

<b>Last Name</b>	<b>First Name</b>	<b>MI</b>
<b>Student ID Number:</b>		<b>Total Score</b>
<b>Circle the name of your TA:      MIKE      ROB</b>		
<b>Discussion Section – Day:</b>	<b>Time:</b>	

## Chem 30A Winter 2005

### MIDTERM #1 (50 Min)

**Weds February 2nd**

***INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM –  
DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU***

***ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED***

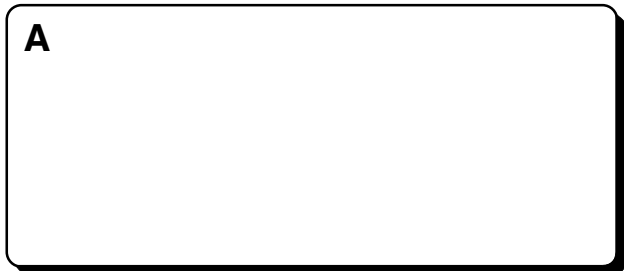
***\*\*\*DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO\*\*\****

<b>Q1</b>	<b>/ 24</b>	<b>Q4</b>	<b>/ 22</b>
<b>Q2</b>	<b>/ 18</b>	<b>Q5 BONUS</b>	<b>/ 5</b>
<b>Q3</b>	<b>/ 36</b>	<b>Q6 BONUS</b>	<b>/ 10</b>
		<b>Total</b>	<b>/ 100</b>

*"A common mistake that people make when trying to design something completely foolproof is to underestimate the ingenuity of complete fools"*  
- Douglas Adams

Q1. (a) Using **LINE FORMULAE** draw the four different **CONSTITUTIONAL** isomers with the molecular formula  $C_4H_9Cl$  (2 pt each) (b) Name each isomer using **SYSTEMATIC** naming rules, in the knowledge that chloro groups are higher in priority than methyl groups (i.e., they get the smaller positional number if a choice has to be made) (2 pt each)

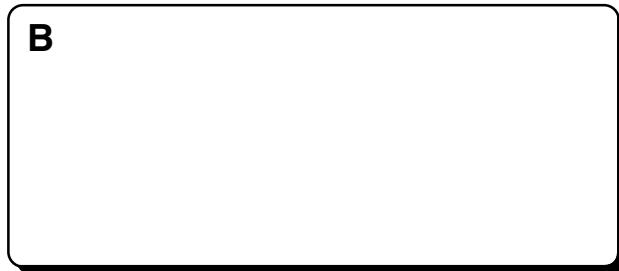
**A**



Name



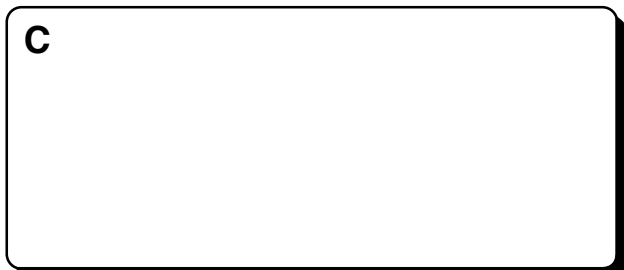
**B**



Name



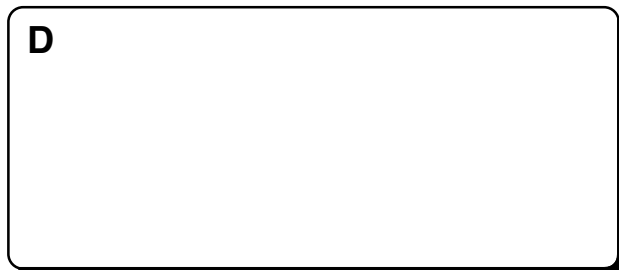
**C**



Name



**D**



Name



(c) Which of the constitutional isomers of  $C_4H_9Cl$  (A–D) has the highest boiling point (79 °C)? (2 pt)

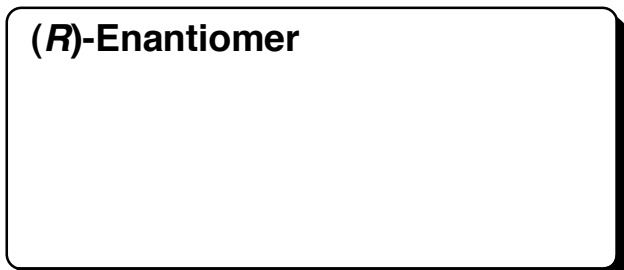


(d) Which of the constitutional isomers of  $C_4H_9Cl$  (A–D) has the lowest boiling point (51 °C)? (2 pt)

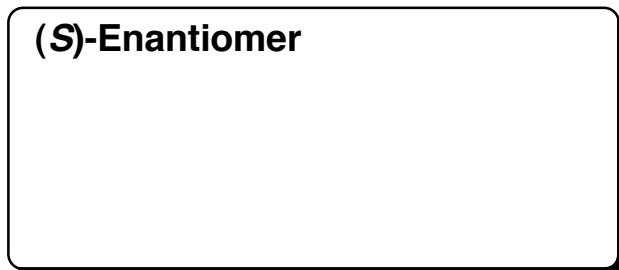


(e) One of the constitutional isomers of  $C_4H_9Cl$  can exist in two stereoisomeric forms (enantiomers). Draw these two non-superimposable mirror images in the appropriate boxes below. (2 pt each)

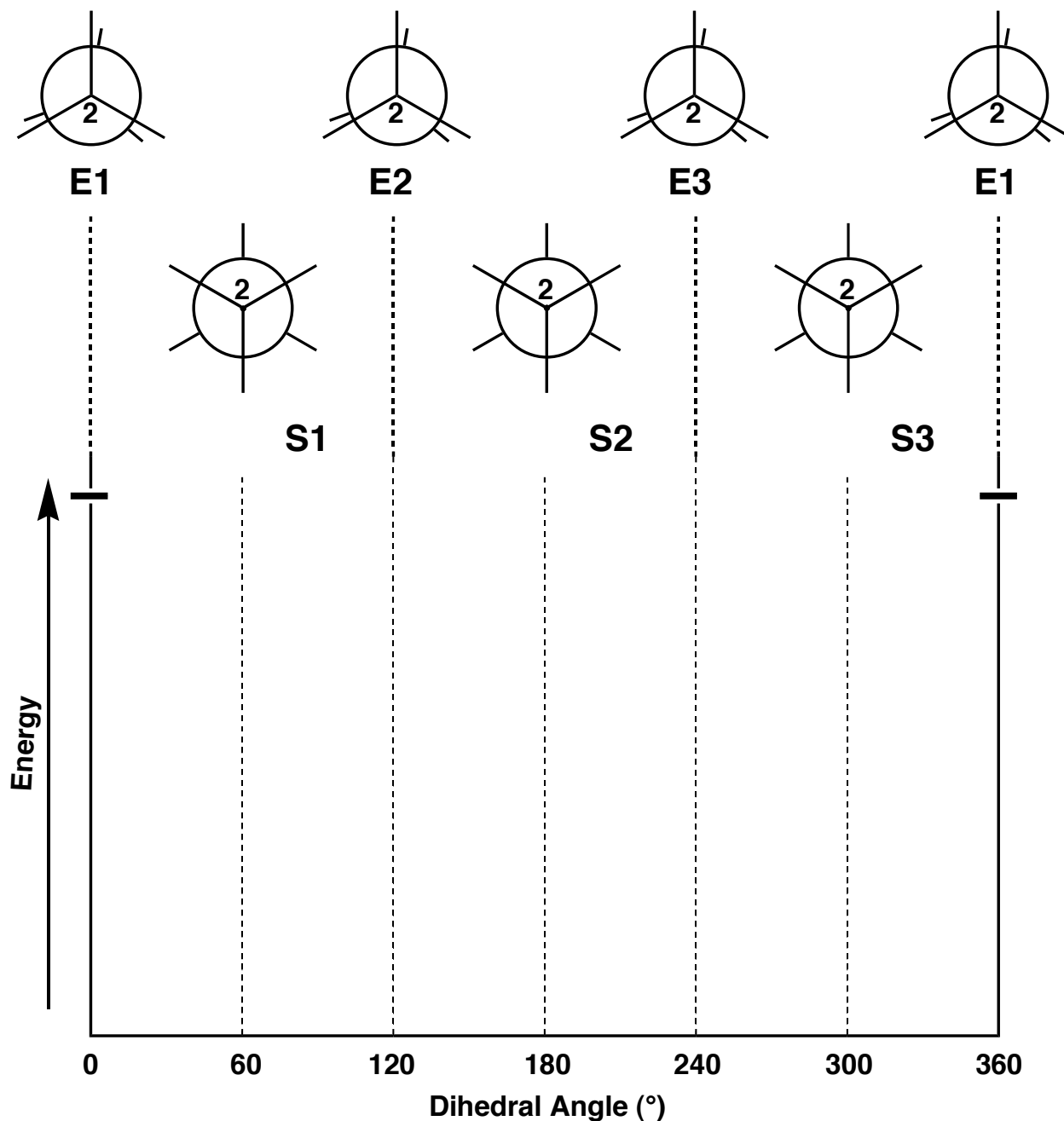
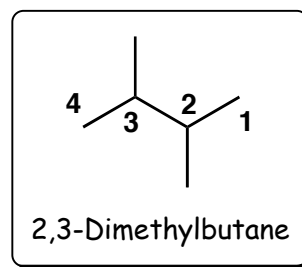
**(R)-Enantiomer**



**(S)-Enantiomer**

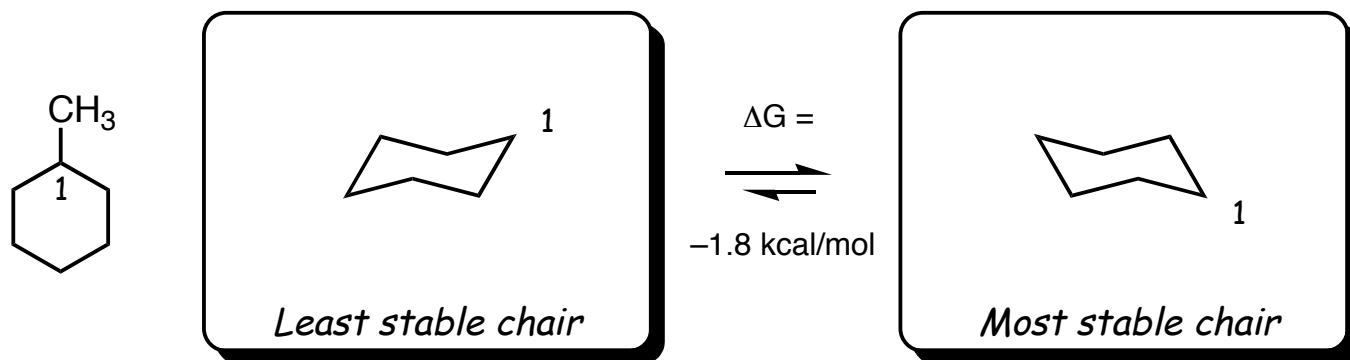


Q2. (a) Above the  $0^\circ$  line on the graph below, fill in the groups on the Newman projection of the **MOST UNSTABLE** eclipsed conformation (**E1**) of 2,3-dimethylbutane, as viewed from C2 to C3, i.e., C2 is in the front. By rotating C2 (and the groups attached to it)  $60^\circ$  **CLOCKWISE**, the first staggered conformation (**S1**) is reached, fill in the groups on this Newman projection above the  $60^\circ$  line. Continue this clockwise rotation, and complete the Newman projections of the other eclipsed (**E2**, **E3**) and staggered (**S2**, **S3**) conformations. (2 pt each)

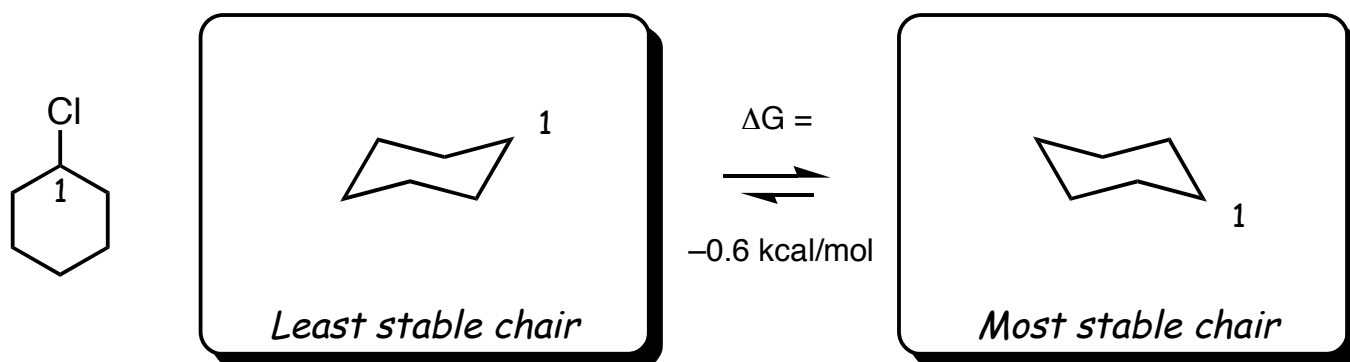


(b) Draw short horizontal bars on the **GRAPH ABOVE** (like those drawn for **E1** at  $0^\circ$  &  $360^\circ$ ), indicating the relative energies of **S1**, **E2**, **S2**, **E3**, and **S3**, and complete the graph by drawing in a curve that shows how the energy changes relative to the dihedral angle. (6 pt)

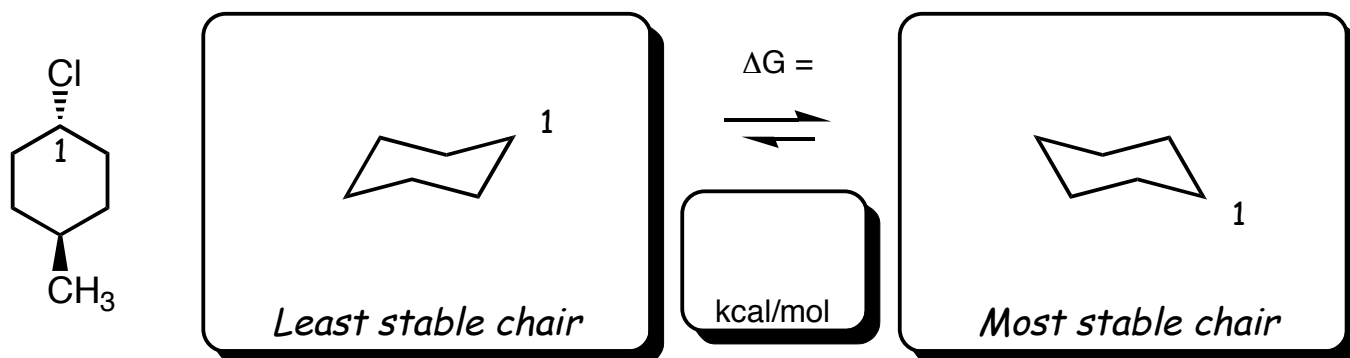
Q3. (a) Methylcyclohexane can exist in two different chair conformations, one of which is 1.8 kcal/mol more stable than the other, i.e., the **A value** for the methyl group is 1.8. In each of the two boxes below, draw in a bond to one methyl ( $\text{CH}_3$ ) group in the appropriate position. (2 pt)



(b) Chlorocyclohexane also exists in two different chair conformations, one of which is 0.6 kcal/mol more stable than the other, i.e., the **A value** for the chloro group is 0.6. In each of the two boxes below, draw in a bond to one chloro ( $\text{Cl}$ ) group in the appropriate position. (2 pt)

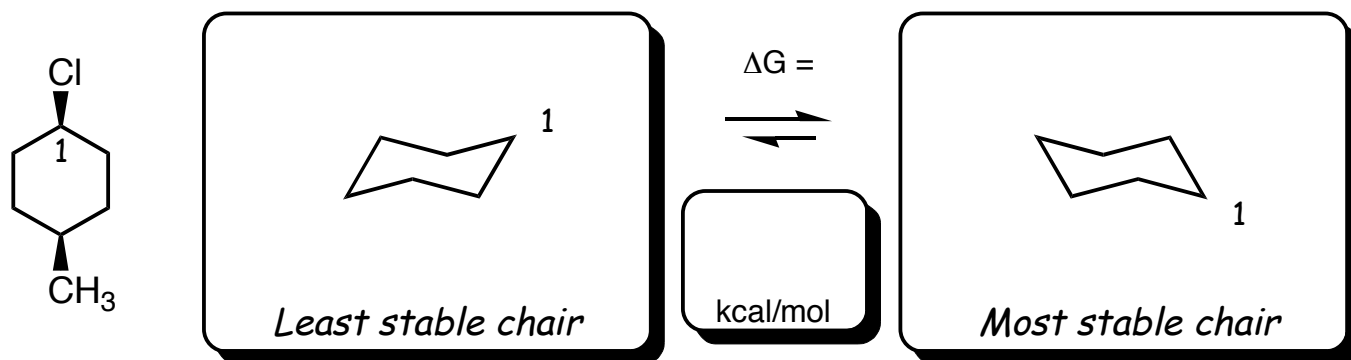


(c) For *trans*-1-chloro-4-methylcyclohexane (shown below), draw in bonds to  $\text{CH}_3$  and  $\text{Cl}$  groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the  $\Delta G$  value will be. (6 pt)

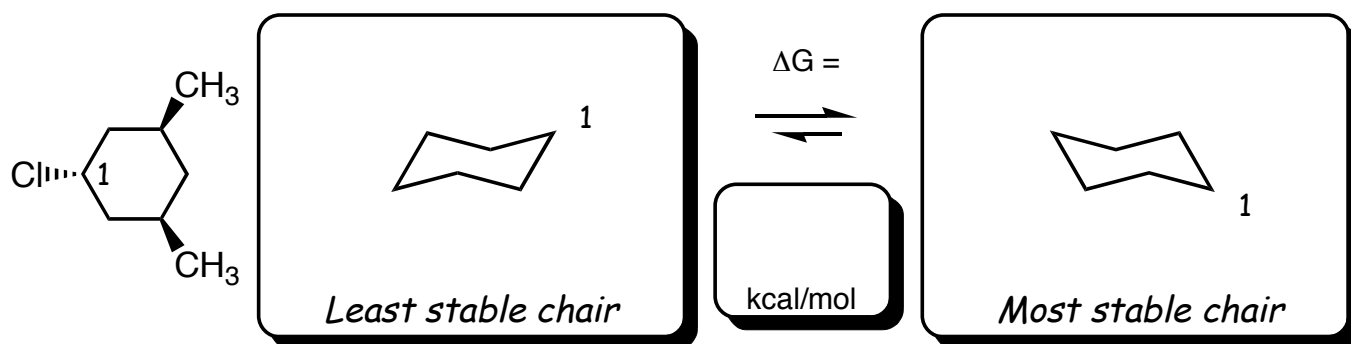


Question 3 is continued on the next page...

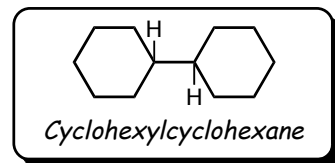
(d) For *cis*-1-chloro-4-methylcyclohexane (shown below), draw in bonds to  $\text{CH}_3$  and  $\text{Cl}$  groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the  $\Delta G$  value will be. (6 pt)



(e) For the isomer of 1-chloro-3,5-dimethylcyclohexane shown below, draw in bonds to  $\text{CH}_3$  and  $\text{Cl}$  groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the  $\Delta G$  value will be. (8 pt)

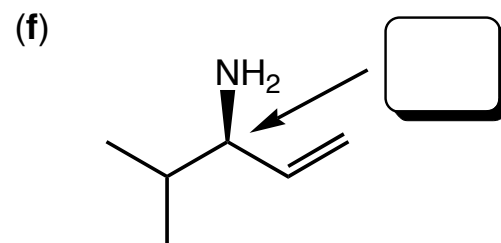
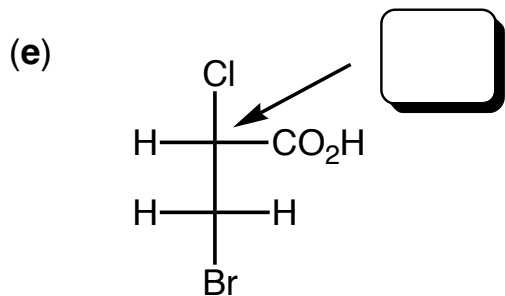
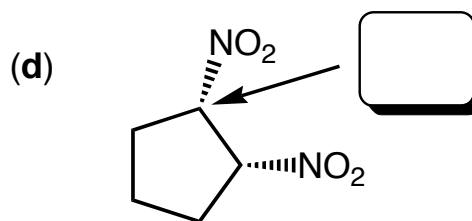
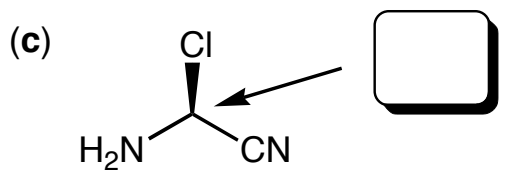
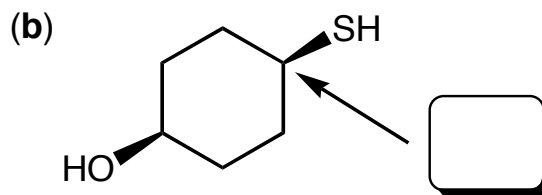
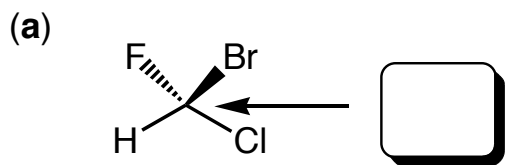


(f) In the appropriate boxes below, draw the three most stable conformations of cyclohexylcyclohexane (shown to the right) in which the indicated H atoms maintain an **ANTI** relationship, i.e., are  $180^\circ$  apart. Once you have drawn these three **different** conformers, use the box below them to briefly explain your answers. (12 pt)

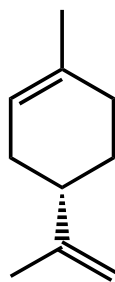
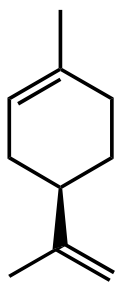


**Explanation:**

Q4. (a)–(f) In each box, write down either *R*, *S*, or *X*, indicating that the carbon atom to which the arrow is pointing has the *R* configuration, the *S* configuration, or is (*X*) not a stereocenter. (3 pt each)

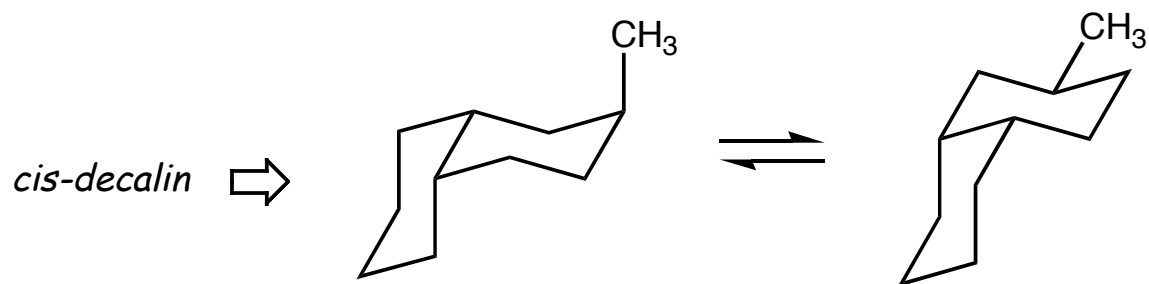
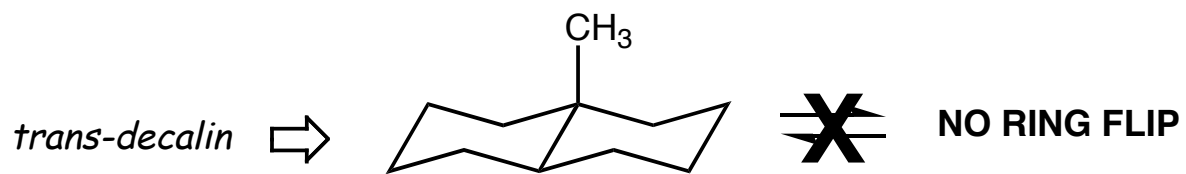


(g) The two enantiomers of limonene have **EXACTLY** the same boiling point, melting point, vapor pressure, and appallingly bad solubility in water. Interestingly, one of them smells of oranges (the *R* isomer) and the other (the *S* isomer) smells like lemons. Explain why they smell different. (4 pt)



(*R*)-limonene    (*S*)-limonene

Q5 (BONUS). Explain why trans-decalin systems cannot undergo chair flips, whereas cis-decalin systems can (examples are shown in the box below). (5 pt)



**Q6 (BONUS).** You've already seen that a chloro-substituent on a cyclohexane ring prefers to be in the equatorial position, i.e., the conformer with the Cl in the **EQUATORIAL** position is favored by 0.6 kcal/mol. Suggest why in the case of 2-chlorotetrahydropyran (shown below), the conformer in which the Cl atom is in the **AXIAL** position is favored by over 2 kcal/mol. (10 pt)

