

CH 637
Midterm Exam
Wednesday, February 15, 2006

Please write your answers in the blue books provided.

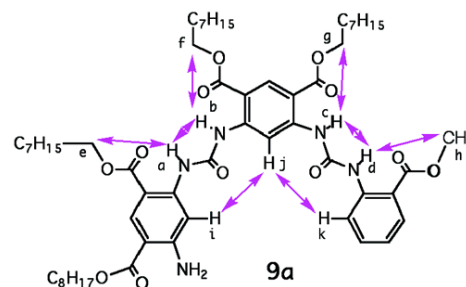
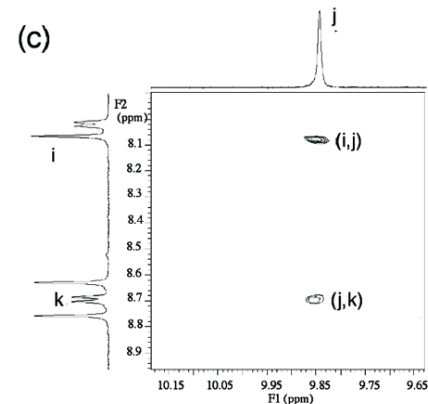
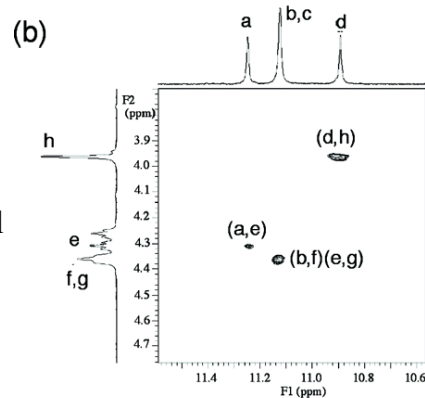
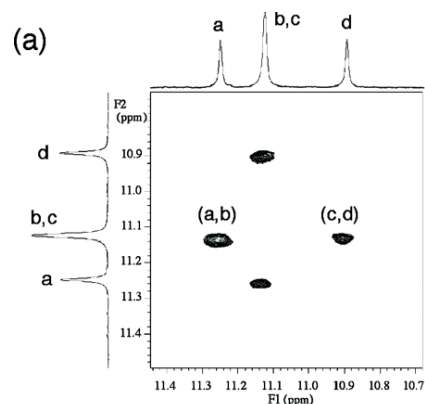
1. (30 points) A recent report (Zhang, A.; Han, Y.; Yamato, K.; Zeng, X. C.; Gong, B. *Org. Lett.*, **2006**, ASAP, <http://dx.doi.org/10.1021/ol0526322>) discusses the properties of oligoureas like the one shown below. Molecular mechanics modeling was employed to evaluate whether the molecule was folding into a helical conformation. The ROESY spectrum provides experimental information about the presence of through-space H-H interactions; the intensity of the cross peak is inversely proportional to the distance between interacting hydrogens.

The two lowest energy conformations of 9a is shown on the following page; energy and metrical parameters (AMBER force field) are in the table included. Answer the following questions based on this data.

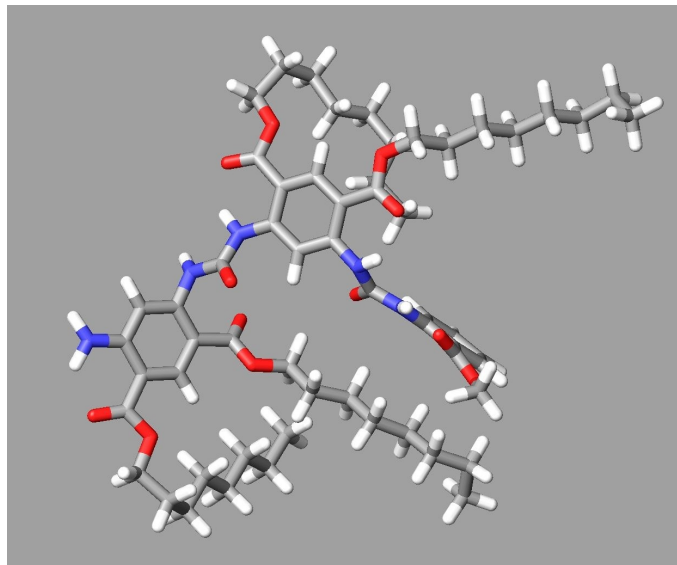
A. Explain how to judge which low-energy conformers are relevant to evaluating the ROESY data.

B. A total of 852 unique structures were found in a conformational search, all more than 5 kcal/mol above the lowest. Should we be concerned about any more of these in evaluating the structural behavior?

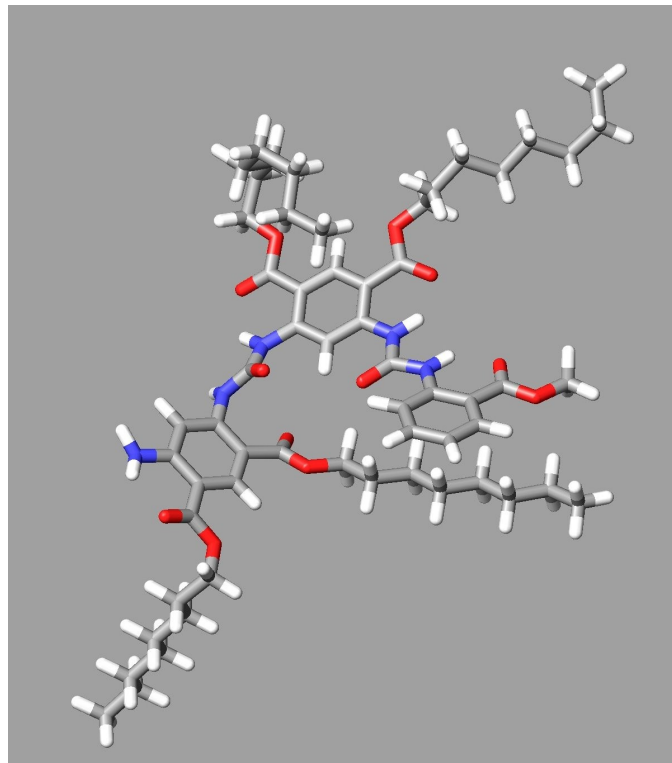
C. AMBER is a force field that was developed for modeling of proteins and other polypeptides. Using your understanding of the constituent elements of a force field, explain why this should be an appropriate model for this and related compounds.



Conformer	Energy (relative, kcal/mol)	a-b	a-e	b-f	c-d	c-g	d-h	i-j	j-k
1	0	2.238	5.177	4.192	2.106	4.377	4.322	6.092	4.805
2.	0.75	2.266	5.246	4.358	2.024	4.316	4.411	5.999	4.354



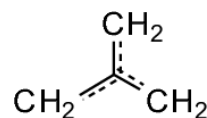
Conformer 1



Conformer 2

2. (40 points) Consider the molecule trimethylenemethane.

A. Set up the secular determinant needed to solve the Simple Huckel Theory approach to finding the pi molecular orbitals for this compound.



B. The roots of the secular equation are $0, 0, \pm\sqrt{3}$. Sketch an energy level diagram showing the MO occupations.

C. The wavefunctions are: (the center carbon is C1)

$$\Psi_1 = 0.707 \varphi_1 + 0.408 \varphi_2 + 0.408 \varphi_3 + 0.408 \varphi_4$$

$$\Psi_2 = -0.408 \varphi_2 - 0.408 \varphi_3 + 0.816 \varphi_4$$

$$\Psi_3 = 0.707 \varphi_2 - 0.707 \varphi_3$$

$$\Psi_4 = 0.707 \varphi_1 - 0.408 \varphi_2 - 0.408 \varphi_3 - 0.408 \varphi_4$$

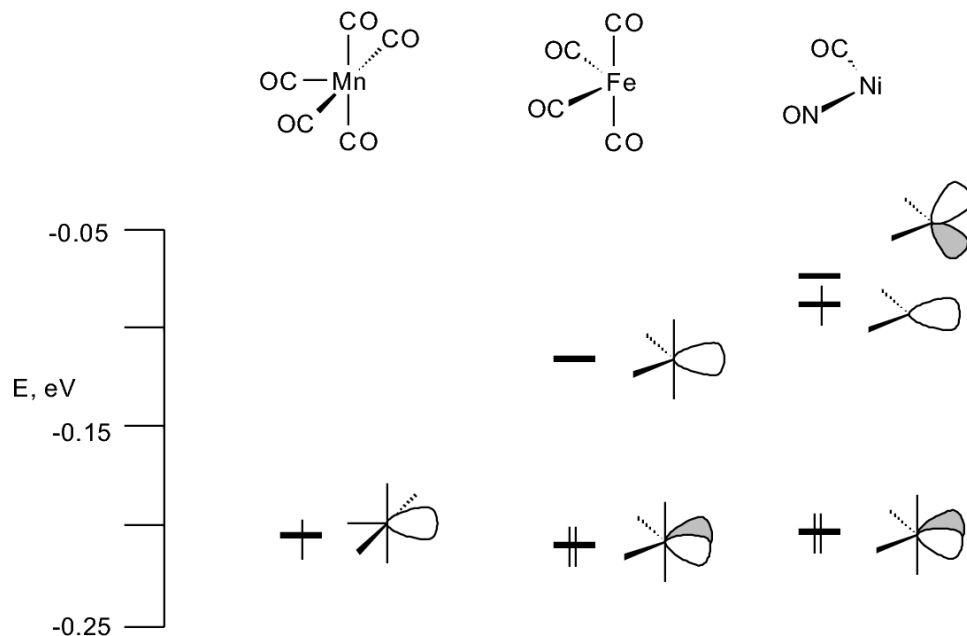
Calculate the total pi energy for the system.

D. Calculate the bond order for all pi bonds.

E. Calculate the atomic charges for all carbon atoms.

F. Describe how you view the stability and reactivity of this molecule based on the MOs.

3. (30 points) Roald Hoffman (Nobel Prize winner, 1981) has used perturbation MO theory to develop a simplified model called the *isolobal analogy* to predict how metal fragments will interact with ligands. Essentially, this says that a metal fragment will have a collection of frontier orbitals that parallels the number and symmetry of frontier orbitals in an organic fragment, and that stable metal complexes will be analogous to stable organic molecules. Several of these are shown below. The energy scale reflects the relative energies of the fragment MOs, and simplified diagrams of the MO's are provided.



A. For each of the three fragments, explain which organic fragment (CH_3- , $\text{CH}_2=$, $\text{CH}\equiv$) provides the best isolobal analogy.

B. Provide a qualitative frontier MO diagram for a carbene (CH_2).

C. Only one of these metal fragments will form a stable carbene complex. Use a perturbation MO approach to choose which one is best, and construct the energy level diagram for this stable carbene complex ($\text{L}_n\text{M}=\text{CH}_2$) for one of these based on this isolobal analogy. Predict the orientation of the plane of the CH_2 group with respect to the metal ligands.