

C7800 Introduction to molecular modelling - seminar

TSM Modeling of molecular structures

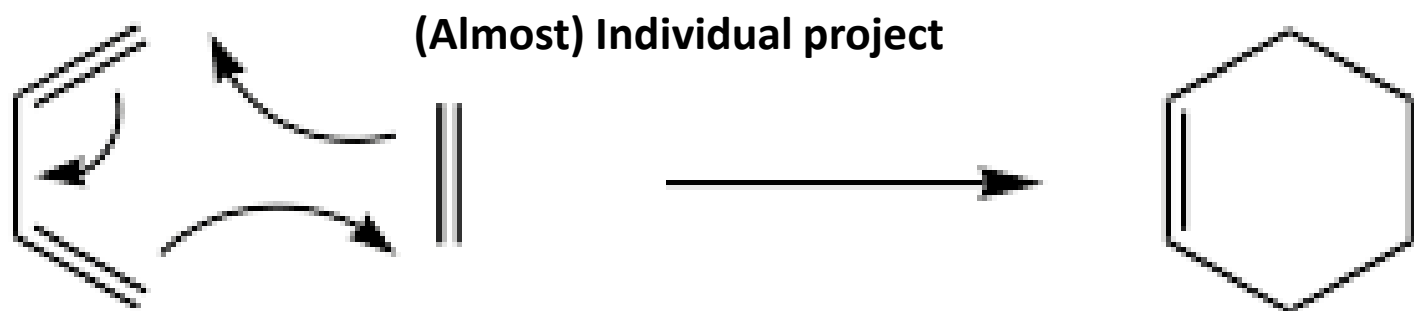
Projects
Project B - Reaction

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Diels-Alder [4+2] Cycloaddition Reaction



- **Reference manuals**
 - Gaussian (QM calculations)
 - Nemesis (preparation, visualization)
 - Infinity (submitting jobs)

How to process results

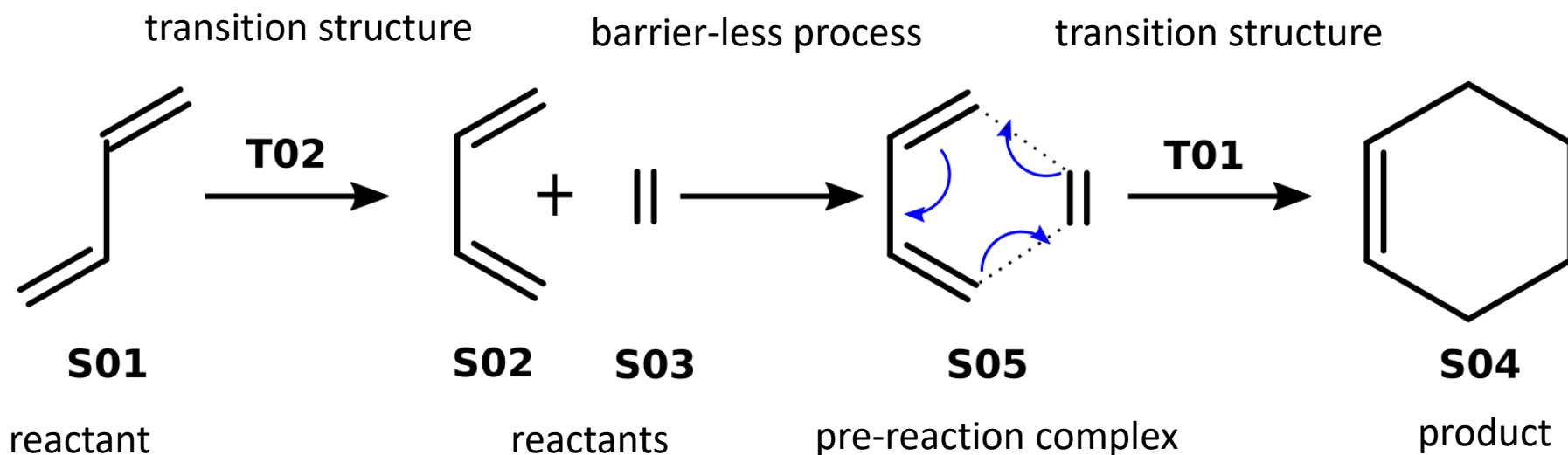
I recommend processing the results in the form of a brief protocol, which should fulfill the following requirements:

- Name and surname, name of the project and date
- For each thematic area:
 - Brief summary of the topic, including a reaction scheme, if appropriate
 - Software used, including versions
 - Results (tables and graphs)
 - Discussion of the results according to the assignment
 - Used literature (e.g., for experimental values)

Tasks

- 1) Model the butadiene molecule (*s*-cis and *s*-trans conformations), ethene and cyclohexene and optimize their geometry using molecular mechanics.
- 2) Optimize the geometry of molecules using the quantum chemical method PM3 (this method does not explicitly state the basis set). Verify that the geometries found are local minima on the PES. Determine the reaction energy.
- 3) Select a suitable candidate (reactants or product) for the single coordinate driving method (SCD). Choose a suitable approximation of the reaction coordinate for the given candidate to find an estimate of the transition state geometry.
- 4) Perform SCD using the PM3 method. Display the energy profile along the reaction coordinate. Visually verify the modeled reaction path.
- 5) Optimize the geometry of the transition state using the PM3 method. Verify that it is a first-order saddle point on the PES (put the imaginary frequency value into the protocol).
- 6) Optimize the geometry of the pre-reaction complex using the PM3 method. Verify that this is the local minimum on the PES.
- 7) Determine the activation energies of the forward and reverse reactions (with respect to pre-reaction complex and reaction product).
- 8) Determine the energy of formation of the pre-reaction complex.
- 9) Compare the calculated energies with the experimental values. Discuss any difference.

Analysis of reaction transformations



Finding T02 - optional part of the project.



Solution

Data organization

01.S01

01.opt

02.freq

02.S02, 03.S03, 04.S04 (similar to S01)

05.SCD01

06.T01

01.opt

02.freq

07.S05 (similar to S01)

08.SCD02

09.T02

01.opt

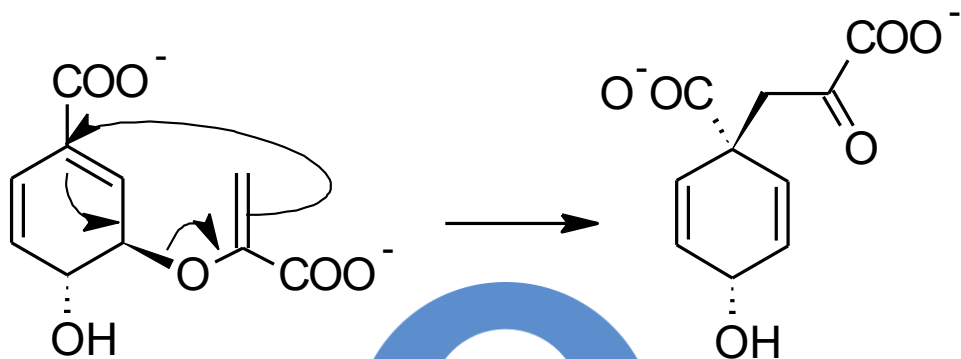
02.freq

- 1) Create models for S01, S02, S03, S04. Pre-optimize their geometry using molecular mechanics (force field MMFF94). Then optimize the geometry by the semiempirical quantum-chemical method PM3 (the basis set is not explicitly stated). Verify that the optimized geometries are local minima on the PES.

Solution, cont.

- 2) Select the appropriate starting structure and rough reaction coordinate (geometric parameter) for the SCD in order to find the T01.
- 3) Load default geometry into project "Build project". In the "Geometry" tool, select the selected geometric parameter and create a property from it (button Property).
- 4) Create an input file for SCD calculation (File->Export Structure as...->Gaussian Input). Set the calculation parameters (method, charge). Select "Single Coordinate Driving" and set the driving method (number of steps and their length). Save the input file (scd.com) and start the calculation.
- 5) Load the scd.log file into Nemesis (Project: **Trajectory**, File->Import Trajectory from...->Gaussian->Geometry 1D driving File). Analyze the course of SCD. Use the structure with the maximum energy value for calculation of T01. Then, select structure with an estimate of the pre-reaction state to find S05.
- 6) Use the selected geometry from the SCD to find the transition state. Create an input file for the calculation (File->Export Structure as...->Gaussian Input). Set the calculation parameters (method, charge). Choose "Transition Structure Optimization". Save the input file (ts.com) and start the calculation.
- 7) Perform vibration analysis for T01 and S05.

[3,3]-sigmatropic rearrangement of chorismate to prephenate



optional

➤ Reference manuals

- Gaussian (QM calculations)
- Nemesis (preparation, visualization)
- Infinity (submitting jobs)

Tasks

- 1) Model the molecule of chorismate and prephenate and optimize their geometry using molecular mechanics. Use Avogadro and try to find the global conformational state for both molecules.
- 2) Optimize the geometries of the chorismate and prephenate using the quantum chemical method PM3. Verify that the found geometries are local minima on the PES. Determine the reaction energy.
- 3) Select a suitable candidate (reactant or product) for the single coordinate driving method (SCD). Choose a suitable approximation of the reaction coordinate for the given candidate to find an estimate of the transition state geometry.
- 4) Perform SCD using PM3. Display the energy profile along the reaction coordinate. Visually verify the modeled reaction path.
- 5) Optimize the geometry of the transition state of the reaction using the PM3 method. Verify that this is a first-order saddle point on the PES (record the imaginary frequency value into a protocol).
- 6) Determine pre-reaction and post-reaction geometries. Compare them with global conformational states and discuss the difference.
- 7) Determine the activation energies of the forward and reverse reactions to pre-reaction and post-reaction state.
- 8) Compare the calculated energies with the experimental values. Discuss any difference.