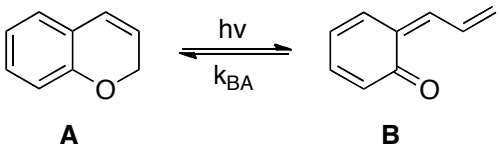
D1CH9116 - MMCO
Molecular Modelling applied to organic chemistry

Practical 7: Photochemical processes

A/ Photochemistry of benzopyran

From F. Castet, R. Méreau, D. Liotard "Photochemistry of Naphthopyrans and Derivatives: A Computational Experiment for Upper-Level Undergraduates or Graduate Students" J. Chem. Educ. ***2014****, 91, 924–928.*

This computational experiment aims to make students familiar with excited-state reaction mechanisms. It addresses the photoisomerization of the benzopyran molecule by means of semiempirical quantum chemical calculations and introduces the concept of conical intersection between potential energy surfaces.



Scheme 1: Photo-induced ring-opening in the benzopyran molecule

a. Simulation of the ground-state 'thermal' reaction mechanism

1. Characterize the reactant A and the product B, optimize their structures and confirm with vibrational frequencies. Visualize the absorption spectrum of A and B, and note the transition energy and oscillator strength toward the first singlet excited states (referred to as A* and B*, respectively).
2. Model the A⇆B reaction mechanism shown on Scheme 3 in the ground electronic state by using the CHAIN method.
3. Confirm the optimized transition-state structure by a frequency calculation.
4. Perform intrinsic reaction coordinate (IRC) calculation on the forward and reverse directions and visualize the reaction energy profile.
5. Use the results to calculate the reaction enthalpies and barriers.

B. Simulation of the excited-state reaction mechanism

1. Optimize A in the first excited singlet state and check that the optimized structure keeps a closed form.
2. Optimize B in the first excited singlet state to obtain structure B^x, and verify that B and B^x have similar geometries.
3. Model the A*⇆B^x reaction mechanism on the excited PES by using the CHAIN method. Visualize the A*⇆B^x reaction path using the graphical interface, and locate the intermediate minimum C.

C. Relaxation from the excited state to the ground state

1. Calculate the fluorescence spectrum of C. Note the transition energy and oscillator strength toward the ground state, and draw conclusions about the radiative or non-radiative character of the electron transition toward the ground state.
2. Model the C→B reaction mechanism on the ground state PES by using the CHAIN method. Comment on the possibility to form B from the thermal relaxation of C.

3. Use the same method to model the C→A reaction mechanism on the ground state PES. Comment on the possibility to back form A from the thermal relaxation of C, and on the consequences on the quantum yield of the photochemical process.

D. Results summary

Summarize graphically the photochromic reaction mechanism predicted by the CI/AM1 calculations.