Chemistry 261: Organic Chemistry

Examination #1

September 23, 2013

Name:

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.

(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.

(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.

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)?

$$NH_4^+ \quad + \quad NH_2^- \quad \rightleftharpoons \quad 2\ NH_3$$

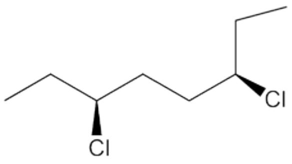
(B) Hydrogen cyanide (HCN) has a C–H bond length of 1.07 Å and a C–N length of 1.17 Å. Molecular orbital calculations suggest a partial charge on H of about +0.28 e^- and a charge on N of roughly -0.28 e^-, while the C is close to neutral. Use these values to estimate the molecular dipole moment of HCN.

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

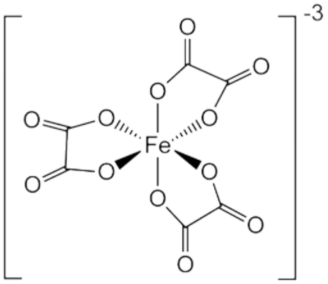
(D) The entropy of vaporization (boiling) for essentially all liquids lies in the narrow range from +85-88 J/mol/K. This is sometimes referred to as Trouton’s Rule. What is the physical explanation for consistency in the entropy of vaporization? Do intermolecular interactions, such as hydrogen bonding, play a larger role in determining enthalpy or entropy of vaporization? Explain briefly.

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

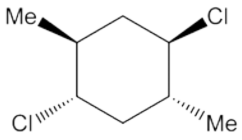
(A) For each structure below, indicate whether the molecule is chiral or achiral.



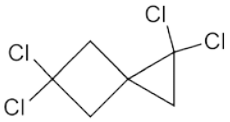
(1)



(2)

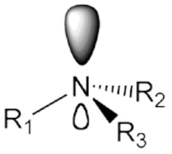


(3)

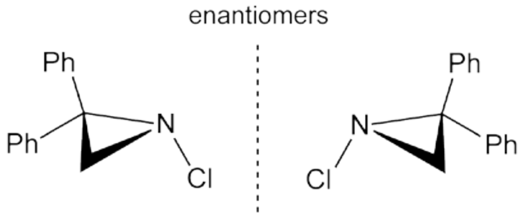


(4)

(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.]*

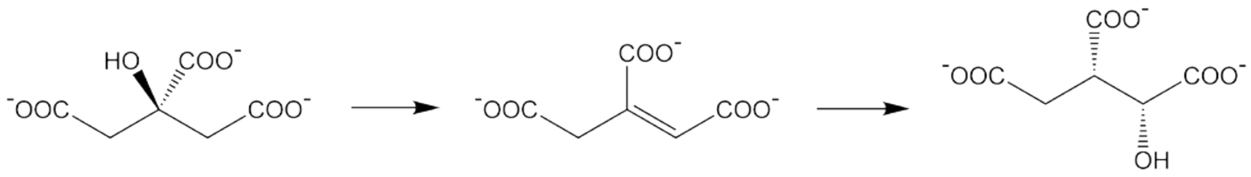


Amine



Chiral Aziridines

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.

(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?

(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.

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?

(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?

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

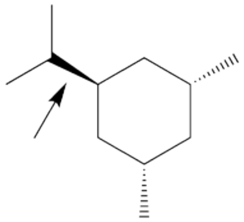
(H) Considering all three molecules, which C–N bond is the longest? Which C–N bond is the shortest?

(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?

(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?

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.



(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.

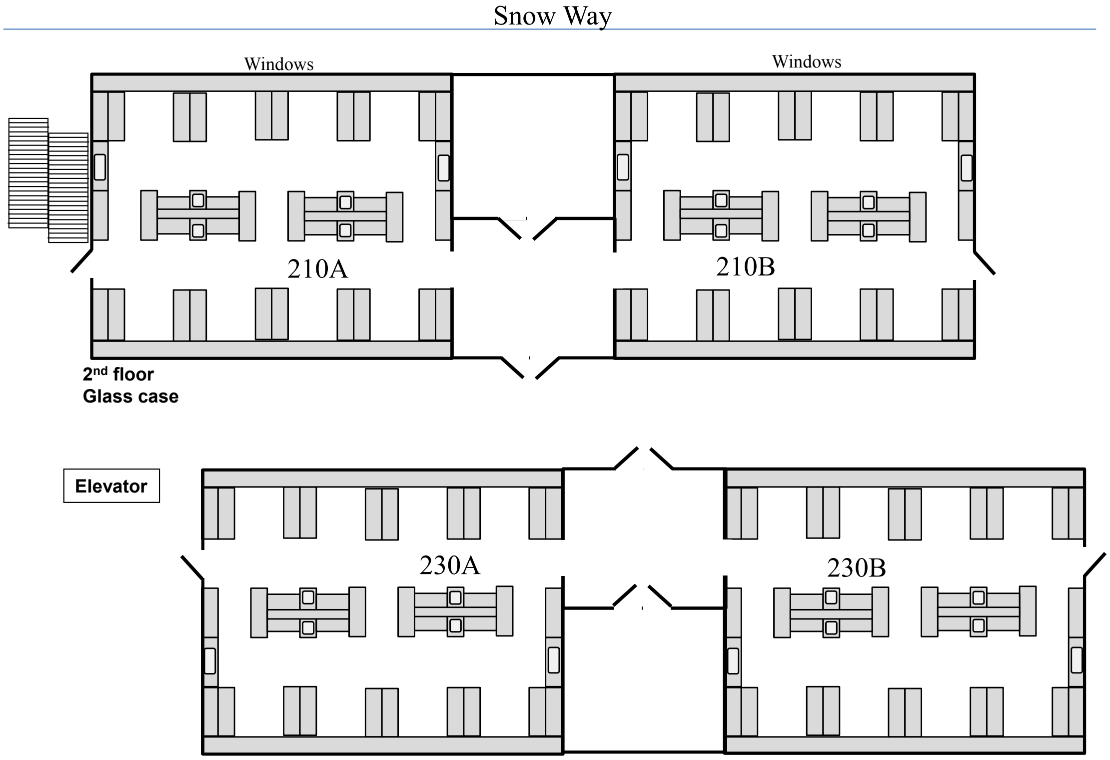
(C) Draw alternative Newman projections looking down the bond indicated by the arrow, in order to show the stable rotational states for this bond. Estimate the difference in energy between the most stable isopropyl conformation and the alternative conformation(s).

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		
The crystals obtained by suction filtration are washed with fresh, hot solvent		
Crystals are obtained by breaking up the solidified mass of an oil which originally separated from the hot solution		
Crystallization is accelerated by immediately placing the flask of hot, filtered solution in an ice bath		

(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.



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.

_____ π C=R   _____ π^* C=R   _____ σ C–R   _____ σ^* C–R

_____ π C=X   _____ π^* C=X   _____ σ C–X   _____ σ^* C–X

_____ *n* C   _____ *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.

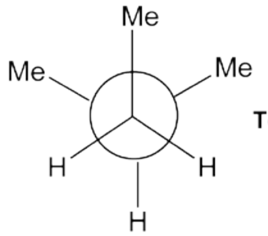
(C) Hydroxide ion, which has lone pair electrons as its HOMO, reacts readily with formaldehyde, while ethylene is unreactive. Suggest an explanation. Which atom of formaldehyde do you think the hydroxide ion will attack?

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

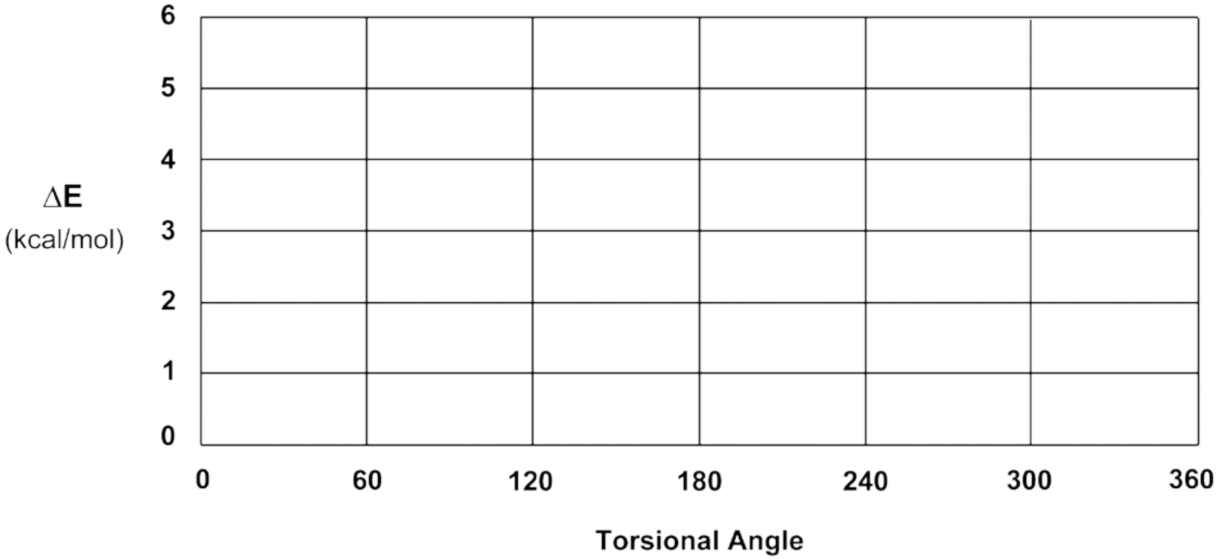
(A) Plot the conformational energy as a function of torsional angle for isopentane. Use the energy values listed to construct your plot (neglect all other interactions). Use the Newman projection shown as the definition of a 0° torsional angle.

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**



Torsional Angle = 0 degrees



(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.

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!]***

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

Score Sheet – Do Not Write on This Page!

/8	**Question 1**
/8	**Question 2**
/7	**Question 3**
/8	**Question 4**
/20	**Question 5**
/8	**Question 6**
/10	**Question 7**
/12	**Question 8**
/12	**Question 9**
/7	**Question 10**
/100	**TOTAL**

The Periodic Table of Elements

6 ← **Atomic Number** = Number of Protons = Number of Electrons
C ← **Chemical Symbol**
CARBON ← **Chemical Name**
12 ← **Atomic Weight** = Number of Protons + Number of Neutrons*

METALS

NON-METALS

1 ☁ **H** HYDROGEN 1																	2 ☁ **He** HELIUM 4
3 ▢ **Li** LITHIUM 7	4 ▢ **Be** BERYLLIUM 9											5 ▢ **B** BORON 11	6 ▢ **C** CARBON 12	7 ☁ **N** NITROGEN 14	8 ☁ **O** OXYGEN 16	9 ☁ **F** FLUORINE 19	10 ☁ **Ne** NEON 20
11 ▢ **Na** SODIUM 23	12 ▢ **Mg** MAGNESIUM 24											13 ▢ **Al** ALUMINUM 27	14 ▢ **Si** SILICON 28	15 ▢ **P** PHOSPHORUS 31	16 ▢ **S** SULFUR 32	17 ☁ **Cl** CHLORINE 35	18 ☁ **Ar** ARGON 40
19 ▢ **K** POTASSIUM 39	20 ▢ **Ca** CALCIUM 40	21 ▢ **Sc** SCANDIUM 45	22 ▢ **Ti** TITANIUM 48	23 ▢ **V** VANADIUM 51	24 ▢ **Cr** CHROMIUM 52	25 ▢ **Mn** MANGANESE 55	26 ▢ **Fe** IRON 56	27 ▢ **Co** COBALT 59	28 ▢ **Ni** NICKEL 59	29 ▢ **Cu** COPPER 64	30 ▢ **Zn** ZINC 65	31 ▢ **Ga** GALLIUM 70	32 ▢ **Ge** GERMANIUM 73	33 ▢ **As** ARSENIC 75	34 ▢ **Se** SELENIUM 79	35 💧 **Br** BROMINE 80	36 ☁ **Kr** KRYPTON 84
37 ▢ **Rb** RUBIDIUM 85	38 ▢ **Sr** STRONTIUM 88	39 ▢ **Y** YTTRIUM 89	40 ▢ **Zr** ZIRCONIUM 91	41 ▢ **Nb** NIOBIUM 93	42 ▢ **Mo** MOLYBDENUM 96	43 ▢ **Tc** TECHNETIUM 🚶 98 ☢	44 ▢ **Ru** RUTHENIUM 101	45 ▢ **Rh** RHODIUM 103	46 ▢ **Pd** PALLADIUM 106	47 ▢ **Ag** SILVER 108	48 ▢ **Cd** CADMIUM 112	49 ▢ **In** INDIUM 115	50 ▢ **Sn** TIN 119	51 ▢ **Sb** ANTIMONY 122	52 ▢ **Te** TELLURIUM 128	53 ▢ **I** IODINE 127	54 ☁ **Xe** XENON 131
55 ▢ **Cs** CESIUM 133	56 ▢ **Ba** BARIUM 137		72 ▢ **Hf** HAFNIUM 178	73 ▢ **Ta** TANTALUM 181	74 ▢ **W** TUNGSTEN 184	75 ▢ **Re** RHENIUM 186	76 ▢ **Os** OSMIUM 190	77 ▢ **Ir** IRIDIUM 192	78 ▢ **Pt** PLATINUM 195	79 ▢ **Au** GOLD 197	80 💧 **Hg** MERCURY 201	81 ▢ **Tl** THALLIUM 204	82 ▢ **Pb** LEAD 207	83 ▢ **Bi** BISMUTH 209 ☢	84 ▢ **Po** POLONIUM 209 ☢	85 ▢ **At** ASTATINE 210 ☢	86 ☁ **Rn** RADON 222 ☢
87 ▢ **Fr** FRANCIUM 223 ☢	88 ▢ **Ra** RADIUM 226 ☢		104 ▢ **Rf** RUTHERFORDIUM 🚶 267 ☢	105 ▢ **Db** DUBNIUM 🚶 270 ☢	106 ▢ **Sg** SEABORGIUM 🚶 271 ☢	107 ▢ **Bh** BOHRIUM 🚶 274 ☢	108 ▢ **Hs** HASSIUM 🚶 277 ☢	109 ▢ **Mt** MEITNERIUM 🚶 278 ☢	110 ▢ **Ds** DARMSTADTIUM 🚶 281 ☢	111 ▢ **Rg** ROENTGENIUM 🚶 281 ☢	112 ▢ **Cn** COPERNICIUM 🚶 285 ☢	113 ▢ **Uut** UNUNTRIUM 🚶 286 ☢	114 ▢ **Uuq** UNUNQUADIUM 🚶 289 ☢	115 ▢ **Uup** UNUNPENTIUM 🚶 289 ☢	116 ▢ **Uuh** UNUNHEXIUM 🚶 291 ☢	117 ▢ **Uus** UNUNSEPTIUM 🚶 294 ☢	118 ☁ **Uuo** UNUNOCTIUM 🚶 294 ☢

57 ▢ **La** LANTHANUM 139	58 ▢ **Ce** CERIUM 140	59 ▢ **Pr** PRASEODYMIUM 141	60 ▢ **Nd** NEODYMIUM 144	61 ▢ **Pm** PROMETHIUM 🚶 145 ☢	62 ▢ **Sm** SAMARIUM 150	63 ▢ **Eu** EUROPIUM 152	64 ▢ **Gd** GADOLINIUM 157	65 ▢ **Tb** TERBIUM 159	66 ▢ **Dy** DYSPROSIUM 163	67 ▢ **Ho** HOLMIUM 165	68 ▢ **Er** ERBIUM 167	69 ▢ **Tm** THULIUM 169	70 ▢ **Yb** YTTERBIUM 173	71 ▢ **Lu** LUTETIUM 175
89 ▢ **Ac** ACTINIUM 227 ☢	90 ▢ **Th** THORIUM 232 ☢	91 ▢ **Pa** PROTACTINIUM 231 ☢	92 ▢ **U** URANIUM 238 ☢	93 ▢ **Np** NEPTUNIUM 🚶 237 ☢	94 ▢ **Pu** PLUTONIUM 🚶 244 ☢	95 ▢ **Am** AMERICIUM 🚶 243 ☢	96 ▢ **Cm** CURIUM 🚶 247 ☢	97 ▢ **Bk** BERKELIUM 🚶 247 ☢	98 ▢ **Cf** CALIFORNIUM 🚶 251 ☢	99 ▢ **Es** EINSTEINIUM 🚶 252 ☢	100 ▢ **Fm** FERMIUM 🚶 257 ☢	101 ▢ **Md** MENDELEVIUM 🚶 258 ☢	102 ▢ **No** NOBELIUM 🚶 259 ☢	103 ▢ **Lr** LAWRENCIUM 🚶 262 ☢

KEY

▢ = **Solid** at room temperature
💧 = **Liquid** at room temperature
☁ = **Gas** at room temperature
☢ = **Radioactive**
🚶 = **Artificially Made**

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* The atomic weights listed on this Table of Elements have been rounded to the nearest whole number. As a result, this chart actually displays the **mass number** of a specific isotope for each element. An element's complete, unrounded atomic weight can be found on the It's Elemental web site: http://education.jlab.org/itselemental/index.html