

Spectral Properties of Spiro[chromene-2,2'-indole]-Based Photochromic Molecules

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Abstract

Light-driven molecular switches are components of photochromic systems that undergo structural changes when irradiated with UV light and revert to the original state after another light-exposure or via thermal routes. A new class of ultrafast light-driven molecular switches based on spiro[chromene-2,2'-indole] has been designed and synthesized recently; fast and reversible photoinduced chromene bond-cleavage processes were discovered for five compounds of this class [1]. The relaxation lifetime of the four of the compounds is found to be in range of 20–27 ns while the lifetime of the last compound is 484 ns. The aim of the presented work is to explain how the differences in relaxation lifetimes are related to the structural and spectral properties of the molecules.

It was shown recently that modeling of the potential energy surfaces (PES) of the ground and excited electronic states allows to qualitatively explain experimental results in similar systems [2]. In this work density functional theory (DFT) and time-dependent DFT are used to investigate the PES of the two spiro[chromene-2,2'-indole] compounds with different observed properties. The wavefunction is constructed from cc-pVDZ basis set, and the results obtained by the use of three functionals – B3LYP, CAM-B3LYP and PBE0 – are compared.

The structural changes of the compounds upon light-excitation are found to be driven by a barrierless C–O bond dissociation in the first excited state. Similar mechanism of the photochemical conversion of spiropyran to merocyanine was proposed recently [3]. Changes in the absorption spectrum are shown to arise due to the formation of a second chromophore in the longer-lived compound. Electronic excitation is also accompanied by partial charge redistribution that persists in the ground-state open-ring form of the compounds. Presence of an electron-withdrawing moiety in one of the compounds results in higher transition-state energy barrier between ground-state structures, which explains the decrease of thermal cyclization reaction rate.

References

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