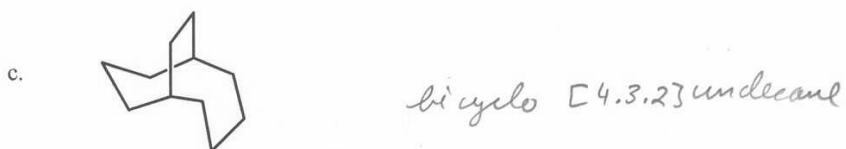
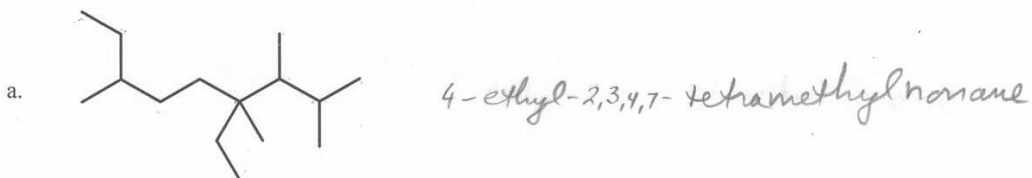
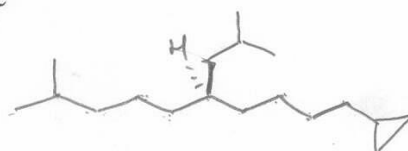


1. Provide names for the following compounds (don't worry about stereochemistry – yet). (15 points)

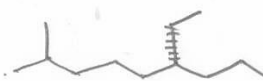


2. Draw the *bond-line* structures for the following compounds. (15 points)
Extra Credit. How many stereoisomers are possible for the structure in c. (5 EC points)

a. (S)-1-cyclopropyl-5-(2-methylpropyl)-9-methyldecane



b. (R)-6-ethyl-2-methylnonane



c. 7-methylbicyclo[4.3.1]decane

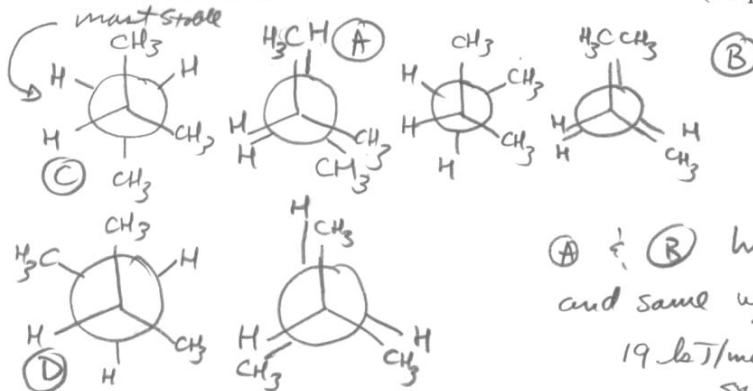


EC – assuming no geometric constraints, $2^3 = 8$ isomers

3. Draw all six conformations of 2-methylbutane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, as viewed down the C2-C3 bond, using Newman projections. Indicate the *least stable* and the *most stable* conformations. If any of the conformations have the *same energy* then show which ones do. Finally, use the provided data to estimate the total barrier to rotation about the C2-C3 bond. (25 points)

Strain interactions

H/H eclipsed	4 kJ/mol
CH_3/H eclipsed	6 kJ/mol
CH_3/CH_3 eclipsed	11 kJ/mol
CH_3/CH_3 gauche	3.8 kJ/mol



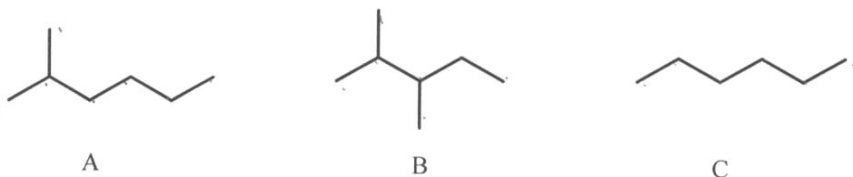
barrier $19 - 3.8 = 15.2 \text{ kJ/mol}$ (difference between highest and lowest points)
 C & D lowest E w/ 3.8 kJ/mol strain

4. Which hydrocarbon has the higher boiling point, octane or 2,2,4-trimethylpentane? Explain why in terms of intermolecular forces. (10 points)



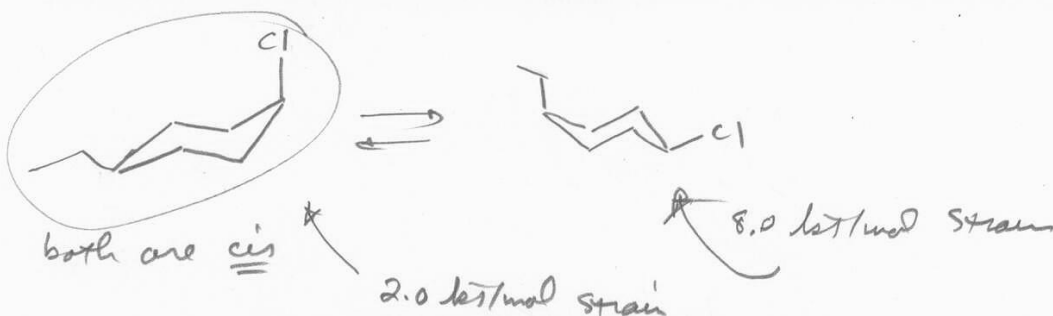
since octane has more surface area for same MW,
 Greater amount of London dispersion forces, so more intermolecular attractive forces

5. Which molecule A or B below has the greatest value for heat of combustion (ΔH_{comb})? Explain. Why can't the value of ΔH_{comb} for molecule C be compared to A or B? (10 points)



A is less branched than B, so should have the largest (negative) value for ΔH_{comb} . - more branched is most stable
 C can't be compared directly since it doesn't have the same # of carbons -

6. Draw both *chair* conformations of *cis*-1-chloro-4-ethylcyclohexane. Circle the most stable chair conformation. (Don't forget stereochemistry and remember you get points for a good looking chair) (10 points)



7. Given the data below, calculate ΔG and K_{eq} for the equilibrium between the two chairs from Question 6, at 25°C, from the highest to lowest energy chair! ($K_{eq} = e^{-\Delta G/RT}$, $R = 8.314 \text{ J/mol K}$, $K = C + 273.15$) (15 points)

1,3-diaxial interactions

-Cl	2.0 kJ/mol
-CH ₂ CH ₃	8.0 kJ/mol

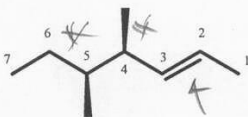
$$\Delta G = (2.0 - 8.0) \text{ kJ/mol} = -6.0 \text{ kJ/mol} = -6000 \text{ J/mol}$$

lowest strain is w/ equatorial ethyl

$$T = 273.15 + 25 = 298.15 \text{ K}$$

$$K_{eq} = e^{-(-6000 \text{ J/mol}) / (8.314 \text{ J/mol} \cdot \text{K})} = 11.3$$

8. How many *stereoisomers* in total are possible for this compound (one of them is shown)? (5 points)

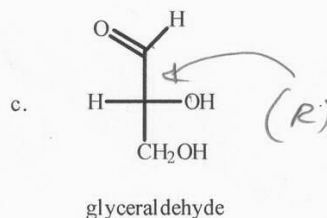
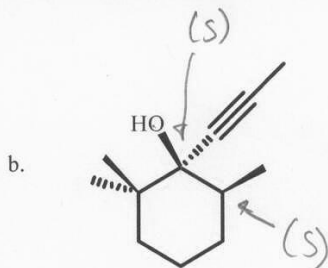
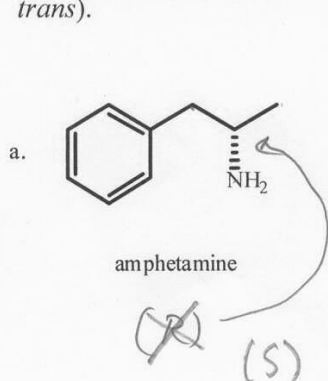


$$\text{So, } 2^3 = 8 \text{ isomers}$$

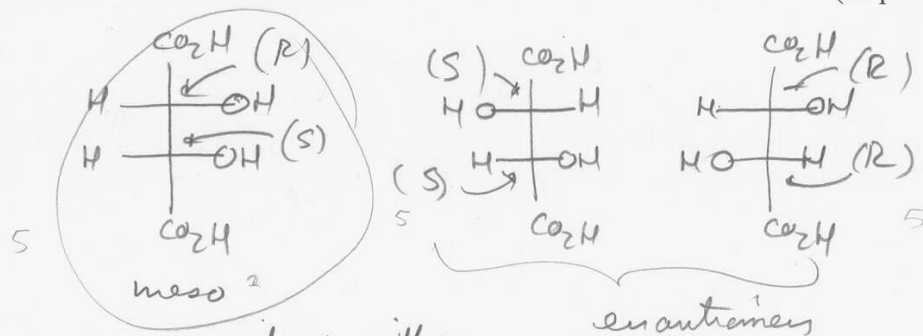
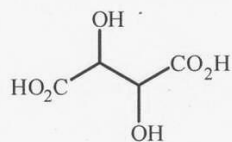
2 asymmetric carbon can be either R or S

1 double bond can be either E or Z (cis or trans)

9. Assign the stereochemistry in the following compounds with the appropriate notation (*R*), (*S*), *cis* or *trans*). (15 points)



10. Show *all* of the stereoisomers for tartaric acid (shown below). Label each asymmetric carbon with the corresponding *configuration*. Indicate the relationship between each pair of isomers as *enantiomers* or *diastereomers*. If one of the isomers is a *meso* compound, then circle and label it. Use either bond-angle perspective drawings or Fisher projections to show the structures. (20 points)

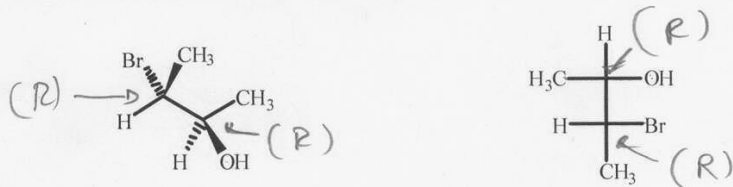


meso compound of either
 of the enantiomers are
 diastereomers 2

11. Indicate whether the following statements are *absolutely* true or false. (12 points)

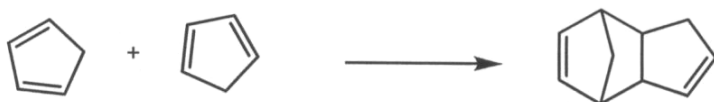
- a. All *enantiomers* are optically active. T
- b. (2*R*,3*R*)-pentane-2,3-diol is the *enantiomer* of (2*S*,3*S*)-pentane-2,3-diol. T
- c. If a molecule lacks a sigma plane (σ) then it is chiral. F
- d. All *meso* compounds are optically active. F
- e. *trans*-1,3-dimethylcyclobutane is chiral. F
- f. If a molecule with one asymmetric carbon has a positive (+) rotation then the absolute configuration must be (*R*). F

12. What is the relationship between the following two structures: they are *enantiomers*, *diastereomers*, *constitutional isomers*, or *identical*? (5 points)



identical

13. How is the following reaction sensitive to temperature? Clearly explain (Hint: consider ΔH and ΔS) (10 points)



σ bonds are much stronger than π

3 π bonds are converted to 2 σ + 1 π
so ΔH should be negative ($\Delta H = \ominus$)

2 molecules become 1 molecule as a product, so
 $\Delta S = \ominus$

$$\Delta G = \Delta H - T\Delta S$$

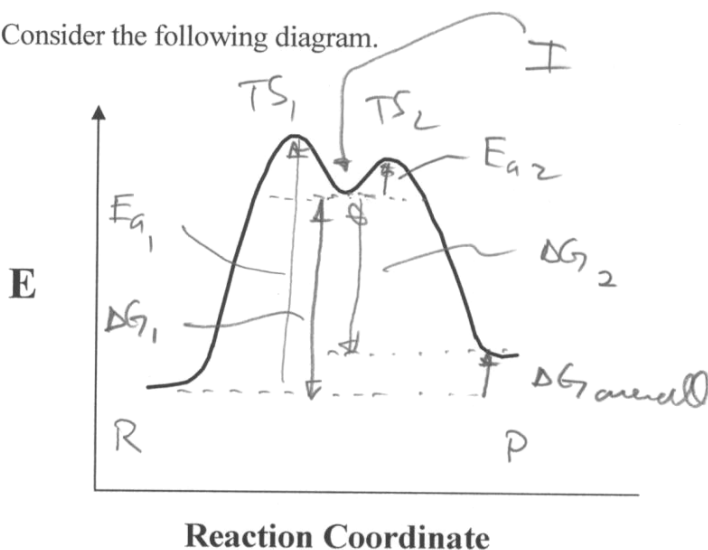
At low temperatures $\Delta G = \ominus$ since ΔH dominates

At high temperatures $\Delta G = \oplus$ since $-T\Delta S$, which is positive (\oplus) dominates

At high temperatures the reverse reaction is favored

14. Consider the following diagram.

(33 points)



Show the following on the energy-level diagram above:

- The activation energy for each step (E_{a1} and E_{a2})
- The Gibbs free energy for each step (ΔG_1 and ΔG_2)
- The overall free energy ($\Delta G_{\text{overall}}$).
- Where the transition states for each step (TS_1 and TS_2) are.
- Where the reagents, intermediates, and products would appear on the graph.

Answer the following questions about the reaction depicted in the diagram:

- Is the overall reaction spontaneous in the forward direction? Explain. *No, $\Delta G = \oplus$ non-spontaneous*
- Which step is rate-limiting? Explain. *1st Step*
- For the overall reaction, is K_{eq} large (>1) or small (<1)? Explain.

$K_{\text{eq}} < 1$ since $\Delta G_{\text{overall}} = \oplus$

$K_{\text{eq}} = e^{-\Delta G/RT}$

< 1 for $\Delta G = \oplus$