Chemistry 430 — Simulation in Chemistry & Biochemistry

Laboratory #8 — Computing the 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: the standard Gaussian program via terminal command line batch jobs, and (optionally) the QChem program via the Spartan graphical interface. Hydrazine is a colorless, flammable, highly toxic liquid with an odor similar to ammonia. It is a "high energy" molecule, used as a rocket fuel for various military missiles and deep-space rockets.

Protocol

(1) Download the **hydrazine.com** file from the lab section of the course web site (use a "right click" on the mouse to download). This is a Gaussian input file for the molecule hydrazine, and will run a molecular orbital calculation at the Hartree-Fock level using the 3-21G basis set. Open the file in a text editor, and take a look at the file so that you understand how it is structured. Note the molecule is specified in a Z-matrix format, and the value of the H-N-N-H dihedral angle is 180 degrees as given by the variable **`HNNH`** on the last line of the file.

(2) Submit a Gaussian 09 calculation from a Terminal window by issuing the command:

g09 < hydrazine.com >& hydrazine.log &

The program will optimize the molecular geometry, holding the H-N-N-H torsional angle fixed at 180 degrees, but allowing all of the bond lengths and bond angles to vary. Examine the output file, hydrazine.log, and find the final value of the energy in the lower part of the file (it should be -110.5461182 Hartrees). The large negative energy represents the stability of the hydrazine structure relative to infinitely separated nuclei and electrons.

(3) In addition to the **hydrazine.log** output file, Gaussian creates a "checkpoint" file named **hydrazine.chk**, which contains a summary of the numerical results in a binary format. This file can be converted to a human-readable form using a Gaussian utility via the command:

formchk hydrazine.chk

This command will create a file **hydrazine.fchk**, which is a formatted checkpoint file. The Avogadro program, which can be downloaded from the Software Resources section on the course website, will read **`.fchk`** files and display the molecular orbitals from a Gaussian calculation. Try this. What is the nature of the HOMO for hydrazine? *(Note: if Avogadro shows the orbital as a black mesh, try "Reset Display Types" from the Avogadro "View" menu)*

(4) Run a series of Gaussian calculations, varying the H–N–N–H dihedral angle from 0 to 180 degrees. As noted the constrained value of the dihedral angle is given as HNNH on the last line of the Z-matrix input file. You will need to vary this values using a text editor. Perform a calculation for each dihedral value, 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- or 15-degree increments in order to produce a smooth plot.

(5) Now repeat the full series of calculations with electron correlation and a larger basis set. To do this, literally replace **`HF/3-21G`** with **`MP2/cc-pVDZ`** near the top of the **`hydrazine.com`** file. This will perform a more involved calculation including MP2 correlation and the larger, "correlation consistent" cc-pVDZ basis set.

(6) The Spartan Student program is installed on the iMac computers in the Chem 430 lab. Try the same hydrazine calculations using the QChem program, which is the computational engine underneath the Spartan Student graphical interface. You can simply draw the structure using the graphical interface, and then submit a similar Hartree-Fock (HF) calculation using the 3-21G basis set. In addition, you can set constraints on the H-N-N-H angle via the Spartan interface to replicate the dihedral angle *vs*. energy curves computed with Gaussian. Documentation for the Spartan Student program and a tutorial exercise is provided on the course website.

(7) Use a plotting program (Excel, MATLAB, gnuplot, *etc*. are available on the lab iMac computers) to produce plots of the energy of hydrazine as a function of the torsional (dihedral) angle. Note that most quantum chemistry programs use atomic units for energy (*i.e*., 1 Hartree = 627.5 kcal/mol).

Questions

(1) Inspect the hydrazine.log file. How many total gaussian basis functions are used in this calculation? How many iterations were required to converge the first Hartree-Fock SCF calculation? How many cycles of structural optimization were needed to arrive at the minimum energy structure, and what criteria were used to monitor structural convergence?

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

(3) Provide a molecular orbital rationale to explain the hydrazine minimum energy conformation. Use frontier orbital (*i.e*., HOMO/LUMO) arguments and/or detailed analysis of the actual hydrazine wavefunction to illustrate your answer. There is an original research paper, **jctc-1-394-05.pdf**, on the course site for this lab that discusses these issues.

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

(5) The calculations initially done in the lab were using the Gaussian program at the HF/3-21G level. What do the toal energy values from the Gaussian calculations represent? If you were able to run calculations with Spartan Student, did that program give exactly the same total energies?

(6) In step 5 of the protocol, you repeated the rotational barrier calculations at the higher MP2/cc-pVDZ level of theory. Compare the results for these two theory levels.

(7) Do you think a "classical" molecular mechanics model would be able to reproduce the hydrazine rotational profile? What terms in a molecular mechanics model would control such rotational barriers?

(8) ***(OPTIONAL)*** If you have time, try computing the hydrazine rotational profile using coupled cluster theory – for example, at the CCSD(T)/aug-cc-pVTZ level of theory. How much time is needed to run these calculations on the lab iMac workstations?