Molecular Quantum Chemistry: Practical 3 Chem0025 2021: Assessment 2

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1. Instructions

Below is a series of tasks involving performing and analysing calculations in order to gain some chemical insight. You must complete the tasks and submit a 2 to 3 page report based on them. The report must contain three main sections:

1.1. Introduction

Here, you will briefly comment on the possible uses for computational modelling in Chemistry and you will present the structure of your report.

- **10/100**
  - 5/10 for clarity and presentation
  - 5/10 for understanding the role of Computational Chemistry

1.2. Methods

Here, you will detail *how* to carry out the work you've done. The detail should be enough to allow a classmate with no experience in Computational Chemistry to reproduce your results.

- **30/100**
  - 15/30 for clarity and presentation
  - 15/30 for completeness (did you cover each element of each calculation?)

1.3. Results

Here, you will report and discuss the results of each of the tasks.

- **50/100** (10/100 for each of the first three taskts, double for the final one)
  - 4/10 for clarity and presentation
  - 4/10 for linking the calculations with chemical knowledge

– 2/10 for accuracy of the results

A final **10/100** will be awarded for overall coherence of your report (consistent typesetting, transitions between sections etc.).

2. Tasks

For the first three calculations, use NWChem with the B3LYP functional and the basis set 3-21G. For 2.4., useGaussian with HF (Hartree-Fock) and the basis set 3-21G.

2.1. Pyridine

Pyridine has three symmetrically unique carbon sites. Which of these sites would allow an electrophilic substitution, an which ones would allow a nucleophilic substitution?

Base your answer on the distribution of charge around the molecule.

2.2. Butadiene and ethene

Report the reaction energy for the Diels-Adler reaction between butadiene and ethene, producing cyclohexene.

Is this reaction allowed under frontier molecular orbital theory? Include a visualisation of the frontier orbitals involved for your explanation.

2.3. Propene and hydrobromic acid

Propene and hydrobromic acid can react to produce 1-bromopropane or 2-bromopropane. Report the reaction energies for both cases. Which one will be favoured? Which rule does this reflect for addition reactions?

2.4. Cyclohexane conformers

Warning: for these calculations, use Gaussian with HF 3-21G.

Cyclohexane has three stable conformers: chair, twist, and boat. Compare the energies and geometry of each conformer, using descriptive bond lengths, bond angles, and dihedral angles.

Probe the potential energy surface of the isomerisation between chair and twist by performing a relaxed scan of a tactically chosen dihedral angle coordinate. In order to find the transition that you care about, you will likely have to freeze another dihedral angle.

First, sample 4 points along the relevant coordinate: chair, boat, and two in-between points. Identify the point of highest energy, and the points at either side: A and B.

Then, perform a finer scan of four points around the peak: A, B, and two in-between points.

Plot all of your calculated points as a potential energy surface. What is the energy barrier for isomerisation?