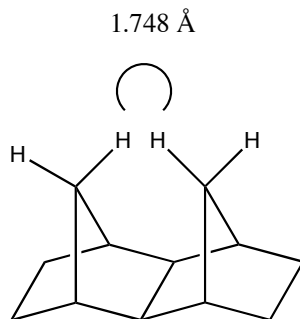
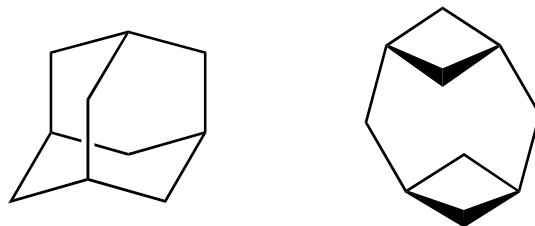


Using PC Model, answer the questions below.

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.
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).

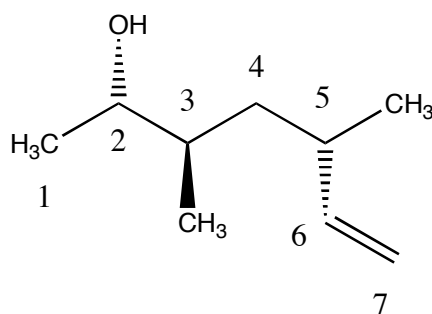


3. Below are two isomeric geometries that we will look at with various levels of theory to see how they compare. On the left is an adamantane framework, and on the right is a mildly exotic tricyclic isomer. We will consider both the all-carbon and all-silicon skeletons, i.e., $C_{10}H_{16}$ and $Si_{10}H_{16}$. 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.

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.

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 ${}^3J_{\text{HH}}$ between the H atoms on C(2) and C(3)? What is the value of ${}^3J_{\text{HH}}$ for each of the three structures that you found on your own?

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.