Chemistry 4021/8021 **Computational Chemistry** 3/4 Credits

Spring Semester 2014

(Due 2 / 26 / 14)

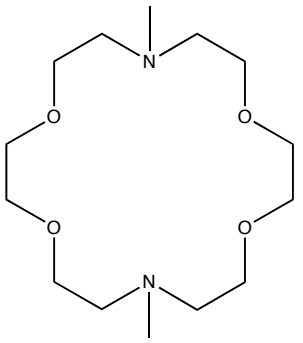
Using PC Model, answer the questions below. If you have questions/issues working on this Problem Set, do please consider using Piazza to address them.

1. What are the parameters for the force constant (mdyne/Å) and equilibrium bond length (Å) for the bond between a carbonyl carbon and a carbonyl oxygen in each of the MM3, MMX, and MMFF94 force fields? What is the parameter for the equilibrium bond length between two sp3 carbon atoms in the MMX force field? If you were to pick a "canonical" value for a C–C single bond between two sp^3 carbon atoms, what would it be to the nearest hundredth of an angstrom (explain how you made your choice)? How does that compare to the MMX parameter? Run a geometry optimization of ethane with the MMX force field. Is the optimized C–C bond length equal to the MMX equilibrium bond length parameter? If not, explain why not.

2. Oh no! Someone spilled a solution of plutonium salts onto the Chemistry Department's softball trophy from that famous 1934 championship that saw Mathematics and Chemistry go 73 scoreless innings over the course of four days before I. M. Kolthoff himself powered one over the left field fence, shattering the windshield of the Dean's Cadillac V16 Aerodynamic Coupe.

   You probably know that plutonium (Pu) is one of the deadliest substances on Earth in addition to being highly radioactive. But, we can't throw away the trophy! The only remedy will be to soak the wooden base, into which the Pu has leached, in a solution containing a sequestering agent that will extract the Pu from the wood until the remaining amount of Pu in the wooden base falls below femtogram levels. The organic and inorganic chemists have huddled together, and propose the 3 molecules shown on the next page, each of which can be synthesized for the indicated cost per gram. Given that this money has to come out of the seminar donut fund, they want to choose the most cost effective option. Which molecule should they make? Justify your answer on the basis of molecular mechanics calculations, explaining precisely and in detail what you did in order to come to some

conclusion. (As it is mildly tricky to interpret stereochemistry for the final structure, absolute assignments at each position are provided for completeness.) For purposes of this exercise, let's assume the speciation of Pu is entirely high-spin Pu(IV).



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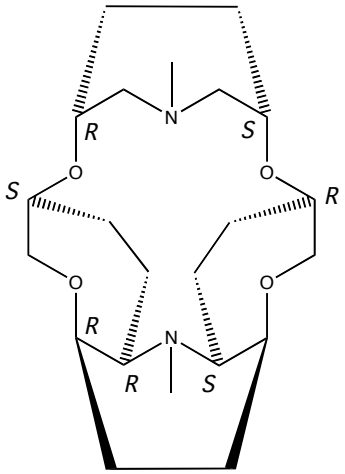

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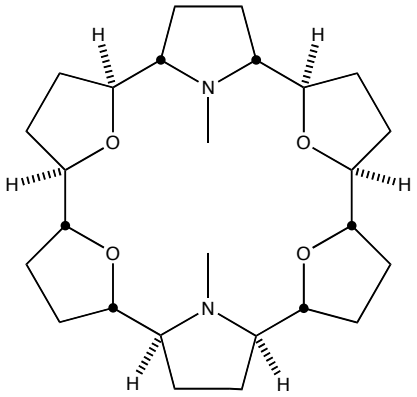

$10.00

3. Consider the interaction between two molecules of pyrazine (i.e., the pyrazine dimer). What geometries do pyrazine dimers adopt and what are their associated complexation energies as calculated with the MMX, MM3, and MMFF94 force fields? Compare/contrast the different force-field results. From the components that contribute to your results, what can you say about the nature of the intermolecular interactions in this dimer (i.e., what type of interaction(s) is/are dominant?)

Now, assume that you would like to create a force field *specific* to the pyrazine dimer. And, assume that you have access to supercomputing

resources that allow you to compute "exact" interaction energies for any geometry, but the timeline of the project limits you to the calculation of no more than 100 single-point energies. The ultimate goal of the project is to design a force field that will approximate the exact interaction energies in a coarse-grained fashion; that is, think about how you might reduce the number of variables from 54 ($3N - 6$ for two pyrazine molecules) to a much smaller number, and then how would you sample over those variables and come up with an overall function fitting the relevant energies. How would you choose your 100 points?