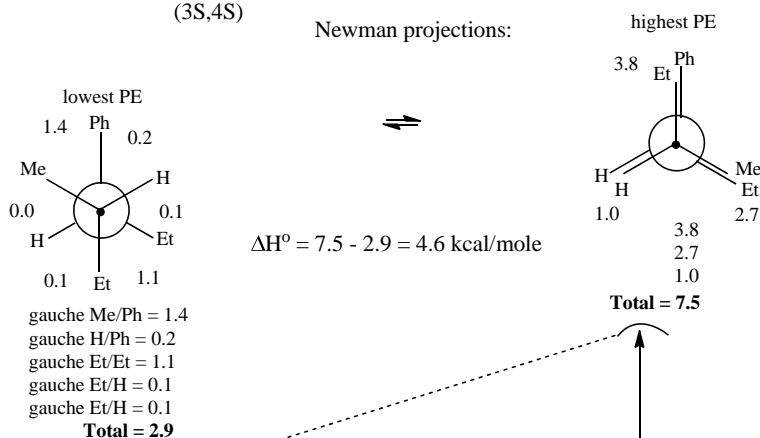$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

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

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

3-methyl-4-phenylhexane

CH₃ = Me
CH₃CH₂ = Et
C₆H₅ = Ph

$C_3 \rightarrow C_4$

(3S,4S)

This is the same problem as the sample exam key!

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. I did not do this in this key.

Newman projections:

lowest PE

Me   Ph 1.4   0.2
0.0   H
H   0.1
   0.1 Et   Et 1.1

gauche Me/Ph = 1.4
gauche H/Ph = 0.2
gauche Et/Et = 1.1
gauche Et/H = 0.1
gauche Et/H = 0.1
Total = 2.9

ΔH^o = 7.5 - 2.9 = 4.6 kcal/mole

highest PE

3.8 Et Ph
H   Me
H   Et
1.0   2.7

3.8
2.7
1.0
Total = 7.5

7.5 kcal/mole

2.9 kcal/mole

$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}} = K_{eq} = 10^{\frac{-4600}{1380}} = 10^{-3.33} = 4.7 \times 10^{-4} = \frac{1}{2340}$$

9. Use the given formula to illustrate the requested example. Formula = $C_6H_{10}Br_2$ (25 pts)
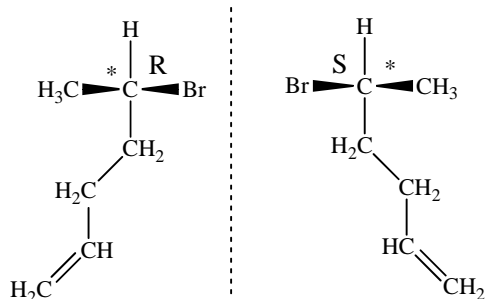
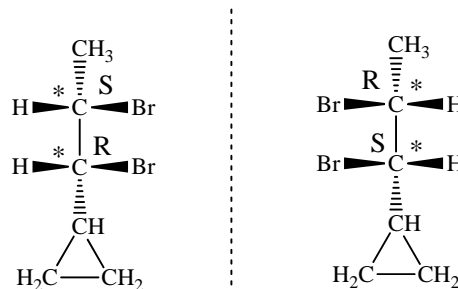degree of unsaturation = 2 x 6 + 2 = 14

Formula = $C_6H_{10}Br_2$
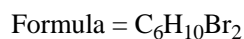
- 12 single bonding groups
= 2 / 2 = 1° unsaturation

a. Draw a 3D structure with one chiral center and its enantiomer. Specify chiral centers as R or S.
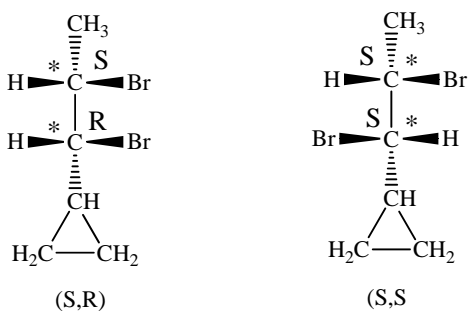
enantiomers are stereoisomers that are 'different' mirror images

b. Draw a 3D structure with two chiral centers and its enantiomer. Specify chiral centers as R or S.
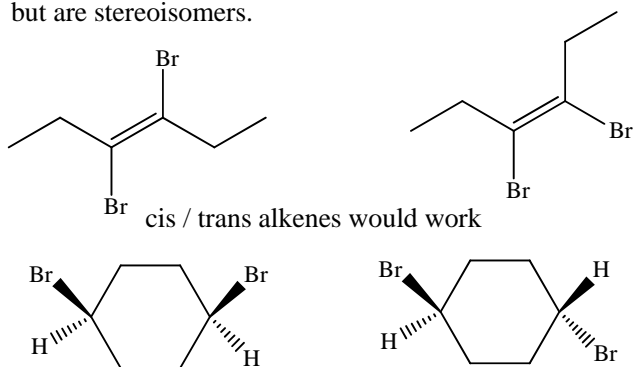
enantiomers are stereoisomers that are 'different' mirror images

c. Draw a 3D structure with two chiral centers and a diastereomer. Specify chiral centers as R or S.

(S,R)   (S,S

diastereomers are stereoisomers that are not mirror images and not identical

d. Draw two structures that do not have any chiral centers, but are stereoisomers.

cis / trans alkenes would work

Even carbon rings substituted cis/trans on opposite sides do not have any chiral centers, but are diastereomers.
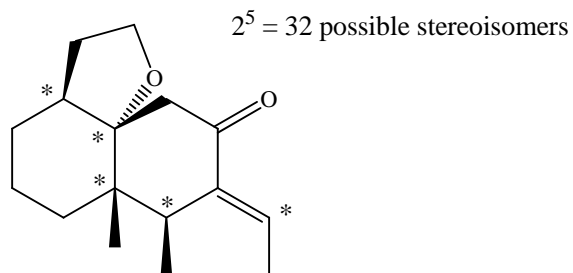
e. Draw a structure that has chiral centers, but is not chiral.
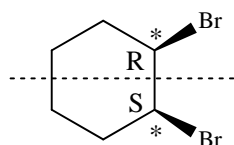
Compounds with 2 or more chiral centers, but having a mirror plane of symmetry down the middle are meso and achiral.

f. Circle all stereogenic centers in following molecule and calculate the maximum number of stereoisomers possible.

$2^5 = 32$ possible stereoisomers

You cannot teach people anything. You can only help them discover it within themselves.   Galileo