Chemistry 125   First Semester   Name _____

**December 18, 2006**   Final Examination

This exam is budgeted for 150 minutes, but you may have 180 minutes to finish it. Good Luck.

1. (56 minutes).   On pages 1 and 2 are 18 diagrams, models, formulas, or other illustrations (labeled **A-R**).
 In a blue book describe very briefly the **principal point** that each of **14** (**FOURTEEN ONLY**) of them was designed to show:
You should **omit 4** of the examples. Only the first 14 answers will be graded.

(A)

(B)

(C)

(D)

(E)

(F)

(G)

(H)
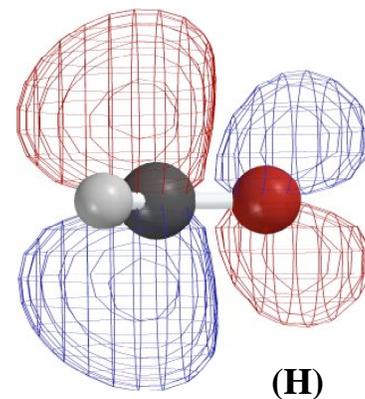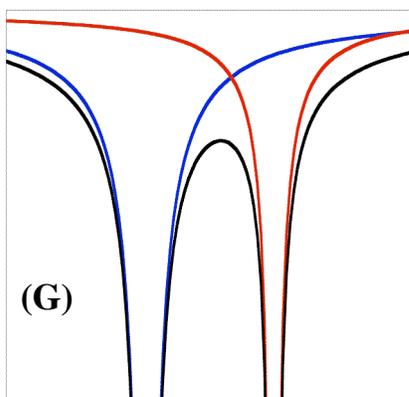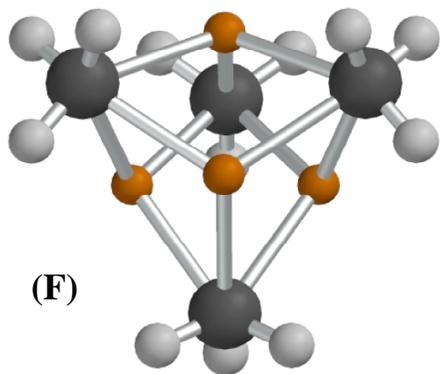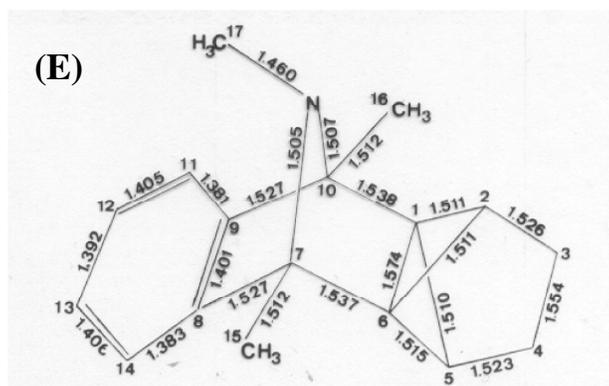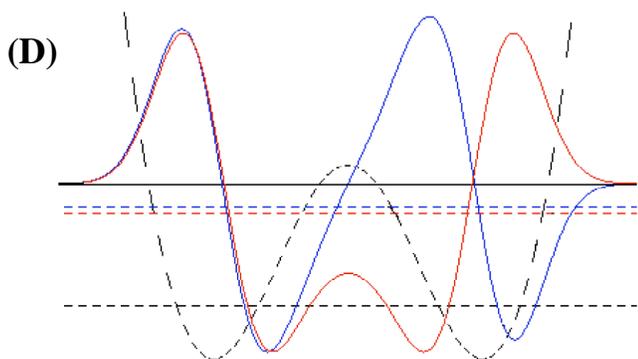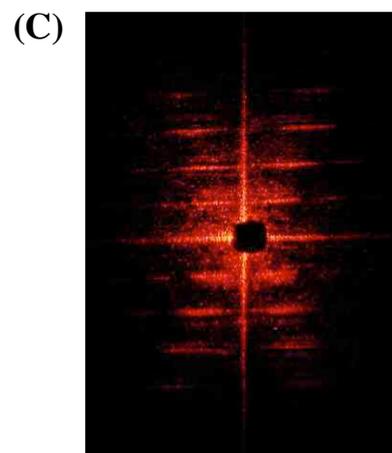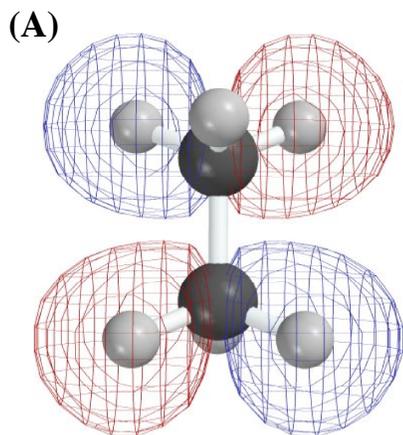
Question 1 (continued)

(I)

(J)

(K)

(L)

(M)

(N)

(O)

(P)

(Q)

(R)
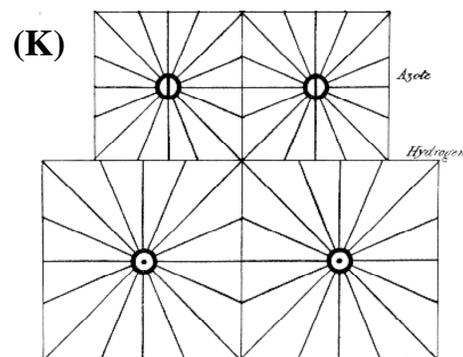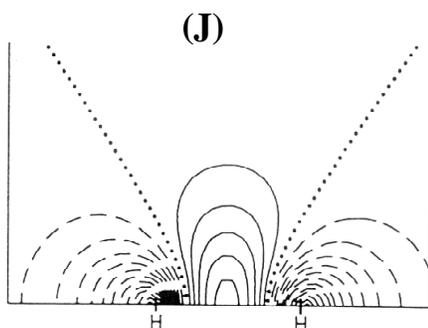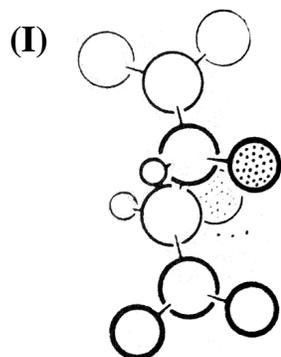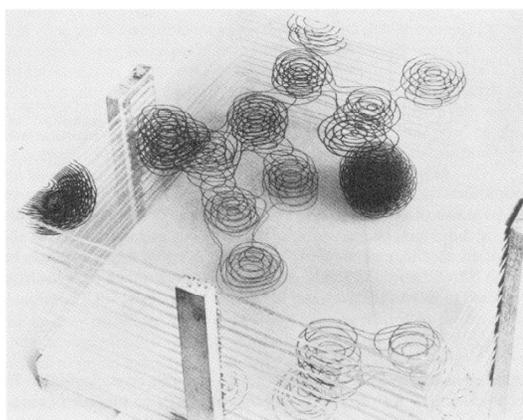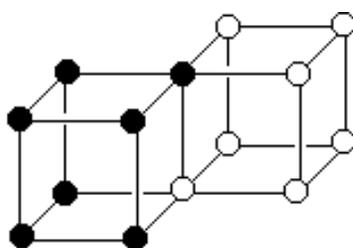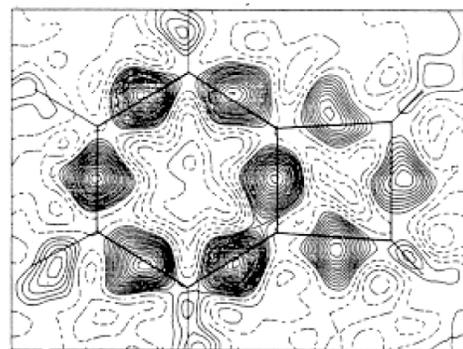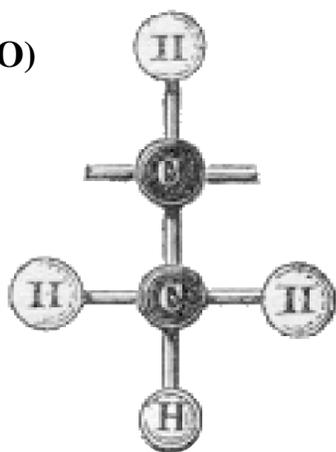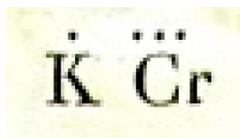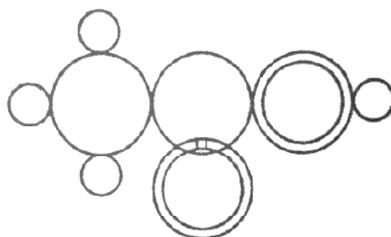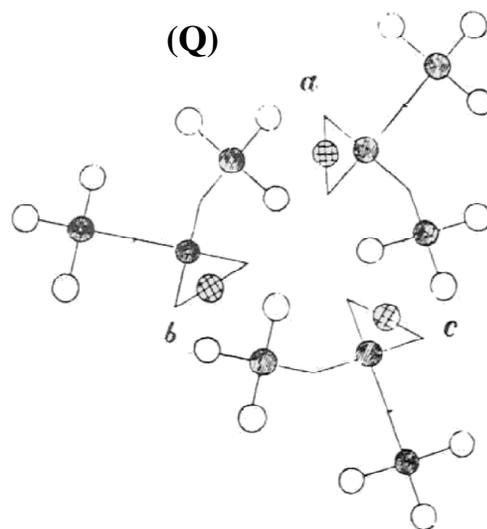
2.   "Brevibloc" or "Esmolol Hydrochloride" (formula at the right from a pharmaceutical
website) is a "beta-blocker" that may be administered intravenously as an aqueous
solution to a patient during surgery to slow abnormally rapid beating of the heart.

   The website also gives a more systematic name for the drug:

(±)-4-(2-Hydroxy-3-((1-methylethyl)amino)propoxy)phenylpropionic acid, methyl ester.
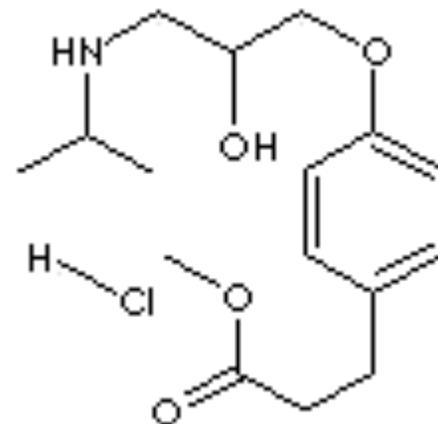
   A. (2 min)   **Label specific atoms** in the structure 1, 2, 3, and 4 corresponding to the
   numbers used in the systematic name.

   B. (1 min)   Give the **trivial name for 1-methylethyl**: _____

   C. (2.5 min) List the **names of five functional groups** in Esmolol (neglecting the HCl)

   D. (4 min)   **Explain** briefly **in HOMO/LUMO terms** which of these functional groups involve (or are involved in)
   "resonance".

   E. (4 min) Generic versions of Esmolol are on the market. Suppose a manufacturer proposed a **"chiral switch"**, and you
   were an officer of the U.S. Food and Drug Administration in charge of supervising **clinical trials**.   Would you suggest
   comparing equal **concentrations of the old and new forms** (1:1), or twice as much of the old form (2:1), or twice as
   much of the new form (1:2)? **Give a reason** for your recommendation.

   F. (4 min) Explain how *d*-tartaric acid might be useful in preparing material for research relevant to this chiral switch.

Question 2 (cont.)

G. (3.5 min) Directions for intravenous administration of the drug caution "BREVIBLOC SHOULD NOT BE ADMIXED WITH SODIUM BICARBONATE". Given that bicarbonate is a weak base and not normally harmful during injection, why do you think the admixture might be dangerous? (Hint: the structure showing HCl floating free is erroneous. Bad idea to inject raw HCl.)

3. The synthetic cancer drug candidate E7389 (right) is remarkable because it possesses so many chiral centers.

A. (3 min) Draw a **small circles around each chiral center** in the formula.

B. (4 min) Redraw below enough of the **chiral center that is nearest the top** in the formula so that you can **label priorities**, and then **give a systematic CIP name** to its configuration.
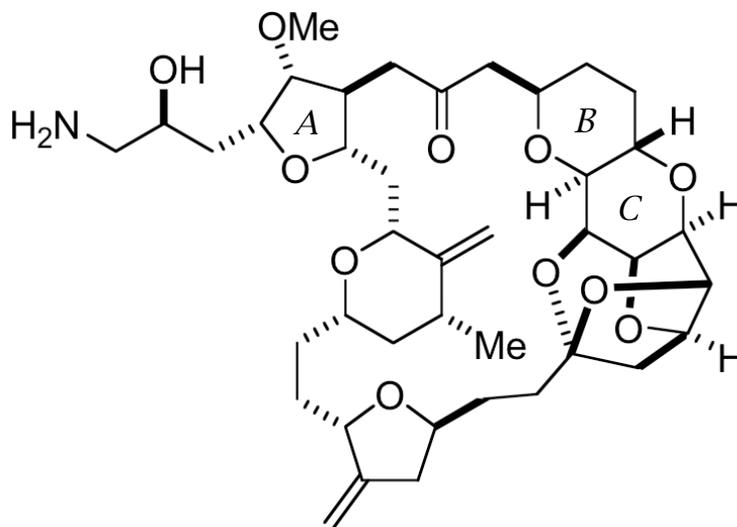
C. (8 min) The fused 6-membered rings labeled "*B*" and "*C*" in E7389 have a conformation similar to that of "trans-decalin". The partial structure below shows **Ring C** with most of the atoms attached directly to it. **Complete this structure to include Ring B and all the atoms attached directly to it**. Don't worry about shading the bonds realistically, but do be careful to **draw lines at the correct angles**.   [The small Ring *C* is for practice.]
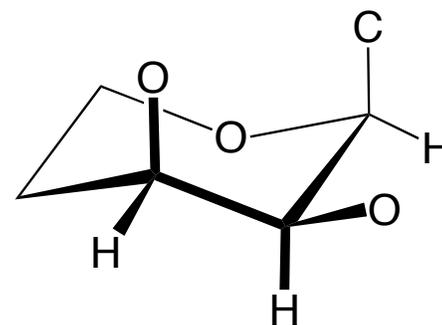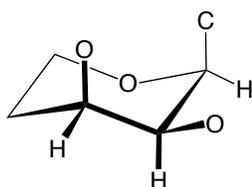
Question 3 (cont.)

D. (2 min) Is it possible that the formula of E7389 represents a *meso* configuration?

E. (6 min) What are the **likely sources of significant strain** involving the **5-membered ring "*A*"** near the top left of the formula for E7389? **Explain whether** you expect this ring to be **planar**.

4. (8 min) Why was it important to measure the heat of formation of carbon atoms in order to be able to use constitutional formulas to estimate molecular energy? (Try to mention two other "kinds" of heat in your answer. A diagram may help.)

5. (10 min) Use the circles to draw **Newman projections** for the *anti, anticlinal-eclipsed*, and *gauche* conformations of butane. Give **numerical** values for their relative **energies** (defining anti as 0). Use these numbers to **estimate one equilibrium** constant **and one rate** constant.

anti

Energy = 0

anticlinal-eclipsed

Energy = _____

Gauche
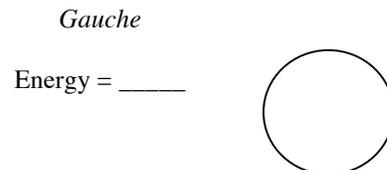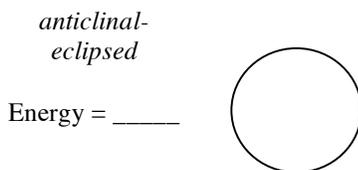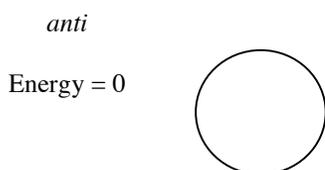
Energy = _____

Rate Constant *k*

Equilibrium Constant *K*

6. (4 min) Explain a way in which "correlation energy" and "strain energy" might be considered to be **analogous** concepts.

7. (4 min) Write a **mathematical** formula for a $2p_x$ orbital.
                        (don't worry about constants).

8. (15 min) Identify the "intramolecular HOMO-LUMO mixing" within the **amide** functional group, and **explain how it affects** each of the listed molecular properties:

Identify HOMO/LUMO mixing:

 heat of formation:

bond distances:

bond angles at N:

ease of rotation about the C-N bond:

reactivity as an acid:

reactivity as a base:

9. (9 min)   Choose **any reaction process that involves several steps** and draw a mechanism using curved arrows to show every electron (pair) shift involved   (*e.g.* alkene + Cl_2 → dichloroalkane; **or** alkane + Cl_2 → alkyl chloride + HCl; **or** NH_3 + Cl_2 → NH_2Cl + NH_4Cl; **or whatever**). No discussion of HOMOs and LUMOs required, but draw the arrows carefully.