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

Spring Semester 2010

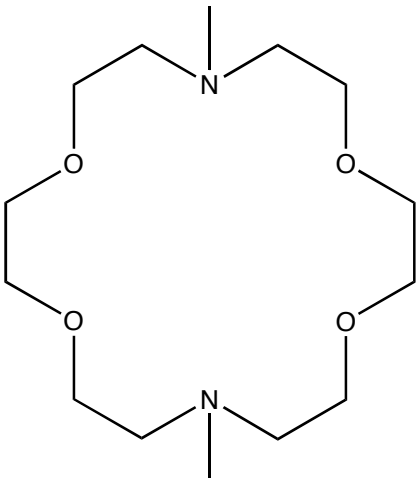
(Due 2 / 22 / 10)

Using PC Model, answer the questions below.

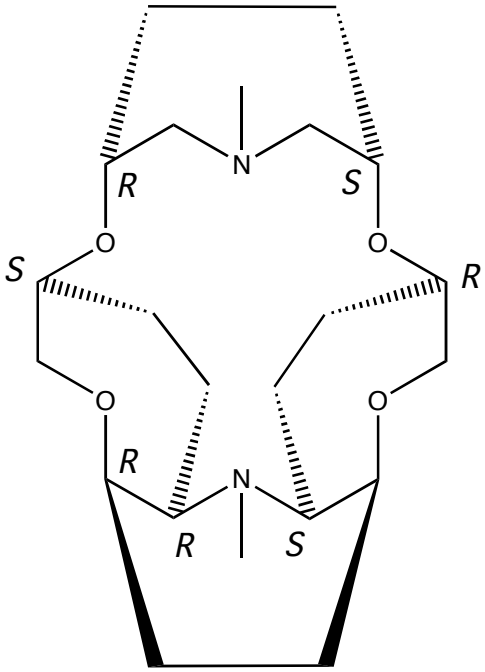
1. In the AMBER and MMFF94 force fields, what are the parameters for the force constants and equilibrium bond lengths for the bond between an alkyl carbon and an amine nitrogen? How closely do the two force constants agree? Optimize methyl amine using the AMBER force field. What is the C–N bond distance and what is the bond stretching strain? Now, fix the C–N bond to a *different* bond length at least 0.05 Å longer and compute the bond stretching strain. Is it equal to the expected value? Explain how you carry out this calculation and how you compute the "expected value". Stretch the C–N bond by the same amount with MMFF94. Is the increase in bond stretch strain for MMFF94 consistent with the AMBER value and the relative force constants for the two force fields? If not, 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.

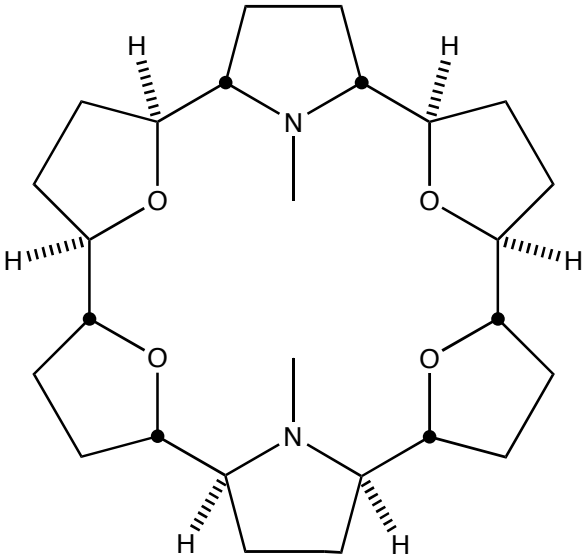
   You probably know that plutonium (Pu) is one of the deadliest substances on Earth in addition to being highly radioactive. But, we can't throw away the trophy! The only remedy will be to soak the wooden base, into which the Pu has leached, in a solution containing a sequestering agent that will extract the Pu from the wood until the remaining concentration 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).



$1.00

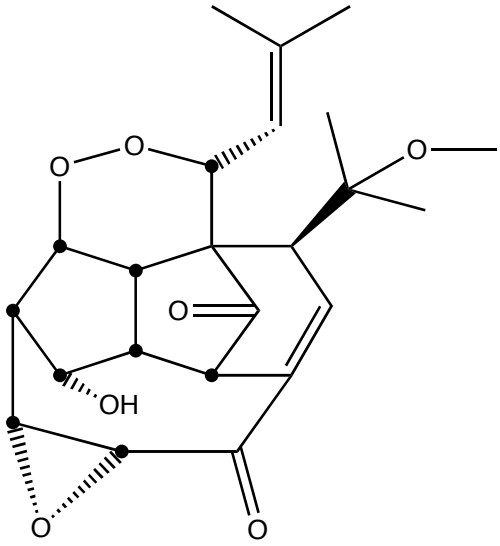


$1000.00

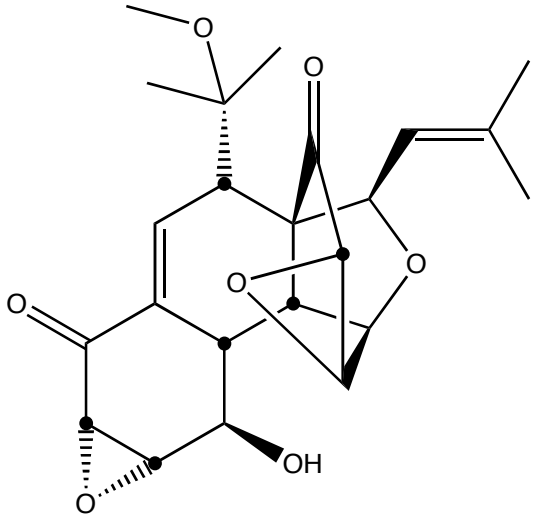


$10.00

3. We will use the MMX force field for this problem.



A



B

If your last name begins with any letter A through M, you are responsible for the structure on the left, **A**. If your last name begins with any letter N through Z, you are responsible for the structure on the right, **B**. Your responsibility is to find the two lowest energy structures that you can for your molecule. As you work, if/when you find a lower-energy structure, save it as a file so that you don't lose it (of course, you can save as many files as you like if you don't want to lose intermediate structures while you're working).

You may decide that you want to use the GMMX utility to sample the conformational possibilities more completely. You will need to add rings and/or rotatable bonds to the search criteria using the appropriate buttons in the GMMX dialog box. You might want to play with GMMX a bit in a simpler system to get a feel for what it does, and choose fewer than 100,000 steps unless you want to wait a LOOOOOONNNNNNGGGGG time. If you DO use GMMX, look carefully at your final structures to ensure that no stereochemistry was changed during the stochastic search process—it *can* happen.

Full credit for this problem consists of emailing me PC Model text files corresponding to your two *lowest-energy* structures (so that I can run the molecules, too, and verify your steric energies). A PC Model text file looks like, for example:

{PCM Untitled
NA 9
FL EINT4 UV1 PIPL1 DIELC1.000000
ATOMTYPES 7
SSNAME UNTITLED
AT 1 1 -1.6071 -0.7522   0.1458 B 2 1 4 1 5 1 6 1 S 0
AT 2 1 -0.3666 -0.3530 -0.6244 B 1 1 3 1 7 1 8 1 S 0 C 0.28
AT 3 6   0.3059   0.6775   0.0838 B 2 1 9 1 S 0 C -0.68
AT 4 5 -1.3425 -1.1024   1.1490 B 1 1 S 0
AT 5 5 -2.2743   0.1066   0.2746 B 1 1 S 0
AT 6 5 -2.1504 -1.5465 -0.3735 B 1 1 S 0
AT 7 5 -0.6345   0.0190 -1.6178 B 2 1 S 0
AT 8 5   0.3098 -1.2062 -0.7317 B 2 1 S 0
AT 9 21   1.0950   0.9114 -0.4339 B 3 1 S 0 C 0.4
mmenergy MMFF94 -1.517098
dipole_moment 2.245643
moment_inertia 2.340497 9.029104 10.319803
}