General scheme for computational laboratory sessions

Introduction

The goal of these computational laboratory sessions is to practice your skills in the geometry optimization of minima and transition states, as well as your ability to connect the computational results with general chemistry concepts.

Description of work

All assignments consist of the comparison between the results of two different calculations, that have to be carried out. The practices are diverse: the comparison can be between two different mechanisms (conrotatory, disrotatory) for the same reactant; or between two different reactants (different leaving groups) for the same mechanism.

In all cases, the work starts with geometry optimization of reactants and products, and continues with location of transition states. The transition state search is the most demanding part, and the selection of the initial structure for the geometry optimization will be done through the reaction coordinate method. The correct choice of the reaction coordinate may be not trivial.

An important part of the assignment, that will not be carried out in the laboratory, concerns the interpretation of the results. Was the result obtained to be expected? Why? Is there some Woodward-Hoffmann rule involved? Is there some orbital analysis to be carried out? Are there any bibliographical references supporting the results you have obtained?

Computational methods

Due to limitations in computational power, the first set of all calculations will be carried out with the semiempirical method AM1.

Then, these results will be validated against single-point DFT calculations (B3LYP 6-31G) on the AM1 optimized geometries.

The need for B3LYP reoptimization of geometries will be evaluated together

with the lecturers.

Technical aspects

Calculations will be carried out with the Gaussian03 program. The recommended graphical interface is GaussView 3.0. It is recommended to save your files in your own pendrives at the end of each session.

Recommended schedule

There will be three supervised sessions in the laboratory. Probably this will not be enough for all calculations, which will have to be completed at your local institutions.

However, in order to be able to better assist you in tackling the technical problems, it would be desirable to keep the following schedule:

Day 1 Geometry optimization of reactants and products. Evaluation of ΔV (potential energy), ΔG (free energy). Initial analysis of possible reaction coordinates

Day 2 Application of the reaction coordinate method to search for starting geometries for transition state search

Day 3 Direct geometry optimization of the transition states. Evaluation of $\Delta V^{\ddagger}$, $\Delta G^{\ddagger}$