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Overview

A new class of ultrafast light-driven molecular switches based on 10,3,30,4-tetrahydro-spiro[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 experimentally [1]. Fast and reversible photo-induced chromene bond-cleavage processes were discovered for these compounds. It was shown that the relaxation lifetime of one compound (R=CH₃, R'=CH₃, see Fig. 1) is 22 ns while the lifetime for the different compound (R=CH₂CH₃, R'=NO₂) is 484 ns.

It was shown in earlier work [2] that modeling of potential energy surfaces (PES) of the ground and excited electronic states allows to qualitatively explain experimental results in similar compounds. The current study aims 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.

The structure optimizations were performed using density-functional theory (DFT) at the B3LYP/cc-pVDZ level. Excited state calculations employed time-dependent DFT at the same level of theory. All calculations were carried out using *Gaussian09* [3] package.

Experiments [1]

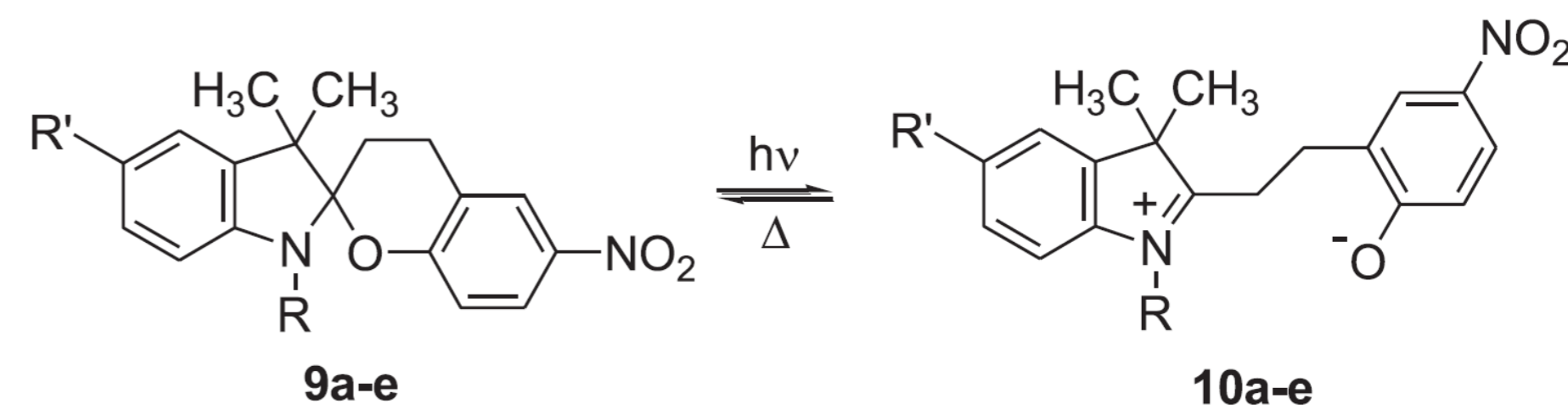
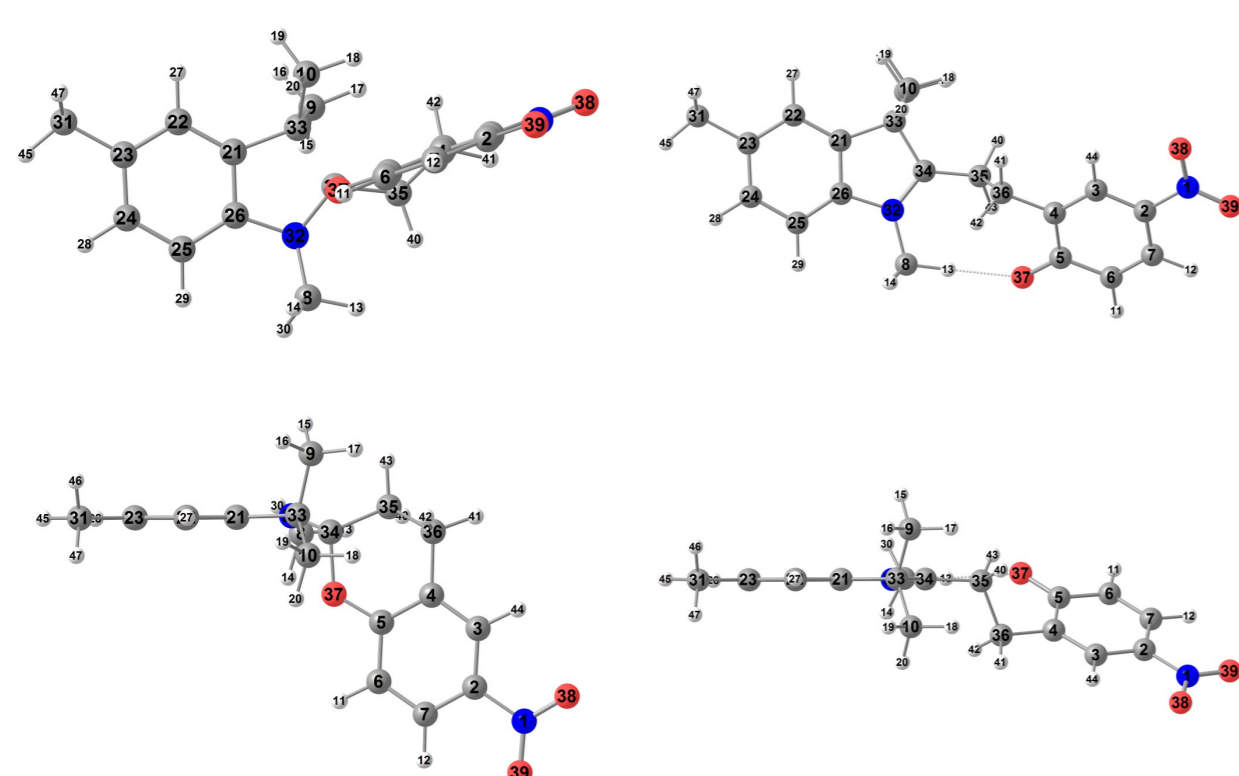


Figure 1. Photochromism of 6-nitro-1',3'-dihydro-spiro[chromene-2,2'-indoles].

Table 1. Summary of experimental data for the investigated photochromic compounds.

Compound	R	R'	Closed form: abs., nm	intensity	Open form: abs., nm	Relaxation time, ns
9c	CH ₃	CH ₃	245 313	15,7 13,6	450	22
9e	CH ₂ CH ₃	NO ₂	330 (shoulder) 380	14,6 22,1	420	484

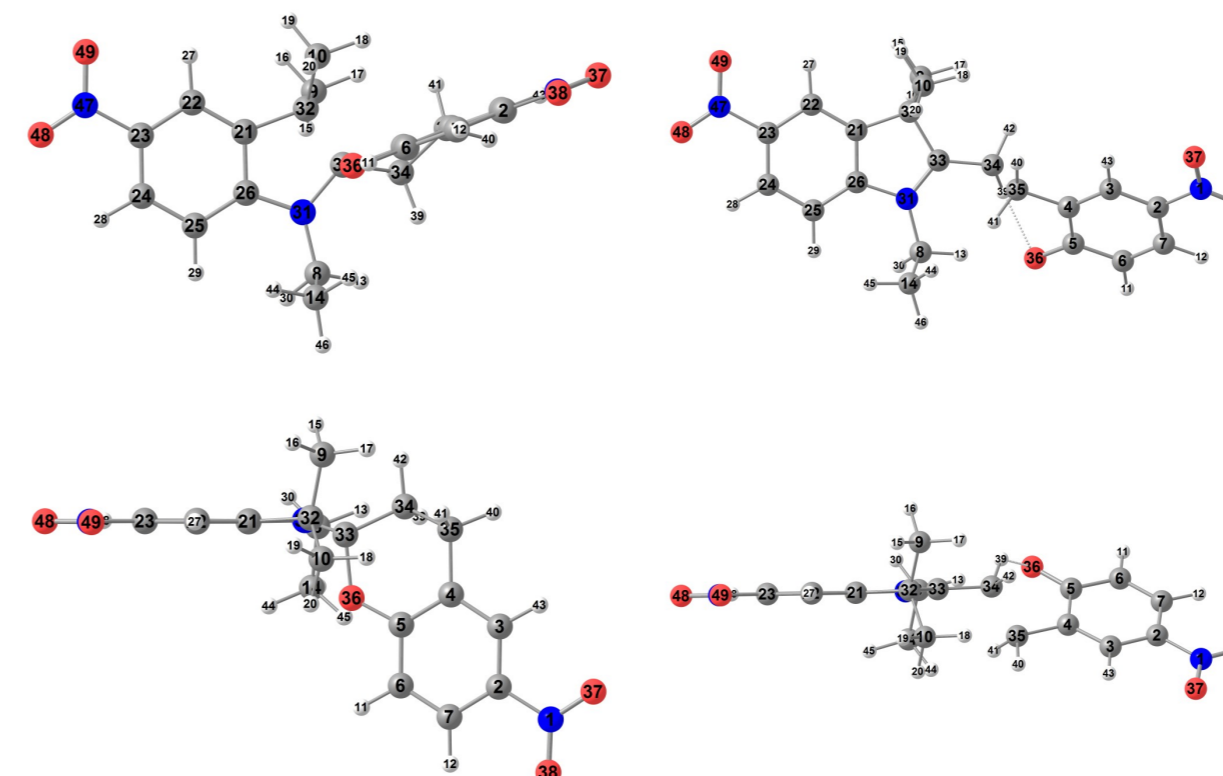
9c: methylindole + nitroisochroman



Structure	E (S ₀), eV
10c	0,98
TS	1,12
9c	0,00
TS	0,22
9c'	0,14
TS	1,35
10c'	1,16

Figure 2. Molecular structure of 9c compound: closed form (left), open form (middle) and relative ground-state energies of various conformations (right).

9e: nitroindole + nitroisochroman



Structure	E (S ₀), eV
10e	1,29
TS	1,53
9e	0,00
TS	0,31
9e'	0,13
TS	1,62
10e'	1,44

Figure 3. Molecular structure of 9e compound: closed form (left), open form (middle) and relative ground-state energies of various conformations (right).

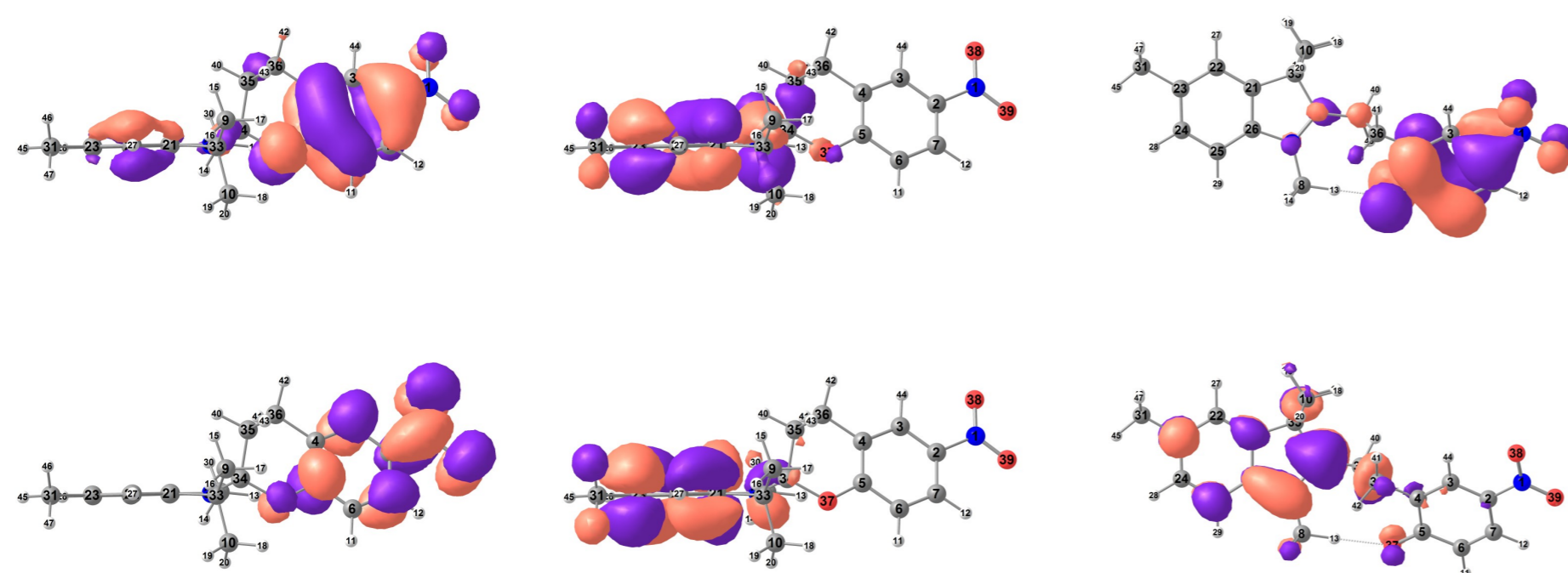


Figure 4. Molecular orbitals corresponding to the most important electronic excitations of 9c compound: lowest optically-allowed transition of both closed and open forms (left), second optically-allowed transition of closed form (middle), charge-transfer state of open form (right).

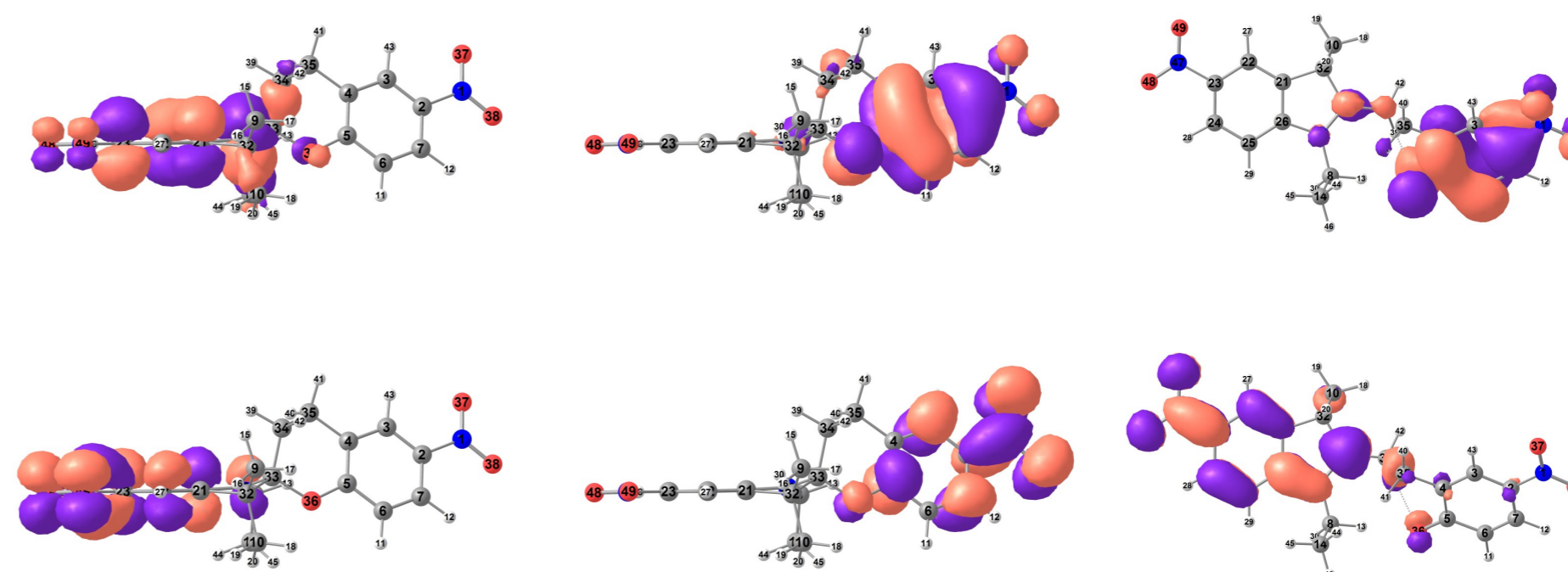


Figure 5. Molecular orbitals corresponding to the most important electronic excitations of 9e compound: lowest optically-allowed transition of closed form (left), second optically-allowed transition of closed form and lowest allowed transition of open form (middle), charge-transfer state of open form (right).

Discussion

The two investigated compounds, 9c and 9e, exhibit remarkably similar molecular structure (Figs. 2, 3). The similarities also extend to the various conformations of the ground state, i. e., local minima and transition states. Exchange of methyl group (R) with ethyl group seems to have no significant effect.

Addition of NO₂ group to the indolium moiety, however, results in the molecular group (nitroindole) with different optical properties that partly resemble those of the adjacent nitroisochroman. In addition to the nitrophenol absorption present in both compounds (exp. 313 and ~330 nm, calc. 4,2 eV), 9e also absorbs light of slightly lower energy (exp. 380 nm, calc. 3,8 eV) via the similar excitation of the nitroindole moiety (Fig. 5, left).

After the C-O bond cleavage and pyran ring dissociation, the resulting nitrophenolate moiety tends to move with respect to the indole group and, after relaxation, forms opening structures corresponding to the local minima of the ground-state potential energy surface. During the ring dissociation partial charge-separation (calculated to be around 0,5–0,6 e) also occurs; this corresponds to the emergence of low-energy excited states in the calculated electronic spectrum (Table 2; Figs. 4, 5, right). Because of the electron-withdrawing NO₂ group present in the nitroindole, both the charge-separated excited state and the resulting ground-state conformation seem to be more stable in the case of 9e compound, as evidenced by the excited-state energies (1,35 vs. 1,12 eV) and the ground-state transition barriers (0,14 vs. 0,24 eV), respectively. The presence of the meta-stable excited state would also explain the broad measured absorption of the 9e compound [1]. Thus, the changes to the optical properties of the indolium moiety induced by the NO₂ group are most likely responsible for the observed sharp decrease of thermal cyclization reaction rate in this compound.

Table 2. Calculated properties of excited electronic states for the investigated photochromic compounds.

Compound	Closed form: abs., eV (nm)	intensity	Open form: abs., eV (nm)	intensity
9c	4,16 (298)	0,35	1,35 (918)	0,13
	5,26 (236)	0,23	3,73 (332)	0,39
			4,18 (296)	0,12
9e	3,83 (324)	0,32	1,12 (1106)	0,15
	4,24 (292)	0,27	3,69 (336)	0,30
			4,30 (288)	0,17

References

- [1] M. Dagilienė et al., *Tetrahedron* **69** (2013) 9309.
- [2] S. Toliautas et al., *Chem. Phys.* **404** (2012) 64.
- [3] *Gaussian 09*, Revision **D.01**, Gaussian, Inc., Wallingford CT (2013).

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