

SPECTRAL PROPERTIES OF SPIRO[CHROMENE-2,2'-INDOLO]-BASED PHOTOCHROMIC MOLECULES

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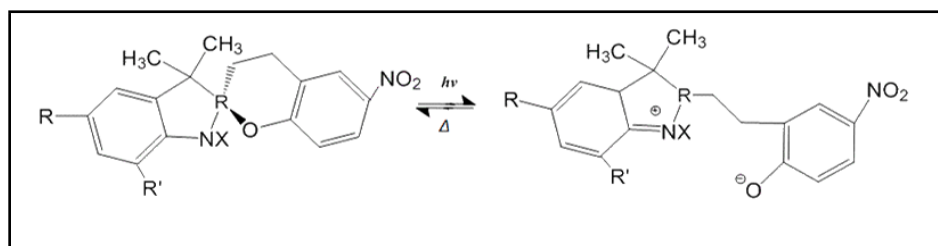
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Light-driven molecular switches are components of photochromic systems that undergo reversible structural changes when irradiated with UV light and revert to the original state when exposed to light of a different wavelength or via thermal routes. A new class of ultrafast light-driven molecular switches based on 10,3,30,4-tetrahydrospiro[chromene-2,20-indole] has been designed and synthesized recently. The spectroscopic properties and nanosecond-resolved photoinduced dynamics of five compounds in the aforementioned class were investigated experimentally¹. Fast and reversible photoinduced chromene bond-cleavage processes were discovered for these compounds. It was shown that the relaxation lifetime of one compound (R=CH₃, R¹=H, see figure) is 27 ns while the lifetime for the different compound (R=CH₂CH₃, R¹=NO₂) is 484 ns. The aim of this work is to explain how the differences in relaxation lifetimes are related to the structural and spectral properties of the molecules as well as features of the potential surfaces of their excited electronic states. It was shown earlier that modeling of potential energy surfaces (PES) of the ground and excited electronic states allows to qualitatively explain experimental results in similar compounds². In this work density functional theory (DFT) and time-dependent DFT computations at (CAM-)B3LYP/cc-pVDZ level are used. Similar mechanism of the photochemical conversion of spiropyran to merocyanine was recently investigated theoretically³. We achieved the similar result for PES of investigated compounds: starting at the ground-state geometry, the energy of the first excited state decreases in the direction of the C–O bond dissociation while the ground-state energy increases. This leads to a barrierless C–O bond dissociation in the first excited state. Further relaxation leads to a conical intersection of the ground state and the first excited state. After passing the conical intersection, the reaction continues on the ground-state PES.

Electronic excitation is accompanied by significant charge transfer. Spectral and PES properties of the reaction path intermediates were determined. Thermal pathways of the reverse cyclization reaction were investigated. Results suggest that the decrease of thermal cyclization reaction rate in compounds containing electron-withdrawing moieties is related to the higher transition-state energy barriers for the conformational changes between open-ring ground states.



KEYWORDS: Molecular switches; Excited states; TDDFT.

¹ M. Dagilienė, V. Martynaitis, M. Vengris, K. Redeckas, V. Voiciuk, W. Holzer, A. Šackus, *Tetrahedron* **69** (2013) 9309–9315.

² S. Toliautas, J. Sulskus, L. Valkunas, M. Vengris, *Chem. Phys.* **404** (2012) 64–73.

³ S. Prager, I. Burghardt, A. Dreuw, *J. Phys. Chem. A* **118** (2014) 1339–1349.