EXPERIMENT #4

Molecular Modeling Part II

Introduction

In this lab you will continue to hone your modeling skills using the Spartan program. Several key concepts that were recently covered in class will be examined computationally and compared with known experimental data. As with the other experiments, the goal here is not to simply get the "right" or "expected" answer, but to gain an appreciation for the techniques that organic chemists employ to solve problems. If necessary, please look up your notes from Molecular Modeling I to reacquaint yourself with Spartan and review some of its basic commands.

Part I. Substituted cyclohexanes

In this part, you can explore the relative stabilities of several substituted cyclohexanes and also investigate their chirality. In all cases, you should minimize your molecule in the Builder, then optimize the geometry using the semi-empirical AM1 method. Feel free to turn the structures around as much as you wish and make sure that you see the interactions that might stabilize or destabilize the individual conformer. The cyclohexane template provided under the "Rings" menu is a useful tool for building your structures.

• Build and optimize both chair conformers of methylcyclohexane and record their heats of formation. Using the difference in the heats of formation, calculate the amount of each species present at equilibrium. Repeat this calculation for tert-butylcyclohexane. Refer to the beginning of Chapter 8 of your text if you are unsure how to proceed. For your calculations, assume ΔG ≈ ΔH_{rxn}, and set up your calculations so that K = [equatorial]/[axial].

• Build and optimize both chair conformations of cis-1,3- and trans-1,3-dimethylcyclohexane. As before, record their heats of formation and compute the equilibrium ratios of the conformers for each compound. Note how these structures are related to each other and determine whether each structure is chiral.

Part II. Investigating relative acidities with electrostatic potential maps

As you might expect, the hydrogen in a stronger acid has a greater partial positive charge than that in a weaker acid. In other words, a stronger acid has a more "electron poor" hydrogen than a weaker one. In this exercise, you will assess the acidity of various compounds by examining their electrostatic potential maps. The electrostatic potential maps will let you identify electron poor (blue) and electron rich (red) regions of the molecule.

• Comparing the acidities of ethane, ethylene, and acetylene: Build these three compounds and optimize using the semi-empirical AM1 method. Be sure to request the electron density (for surface) and electrostatic potential (for property) before submitting the calculation. Display the electrostatic potential map of all three molecules on the same screen and record the most positive value of the potential at the hydrogen for each compound.
• Effect of substituents on acidity: Build acetic acid, trifluoroacetic acid, and trichloroacetic acid. Submit the calculations as before and record the most positive value of the potential at the carboxyl hydrogen for each compound.
• Acidity of alcohols versus phenols: Repeat the above calculations for ethanol and 2-methylphenol and record the appropriate potential values for each.

Part III. Relative stabilities of cations

Build models of 1°, 2°, and 3° butyl cations. Submit a calculation using the AM1 method. Be sure to specify that the molecule has a positive charge before submitting the job. Record the heats of formation for each cation.

Part IV. Bridgehead alkenes and cations

Build and optimize the following four species using the AM1 method. Record the heats of formation in each case. Also note the angles around the positively charged carbon in the bridgehead cation. For the bridgehead alkene, note the H-C=C-C dihedral angles.

Part V. Reactivity of Alkenes

Build and optimize the two isomeric alkenes 2-methyl-1-butene and 2-methyl-2-butene. Before submitting the calculation, request that the HOMO and LUMO surfaces be computed (just as you did in Experiment 3). Record the heat of formation and the HOMO and LUMO energies for each compound, and then display the HOMO and LUMO orbital surfaces for each. Examine these orbitals carefully, and sketch them in your notebook.

Prelab

(1) Write both chair conformations for cis-1,3- and trans-1,3-dimethylcyclohexane. Label each conformer as chiral or achiral. Are the cis-1,3- conformers diastereomers or enantiomers of each other? What is the relationship between the trans-1,3- conformers?

(2) Look up the pKa values of ethane, ethylene, acetylene, acetic acid, trifluoroacetic acid, trichloroacetic acid, ethanol, and phenol. Record these values in your notebook.
Report

Part I.
Tabulate the energies and equilibrium ratios of the substituted cyclohexanes. Remember that the set up of your calculations is required.

Part II.
Tabulate the most positive value of the electrostatic potential and the pKa value for each of the compounds in this part.

Part III.
Arrange the cations according to stability using their AM1 heats of formation.

Part IV.
Tabulate the heats of formation for all four species, the angles around the bridgehead cation, and the dihedral angles of the bridgehead alkene.

Part V.
Tabulate the heats of formation and orbital energies (converted to kcal/mol) for the two alkenes.

Questions
1. How do the calculated equilibrium ratios for methylcyclohexane and tert-butylcyclohexane compare with the experimental values reported in your text?

2. Explain the observed trend in the pKa values of ethane, ethylene, and acetylene. Compare this trend with the electrostatic potentials that you calculated.

3. Explain the effect of substituents on acidity in going from acetic acid to trichloroacetic acid to trifluoroacetic acid.

4. Using your pKa values, account for the trend in the relative acidities of a phenol, ethanol, and acetic acid. Does your computational work completely correlate with the pKa values? If not, what might be the source of the discrepancy?

5. Explain the relative stabilities of the cations you modeled in Part III.

6. Explain the differences in the heats of formation of the two alkenes modeled in Part IV. Explain the differences in the heats of formation of the two cations modeled in Part IV.
7. Compare the heats of formation of 2-methyl-1-butene and 2-methyl-2-butene. Are these values consistent with what you would expect?

8. What do the images of the HOMO and LUMO surfaces of 2-methyl-1-butene and 2-methyl-2-butene tell you about the bonding in multiple bond-containing compounds? Does this change the way you think about bonding?

9. Carefully compare the HOMO orbital energies of 2-methyl-1-butene and 2-methyl-2-butene. What does this tell you about the reactivity of the two molecules in an addition reaction with a species such as HBr? Is this what you might expect, considering your answer to question 7?