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

Spring Semester 2007

(Due 2 / 20 / 04)

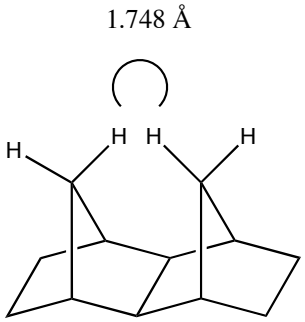
Answer Key

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 sp^3 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? 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 equilibrium bond length parameter? If not, explain why not.

   C=O parameters: MM3, 10.1 mdyne/Å, 1.208 Å; MMX, 10.8 mdyne/Å, 1.208 Å; MMFF94, 12.95 mdyne/Å, 1.222 Å.

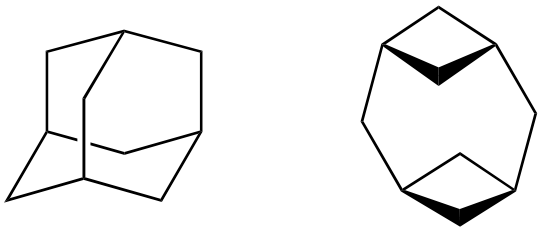
   MMX C–C equilibrium bond length: 1.523 Å. The usual value in textbooks for a C–C single bond between two sp^3 carbon atoms is 1.54 Å, which is longer. However, the geometry optimization with MMX leads to a value of 1.532 Å. The reason it is longer than the parameter is that there are other strain contributors that must be minimized other than just bond stretch (primarily the repulsive non-bonded van der Waals interactions between the H atoms on the two different methyl groups, which contribute 0.679 kcal/mol worth to the total strain of 0.816 kcal/mol).

2. Neutron diffraction establishes the very short non-bonded distance between the two hydrogen atoms shown below. The geometry of this molecule was used in the parameterization of one of the force fields in PC Model. Which one? Explain how you arrived at your answer (you shouldn't have to do any literature searching here).



The predicted H–H interatomic distances (Å) are: MMX, 1.890; MM3, 1.750; MMFF94, 1.839; AMBER, 1.977; OPLS, 1.968. It is fairly clear that MM3 is the only force field that included the geometry of this molecule in its error function, since all of the others predict repulsive forces to push these two atoms much further apart.

3. Below are two isomeric geometries that we will look at with various levels of theory to see how they compare. On the left is an adamantane framework, and on the right is a mildly exotic tricyclic isomer. We will consider both the all-carbon and all-silicon skeletons, i.e., $C_{10}H_{16}$ and $Si_{10}H_{16}$. Before doing any calculations, which structure do you expect to be more strained than the other in the case of C? What about Si? Explain your rationale. Furthermore, do you expect the magnitude of the difference in strain between the two systems to be affected by whether the framework is C or Si? Again, explain your answer. Note that I'm not looking for a "right" answer, I'm asking for your chemical instincts.



Now, using the MMX force field, compute the MMX energies for all 4 cases. Report your results. Comment on your ability to make predictions about any isomeric equilibrium that might exist in the C or Si species. Discuss the relative levels of confidence you may have in your results.

Your gut feelings are, of course, your own, and there is no penalty for being wrong. But, most people will probably feel that the presence of two 4-membered rings will make the structure on the right higher in energy than the adamantyl framework. Moreover, since C–C bonds are shorter

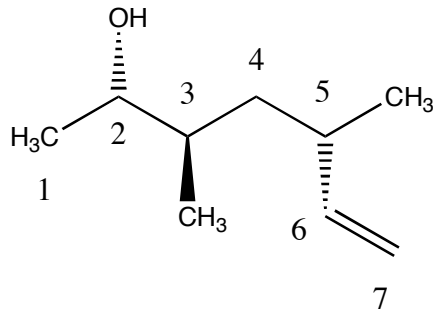
than Si–Si bonds, one might suspect that the strain will be worse for Si than for C, so that the energetic separation might be increased for the second-row atom compared to the first.

The MMX energies (kcal/mol) computed for the two structures are, respectively: C, 17.1 and 72.9; Si, –7.0 and 50.0. Thus, there is more strain in the joined 4-ring system than in adamantane, by 57.8 and 57.0 kcal/mol for C and Si, respectively. This suggests little difference between Si and C.

One potential source of concern would be whether the atom types in the two molecules are the same (if they are not, comparison of strain energies is not meaningful). However, the reported heats of formation (kcal/mol), which take into account any difference in atom types, are –31.5 and 24.0 for C and –4.6 and 52.4 for Si, which represents a negligible change.

One's confidence in the results is probably higher for C than for Si, since the hydrocarbons are not that unusual (adamantane is a commodity chemical) and molecules in the parameterization set include substructures found in the targets. For Si this is not true, and one can wonder, indeed, how parameter for SiH bonds, angles, etc., were developed. We'll explore this more in the next problem set.

4. Read the case study at the end of Chapter 2 of the textbook carefully. We will consider a slight variation of the molecule discussed there, as illustrated below:



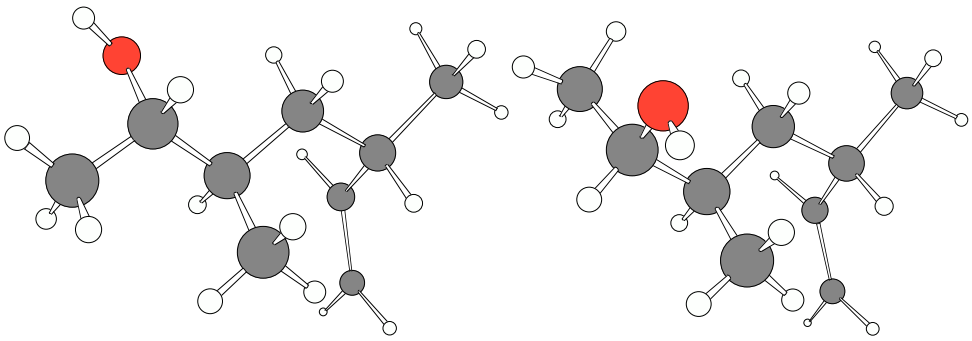
Using the MMX force field, optimize 3 different structures for this molecule, print them as tube structures, and label each page with the energy of the illustrated structure.

Any set of 3 structures is acceptable.

Now, use the GMMX utility to characterize the conformational possibilities more completely. You will need to add the 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. Play with the Setup queries a bit and look at the output files that get generated with a text editor.

After completing the GMMX survey, answer the following questions: 1) What is the global minimum and its energy (print it out and label it)? Was this one of the three structures you found on your own? 2) What fraction of the 300 K population does the global minimum comprise? 3) Is one of the structures that you *did* find (that is *not* the global minimum) amongst those found by GMMX? What fraction of the 300K population does *it* comprise? 4) What is the 300 K Boltzmann-averaged coupling constant $^3J_{HH}$ between the H atoms on C(2) and C(3)? What is the value of $^3J_{HH}$ for each of the three structures that you found on your own?

Below are two structures that are essentially degenerate and represent the lowest energy species found by GMMX. Either is acceptable as the optimized global minimum from GMMX:



1) The MMX Steric Energy is 8.4 kcal/mol and the Heat of Formation is predicted as –68.85 kcal/mol.
2) 15.6%
3) per your own results.
4) 6.3 Hz for the average, the three conformers per your own results.

What if the stereochemistry at C(2) were to be uncertain? Describe, based on your calculations thus far, what combination of modeling and spectroscopy might be done to resolve the absolute configuration at C(2). You don't have to do any additional calculations, just describe what you *could* do.

One could do the same thing for the other C(2) epimer and examine whether the relevant coupling constant (or indeed any *coupling constant) was significantly different for the two stereoisomers. Comparison to experimental NMR data would then presumably settle which was correct.*