

Photochemical Reversibility of Ring-Closing and Ring-Opening Reactions in Diarylperfluorocyclopentenes

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1. Introduction

Time dependent density functional theory (TDDFT) is used to study the important factors that control the photo-isomerization of diarylperfluorocyclopentenes. The calculations are carried out for free molecules and for diarylperfluorocyclopentenes perturbed by gold atoms. Potential energy surfaces for the cyclization reaction are obtained for the ground state and for the excited states involved in the photoswitching. Analysis of the computed UV/Vis spectra, the excitation energies, and the spatial distribution of the frontier orbitals of both unperturbed and perturbed molecules give an inside view of the ring opening and the ring closing. The bonding interaction in the unoccupied orbitals is considered to be the driving force for the photochemical cyclization while the antibonding interaction significantly hinders the reaction. The obtained theoretical results are in good agreement with the experimental data and provide explanation of the one-directional and bidirectional photoswitching of diarylperfluorocyclopentenes attached to gold surface.

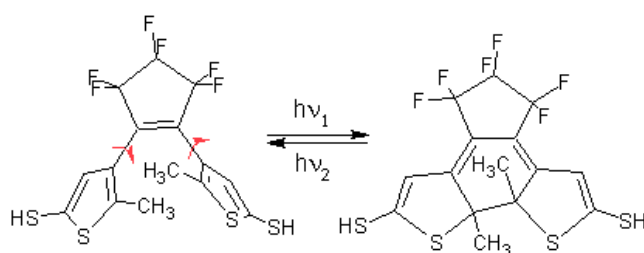


Figure 1: Diarylperfluorocyclopentenes.

2. Woodward-Hoffmann rules applied for cyclization of diarylperfluorocyclopentenes

The photoswitching of diarylethenes is a cyclization reaction for which the Woodward-Hoffmann rules are fulfilled. A hexatriene structure takes part in the cyclization reaction. For a system with $4n+2$ π -electrons the symmetry-allowed ground-state rotation is disrotatory. The disrotatory rotation leads to bonding interaction of the terminal atoms within the HOMO, as shown in Figure 2. However, such rotation will bring the methyl group attached to one of the terminal C atoms very close to the closing ring. This steric hindrance

will block the ground-state reaction. In the excited state an electron is promoted from the HOMO to LUMO. The Woodward-Hoffmann rules say that for a system with $4n+2$ π -electrons the symmetry-allowed excited-state rotation is conrotatory. The conrotatory rotation leads to bonding interaction of the terminal atoms within the LUMO, as shown in Figure 2. In the case of conrotatory rotation, the two methyl groups move away from the closing ring and do not disturb the reaction.

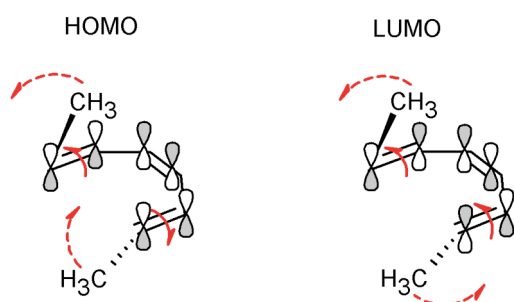


Figure 2: Woodward-Hoffmann rules applied for cyclization of diarylperfluorocyclopentenes.

3. Potential energy surface scans

Purpose of our study is to determine the reason for the higher photochemical activity of the open-ring form compared with that of the closed-ring form. We have performed a PES scan along the reaction coordinate – the distance between the two terminal C atoms that participate in the bond formation. The results of the PES scans for the ground state and for the first excited state are summarized in Figure 3.

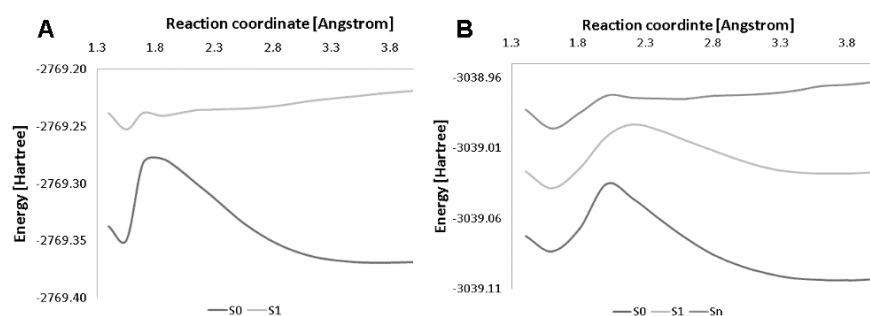


Figure 3: PES scans of diarylperfluorocyclopentene. A: unperturbed system; B: perturbed system.

4. Conclusions

The UV/VIS spectra and the oscillator strengths play an essential role for the photochemistry of the diarylperfluorocyclopentenes. Different substituents can alter the optical properties of the compounds, which allow high flexibility for the experimental design. We believe that the suggested theoretical model will provide good support to the experimentalists in their search for photoswitching systems with better reversibility and usability.