

Effect of methoxy group substitution on energetic landscape of 3H-naphthopyrans and its spectroscopic implications on fading time and photoisomerization reaction

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Introduction

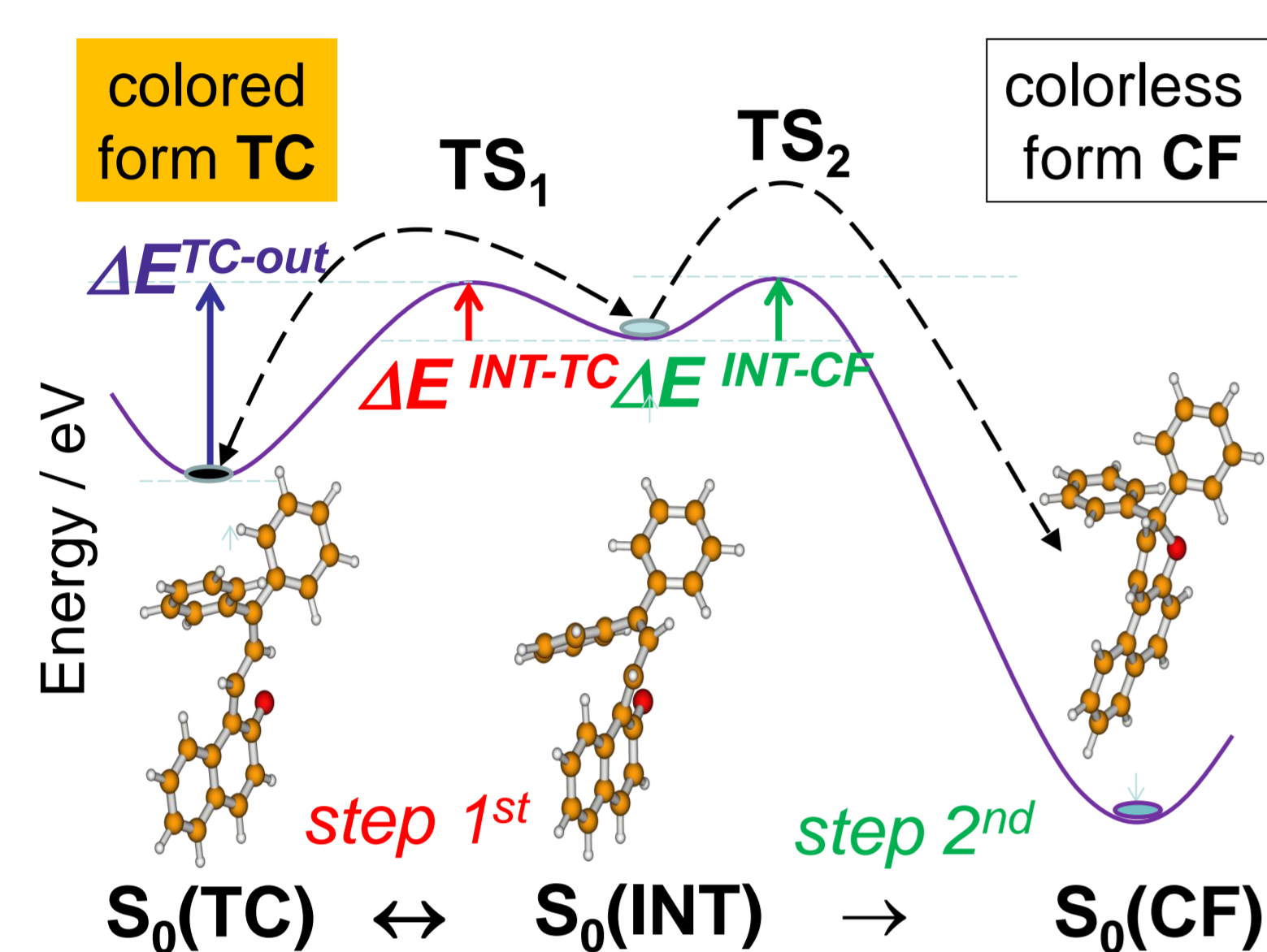
3H-naphthopyrans (NP) are valuable photochromic compounds that have been applied mostly in commercially available photochromic lenses.[1] They become coloured due to UV-light irradiation that initiates a pyran ring opening reaction by photodissociation of the C₃-O₄ bond in the closed form (CF). As a consequence, it is leading to generation of two colored isomers: short-lived *transoid-cis* (TC), see **Scheme 1**, and long-lived *transoid-trans* (TT), see **Scheme 2**. [2, 3]

Fading process is based on depopulation of TC (lifetime ~seconds) and of TT (lifetime ~minutes/hours) in solution. The depopulation of colored TC towards colorless CF form undergoes in the ground electronic state through the high-energy *cisoid-cis* intermediate INT. The fading rate of TC depends on the relative barriers separating INT from the surrounding minima. Long-lived TT form is unwanted species in the photoreaction. As TT is photoproducted in the *single-twist* photoisomerization reaction we would like to present the strategy how to reduce TT contribution by favouring *bicycle-pedal* photoisomerization process that suppress TT formation in the 10-OCH₃-NP molecule. [4, 5]. We present here how chemical modification of the NP structure may influence both fading time and yield of the TT form in the photoprocess.

Methodology

Ground-state equilibrium geometries and energy profiles were computed with the MP2 method. Excited-state geometries and minimum potential-energy surfaces were calculated with the ADC(2) method, a simplified and cost-effective variant of the coupled-cluster method with single and double excitations. ADC(2) can be considered as an MP2 equivalent for excited states. The cc-pVDZ basis set was used throughout the calculations.

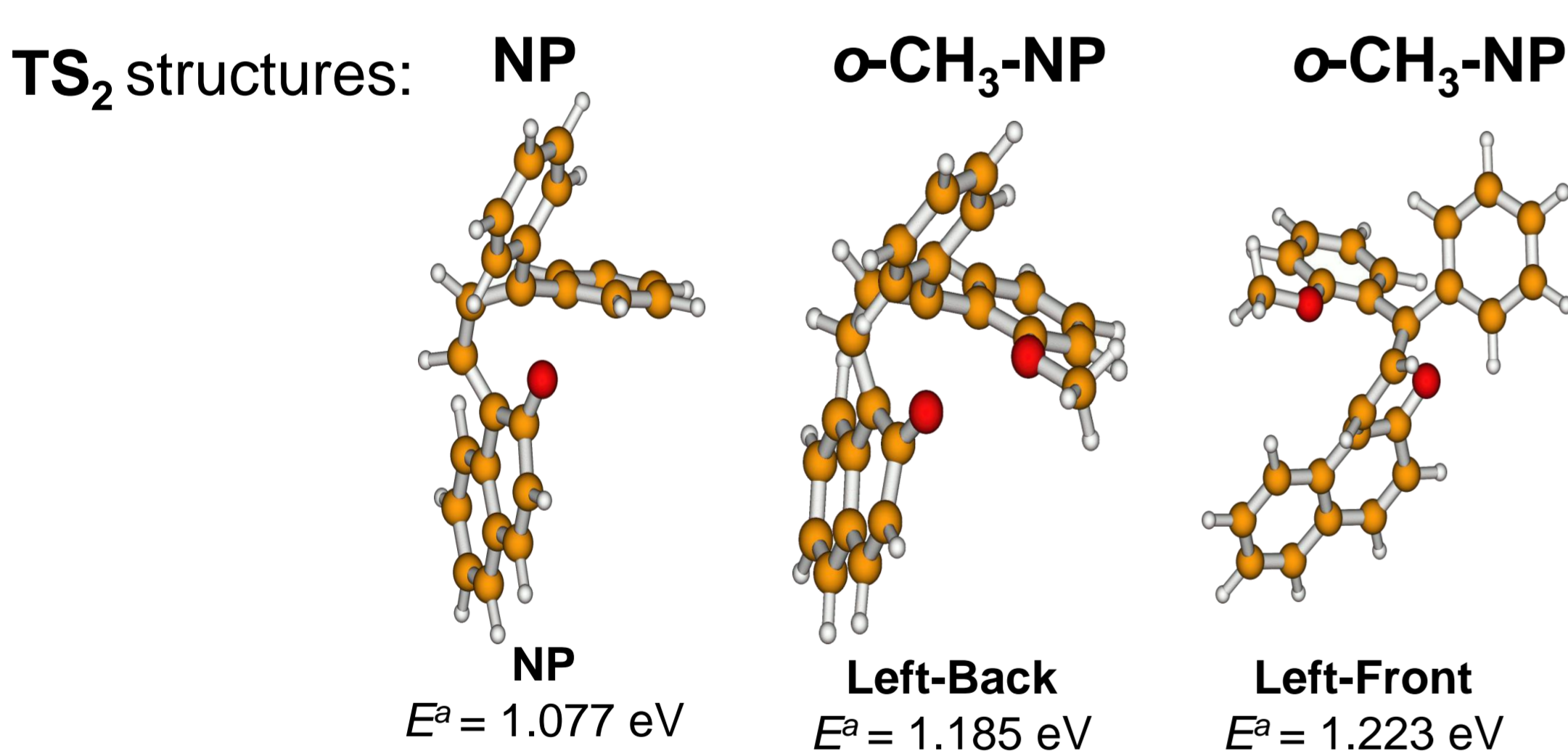
Ground (S₀) - state decoloration proces TC → INT → CF



Scheme 1. Mechanism of the two-step TC form depopulation process towards CF incorporates highly-energetic *cisoid-cis* intermediate INT. INT plays a crucial role in fading rate of different derivatives of NP, see Table 1.

Table 1. Decoloration proces of the TC form. S₀-state adiabatic energies, E^a, and potential-energy barriers (marked *italic*), ΔE, in eV.

| Derivative | TC | ΔE ^{TC-out} | TS ₁ | ΔE ^{INT-TC} | INT | ΔE ^{INT-CF} | TS ₂ | CF | τ (S ₀ TC) c-hexane |
|-----------------------|-------|----------------------|-----------------|----------------------|-------|----------------------|-----------------|-------|--------------------------------|
| NP | 0.588 | +0.452 | 1.040 | +0.196 | 0.844 | +0.233 | 1.077 | 0.000 | 9.3 sec |
| 10-methoxy | 0.578 | +0.458 | 1.036 | +0.191 | 0.845 | +0.218 | 1.063 | 0.000 | 9.3 sec |
| <i>ortho</i> -methoxy | | | | | | | | | |
| Left-Back | 0.626 | +0.380 | 1.005 | +0.161 | 0.844 | +0.341 | 1.185 | 0.056 | 1200 sec |
| Left-Front | 0.634 | +0.390 | 1.024 | +0.166 | 0.858 | +0.364 | 1.223 | 0.064 | 1200 sec |
| Right-Down | 0.669 | +0.476 | 1.145 | +0.207 | 0.938 | +0.203 | 1.141 | 0.113 | 20 sec |
| Right-Up | 0.655 | +0.415 | 1.070 | +0.164 | 0.906 | +0.254 | 1.160 | 0.000 | 20 sec |



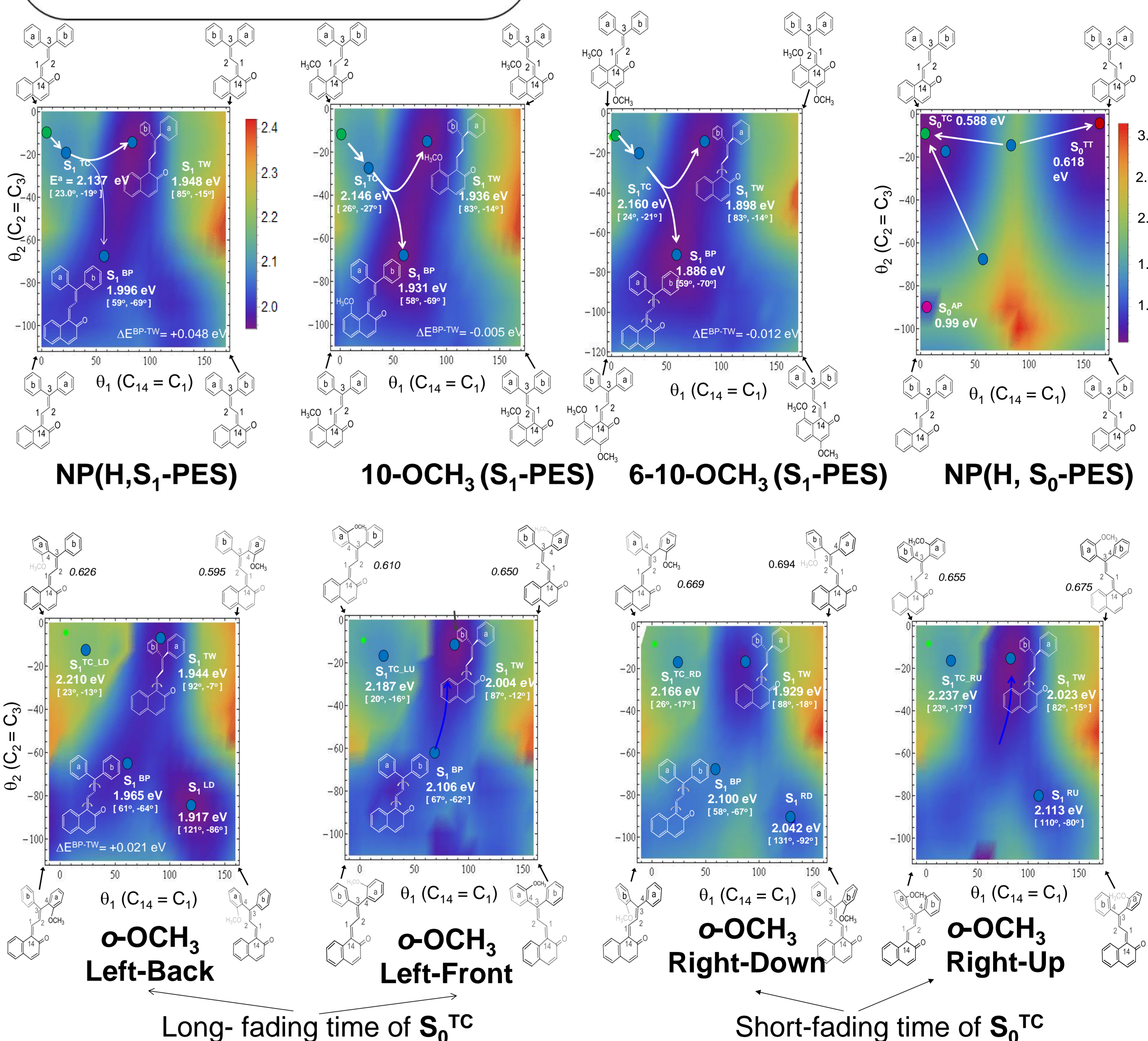
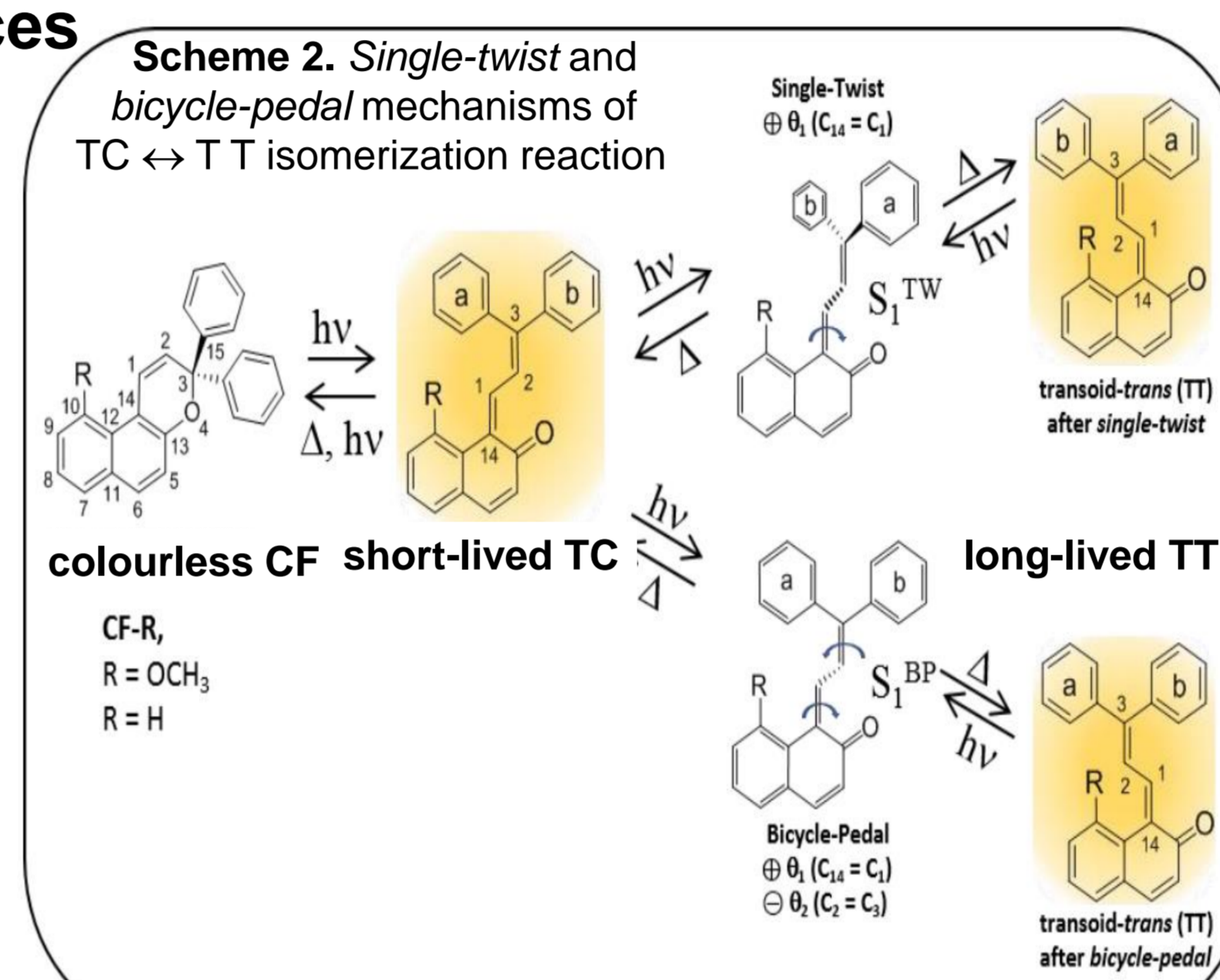
Methoxy group causes steric effects in the transition-state structures, TS₂, and is responsible for increase of the ΔE^{INT-CF} barrier in the *o*-OCH₃ molecule in which the methoxy group is substituted to the left phenyl π-stacking with naphthalenone moiety vs. unsubstituted NP molecule.

Conclusions – Fading process

- The fading process leading coloured open TC form to colorless closed-pyran ring CF form is determined by the S₀-state energy landscape. It is a two-step reaction. The TC and CF minima are separated by highly-energetic *cisoid-cis* intermediate INT (see **Scheme 1**), which plays a crucial role in decoloration rate.[6] The shape of the energetical landscape is correlated with the fading kinetics.
- S₀-state energy barriers, ΔE^{INT-TC} and ΔE^{INT-CF}, separating the intermediate S₀(INT) from the S₀(TC) and S₀(CF) minima, respectively, determine the rate of the fading process.
- In the *o*-OCH₃ molecule, S₀(TC) lifetime is increased in the system with left-phenyl *o*-methoxy-substituted due to oxygen-oxygen repulsion in the transition state TS₂ increasing ΔE^{INT-CF} barrier vs. NP.

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Excited-state (S₁) photoisomerization proces TC → TT seen on minimum potential-energy surfaces



Conclusions – photoisomerization reaction

- Relative energies of the S₁^{TW} and S₁^{BP} minima determine the mechanism of the photoisomerization proces. TT form is produced along *single-twist* - sole (C₁₄ = C₁) rotation. TT form is suppressed when *bicycle-pedal* (C₁₄ = C₁) and (C₂ = C₃) concerted rotations are favoured over *single-twist* and the process is stopped in halfway due to a fast internal conversion to the S₀(TC) state.
- In comparison to unsubstituted compound, NP(H), the presence of the methoxy group in 10-OCH₃ favors the *bicycle-pedal* pathway over the *single-twist* TC→TT photoisomerization. The *bicycle-pedal* pathway is halfway aborted due to S₁→S₀ internal conversion process inducing the structural transformation back to the initial TC form.[5]
- In contrary, *ortho*-methoxy-phenyl substitution to NP changes the S₁-state energetical landscape in a way that *single-twist* mechanism is dominating over *bicycle-pedal*, thus TT formation is enhanced in *o*-OCH₃ molecule.
- Theoretical calculations were strongly motivated and supported by experimental findings and correlated with the ground and excited state lifetimes obtained in UV-vis and mid-IR transient absorption spectroscopy.

Literature

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