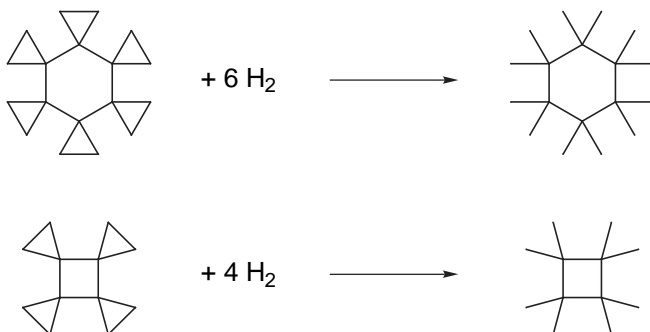


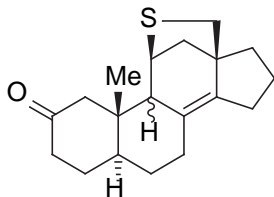
Using PC Model, answer the three questions below.

1. Using the MMX force field, compute the 298 K enthalpies of reaction for the two reactions below:



What is the enthalpy change per cyclopropane unit in each case? Examine the term-by-term change in each case and provide a physical explanation for the difference in the per-cyclopropane-bond change in the two molecules.

2. You have made the steroid derivative shown below, but are not certain of the stereochemistry of the indicated ring-junction proton. Happily, this proton is readily seen in the NMR spectrum, since it is allylic and coupled to only a single other proton. The doublet coupling constant is 4 Hz. Which isomer did you make? Explain how you arrived at your answer.



If you had carried out the reaction under thermodynamic conditions (i.e., conditions that would give an equilibrium distribution of the two epimers) what ratio of the two products would you expect at 298 K based on MMX, MM3, and MMFF calculations (show your computations, please)? What assumption(s) did you use in arriving at these answers? Finally, for one of these force fields, switch from using a charge-charge electrostatic term to a bond-dipole/bond-dipole term.

How would your answer change vis a vis the equilibrium distribution? What if you maintain a charge-charge term, but change the dielectric constant to 4.0?

3. Polyalanine is well known to form  $\alpha$  helices in aqueous solution, while polyglycine has less of a tendency to do so. Construct  $\alpha$ -helical structures of (Ala)<sub>6</sub> and (Gly)<sub>6</sub>, end-capped with *N*-acetyl and MeNH groups at the N and C termini, respectively (don't try to cap the ends until you've already fully built the structure). With mark H-bonds turned on, minimize these structures. Evaluate your final structures with some care to ensure the optimization proceeded to give a reasonable  $\alpha$  helix. Now, do the same thing, but for  $\beta$  sheet structures of both hexamers. Are the computed energy differences between  $\alpha$  helix and  $\beta$  sheet for the two cases consistent with the experimental observation noted above? Examining the term-by-term contributions to the MMX energies, what is different about Ala and Gly (i.e., what causes the computed difference)? Provide a chemical interpretation of this difference and justify that interpretation. An experiment that may help you in your thinking is to try to optimize a  $\beta$  sheet structure for (Val)<sub>6</sub>. Finally, how do the computed dipole moments for the  $\alpha$  helices and the  $\beta$  sheets compare? What is the importance of any difference?