

Last Name ANSWER	First Name KEY	MI
Student ID Number:		Total Score
Circle the name of your TA: HEATHER / LINH / SUSAN		115
Discussion Section – Day:	Time:	/ 100

Chem 30A Spring 2005

MIDTERM #1 (50 Min)

Weds April 27th

**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

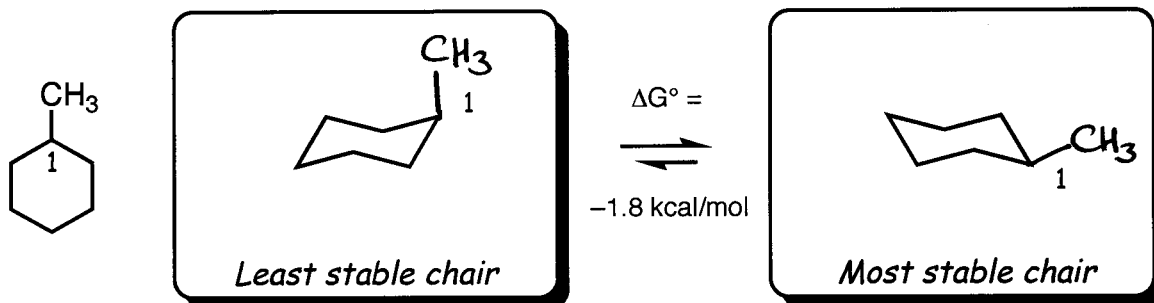
*****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO*****

Q1	30 / 30	Q3	55 / 55
Q2	30 / 30	Total	115 / 100

"Passive acceptance of the teacher's wisdom is easy to most boys and girls. It involves no effort of independent thought, and seems rational because the teacher knows more than his pupils; it is moreover the way to win the favour of the teacher unless he is a very exceptional man. Yet, the habit of passive acceptance is a disastrous one in later life. It causes man to seek and to accept a leader, and to accept as a leader whoever is established in that position"

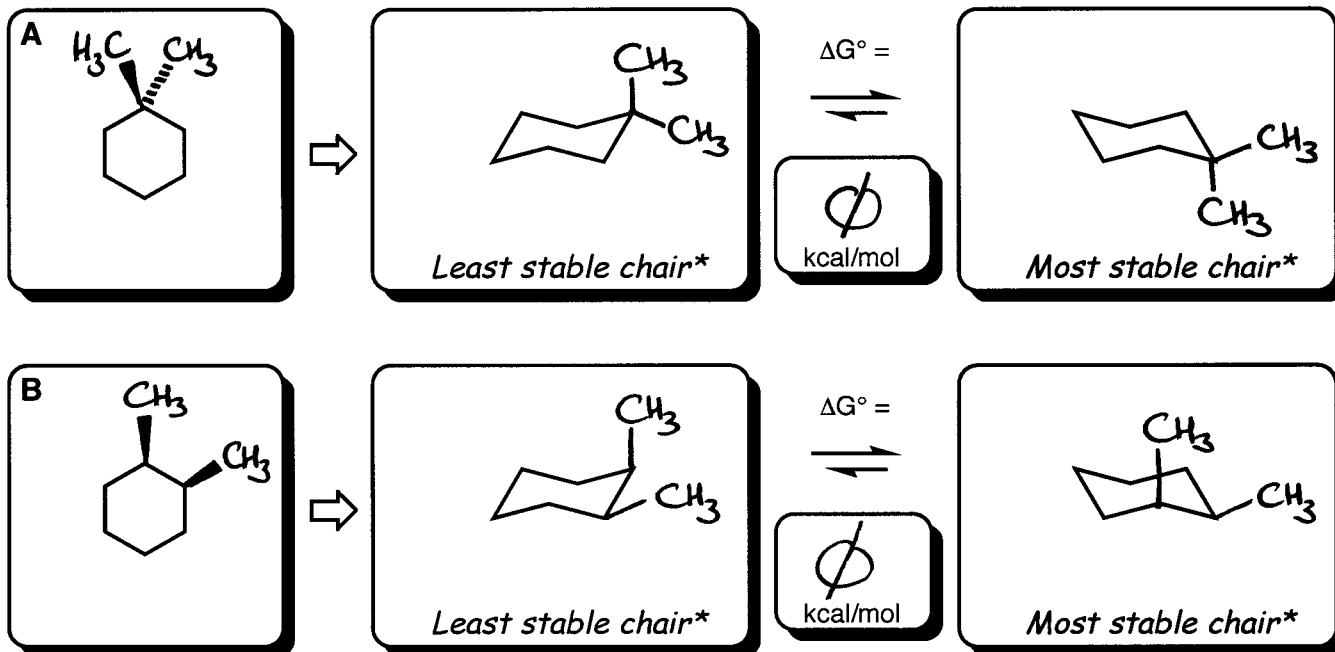
- Bertrand Russell (Author, Mathematician, Philosopher; 1872-1970)

Q1. (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)

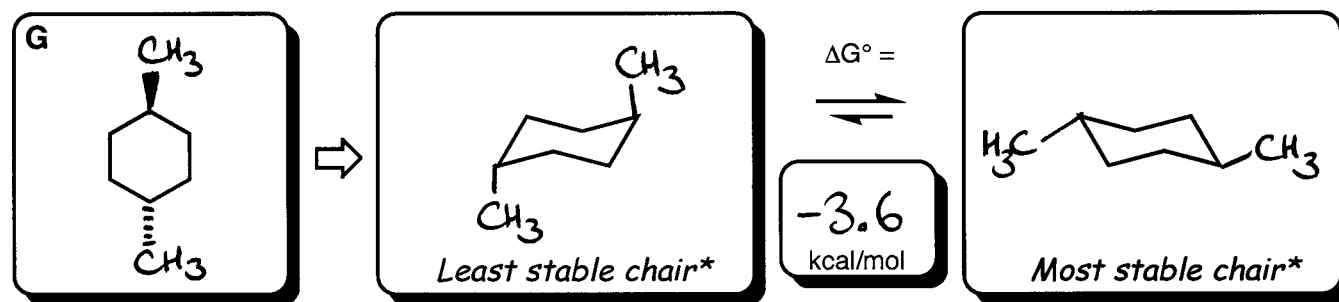
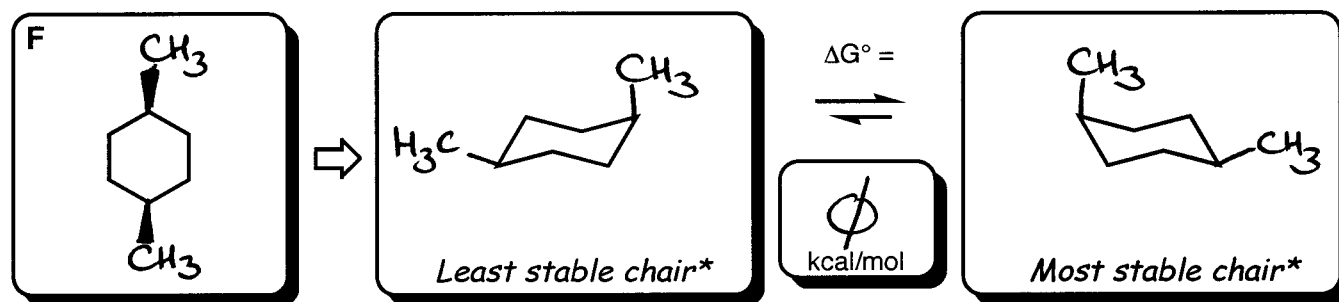
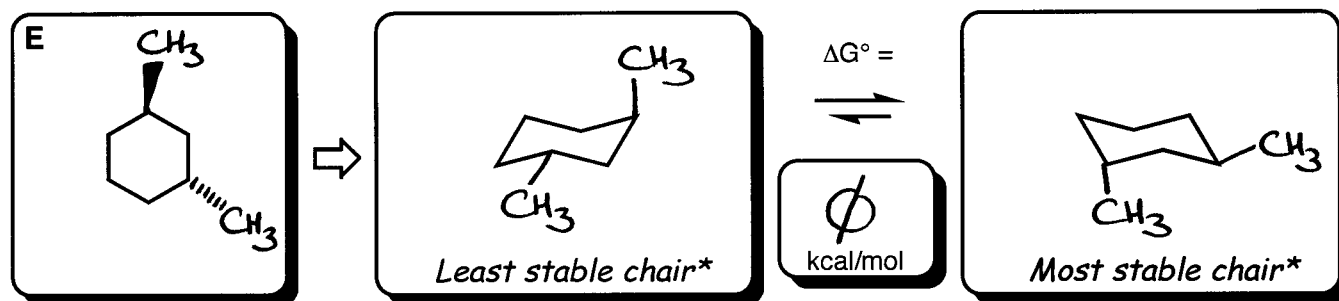
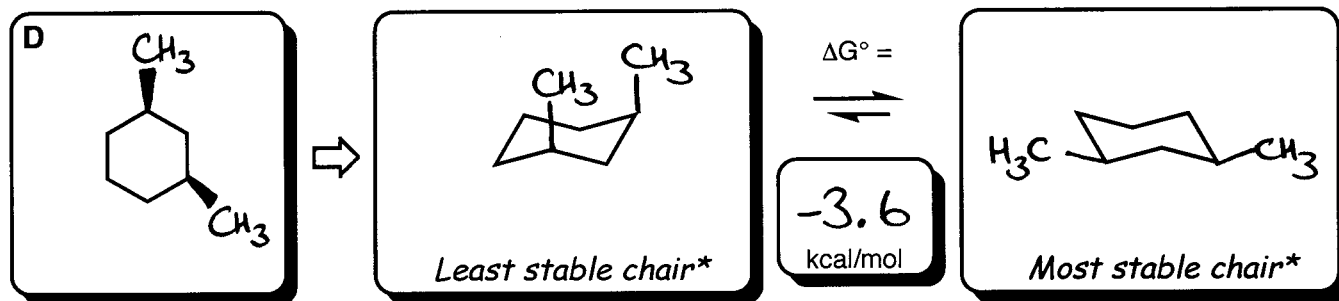
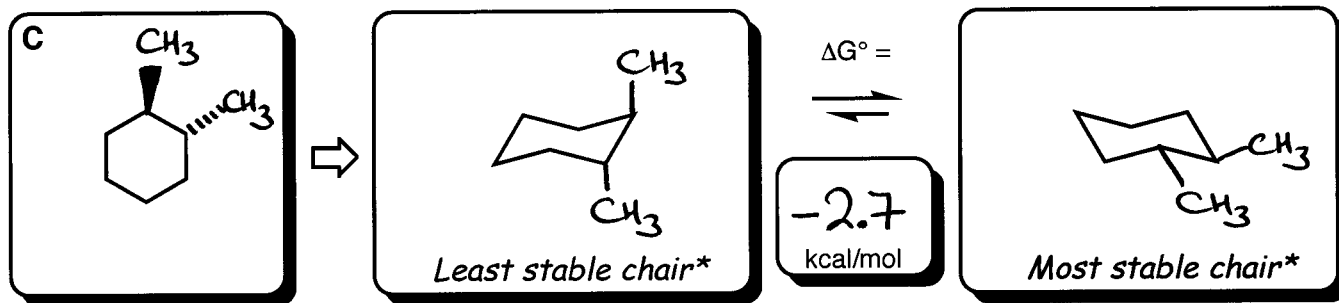


(b) There are SEVEN isomers (ignoring enantiomers) of dimethylcyclohexane. (28 pt)

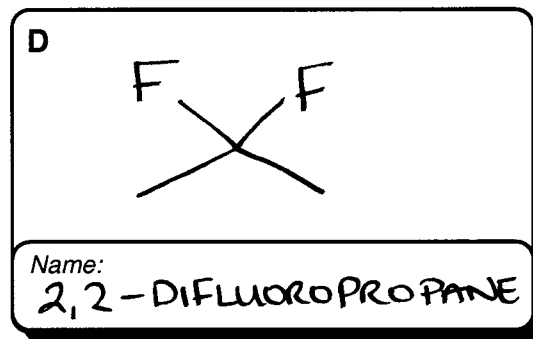
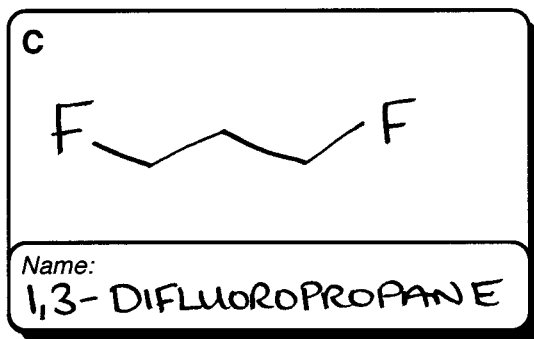
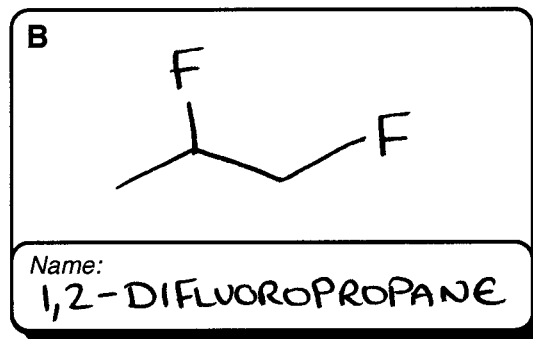
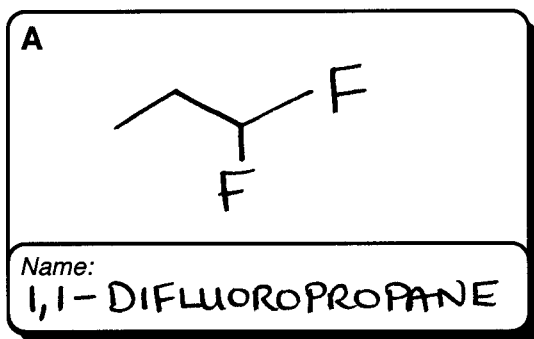
- In the **lettered** boxes below (A-G), use *wedge and dash notation* to draw these different compounds.
- For each of these isomers, complete the two alternate chair conformations by drawing in bonds to CH_3 groups as appropriate (DO NOT USE WEDGES OR DASHES IN THE CHAIR STRUCTURES).
- Assuming that **A values** are additive (and hence subtractive if necessary...), predict what the ΔG° value will be in each case, and remember that a butane gauche interaction (if present) is destabilizing by 0.9 kcal/mol.
- (* In some cases the two chair conformations are of equal energy, so the descriptors 'least stable' and 'most stable' are moot).



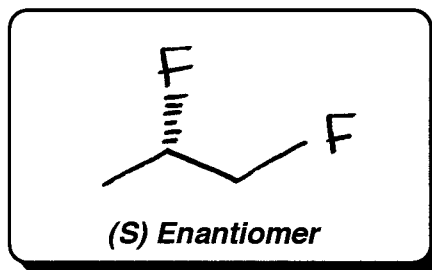
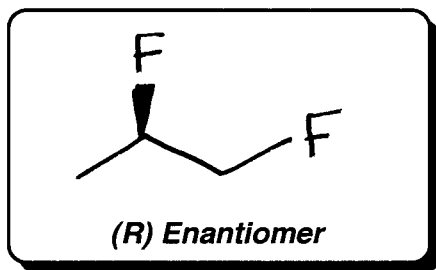
Question 1 is continued on the next page...



Q2. (a) There are four constitutional isomers that have the molecular formula $C_3H_6F_2$. Draw a different constitutional isomer in each of the boxes below – USE LINE FORMULAE. In each case, name the compound according to systematic IUPAC rules. (2 + 2 pt each)

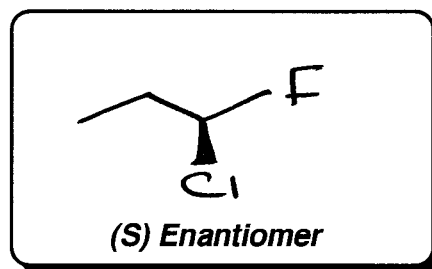
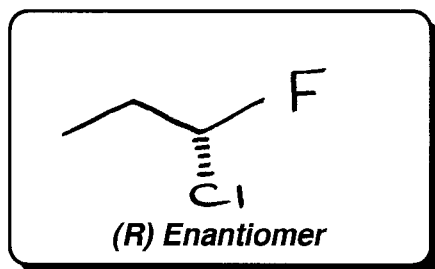


(b) One of the constitutional isomers of $C_3H_6F_2$ can exist in two non-superimposable mirror image forms, i.e., it exists as a pair of enantiomers. In the appropriately labeled boxes below, draw the *R* and *S* enantiomers of this compound – making sure to clearly indicate the orientation of the groups attached to the chiral center by using wedged and dashed lines as necessary. (3 pt each)

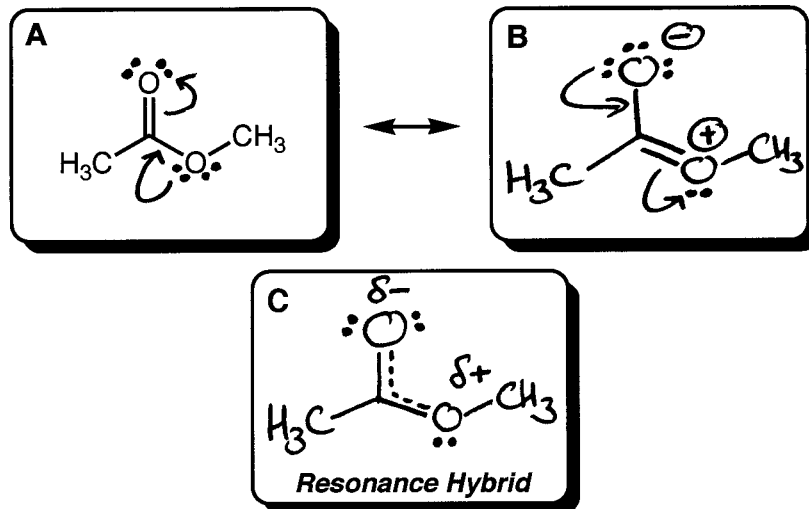


(c) One (and ONLY one) of the ACHIRAL constitutional isomers of $C_3H_6F_2$ would become CHIRAL if ONE of the fluorine atoms was replaced by a chlorine atom. Indicate which of the original constitutional isomers (A–D) has this property, and in the appropriately labeled boxes below, draw the *R* and *S* enantiomers of this new compound – making sure to clearly indicate the orientation of the groups attached to the chiral center by using wedged and dashed lines as necessary. (2 + 3 + 3 pt)

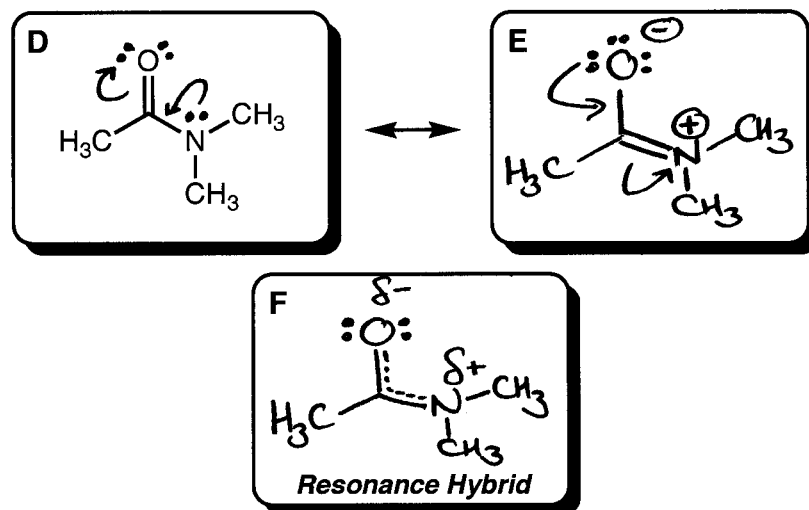
A, B,
C, or D?
↓
A



Q3. (a) Where appropriate, draw lone pairs of electrons on the structure of methyl acetate in **Box A** below. In **Box B**, draw a resonance form of methyl acetate that does NOT have any open octets (i.e., all octets are filled) – include all electron pairs and non-zero formal charges (if appropriate). For the resonance forms drawn in **Boxes A** and **B**, add curly arrows to them, showing how they interconvert. In **Box C**, draw the resonance hybrid of resonance forms **A** and **B**, indicating partial charges and partial bonds. (1 + 3 + 3 pt)



(b) Complete exactly the same analysis for *N,N*-dimethylacetamide (**Box D**) as you did for methyl acetate in the previous part of this question. (1 + 3 + 3 pt)

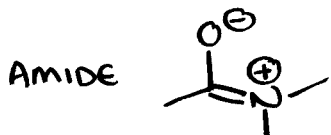
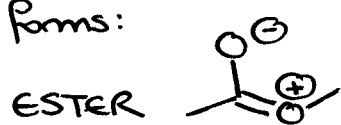


(c) In each of the three compounds below, one of the bonds has been highlighted in bold, and the energy barrier associated with rotation about that bond is indicated below each structure, as well as the frequency of rotation about that particular bond. In the box on the next page, briefly explain the origin of the trends observed in the energy barriers, and hence frequency of rotation. (8 pt)

	$\text{H}_3\text{C}-\text{CH}_3$	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)_2$
Barrier to Rotation (kcal/mol)	3	11	16
Rotations / sec	10^{10}	10^4	1

Question 3 is continued on the next page...

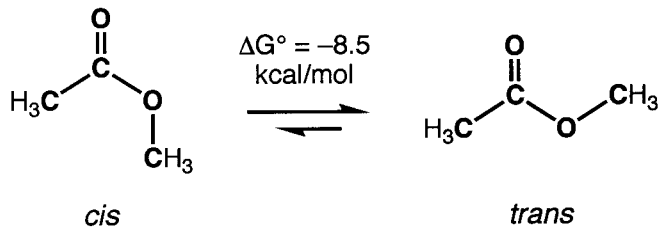
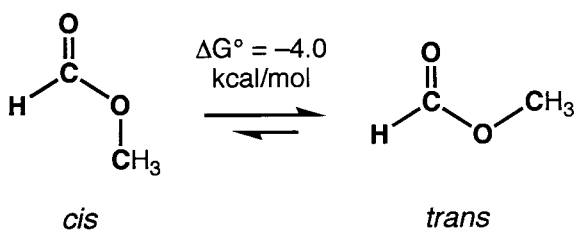
Explanation Rotation in $\text{CH}_3\text{-CH}_3$ is FAST, because we are considering rotation about a C-C SINGLE BOND. In both the ESTER and AMIDE structures, there is partial double bond character to the bonds in question, because of the following resonance forms:



There is more double bond character for the amide, as its DOUBLE BONDED resonance form is more significant than in the case of the ester, as N is more able to handle the positive charge. More DOUBLE BOND CHARACTER means more π OVERLAP \rightarrow harder to rotate the bond.

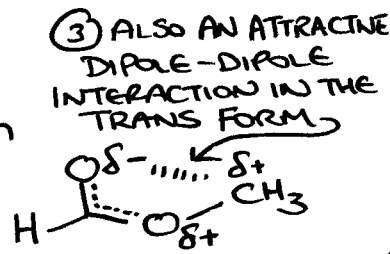
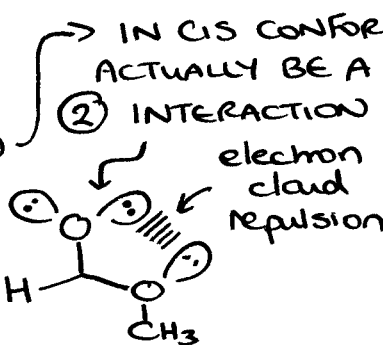
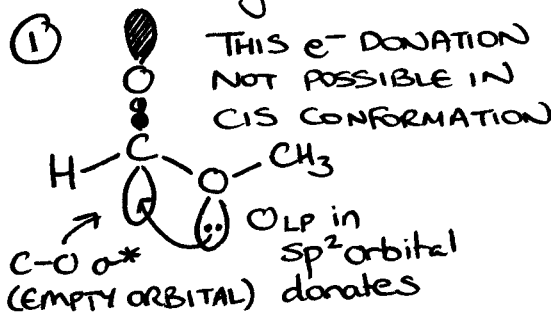
(d) Both methyl formate and methyl acetate adopt two low energy planar conformations (in each structure, the bold atoms lie in the same plane) in which the two methyl groups have either a *cis* or *trans* relationship. In each case, the *trans* conformation is more stable than the *cis* one – for methyl formate, the difference in energy between the *cis* and *trans* conformations is ~ 4.0 kcal/mol, whereas for methyl acetate, the difference in energy between the two conformations is much higher, ~ 8.5 kcal/mol. (Note: in each of these compounds, the oxygen atom that is bonded to the methyl group is best considered to be sp^2 hybridized). \Rightarrow UNHYBRIDIZED PORBITAL IS USED TO FORM π BOND IN THE

Methyl formate **RESONANCE FORM YOU DREW IN PART B** Methyl acetate



(i) Briefly explain in the box below (using words and illustrations as you deem necessary), why the *trans* conformation of methyl formate is more stable than the *cis* conformation of methyl formate. (8 pt)

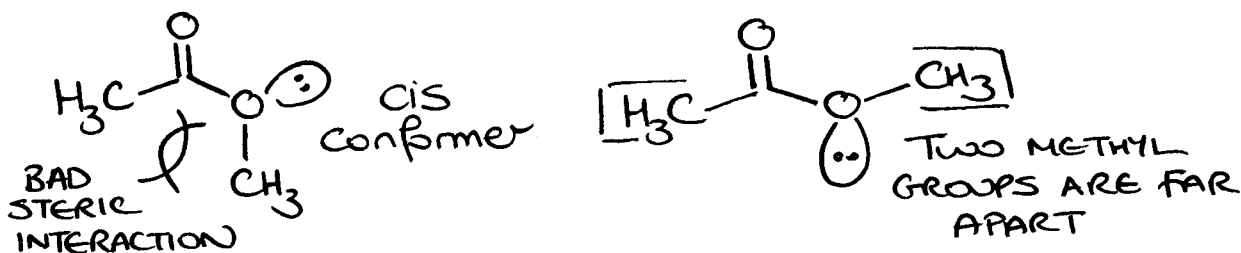
Explanation We can rule out STERICS from the start because we know that O is bigger than H, so based on STERIC arguments, the TRANS conformation would actually be less stable, so let's consider electronic arguments:



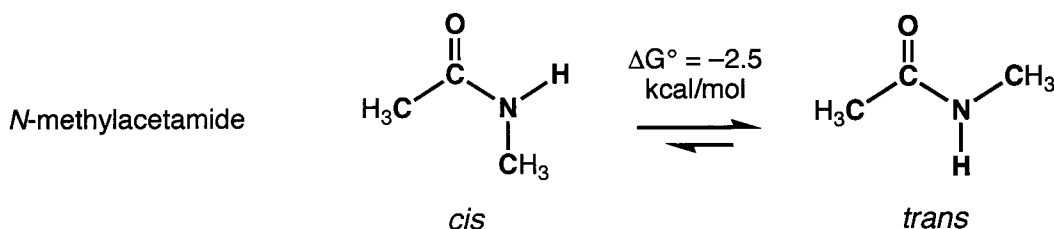
Question 3 is continued on the next page...

(ii) Briefly explain in the box below (using words and illustrations as you deem necessary), why the difference in energy between the *cis* and *trans* conformations of methyl formate is smaller in magnitude than the corresponding value for methyl acetate, i.e., 4.0 vs. 8.5 kcal/mol, respectively. (6 pt)

Explanation ALL OF THE SAME FACTORS ARE IN PLAY, BUT THE TRANS CONFORMATION IS FURTHER REINFORCED BY A BAD $\text{CH}_3 \cdots \text{CH}_3$ STERIC INTERACTION IN THE CIS CONFORMATION

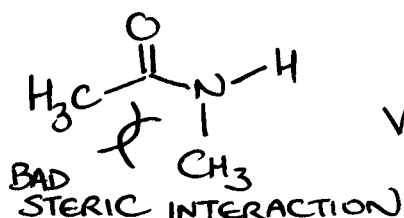


(e) *N*-Methylacetamide also adopts two low energy planar conformations (in each structure, the bolded atoms lie in the same plane) in which the two methyl groups have either a *cis* or *trans* relationship. The *trans* conformation is more stable than the *cis* one – by ~2.5 kcal/mol.

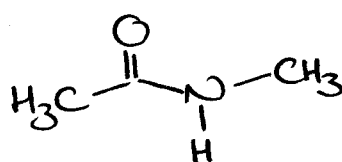


Briefly explain in the box below (using words and illustrations as you deem necessary), why the *trans* conformation of *N*-methylacetamide is more stable than the *cis* conformation. (Note: in this case, the nitrogen atom that is bonded to the methyl group is best considered to be sp^2 hybridized). In addition, suggest a reason why the conformational preference for the *trans* conformation is not as strong in the case of this amide, as compared with the two esters you saw earlier in this question. (6 pt)

Explanation IN THIS CASE, THERE IS NO LONE PAIR TO DONATE INTO THE C-O σ^* ORBITAL (THE ONE LONE PAIR ON THE N ATOM IS INVOLVED IN THE C=N π BOND IN ONE OF THE RESONANCE FORMS), IN THIS CASE, IT IS JUST A STERIC EFFECT



VS



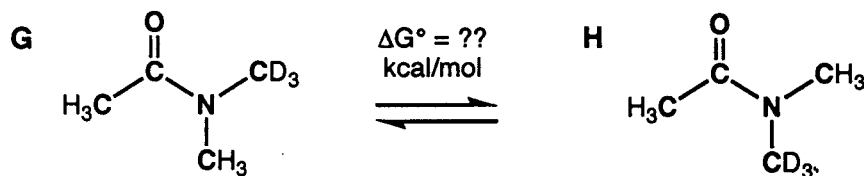
METHYL GROUPS FAR APART

HENCE, NOT SUCH A MARKED PREFERENCE

(ESTER HAS STERIC+ELECTRONICS)

Question 3 is continued on the next page...

(f) If one of the *N*-methyl groups of *N,N*-dimethylacetamide is labeled with deuterium (D) atoms (deuterium is just a heavier isotope of hydrogen (H) and behaves in exactly the same manner), then two different planar conformations are observed – namely, G and H.

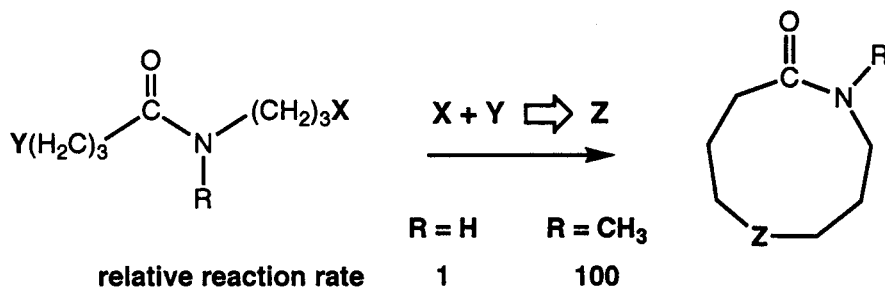


Assuming that deuterium has exactly the same electronic and steric requirements as hydrogen (which isn't actually far from the truth...), what is the difference in energy between these two conformations, and what would the ratio of G to H be in a sample of this compound at room temperature? (3 pt)

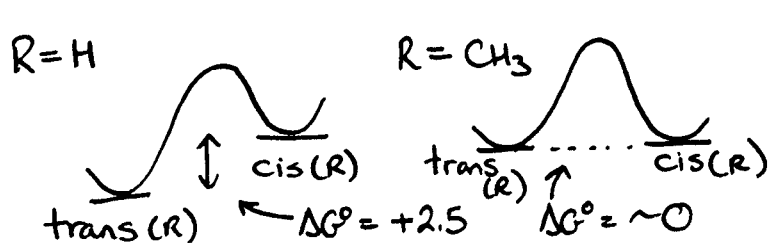
Difference in Energy (ΔG°) in kcal/mol
 \emptyset

Ratio of G:H
 1:1

(f) Two functional groups, X and Y, react together to give Z. This reaction can be used to make cyclic compounds via an intramolecular reaction (as shown below). When a substrate is chosen in which R = H, the reaction is 100 times slower than when R = CH₃. In the box below, explain this difference in reaction rate, using words and illustrations as necessary. (10 pt)



Explanation THE AMIDE IN THE PRODUCT IS IN THE CIS CONFORMATION, AND SO THE STARTING MATERIAL MUST REACT VIA THE CIS CONFORMATION. WHEN R=H, MOST OF THE STARTING MATERIAL ADOPTS THE LOWER ENERGY TRANS CONFORMATION, BUT FOR R=CH₃, THERE IS LITTLE PREFERENCE FOR EITHER CONFORMER, SO MORE OF THE NECESSARY CONFORMATION IS AVAILABLE FOR THE REACTION TO PROCEED.



FOR R=H, HIGHER ENERGY (HENCE LESS POPULATED) CONFORMER IS REQUIRED FOR THE REACTION TO OCCUR, SO REACTION IS SLOWER.