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

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Object: spirochromenes
✔ Class of organic light-driven molecular switches
✔ Exhibit fast, reversible and stable bond cleavage processes
✔ Studied group has an outlier (different absorption, 20° lifetime)

Goal
✔ Compare properties of the compounds and explain the outlier

Tools
✔ Potential energy surface (PES) model for ground and excited electronic states (successful for similar compounds)
✔ Including excited-to-ground-state conic intersection search
✔ Ground-state and time-dependent DFT (basis: cc-pVDZ)
✔ PCM solvent model for acetonitrile
✔ Gaussian09 and GAMESS® packages

Experiments: group of 5 compounds

<table>
<thead>
<tr>
<th>Compound (closed/open)</th>
<th>R</th>
<th>R'</th>
<th>Closed: absorption (nm)</th>
<th>Intensity</th>
<th>Open: absorption (nm)</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9c / 10c</td>
<td>CH₂</td>
<td>CH₂</td>
<td>206 / 245</td>
<td>313</td>
<td>46.3 / 15.7</td>
<td>13.6</td>
</tr>
<tr>
<td>9e / 10e</td>
<td>CH₂CH₃</td>
<td>NO₂</td>
<td>~230 / 330</td>
<td>380</td>
<td>14.1 / 14.6</td>
<td>22.1</td>
</tr>
</tbody>
</table>

Study: 2 compounds

9c: methylindole (MI) + nitrosochroman (NC), 9e: nitroindole (NI) + nitrosochroman
9 and 9e – closed ring conformers (cf. 20°), 9e – ethyl group (R) conformers
TS – transition state (barrier), CI – conic intersection, 10° – ground-state intermediate

Conclusions
✔ Presence of the NO₂ group yields a second chromophore in 9e
✔ Calculations correctly reproduce spectral shape and features
✔ Accounting for solvent also results in good quantitative agreement

Molecular orbitals of 9e

Single barrier case

Intermediate conformation

No notable differences in barrier height seen between 10c and 10e compounds, regardless of energy estimation method

Structural deformation is complicated due to a flexibility of the CH₂–CH₂ bridge

Absorption of optimized open form(s) shows no meaningful differences

Spectrum consists of nitrochromene peak and dark charge-separated states (not shown); all tested functionals reported the same qualitative picture

Direct path (→ left) and presence of intermediates (right →) were studied

Several local minima found in ground-state PES

Respective barrier heights are very similar for 9e and 9c compounds (→ no differences in calculated spectrum)

9e has more potential energy both after excitation (ΔE) and at the CI (ΔE) (→ faster relaxation/ shorter trap escape time)

References