Chemistry 261: Organic Chemistry

Examination #1

September 23, 2013

Name: *ANSWER KEY*

Student ID Number:

Exams will be returned via the Chem 261 wall-mount racks outside Lab Sci 300.

☐ Please check the box if you would prefer to pick up your graded examination directly from Prof. Ponder during office hours.

Problem 1 (8 points; A = 2 points, B = 2 points, C = 4 points).

(A) An enterprising organic chemistry student decides to study a molecule "named" 2-*tert*-butyl-3,3-diethylpropane. Provide a line-angle structure for this constitution.


(+2) FOR ANY CORRECT LINE-ANGE
DRAWING OF THIS CONSTITUTION

(B) The above "name" does, indeed, describe an alkane. However, it is not the correct systematic name. Suggest the best possible formal name for this alkane, following the IUPAC nomenclature rules.

4-ethyl-2,2,3-trimethylhexane

(+1) FOR A "HEXANE"   (+1) FOR FULL CORRECT NAME

(C) Draw all possible stereoisomers for this molecule, and label any chiral centers as *(R)* or *(S)* in accord with the Cahn-Ingold-Prelog convention.

(+1)
(R) CENTER
UNDER KAHN-INGOLD-PRELOG

(+2) FOR
BOTH
STRUCTURES

(S) CENTER (+1)
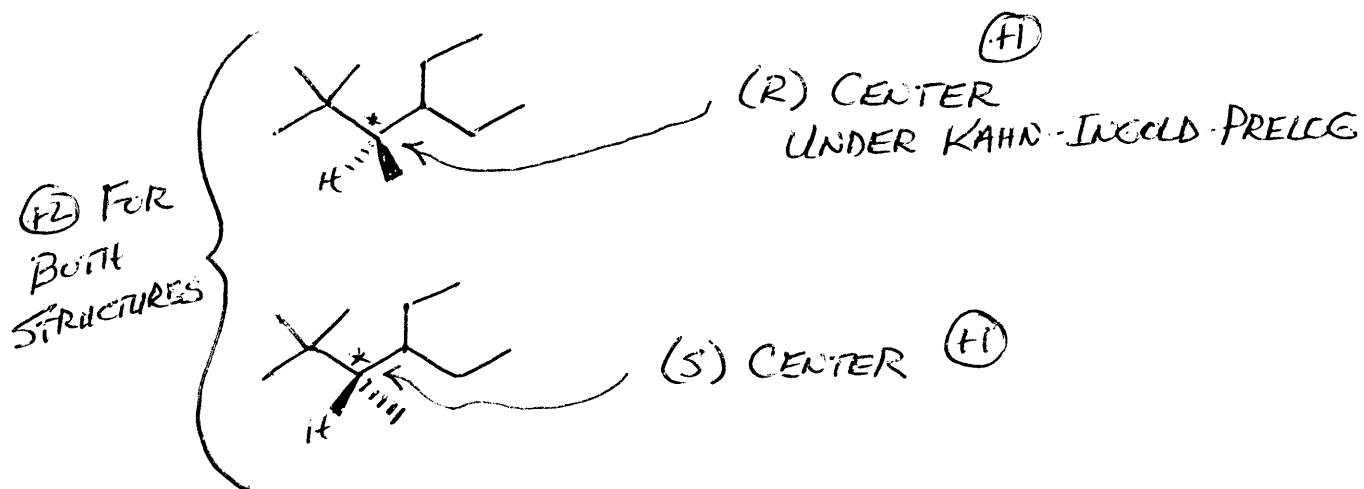
Problem 2 (8 points; A–D = 2 points each).

(A) The pK_a of ammonia is about 33, while the pK_a of ammonium ion is 9.24. What is the ΔG associated with the reaction below at room temperature of 25°C (298K)?

$$NH_4^+ \;+\; NH_2^- \;\rightleftharpoons\; 2\,NH_3$$

(+1) $\quad \Delta G = -RT \ln K$

$\Delta G = -0.592 \cdot \ln 10^{33-9.24}$ (+1)

$\quad = -0.592 \cdot \ln 10^{23.76} = -32.4 \; Kcal/mol$

(B) Hydrogen cyanide (HCN) has a C–H bond length of 1.07 Å and a C–N length of 1.17 Å. Molecular orbital calculations suggest a partial charge on H of about +0.28 e⁻ and a charge on N of roughly -0.28 e⁻, while the C is close to neutral. Use these values to estimate the molecular dipole moment of HCN.

(+1) $\quad \mu = 4.8 \cdot \Delta e^\ominus \cdot Bond\,Length$

$\mu = 4.8 \cdot 0.28 \cdot 2.24 = 3.01 \; Debye$

$H-C \equiv N$ is $Linear$, H to N $Dist.$ is $1.07 + 1.17 = 2.24 \; Å$

(C) The entropy of fusion (melting) of water is +22 J/mol/K. Calculate the enthalpy of fusion of water at 0°C.

$$\Delta G = \Delta H - T\Delta S$$
$\Delta G = 0 \; @ \; 0°C, \; THEN \; 0 = \Delta H - (273)(22)$

$\Delta H = 6.01 \; kJ/mol$
(+1)

(D) The entropy of vaporization (boiling) for essentially all liquids lies in the narrow range from +85-88 J/mol/K. This is sometimes referred to as Trouton's Rule. What is the physical explanation for consistency in the entropy of vaporization? Do intermolecular interactions, such as hydrogen bonding, play a larger role in determining enthalpy or entropy of vaporization? Explain briefly.
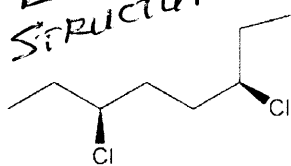
(+1) MOST OF ΔS_{VAP} IS ROTATIONAL/TRANSLATIONAL FREEDOM IN THE GAS, WHICH IS ROUGHLY SIMILAR FOR ALL MOLECULES

(+1) INTERMOLECULAR INTERACTIONS (SUCH AS H-BOND) CONTRIBE MOST TO ΔH_{VAP}

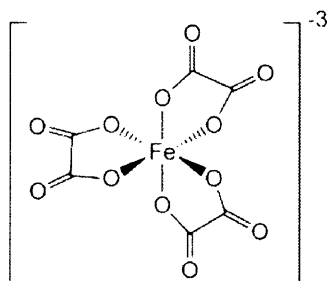## Problem 3 (7 points; A = 4 points, B = 3 points).

(A) For each structure below, indicate whether the molecule is chiral or achiral.
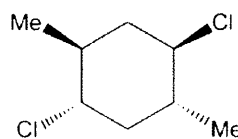
(+1) EACH STRUCTURE

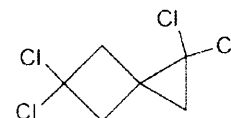|			
(1)	*(2)*	*(3)*	*(4)*
ACHIRAL	CHIRAL	ACHIRAL	ACHIRAL
(MESO, PLANE OF SYMMETRY)	("HELICAL")	(CENTER OF INVERSION)	(INTERNAL MIRROR PLANE)

(B) The barrier to inversion in ammonia is 5 kcal/mol, and inversion occurs rapidly at room temperature. For this reason, most amines containing three different substituents are achiral (see below, where R_1, R_2 and R_3 can be three different alkyl groups). In contrast, aziridines (such as the pair of molecules shown on the right below) can often be separated into pure enantiomers at room temperature. Suggest a reason for this behavior of aziridines. *[Note: An aziridine is an amine in a 3-membered ring.]*
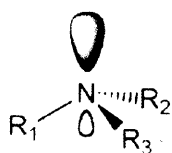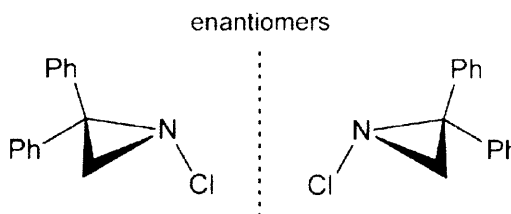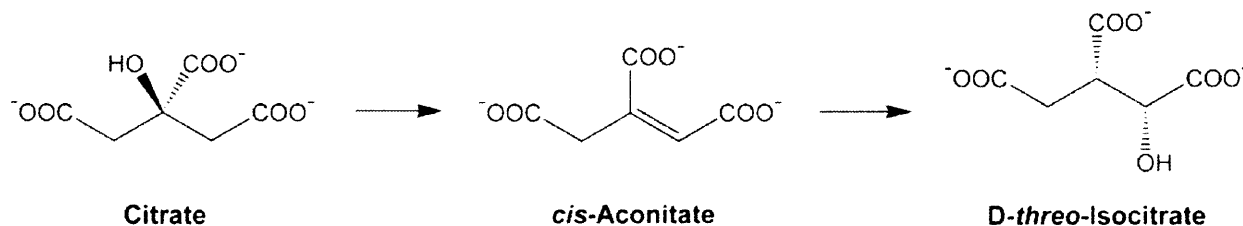
enantiomers

Amine   **Chiral Aziridines**

(+1) EACH

- INVERSION IN AZIRIDINES IS HINDERED BY RING STRAIN
- STRAIN IS GREATEST WHEN N IS FLAT (sp^2), WHICH IS THE INVERSION TRANSITION STATE
- THUS, INVERSION BARRIER IS $\gg$ 5 KCAL/MOL & ENANTIOMERS CAN BE SEPARATED

Problem 4 (8 points; A & C = 3 points each, B = 2 points). The citric acid cycle is used by aerobic organisms to generate energy via the net oxidation of acetate to CO_2. It also produces some amino acid precursors and the reducing agent NADH. Hans Krebs won the Nobel Prize in 1953 for elucidating the overall cycle. Part of the cycle involves the conversion of citrate to *cis*-aconitate to D-*threo*-isocitrate, as shown below.

Citrate   *cis*-Aconitate   D-*threo*-Isocitrate

(A) For each of these three species, state whether the molecule has alternative stereoisomers, and whether it is chiral.

(+1) • CITRATE ⟹ ACHIRAL   No STEREOISOMERS

(+1) • ACONITATE ⟹ ACHIRAL   cis/trans ISOMERS @ C=C

(+1) • ISOCITRATE ⟹ CHIRAL   2 PAIRS OF ENANTIOMERS

(B) In the citric acid cycle, both of the reactions above are catalyzed by an enzyme called aconitase. What allows an enzyme to produce a chiral product from an achiral starting material? What feature must an achiral starting material have if an enzyme is to transform it into an optically active product?

(+1) • ENZYME MUST BE CHIRAL TO MAKE CHIRAL PRODUCT FROM ACHIRAL STARTING MATERIALS

(+2) • THE ACHIRAL STARTING MATERIAL MUST HAVE PROCHIRAL FACES, ATOMS, GROUPS, etc.

(C) Working in the Chem 261 lab and using only achiral reagents, do you think it might be possible to convert citrate to *cis*-aconitate? What about the conversion of *cis*-aconitate to D-*threo*-isocitrate? Explain.

(+1) • CAN DO CITRATE → ACONITATE (ACHIRAL → ACHIRAL) IN "LAB"

(+1) • CANNOT DO ACONITATE → ISOCITRATE (D, threo) IN "LAB" WITH ACHIRAL REAGENTS (ACHIRAL → CHIRAL)

(+1) • IN GENERAL, CAN'T MAKE CHIRAL PRODUCT FROM ACHIRAL STARTING MATERIAL WITHOUT CHIRAL CATALYST OR REAGENTS

Problem 5 (20 points; A–J = 2 points each). There are several possible species with the general molecular formula CH_2N_2, including diazomethane, cyanamide and diazirine. In diazomethane the C and N atoms are connected in the order C–N–N. In cyanamide the connectivity is N–C–N, while in diazirine the C and N atoms form a 3-membered ring.

(A) Write all the reasonable Lewis dot structures for diazomethane. Indicate whether your structures are resonance forms or constitutional isomers.
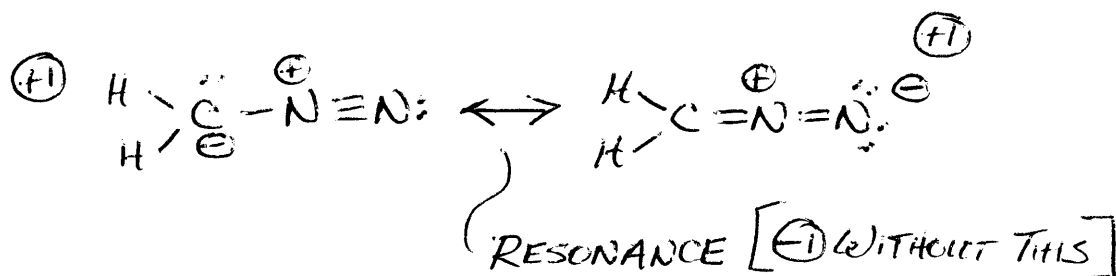

(B) What is the hybridization state of each C and N atom in diazomethane?

(+1) C is sp^2 (+1) BOTH N ARE sp HYBRIDIZED

(C) For both cyanamide and diazirine, there are two possible constitutions. Draw the best Lewis dot structures for both constitutions of both species.
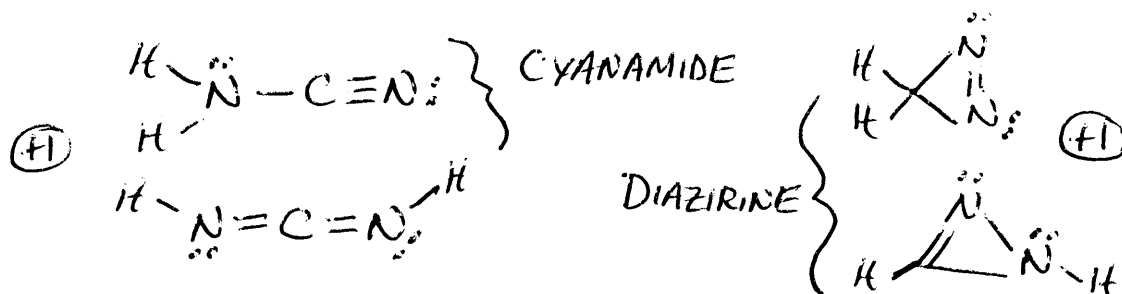
(D) Experiments show that both of the C–N bonds in diazirine have the same length. Which constitution from part (C) is the correct structure for diazirine?
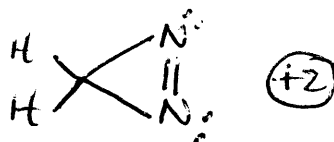
(E) The dipole moments of diazomethane and diazirine are both near 1.5 D, while that for cyanamide is much larger at approximately 3.8 D. Which constitution from part (C) is the correct structure for cyanamide?
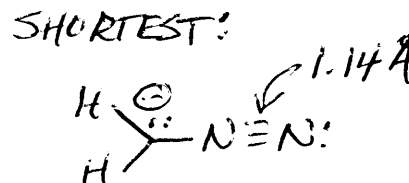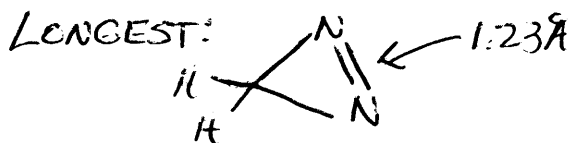
Problem 5 (cont.)

(F) The heat of formation (ΔH_f) is positive for all three molecules. Which has the largest ΔH_f value? Which has the smallest ΔH_f value?
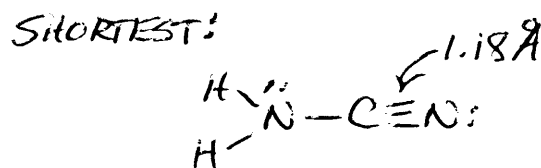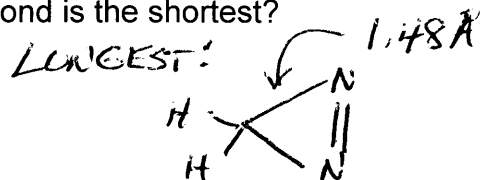
LARGEST ΔH_f IS DIAZIRINE (+1)

SMALLEST ΔH_f IS CYANAMIDE (+1)

**(G)** Considering all three molecules, which N–N bond is the longest? Which N–N bond is the shortest?

LONGEST:

SHORTEST:

(H) Considering all three molecules, which C–N bond is the longest? Which C–N bond is the shortest?

LONGEST:

SHORTEST:

(I) Two of these molecules are gases at room temperature, while the third is a white solid with a melting point of 44°C. Which one is the solid?

CYANAMIDE (*DUE TO MUCH LARGER DIPOLE LEADING TO BETTER PACKING INTERACTIONS*)

(J) Under appropriate conditions, diazomethane decomposes with formation of dinitrogen (N_2). Starting from a Lewis structure for diazomethane, use curved arrows to describe the formation of N_2. What is the other product of this reaction? What category of species does this second product belong to?
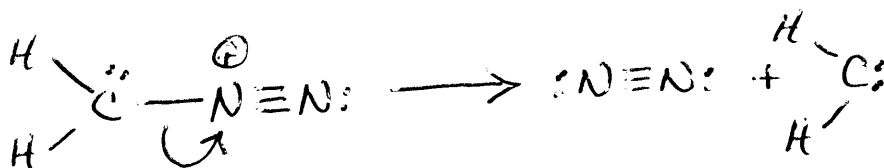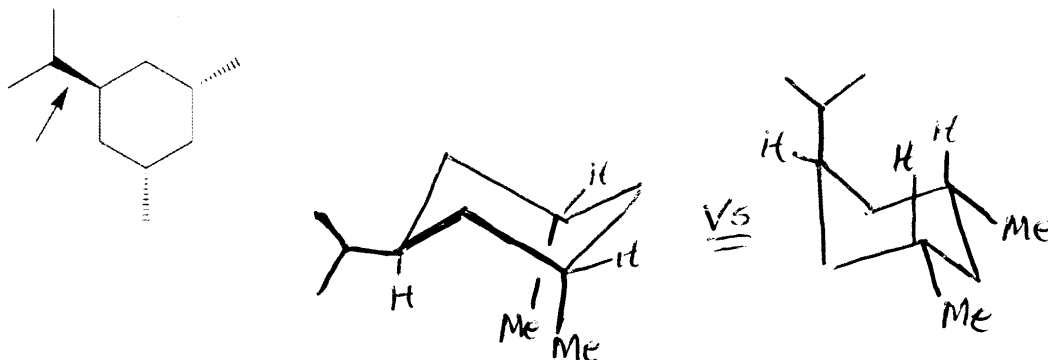
(+1) *FOR CORRECT ARROW*

(+1) *FOR PRODUCTS*

Problem 6 (8 points; A = 3 points, B = 2 points, C = 3 points).

(A)   Make clear 3-D structural drawings of the two stable chair forms of the molecule depicted below.


(+1) EACH STRUCTURE WITH CORRECT SUBSTITUENT STEREOCHEM.
(+1) FOR PROPER CHAIR DRAWINGS

(B)   According to Spartan molecular mechanics calculations, one chair conformation is nearly 16 kJ/mol lower in steric energy than the other. Which conformation is more stable, and why? Remember 1 kcal/mol = 4.184 kJ/mol.

(+1) THE STRUCTURE ON THE RIGHT ABOVE IS _LOWER_
IN ENERGY. THE ONE AT LEFT HAS MORE
GAUCHE INTERACTIONS & A 1,3-DIAXIAL CLASH
(+1)

(C)   Draw alternative Newman projections looking down the bond indicated by the arrow, in order to show the stable rotational states for this bond. Estimate the difference in energy between the most stable isopropyl conformation and the alternative conformation(s).

2 GAUCHE
INTERACTIONS
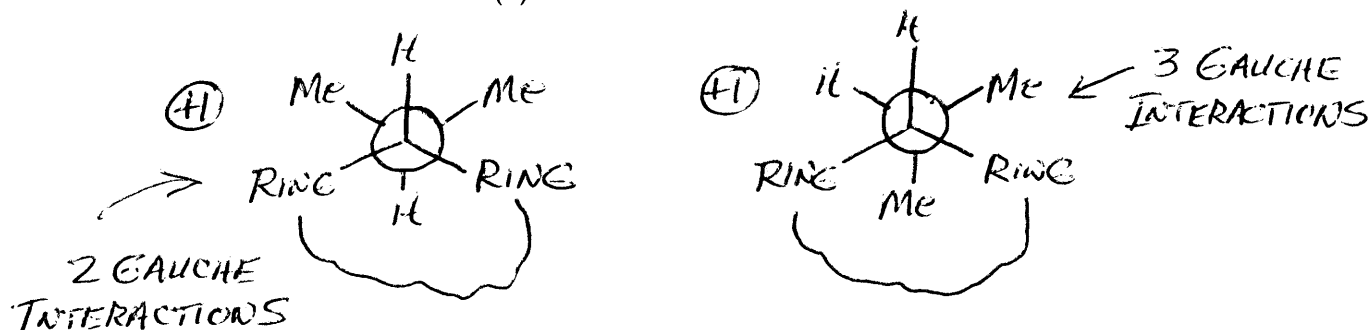
• STRUCTURE ON THE LEFT IS LOWER ENERGY
BY ABOUT 0.9 KCAL/MOL (Δ OF 1 GAUCHE)

## Problem 7 (10 points; A = 8 points, B = 2 points).

(A) Indicate with a checkmark in the appropriate column whether you expect the following procedures to primarily lower the purity or lower the yield of product.

Experimental Procedure	Purity	Yield
The crystals obtained by suction filtration are not washed with fresh cold solvent before drying	X	
The crystals obtained by suction filtration are washed with fresh, hot solvent		X
Crystals are obtained by breaking up the solidified mass of an oil which originally separated from the hot solution	X	
Crystallization is accelerated by immediately placing the flask of hot, filtered solution in an ice bath	X	

(+1) EACH PART

(B) In case of major chemical spills, it is necessary to know the locations of all of the safety showers in or close to your laboratory. On the diagram below, please write the letter "S" to indicate the locations of safety shower(s) in or close to your lab. If you don't remember which lab you are in, show the safety shower location(s) for a lab of your choice.

Snow Way
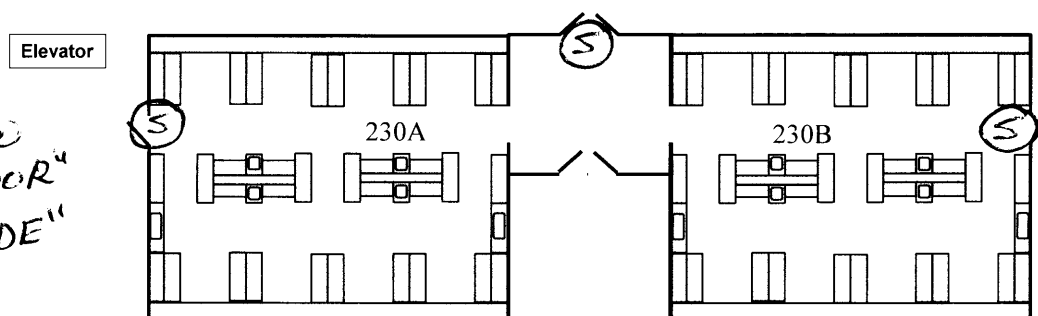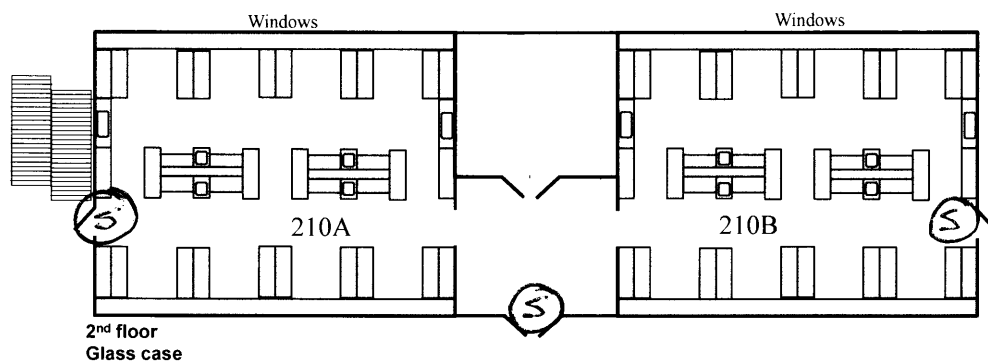
MUST SHOW ONE "MAIN DOOR" & ONE "SIDE" SHOWER

(+1) EACH

Problem 8 (12 points; A = 6 points, B–C = 3 points each). Many organic reactions can be explained in terms of frontier orbital interactions, for example, the HOMO of one molecule interacting with the LUMO of another molecule.

(A) Consider the various types of orbitals found in organic molecules and listed below. Please rank these orbital types from lowest energy to highest energy (1=lowest, 10=highest; write the rank on the line to the left of each orbital type). X is an electronegative atom. R is either an H or a -CH_3 when in C–R, or a =CH_2 when in C=R. Finally, n is a nonbonding orbital; typically a lone pair on X, and either a lone pair or carbocation orbital on C.

ΔE PTS
0-6   6
7-9   5
10-12 4
13-15 3
16-18 2
19-21 1
22+   0

(HL)
POINTS AWARDED
BASED ON "ERROR"
  OVERALL

__4__ π C=R   __8__ π* C=R   __2__ σ C–R   __10__ σ* C–R

__3__ π C=X   __7__ π* C=X   __1__ σ C–X   __9__ σ* C–X

__6__ n C   __5__ n X

(B) Draw pictures of the LUMO for ethylene ($H_2C=CH_2$) and for formaldehyde ($H_2C=O$). Pay attention to the phases and relative sizes of the orbital lobes.
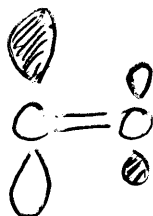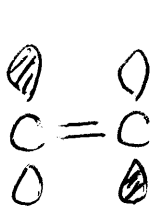
(• π ORBITAL FROM
      p AOs
  • PHASES CORRECT
  • RELATIVE LOBE
      SIZES CORRECT

(+1) EACH

(C) Hydroxide ion, which has lone pair electrons as its HOMO, reacts readily with formaldehyde, while ethylene is unreactive. Suggest an explanation. Which atom of formaldehyde do you think the hydroxide ion will attack?

(+2) • THE C=O LUMO IS LOWER IN ENERGY,
        SO MORE EASILY ATTACKED THAN C=C LUMO

(+1) • OH⊖ WILL ATTACK C OF FORMALDEHYDE
        SINCE HAS THE LARGER LUMO CONTRIBUTION

Problem 9 (12 points; A–B = 6 points).

(A) Plot the conformational energy as a function of torsional angle for isopentane. Use the energy values listed to construct your plot (neglect all other interactions). Use the Newman projection shown as the definition of a 0° torsional angle.

(+1) EACH POINT FROM 0° THRU 300°
(360° IS SAME AS 0°)

Energy for each:

H - H eclipsed	1.0 kcal/mol
H - Me eclipsed	1.3 kcal/mol
Me - Me eclipsed	3.0 kcal/mol
Me - Me gauche	0.9 kcal/mol

Me / Me / Me / H / H / H

Torsional Angle = 0 degrees

ΔE (kcal/mol) vs Torsional Angle plot
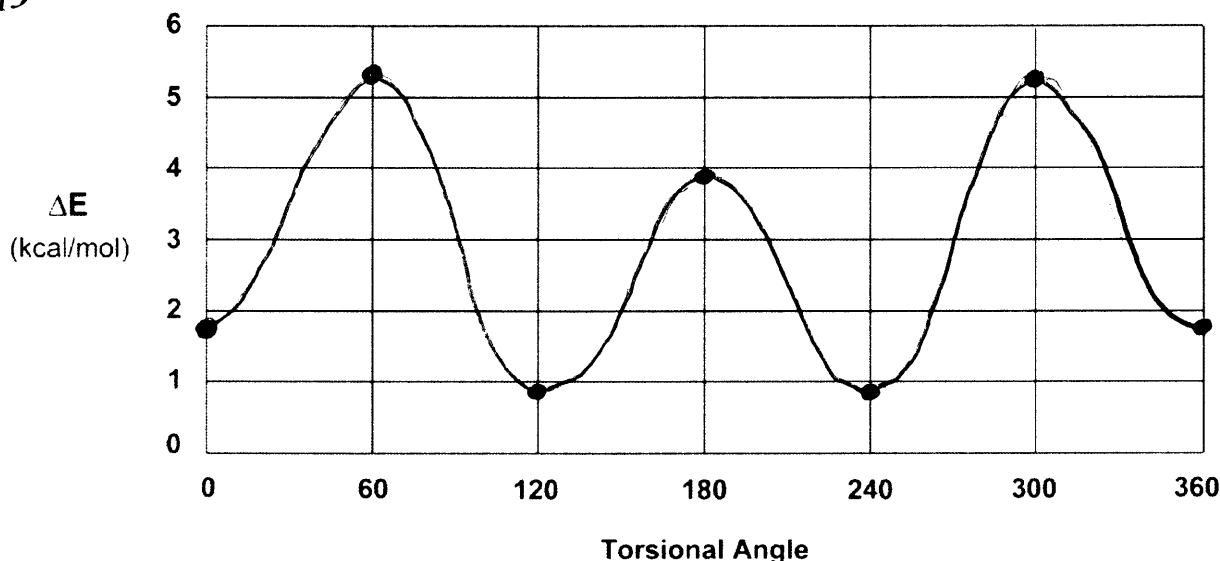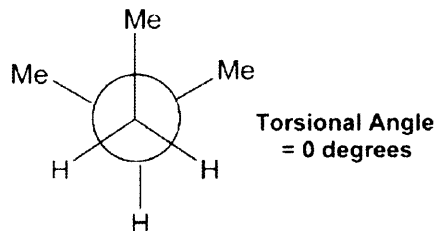
**(B)** Hydrazine ($H_2N–NH_2$) is a dangerously unstable and toxic liquid. Its most famous application in recent years was as the rocket fuel for the NASA space shuttles. The lowest energy conformation of hydrazine is stabilized by hyperconjugation. What is the favored conformation? Provide a molecular orbital drawing to explain the hyperconjugative interactions in hydrazine.

"GAUCHE" CONFORMER IS PREFERRED

(+2)
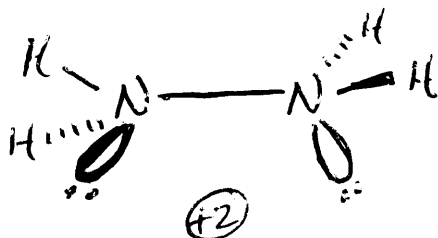
BEST INTERACTION IS n ORBITAL WITH N–H e*

(+4)

NODE
N–H e*
LONE PAIR n

n stabilizes LONE PAIR
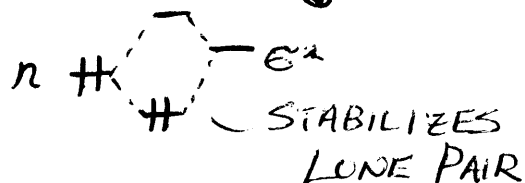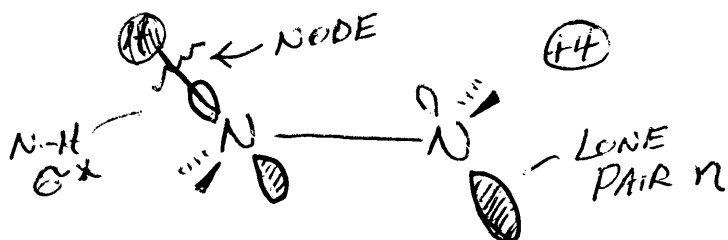
Problem 10 (7 points; A = 3 points, B = 4 points) There are a total of nine possible stereoisomers for the molecule 1,2,3,4,5,6-hexahydroxycyclohexane, commonly known as inositol. Seven of these isomers are achiral, and the remaining two isomers form a pair of enantiomers. Phosphorylated forms of one of the achiral isomers, *myo*-inositol, are involved in many signaling pathways inside eukaryotic cells.
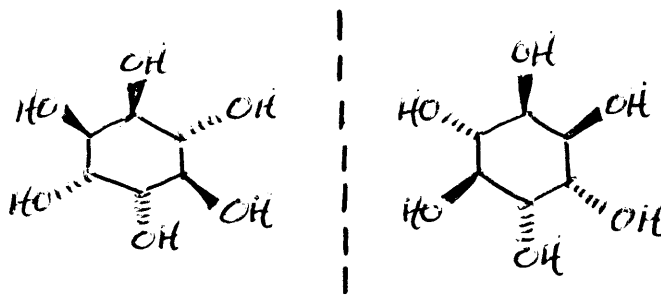
(A) Draw the structures of any three of the seven achiral stereoisomers of inositol. *[Three points of extra credit will be awarded if you can draw all seven!]*
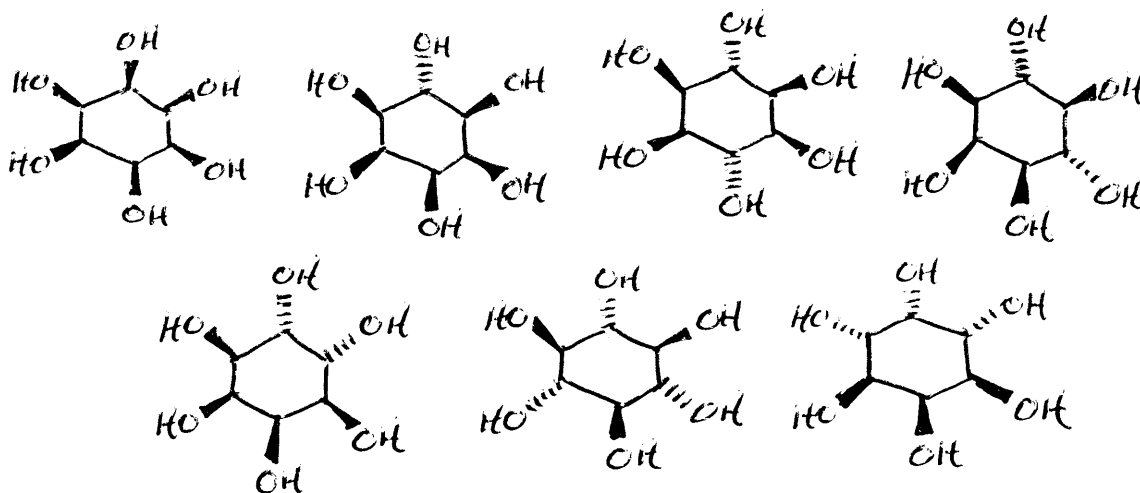
(+1) FOR EACH OF THREE ISOMERS

• MUST HAVE ALL 7 TO GET ANY EXTRA CREDIT

(B) Draw the structures of the pair of enantiomers of inositol along with the mirror plane that interconverts them.

(+2) FOR EACH ENANTIOMER

(−1) IF NO MIRROR PLANE SHOWN