Last Name ANSWER	**First Name** KEY	**MI**

Student ID Number:

Circle the name of your TA: MIKE ROB

Discussion Section – Day: **Time:**

Total Score

/ 100

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****

Q1	24 / 24	**Q4**	22 / 22
Q2	18 / 18	**Q5 *BONUS***	5 / 5
Q3	36 / 36	**Q6 *BONUS***	10 / 10
		Total	115 / 100

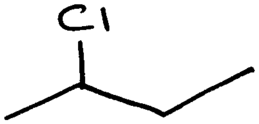
"A common mistake that people make when trying to design something completely foolproof is to underestimate the ingenuity of complete fools"
- Douglas Adams

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

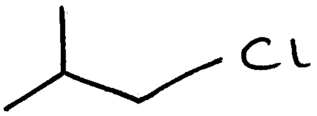
Name
1- CHLOROBUTANE

B



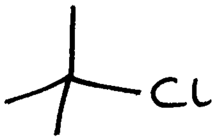
Name
2- CHLOROBUTANE

C



Name
1-CHLORO-2-METHYLPROPANE

D



Name
2-CHLORO-2-METHYLPROPANE

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

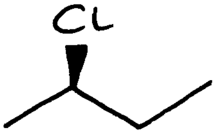
A

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

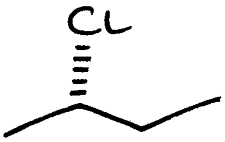
D

(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)

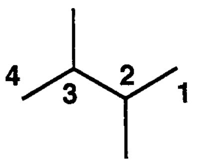
(*R*)-Enantiomer



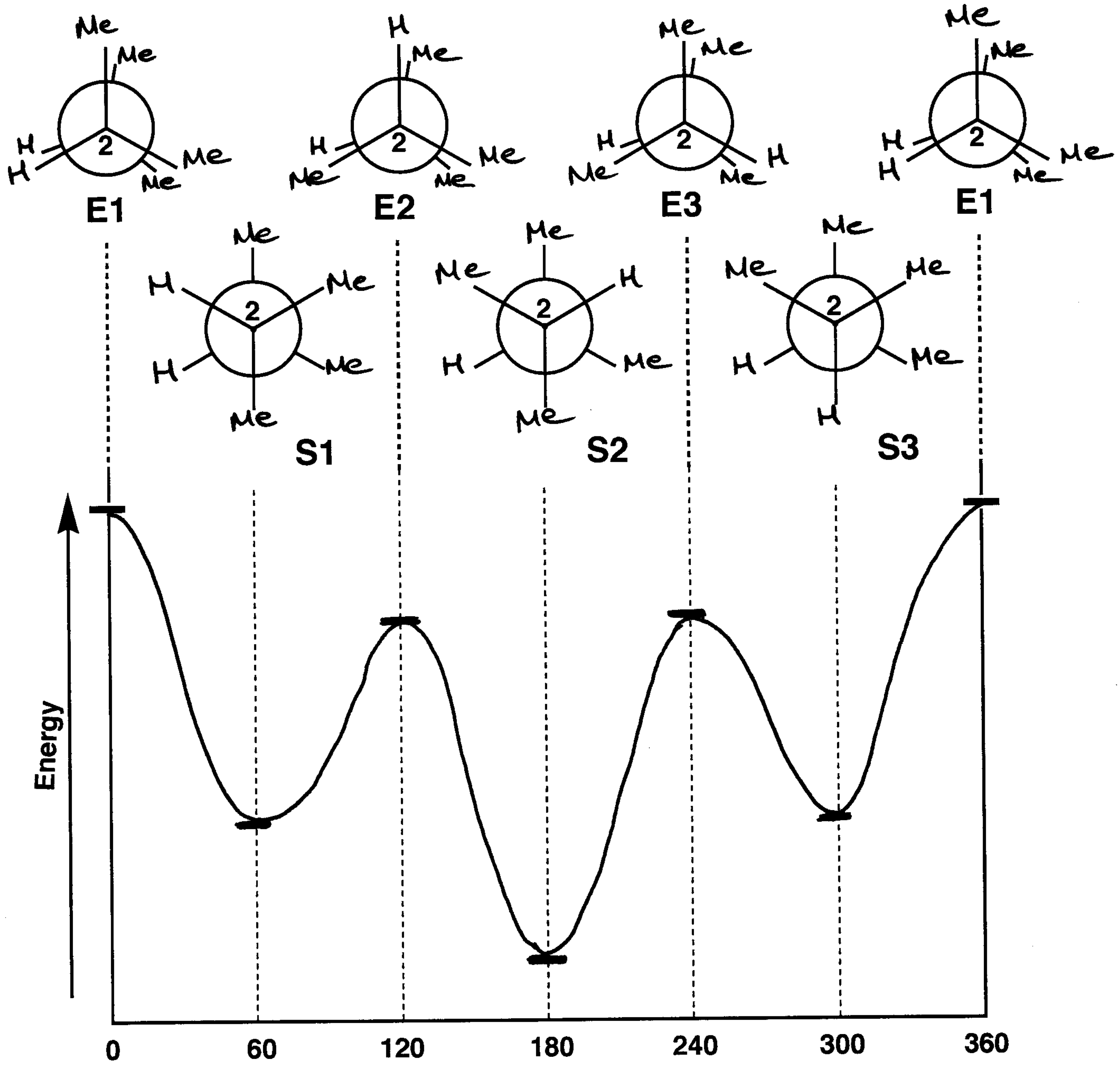
(*S*)-Enantiomer



Q2. (a) Above the 0° 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° **CLOCKWISE**, the first staggered conformation (**S1**) is reached, fill in the groups on this Newman projection above the 60° line. Continue this clockwise rotation, and complete the Newman projections of the other eclipsed (**E2**, **E3**) and staggered (**S2**, **S3**) conformations. (2 pt each)

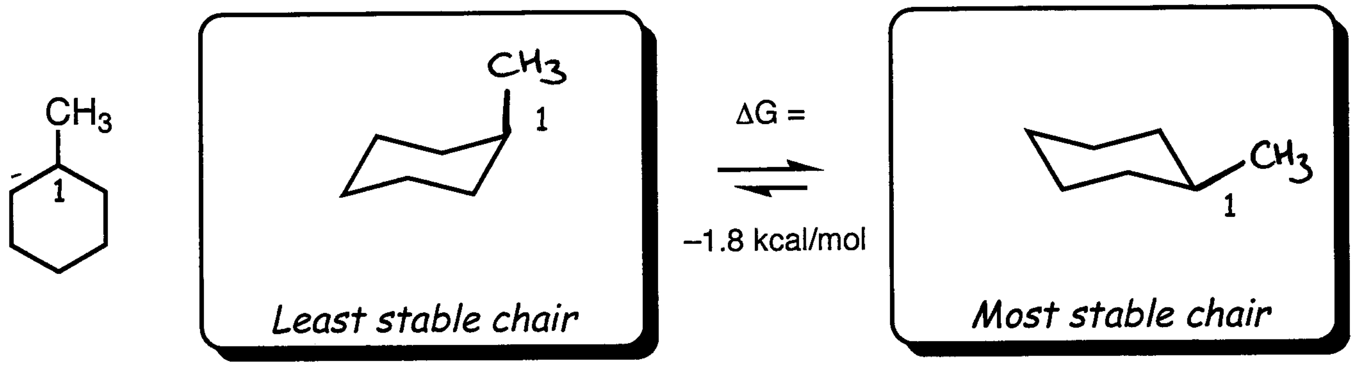


2,3-Dimethylbutane

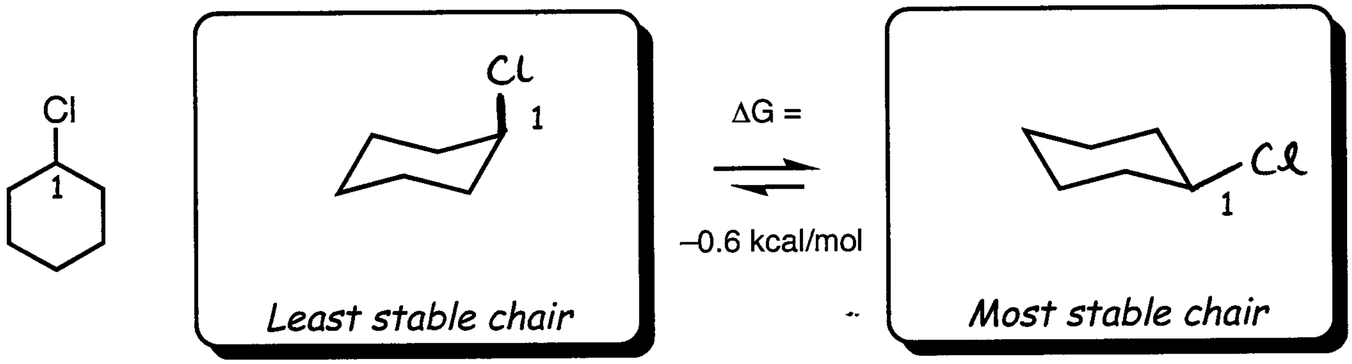


(b) Draw short horizontal bars on the **GRAPH ABOVE** (like those drawn for **E1** at 0° & 360°), indicating the relative energies of **S1**, **E2**, **S2**, **E3**, and **S3**, and complete the graph by drawing in a curve that shows how the energy changes relative to the dihedral angle. (6 pt)

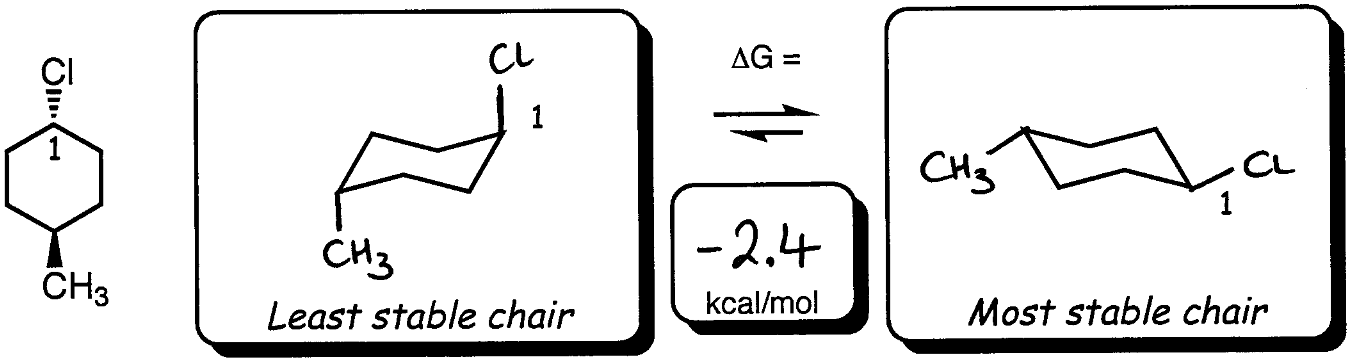
Q3. (a) Methylcyclohexane can exist in two different chair conformations, one of which is 1.8 kcal/mol more stable than the other, i.e., the **A value** for the methyl group is 1.8. In each of the two boxes below, draw in a bond to one methyl (**CH_3**) group in the appropriate position. (2 pt)



(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 (**Cl**) group in the appropriate position. (2 pt)

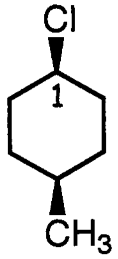


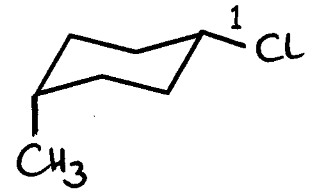
(c) For *trans*-1-chloro-4-methylcyclohexane (shown below), draw in bonds to **CH_3** and **Cl** groups as appropriate, to indicate the least and most stable chair conformers. Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the ΔG value will be. (6 pt)



Question 3 is continued on the next page...

(d) For *cis*-1-chloro-4-methylcyclohexane (shown below), draw in bonds to CH_3 and 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 ΔG value will be. (6 pt)





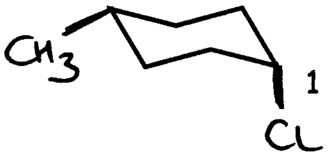
Least stable chair

ΔG =

$\rightleftharpoons$

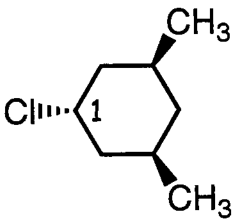
−1.2

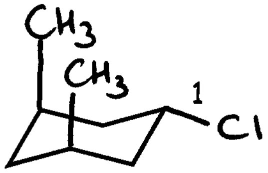
kcal/mol



Most stable chair

(e) For the isomer of 1-chloro-3,5-dimethylcyclohexane shown below, draw in bonds to CH_3 and 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 ΔG value will be. (8 pt)





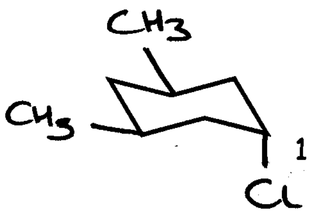
Least stable chair

ΔG =

$\rightleftharpoons$

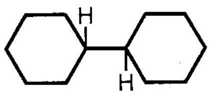
−3.0

kcal/mol

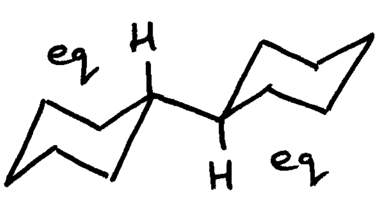


Most stable chair

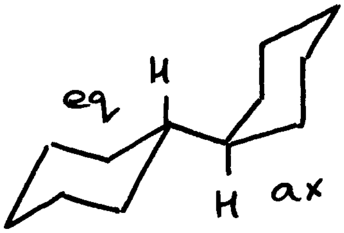
(f) In the appropriate boxes below, draw the three most stable conformations of cyclohexylcyclohexane (shown to the right) in which the indicated H atoms maintain an **ANTI** relationship, i.e., are 180° apart. Once you have drawn these three **different** conformers, use the box below them to briefly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



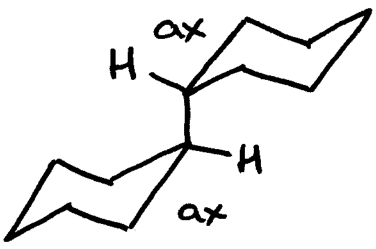
Cyclohexylcyclohexane



Most Stable Conformer



2nd Most Stable Conformer

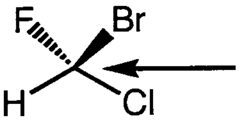


3rd Most Stable Conformer

Explanation: ALL RINGS ARE CHAIRS, BUT CAN BE CONNECTED DIFFERENTLY, EQUATORIAL-EQUATORIAL IS MOST STABLE, AXIAL-AXIAL IS LEAST STABLE, AND EQUATORIAL-AXIAL FALLS INBETWEEN

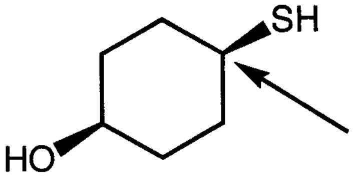
Q4. (a)–(f) In each box, write down either **R**, **S**, or **X**, indicating that the carbon atom to which the arrow is pointing has the *R* configuration, the *S* configuration, or is (**X**) not a stereocenter. (3 pt each)

(a)



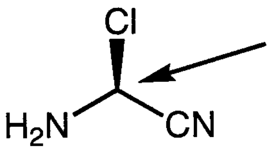
S

(b)



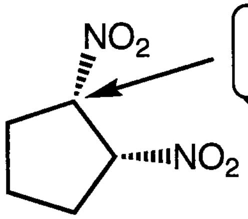
X

(c)



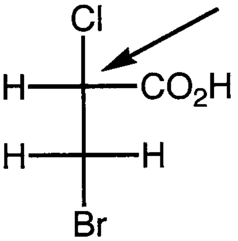
S

(d)



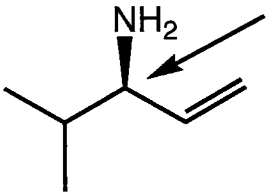
S

(e)



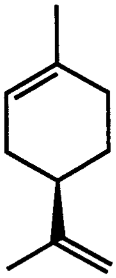
R

(f)

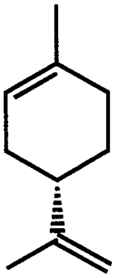


R

(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

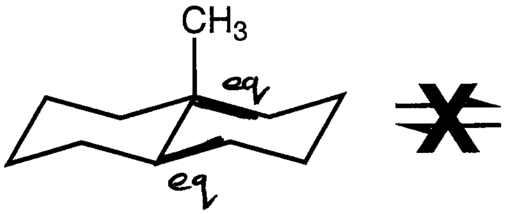


(*S*)-limonene

YOUR NOSE IS CHIRAL! - OR AT LEAST THE 'SMELL' RECEPTORS ARE. SO, ALTHOUGH IN AN ACHIRAL ENVIRONMENT (MP, BP, VP, H_2O SOL), THE (R) & (S) ISOMERS HAVE EXACTLY THE SAME PROPERTIES, IN A CHIRAL ENVIRONMENT THEY RESPOND ('FIT') DIFFERENTLY

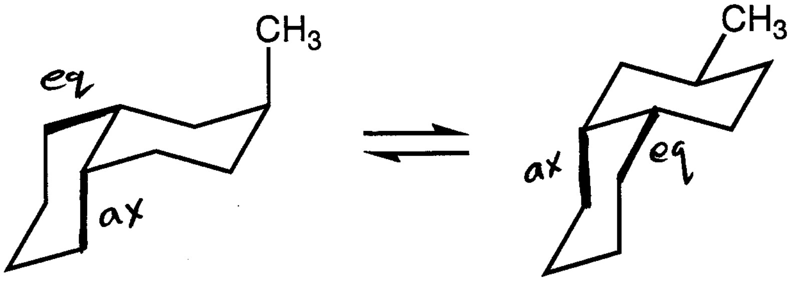
Q5 (BONUS). Explain why trans-decalin systems cannot undergo chair flips, whereas cis-decalin systems can (examples are shown in the box below). (5 pt)

trans-decalin ⇨



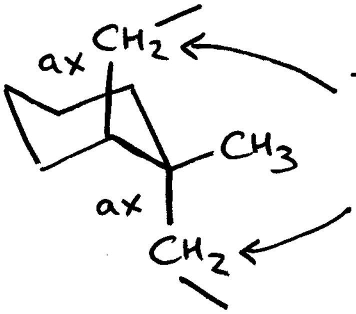
NO RING FLIP

cis-decalin ⇨



- HAS NOTHING TO DO WITH THE METHYL GROUP

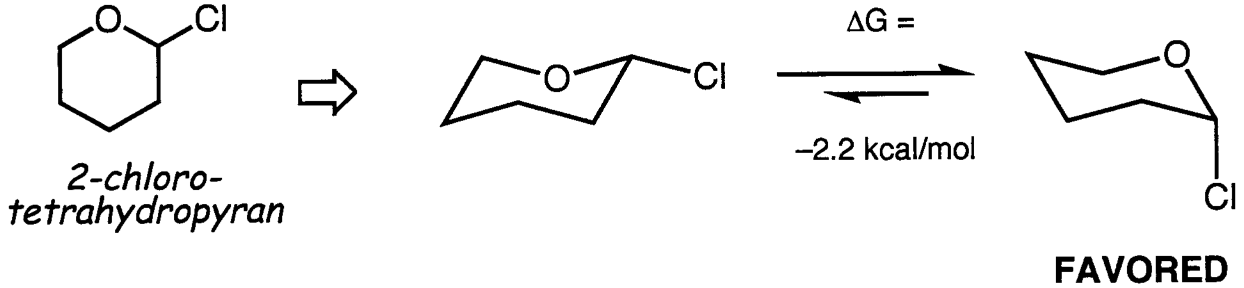
LOOK AT THE LEFT RING OF TRANS DECALIN, IF YOU FLIP IT, YOU GET THE FOLLOWING



THESE ARE NOW TOO FAR APART TO BE BRIDGED BY ONLY <u>TWO</u> MORE CH2 GROUPS, SO THE RING ON THE RIGHT LOCKS THE RING ON THE LEFT AND VICE VERSA, THEY CANNOT FLIP.

HOWEVER, IF YOU LOOK AT CIS DECALIN, THE LEFT RING COMES OFF IN THE AXIAL & EQUATORIAL POSITIONS, SO IT CAN FLIP, AND EQUATORIAL BECOMES AXIAL AND VICE VERSA...

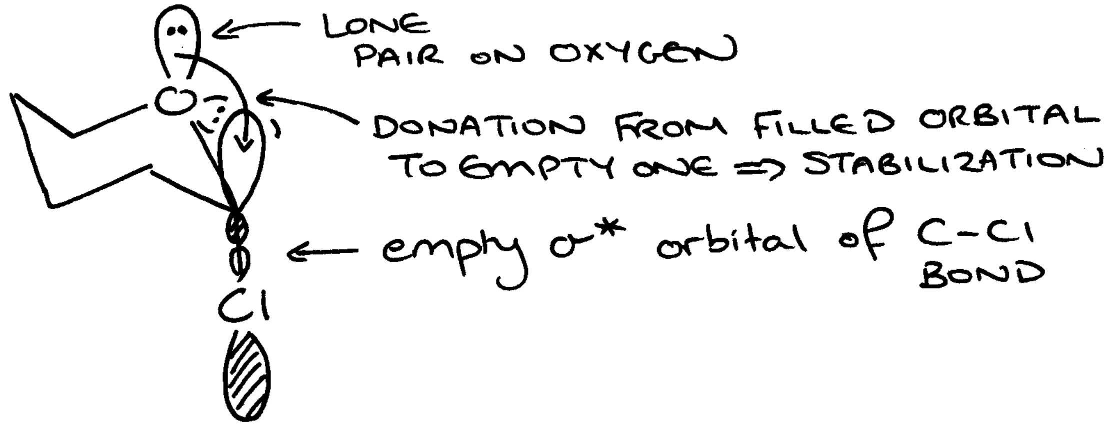
Q6 (BONUS). You've already seen that a chloro-substituent on a cyclohexane ring prefers to be in the equatorial position, i.e., the conformer with the Cl in the **EQUATORIAL** position is favored by 0.6 kcal/mol. Suggest why in the case of 2-chlorotetrahydropyran (shown below), the conformer in which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


2-chloro-tetrahydropyran

NOT A STERIC EFFECT, AS THAT WOULD FAVOR EQUATORIAL OVER AXIAL.

– IT IS AN ELECTRONIC EFFECT

(i)



THIS IS CALLED THE ANOMERIC EFFECT, ONLY IN THIS CONFORMATION IS THE LONE PAIR ON OXYGEN LINED UP WITH THE ANTIBONDING C–Cl σ* ORBITAL → OVERLAP & ELECTRON SHARING LEADS TO STABILIZATION, THIS CANNOT HAPPEN IN THE OTHER CHAIR CONFORMER (WRONG GEOMETRY)

SIMILAR TO THE EFFECT THAT STABILIZES THE STAGGERED CONFORMATION OF ETHANE (LOOK BACK AT YOUR NOTES)

(ii) THIS EFFECT USED TO BE EXPLAINED DIFFERENTLY BY LOOKING AT DIPOLE MOMENTS OF EACH CONFORMER, BUT THE REAL REASON IS THAT ABOVE IN PART (i)