Chemistry 478 — Molecular Modeling

Laboratory #1 — Rotational Barrier in Hydrazine

In this lab you will compute the energy of the hydrazine molecule (NH_2–NH_2) as you rotate about the N–N bond. We will use two standard quantum chemistry packages: QChem (via the Spartan graphical interface) and Gaussian (via command line batch jobs).

Protocol

(1) Download the three "hydrazine" files from the lab section of the course web site. The **`hydrazine.xyz`** file contains coordinates for the molecule in TINKER format. The **`hydrazine.key`** file specifies a molecular mechanics force field to be used with TINKER. Finally, the **`hydrazine.com`** file is a Gaussian 09 input file for the molecule at the Hartree-Fock level using the 3-21G basis set. Take a look at the hydrazine.com file so that you understand how it is structured. You can submit a Gaussian 09 job from a Terminal window by using the command "g09 < hydrazine.com >& hydrazine.log &".

(2) Run a series of Gaussian 09 calculations, varying the H–N–N–H dihedral angle from 0 to 180 degrees. Extract the energy for each structure, and use your favorite plotting program to produce a plot of total energy vs. dihedral angle. You will probably need to run a calculation at 10 to 15 degree increments in the torsion in order to produce a smooth plot. As suggested in question (5) below, you can repeat the series of calculations replacing "HF/3-21G" in the **`hydrazine.com`** file with "MP2/cc-pVDZ". This will perform a more involved calculation including electron correlation at the MP2 level and using the significantly larger cc-pVDZ basis set. *[We will discuss these issues in future lectures.]*

(3) Try the same calculation in Spartan/QChem by running the "Spartan Student" program. You can draw the hydrazine molecule via the graphical interface, and then submit a similar Hartree-Fock calculation using the 3-21G basis set. You can set constraints via the Spartan interface to replicate the torsional curves computed with Gaussian.

(4) Use a plotting program (Excel, MATLAB, gnuplot, etc.) to produce a plot of the energy of hydrazine as a function of torsional angle. Note that most quantum chemistry programs output energies in atomic units (ie, 1 Hartree = 627.5 kcal/mol).

Questions

(1) Were you surprised by the hydrazine rotational profile? What is the barrier to rotation? Is this barrier significant at room temperature? Explain.

(2) Provide a molecular orbital rationale to explain hydrazine minimum energy conformation. Use frontier orbital arguments and/or detailed analysis of the actual hydrazine wavefunction to illustrate your answer.

(3) This lab demonstrates the importance of the so-called “gauche effect”. What other kinds of molecules exhibit this effect?

(4) Would molecular mechanics calculations be able to reproduce the hydrazine rotational profile? What molecular mechanics terms control such barriers?

(5) The calculations initially done in the lab were at the HF/3-21G level. Try repeating the calculations at a higher level of theory such as MP2/cc-pVDZ and compare the results for these two theory levels.