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

Student ID Number:

Circle the name of your TA: HEATHER / CARI / KAUSHIK / RYAN

Discussion Section – Day: **Time:**

Total Score 115 **/ 100**

Chem 30A Fall 2005

MIDTERM #1

(50 Min)

Weds October 26th

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

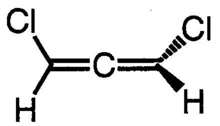
****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO****

Q1	32 / 32	**Q3**	44 / 44
Q2	39 / 39	**Total**	115 / 100

"Once you eliminate the impossible, whatever remains, no matter how improbable, must be the truth." - Sherlock Holmes (by Sir Arthur Conan Doyle)

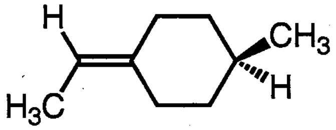
Q1. Indicate whether each molecule drawn below is chiral or achiral by writing either "CHIRAL" or "ACHIRAL" in the box below each one. Be sure of your choices, as each correct answer is worth 2 points BUT each incorrect answer scores –1 point (i.e., don't just guess). *Hint: it may help you to draw the mirror image in each case...*

(a)



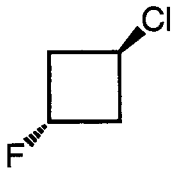
CHIRAL

(b)



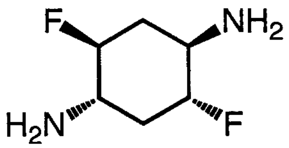
CHIRAL

(c)



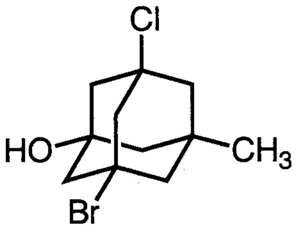
ACHIRAL

(d)



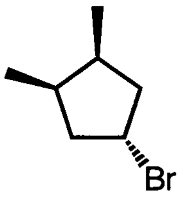
ACHIRAL

(e)



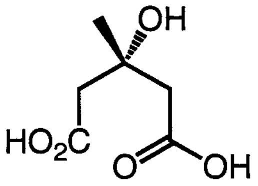
CHIRAL

(f)



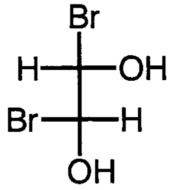
ACHIRAL

(g)



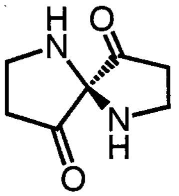
ACHIRAL

(h)



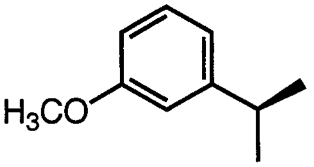
ACHIRAL

(i)



CHIRAL

(j)

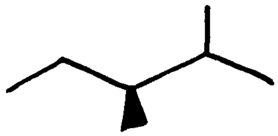


ACHIRAL

Question 1 is continued on the next page...

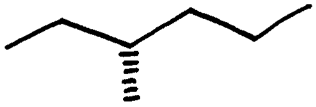
(k) In the box below, draw (using line formula) the structure of the lowest molecular mass ACYCLIC ALKANE (i.e., no rings allowed) that is chiral. No isotopes allowed (i.e., no deuterium etc)! Name the compound according to systematic IUPAC rules. Note: you will only get credit for the compound name if you have the correct compound. (4 pt structure, 2 pt name)

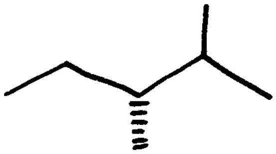
or



(S)-3-METHYLHEXANE

2,3S-DIMETHYLPENTANE



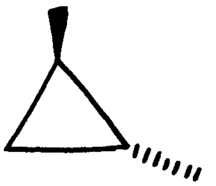


(R)-3-METHYLHEXANE

2,3R-DIMETHYLPENTANE

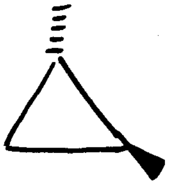
Name:

(l) In the box below, draw (using line formula) the structure of the lowest molecular mass CYCLIC ALKANE that is chiral. No isotopes allowed (i.e., no deuterium etc)! Name the compound according to systematic IUPAC rules. Note: you will only get credit for the compound name if you have the correct compound. (4 pt structure, 2 pt name)



(trans)

1R,2R-DIMETHYLCYCLOPROPANE



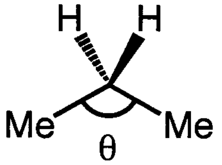
(trans)

1S,2S-DIMETHYLCYCLOPROPANE

Name:

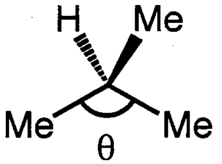
Q2. (a) In the box below, briefly explain the trend observed for the angle labeled as θ in compounds **A**, **B**, and **C**. (2 pt)

A



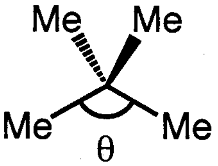
112.2°

B



111.1°

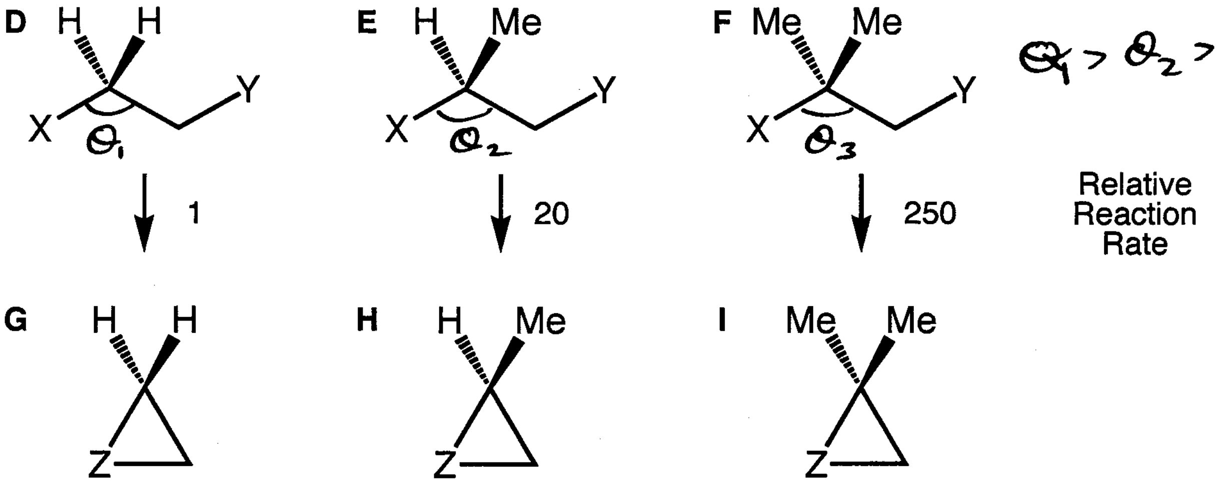
C



109.5°

A METHYL GROUP HAS GREATER STERIC REQUIREMENTS THAN A HYDROGEN ATOM (Me LARGER THAN H). SO, IN C ALL ANGLES ARE IDEAL TETRAHEDRAL (109.5°), BUT IN A AND B THE $\overset{(\mathrm{Me})}{\mathrm{H}}$–C–H BOND ANGLES ARE COMPRESSED, OPENING UP THE Me–C–Me BOND ANGLES.

(b) Compounds **D**, **E**, and **F** undergo cyclization reactions to give compounds **G**, **H**, and **I**, respectively (it doesn't matter what X and Y are, just appreciate that they react together to close the ring at Z). Using an argument based solely upon bond angles, explain briefly in the box below why the reaction of **F** to give **I** is faster than the reaction of **E** to give **H**, which, in turn, is faster than **D** to give **G**. (4 pt)

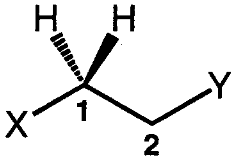


$\theta_1 > \theta_2 > \theta_3$

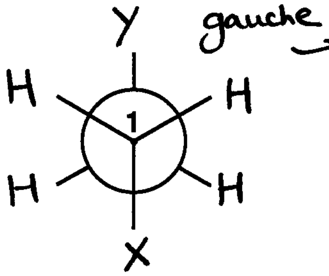
IT'S ALL TO DO WITH PART (a), IN F, THE TWO REACTING GROUPS ARE FORCED CLOSER TOGETHER BY THE GEM DIMETHYL GROUP, IN E THE X and Y GROUPS ARE NOT QUITE SO CLOSE TOGETHER, AND IN D THEY ARE THE FURTHEST APART, SO IT'S A PROXIMITY EFFECT, THE CLOSER X TO Y, THE FASTER THEY REACT, SO F > E > D

Question 2 is continued on the next page...

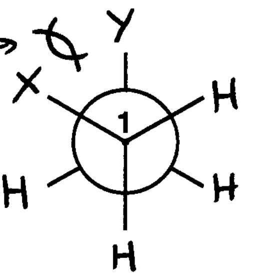
(c) For compound **D**, complete the Newman projections of the three different staggered conformations (**S1**, **S2**, and **S3**). Draw them as if you are looking down the C1–C2 bond (6 pt)



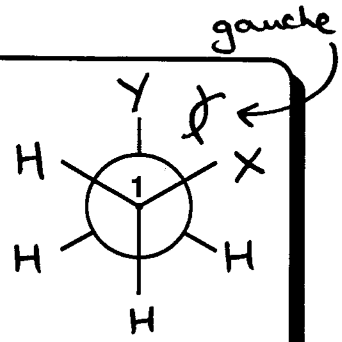
D



S1



S2

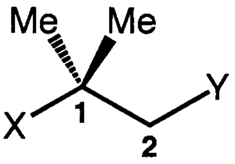


S3

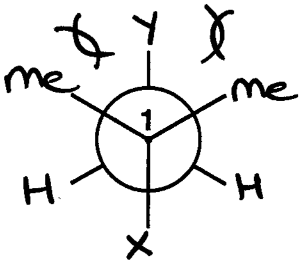
(d) Assuming that the X and Y groups have greater steric demands than hydrogen (H), comment briefly upon the relative energies of conformers **S1**, **S2**, and **S3**. (3 pt)

S1 IS AN ANTI CONFORMATION (X & Y ARE 180° APART) AND SO IS LOWER IN ENERGY THAN BOTH S2 AND S3 IN WHICH THE X & Y GROUPS ARE GAUCHE TO ONE ANOTHER, CAUSING AN UNFAVORABLE STERIC (GAUCHE) INTERACTION

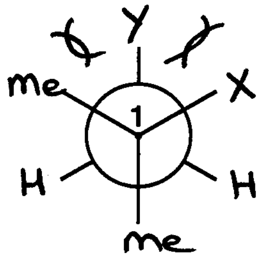
(e) For compound **F**, complete the Newman projections of the three different staggered conformations (**S4**, **S5**, and **S6**). Draw them as if you are looking down the C1–C2 bond (6 pt)



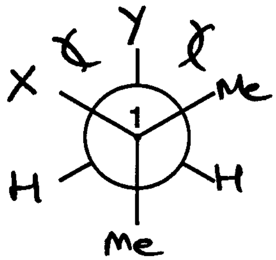
F



S4



S5



S6

(f) Assuming that methyl (Me), X and Y groups all have the same steric demands, comment briefly upon the relative energies of conformers **S4**, **S5**, and **S6**. (3 pt)

EACH OF S4, S5, S6 HAVE TWO GAUCHE INTERACTIONS AND IF WE ASSUME Me, X and Y HAVE THE SAME STERIC REQUIREMENTS, THEY ALL HAVE THE SAME ENERGY

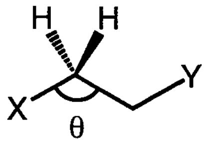
Question 2 is continued on the next page...

(g) After considering the relative energies of the staggered conformations associated with compounds **D** and **F**, construct an argument NOT based upon bond angles to explain briefly why the reaction of **F** to give **I** is faster than the reaction of **D** to give **G.** (8 pt)

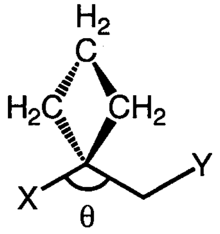
TO FORM A CYCLIC COMPOUND, THE MOLECULES MUST REACT THROUGH THE GAUCHE (OR ECLIPSED) CONFORMATION (i.e. X & Y MUST BE CLOSE ENOUGH TO REACT). IN THE CASE OF D MOST OF THE MOLECULES ARE SPENDING MOST OF THEIR TIME IN THE MORE STABLE ANTI FORM, AND MUST FIRST GO UP IN ENERGY & POPULATE THE GAUCHE CONFORMER. IN THE CASE OF F, 2/3 OF MOLECULES ALREADY HAVE X & Y GAUCHE & THERE IS NO MORE STABLE UNREACTIVE ANTI CONFORMER

(h) Now compare compound **D** with compound **J**. In the box below, indicate which compound you would expect to have the larger value of θ and why. (3 pt)

D



J



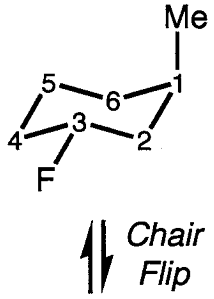
J HAS THE LARGER VALUE OF θ. THE CYCLOBUTANE HAS INTERNAL ANGLES OF ~ 90°, WHICH ESSENTIALLY TIES BACK THE TWO $-CH_2-$ GROUPS, OPENING UP MORE ROOM FOR THE OTHER TWO SUBSTITUENTS (BOTH H IN THIS CASE)

(i) You have given TWO reasons (one in part b and one in part g) to explain why the reaction of **F** to give **I** is faster than the reaction of **D** to give **G.** In the knowledge that **J** cyclizes faster than **D**, comment upon which effect is more important for this series of compounds. (4 pt)

PART (g), THE "REACTIVE ROTAMER" EFFECT IS MORE IMPORTANT, BECAUSE IF THE VALUE OF θ (part b) WAS THE MOST SIGNIFICANT FACTOR, THE LARGER ANGLE OF θ FOR J WOULD SUGGEST THAT J WOULD CYCLIZE MORE SLOWLY, WHICH IS NOT THE CASE... i.e. CONFORMATION IS MORE IMPORTANT THAN ANGLE COMPRESSION.

Q3. (a) *trans*-1-Fluoro-3-methylcyclohexane can exist in two different chair conformations, **A** and **B**. Complete the picture of conformer **B** by drawing in a bond to one methyl (Me) group and one fluorine (F) atom in the appropriate positions. In the two boxes to the right, complete the corresponding Newman projections by filling in methyl (Me) groups, hydrogen (H) atoms, AND fluorine atoms (F) where appropriate. (8 pt)

A



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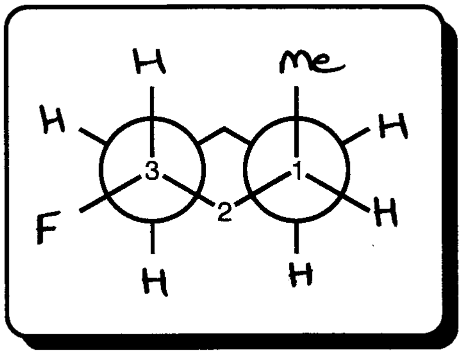
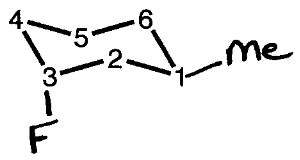


B



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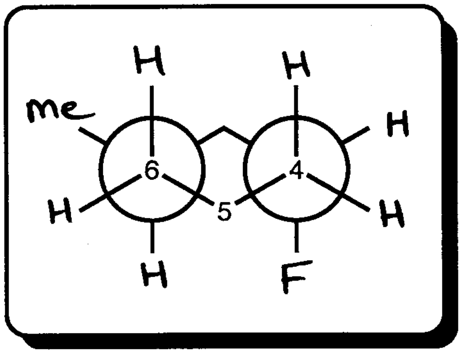
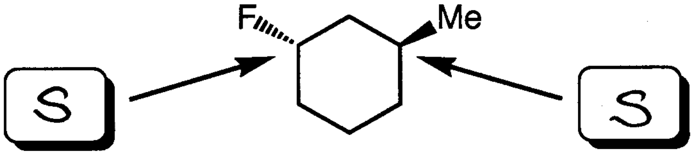


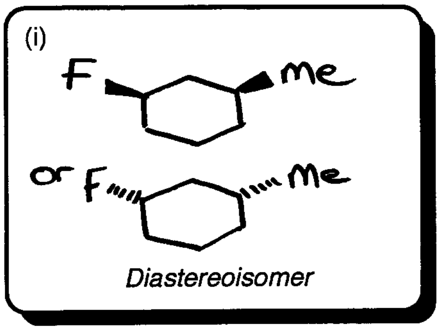
(b) *trans*-1-Fluoro-3-methylcyclohexane is redrawn below. Assign each chiral center either an R or S configuration by writing R or S in each small box. Is this molecule the SAME as that shown in part a, or is it the ENANTIOMER, or a DIASTEREOISOMER? (6 pt)

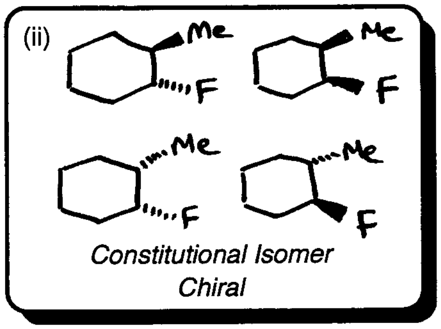


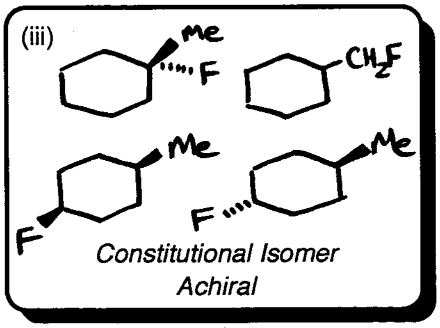
Relationship with part (a)

ENANTIOMER

(c) In relation to the compound shown above in part b, draw in the boxes below, (i) a diastereoisomer, (ii) a chiral constitutional isomer that still contains a cyclohexane ring, and (iii) an achiral constitutional isomer that still contains a cyclohexane ring. (9 pt)

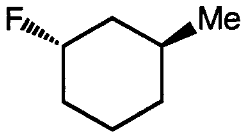






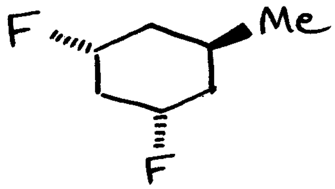
Question 3 is continued on the next page...

(d) By replacing ONE of the hydrogen atoms in *trans*-1-fluoro-3-methylcyclohexane with a fluorine atom, draw in the boxes below (i) a molecule that is achiral, and (ii) a molecule that contains only ONE chiral center. (6 pt)



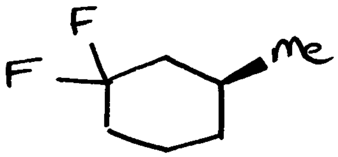
trans-1-fluoro-3-methyl-cyclohexane

(i)



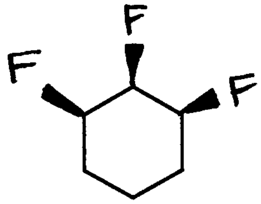
Achiral

(ii)

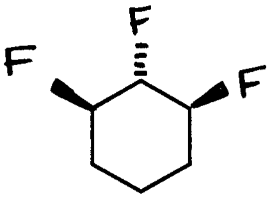


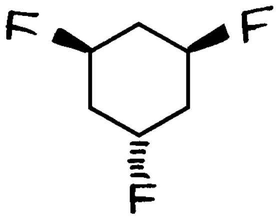
One chiral center

(e) There are five ACHIRAL isomers of trifluorocyclohexane – there are two pairs of diastereoisomers and one compound that exists as a single stereoisomer. In the appropriate boxes below, draw these five structures (you choose in what positions to add three fluorine (F) atoms to the cyclohexane rings drawn in the boxes below – be sure to use wedged and dashed lines where appropriate) (15 pt)

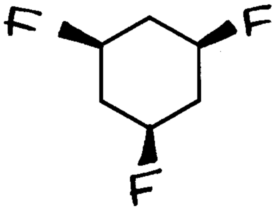


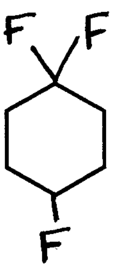
⇦ Diastereoisomers ⇨





⇦ Diastereoisomers ⇨





single stereoisomer