ChemWiki

Third Year TS and Reactivity Lab

Introduction

In this computational lab, you will model several pericyclic reactions by calculating and characterising Transition State (TS) structures.

In your second-year computational labs you have used Quantum Mechanical methods, through the program Gaussian, to calculate and analyse simple molecules. In this lab you will extend on these, using different Quantum Mechanical methods through Gaussian to model reaction pathways for familiar Diels-Alder reactions. You will learn how to calculate TS structures for a reaction and will gain understanding about how reactants, products and TS structures relate to a molecule potential energy surface. By analysing the geometry and MOs of the TS structures, you will gain insight into the reaction mechanism that cannot be gained from experimental organic labs alone. Different reaction paths and barrier heights will also be calculated which will give understanding to the thermodynamics/kinetics of the reactions.

The lab is split into two sections:

1) A tutorial section to work through frst. The tutorial will introduce you to the software, background and methods required to complete the lab.

2) An assessed exercise section where you will apply what you have learnt during the tutorial to model different pericyclic reactions.

Computational Methods

The lab uses Quantum Mechanics to model reaction mechanisms. Gaussian is a compuational chemistry program that will be used to run Quantum Mechanical calculations. You will be using Gaussian to calculate the minimum and transition state structures for several reactions. Two differernt methods will be used for the calculations:

PM6 - A semi-empirical method. This means that the method is parameterised using experimental data which saves computational time and resources but does result in lower accuracy than ab initio methods.
B3LYP/6-31G(d) - Where **B3LYP** is a Density Functional Theory (DFT) method. B3LYP is reasonably fast compared to other DFT or *ab inito* methods and is capable of reproducing chemical data. **6-31G(d)** is a basis set, which generally are a set of functions that typically mimic atomic orbitals and when combined linearly generate molecular orbitals. In a way, they are the building blocks of molecular orbitals. The higher the basis set, the more blocks are available to construct a molecular orbital, at the cost of computational effort.

Both of the methods approximate the Schrodinger Equation in different ways to calculate the energy of a system.

Assessment Information

Lab Objectives

The objectives of the lab are:

- Using Quantum Mechanical calculations (via Gaussian) to calculate and analyse structures and to develop understanding about the methods being used.
- Being able to explain what a Transition State and a Potential Energy Surface are.
- Being able to use chemical intuition to help locate stationary points on a potential energy surface (i.e. relate the energy balance of a reaction to its landscape).
- Being able to discuss the role of sterics and secondary orbital interactions in determining the kinetic and thermodynamic products of a reaction.

Mark Scheme

The break-down for the marks for this lab are as follows:

- **Introduction** 20%
- **Exercises** 60%
- **Conclusions** 20%
    - Main discussion (10%)
    - Further discussion (5%)
    - Presentation and writing style (5%)

Write Up

Generally, try to use clear and concise writing style: short sentences that follow each other logically, with a simple writing style. Label all tables, diagrams, and figures with self-contained captions. Use the appropriate referencing style. Consider moving long lists of images to an SI section.

> **Introduction**: This is where you should discuss the background theory and the computational methods that you have applied in this lab. You should include:
>
> - Potential Energy Surfaces and Transition States:
>
>   - What is a potential energy surface (PES)?
>   - What are the mathematical definitions of minima, maxima and saddle-points on a PES, and how can these features on the PES be related to chemical events/structures.
>
> - Computational methods:
>
>   - A brief introduction to Quantum Mechanical methods
>   - An introduction to the two methods being used including: what are the main approximations of the two methods? How are they different? Why we are using these two methods?

Exercises: Follow the guidelines for the 3 exercises to be completed in the exercise section.

Conclusion: The main part of the conclusions should summarise the key concepts of the lab and your results. You **should** include:

- An evaluation of what your results mean and the chemistry of the reactions.
- An evaluation of the computational methods used.

The further discussion element of the conclusion remains quite open and can be directed by what you found more interesting about the lab. You should consider justified suggestions for improvements or advancements on the systems studied or on the computational methods used in the lab.

Other points that you could consider include:

- Were there any difficulties encountered etc. when locating TSs? In what situations would locating the TS become more difficult?
- The accuracy of the methods, the results and the MOs.
- What ways could you obtain better descriptions of the reactions you have studied?
- Insight provided into the Diels-Alder reactions.
- Can calculations help to understand how to run the reactions studied here in a lab (e.g. reaction conditions)?
- Can calculations help to understand how to improve the reactions by modifying the reactants? (what functional groups would you add to modify the reactions?)

Report Submission

The assigned lab hours are 10.00-17.00 Mon, Tue, Thu, Fri.

The **report deadline is on Wednesday at 12.00 noon**, the second week after the end of your scheduled lab week.

You must submit on Blackboard:

- A written report as a PDF.
- A zip file containing output (.log) files from **all** calculations which you use to answer the questions.

The lab time assigned is sufficient to be able to complete the tutorial, assessed exercises and write up within the lab time. In general, it is advised that:

- The tutorial should be completed before moving on to the assessed section. It is advised that you have started on the assessed exercises by Wednesday mornig at the latest.
- All calculations should be completed by the end of Friday.
- Write up as you go, it will help you keep track of results and answers.
- Submitted reports and output files will be checked for plagiarism
- Name your output files sensibly and use a unique name (e.g. your username or shortcode: hgr16_butadiene.log)
- ChemDraw is recommended to create MO diagrams and reaction coordinates

Demonstrator Sessions

The lab will start with an introduction at 10.00 am on Monday. There will be regular demonstrator sessions on Microsoft Teams lab channel at:

Monday: 10.00 - 12.00 and **15.00 - 16.00**
Tuesday: 10.00 - 12.00 and **15.00 - 16.00**
Thursday: 10.00 - 12.00 and **15.00 - 16.00**
Friday: 10.00 - 12.00 and **15.00 - 16.00**

Outside of the above hours, please use the Year 3 Computational Labs forum, found on the 3rd Year Chemistry Laboratories and Coursework Blackboard page, to post any questions you have on the lab.

Additionally, there is a troubleshooting page for common errors.
