

Prediction of Thermal Cycloreversion and Fatigue-resistance in Photochromic Compounds: A Density Functional Theory Study

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Photocyclization is a reversible process of isomeric transition between the open and closed forms upon irradiation of photochromic compounds accompanied by change in their color. The two isomeric forms differ in various physical and chemical properties and find prospective applications as various optoelectronic devices such as optical memory, optical switching, displays and nonlinear optics.

Some of the most essential properties of the photochromic material which need to be satisfied for their application as optoelectronic devices, are thermal stability of both isomers, fatigue resistance, efficient photochromic reactivity: high sensitivity, rapid response etc. Prediction of these properties based on the molecular structure of the chromophores is an important component of rational design strategy. We applied DFT to predict the equilibrium geometry and absorption spectra for a benchmark set of thermally irreversible (P-type) photochromic compounds, diarylethene derivatives. From our calculations, it is evident that the accurate equilibrium geometry comparison on the basis of bond length alternation (BLA1 and BLA2) values with that of the experimental X-ray geometry and the absorption spectra (λ_{\max}) prediction using TD-DFT is best reproduced is at TD-M05/6-31G*/PCM//M052x/6-31G*/PCM level of calculation. This suggests that the basis set polarization is important to obtain the best geometry and TD-DFT method must employ polarization continuum model (PCM) for accurate spectral data prediction. The thermal cycloreversion process occurs through symmetry forbidden conrotatory electrocyclic mechanism, with transition state of strong diradical character. The activation barrier for thermal cycloreversion process was studied for a set of photochromic compounds and compared to the experimental value to validate a suitable exchange-correlation functionals in DFT method in the study of this phenomenon.

Undesirable chemical reactions occurring during the photochromic rearrangement limits the number of cycles of photochromic reactions and contributes to photochemical fatigue. In order to predict the kinetics of photochemical fatigue in already reported photochromic compounds demonstrating fatigue, we investigated the mechanism of by-product formation. We hypothesized possibility of two different routes to form the by-product – thermal and photochemical. The thermal by-product pathway involves the bicyclohexane (BCH) ring formation as a stable intermediate; while the photochemical by-product formation pathway may involve the methylcyclopentene diradical (MCPD) intermediate. In contrast to the published CAS-SCF study, we found the MCPD to be a stable intermediate. From our preliminary studies performed on the mechanism of byproduct formation, we have found that the by-product is only formed from the closed structure with a barrier of 51.22 kcal/mol between the closed form and the BCH intermediate and 16.16kcal/mol between the BCH intermediate and the by-product at UM052x/6-31G* level.

The quantitative agreement between the experimental and the theoretical data suggests that DFT methods could be successfully employed in the prediction of three out of six properties essential for design of photoswitching and data storage applications: thermal stability, fatigue resistance and absorption spectra.