Last Name	First Name	MI
Student ID Number:		***Total Score***
Circle the name of your TA: CARI / PHIL / ADAM / HEATHER		
Discussion Section – Day: **Time:**		**/ 100**

Chem 30A Fall 2004

MIDTERM #1

(50 Min)

Weds October 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

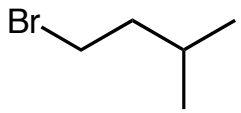
****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO****

Q1	**/ 20**	**Q4**	**/ 20**
Q2	**/ 20**	**Q5**	**/ 20**
Q3	**/ 20**	**Extra Credit**	**/ 15**
		Total	**/ 100**

"Man should practice moderation in all things, including moderation"
– Mark Twain

Q1. (a) Using **LINE FORMULAE** draw the seven other **CONSTITUTIONAL** isomers with the molecular formula $C_5H_{11}Br$ – one has been done for you. (1 pt each) (b) Name each isomer using **SYSTEMATIC** naming rules, in the knowledge that bromo groups are higher in priority than methyl groups (i.e., they get the smaller positional number if a choice has to be made) – one has been done for you. (1 pt each) (c) **THREE** of the isomers contain **CHIRAL** centers, label the small box for these isomers with an **ASTERISK** (*). (3 pt) (d) The highest boiling isomer boils at 130 °C and the lowest at 105 °C – write '**105**' and '**130**' in the small boxes of the isomers you think have these values. (3 pt)

A



Name 1-bromo-3-methylbutane

B

Name

C

Name

D

Name

E

Name

F

Name

G

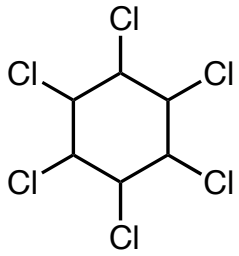
Name

H

Name

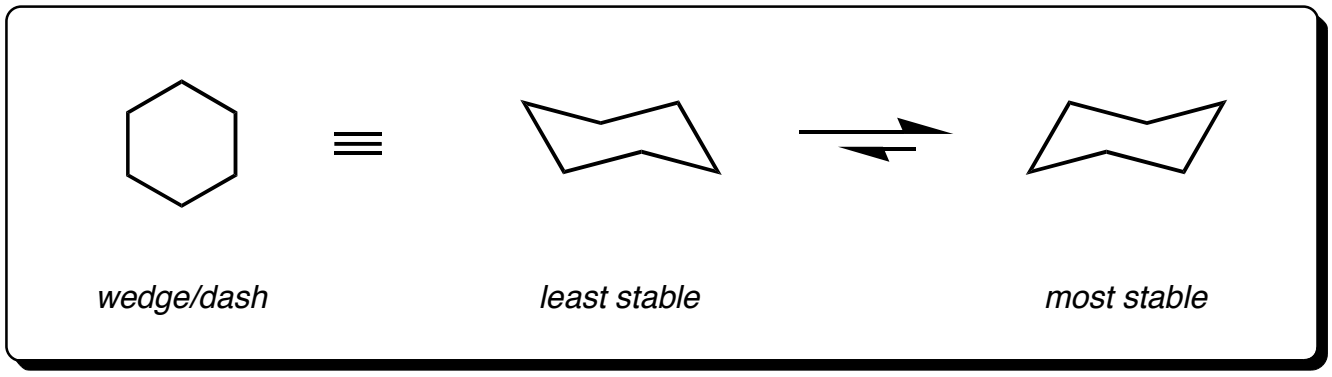
(*Only three asterisks, one '105' and one '130' should appear on this page – otherwise (c) & (d) will not be graded*).

Q2. (a) There are **EIGHT DIASTEREOISOMERS** of 1,2,3,4,5,6-hexachlorocyclohexane – a two-dimensional representation is shown in the center box below. Using **WEDGE** and **DASH** notation, draw these different configurational isomers in the boxes **A–H** below. (2 pt each)

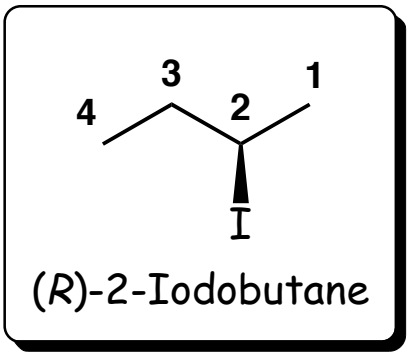
A	**B**	**C**
D		**E**
F	**G**	**H**

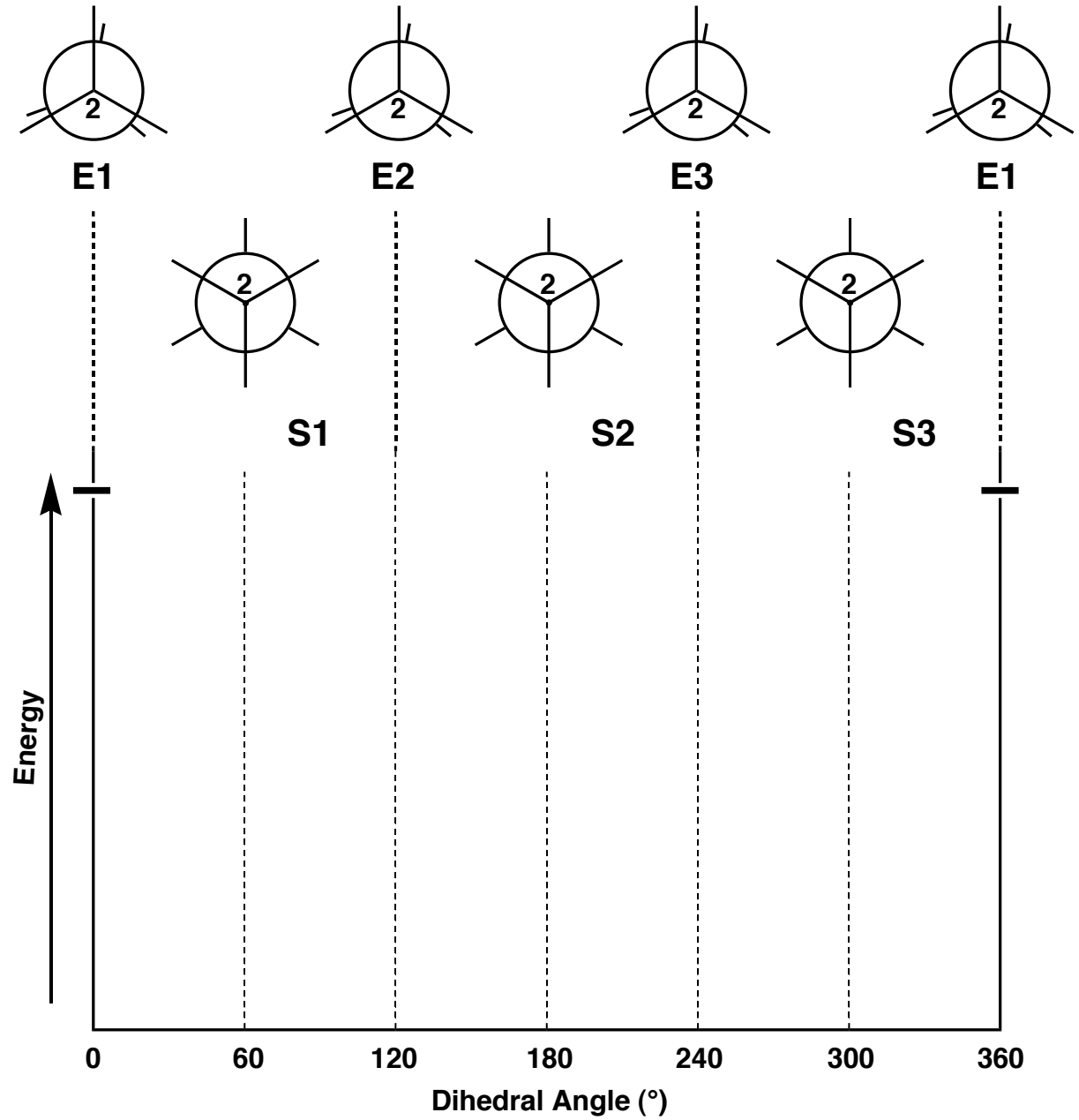
(b) Only one of these diastereoisomers is **CHIRAL**, which box contains this compound? (1 pt)

(c) In the box below, redraw the wedge/dash representation of the **MOST STABLE** of the **EIGHT DIASTEREOISOMERS**, and draw its two alternate **CHAIR CONFORMATIONS** as indicated. (3 pt)



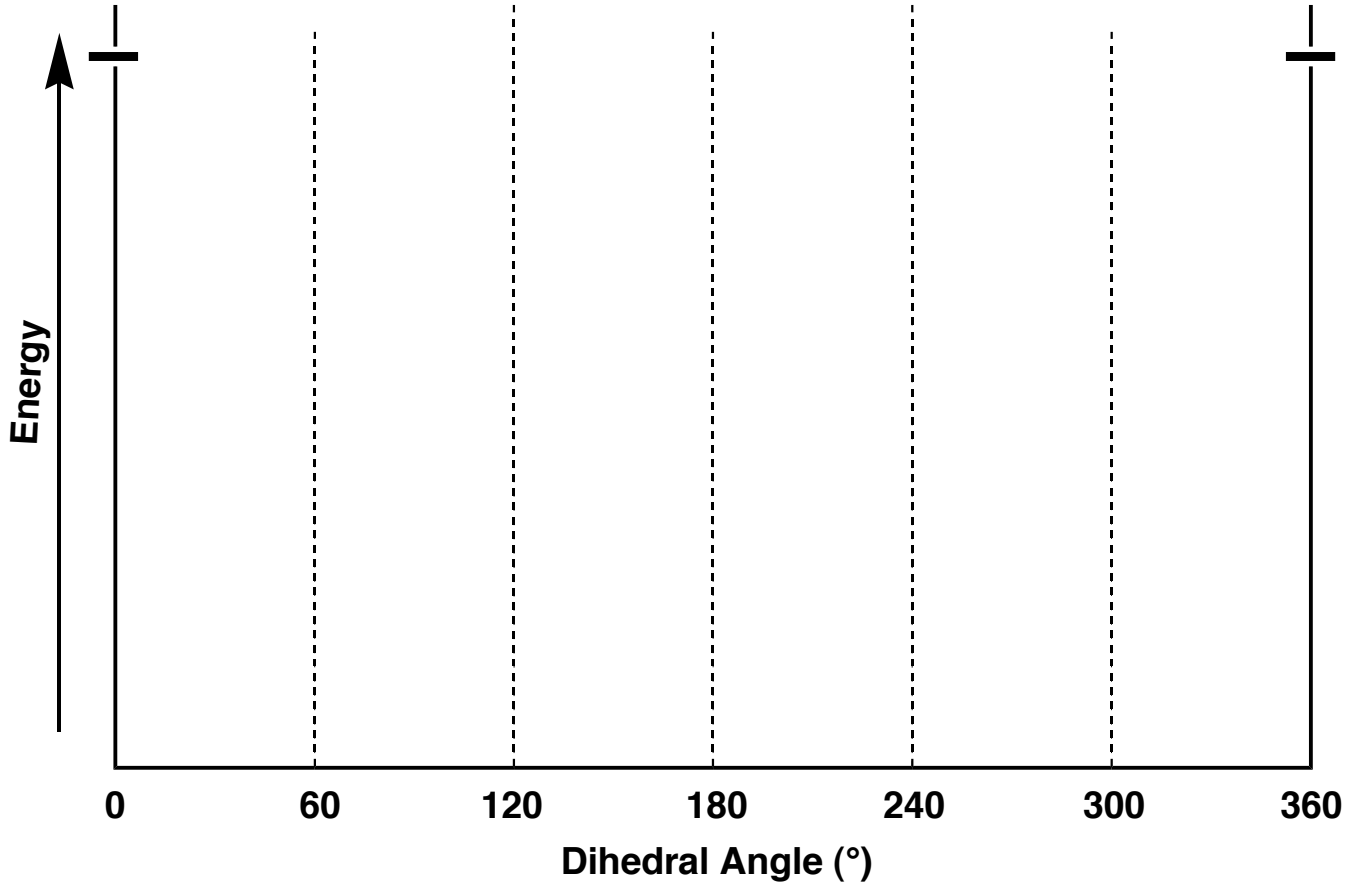
Q3. (a) Above the 0° line on the graph below, fill in the groups on the Newman projection of the **MOST UNSTABLE** eclipsed conformation (**E1**) of (*R*)-2-iodobutane, as viewed from C2 to C3, i.e., C2 is in the front. By rotating C2 (and the groups attached to it) 60° **CLOCKWISE**, the first staggered 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. *(Hint: the A values on a cyclohexane ring for CH_3– and I– groups are 1.74 and 0.45, respectively).* (2 pt each)





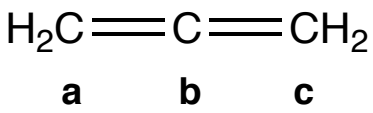
(b) Draw short horizontal bars on the **GRAPH ABOVE** (like those drawn for **E1** at 0° & 360°), indicating the relative energies of **S1**, **E2**, **S2**, **E3**, and **S3**, and complete the graph by drawing in a curve that shows how the energy changes relative to the dihedral angle. (5 pt)

(c) By wasting no more than **TWO MINUTES** of your life, complete the graph below, showing what the energy profile would look like if we had done **EXACTLY THE SAME** conformational analysis (i.e., starting from the most unstable eclipsed conformation, looking from C2 to C3, and rotating C2 in a clockwise fashion, etc.) on (*S*)-2-iodobutane, which is the enantiomer or non-superimposable mirror-image of (*R*)-2-iodobutane... *(Hint: seriously, if this takes you more than TWO MINUTES, give up, do not attempt to repeat the whole analysis step-by-step!)* (2 pt)



(d) If we had done the same conformational analysis with butane instead of 2-iodobutane, we would refer to **S1** and **S3** as conformational enantiomers, how would you describe the relationship between **S1** and **S3** in the case of iodobutane? (1 pt)

Q4. The molecule ALLENE ($H_2C=C=CH_2$) is drawn below.



(a) What is the hybridization state of the carbon atoms labeled **a** and **c**? (1 pt)

(b) What is the hybridization state of the carbon atom labeled **b**? (1 pt)

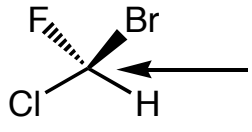
(c) Draw a diagram clearly showing which orbitals overlap to form the carbon-carbon bonds (σ and π) as well as the carbon-hydrogen bonds, in the same style as we did in class for the molecules CH_3–CH_3, $H_2C=CH_2$, and H–C(*TRIPLEBOND*)C–H. Label all orbitals and bonds appropriately. *(Don't worry about antibonding orbitals, when we make bonds, we are just concerned with bonding combinations of orbitals)* (12 pt)

(d) What is the dihedral angle between the two planes defined by H–C_a–C_b and C_b–C_c–H in allene? (2 pt)

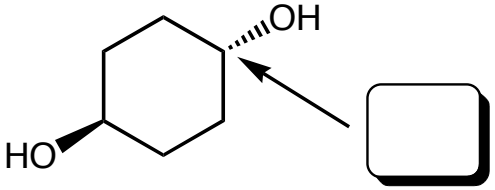
(e) The bonding scheme for allene has significant implications for the geometry the molecule adopts. In the box below, draw, using wedges and dashes as necessary, a representation that more clearly indicates the three-dimensional shape of allene. (4 pt)

Q5. (**a**)–(**f**) In the box next to each arrow, 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. (2 pt each) (**g**) Draw a molecule that is **ACHIRAL**, but contains **TWO** stereogenic (chiral) centers. (3 pt) (**h**) Draw a molecule that is **CHIRAL**, but contains **NO** stereogenic (chiral) centers. (5 pt)

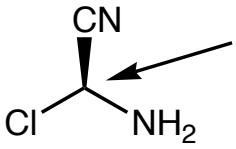
(**a**)



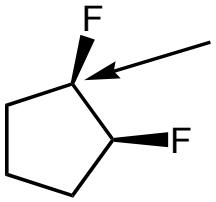
(**b**)



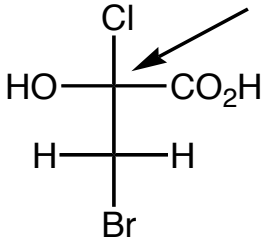
(**c**)



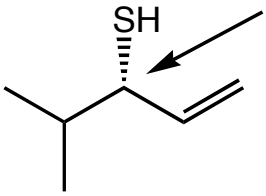
(**d**)



(**e**)



(**f**)



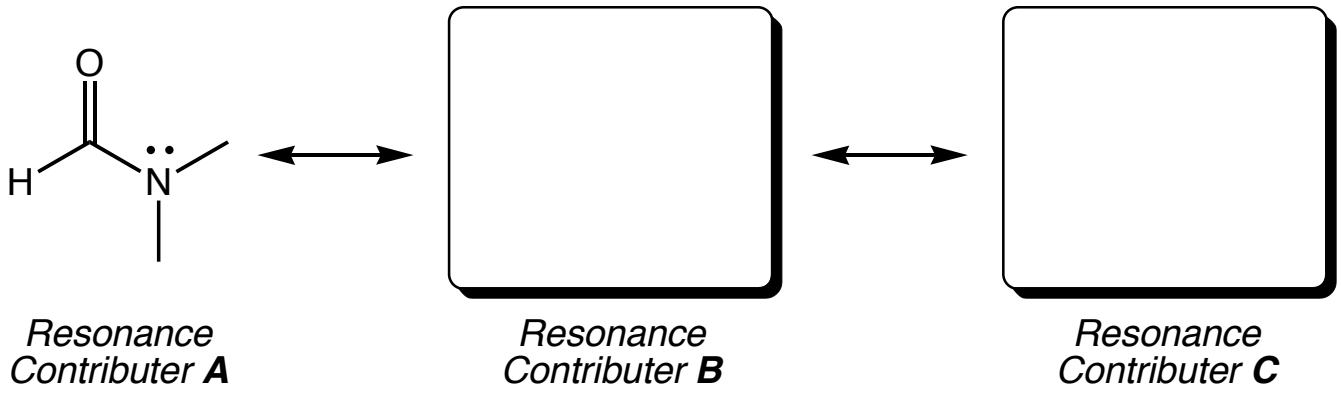
(**g**)

ACHIRAL – with 2 stereogenic centers

(**h**)

CHIRAL – but no stereogenic centers

Extra Credit 1. (a) Draw two reasonable resonance structures (**B** and **C**) for the compound shown below, which is called N,N-dimethylformamide, or DMF for short. (2 pt each)



*Resonance Contributer **A***

*Resonance Contributer **B***

*Resonance Contributer **C***

(b) Draw the structure of the resonance hybrid of DMF (2 pt)

*Resonance **Hybrid***

(c) In ethane (CH_3–CH_3), rotation about the carbon-carbon bond occurs billions of times every second at room temperature, and hopefully you remember that the barrier is about 3 kcal/mol. Rotation about the bond between the sp^2 hybridized carbon atom and the nitrogen atom in DMF happens about once every ten seconds at room temperature!! In DMF the rotational energy barrier for the bond in question is 20 kcal/mol, only 17 kcal/mol more than in ethane – indicating just how dramatic the consequences can be when energy barriers are increased by what seem to be relatively small amounts. Explain why the barrier to bond rotation in DMF is so much higher than in ethane? *(Hint: if you need to write more than what will fit in the box below, the chances are you're on the wrong track).* (4 pt)

Extra Credit 2. Two species, **A** and **B**, for the sake of better names, are in equilibrium with one another. At 300K (room temperature in some of the warmer climes of the world), an equilibrium mixture of these two species consists of 26.9% **A** and 73.1% **B**. The equilibrium constant (K_{eq} = [B]/[A]) is, quite conveniently and without any irony, equal to the mathematical constant *e* (which is about 2.718...). In the knowledge that the gas constant (R) is roughly equal to 2 cal K^{-1} mol^{-1}, and that $\Delta G° = -RT\ln K_{eq}$, answer the following questions:

(a) Which is the more energetically stable species, **A** or **B**? (1 pt)

(b) What is the approximate difference in free energy (i.e., the value of $\Delta G°$) on going from species **A** to species **B**. Give your answer in kcal/mol. *(Hint: the sign of your answer is important)* (4 pt) – if you get the wrong answer, perhaps if you show how you arrive at it, the partial credit Gods may smile down upon you...