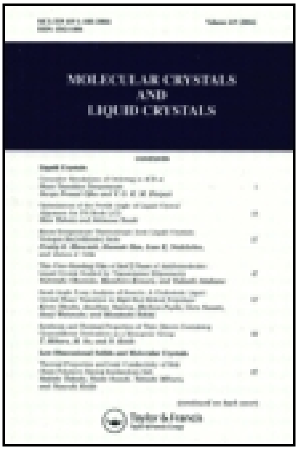

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# Interplay Between Theory and Experiment in Organic Photochromism: Example of Spirooxazine Ring Opening/Closing Equilibrium

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# Interplay Between Theory and Experiment in Organic Photochromism: Example of Spirooxazine Ring Opening/Closing Equilibrium

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*The contribution of quantum chemistry for understanding the mechanism involved in the photochromism of spirooxazines is illustrated from the calculation of three different physical properties. It is shown that the calculation of spectroscopic properties (NMR chemical shift and UV-visible absorption spectrum) and barriers of activation, the results of which are compared to the experimental data, provide a fruitful discussion basis. Confrontation of both data could lead to improve our knowledge on the complex mechanism involved in photochromism of spirooxazines.*

**Keywords:** spirooxazines; TD-DFT calculations

## INTRODUCTION

Recent advances in Density Functional Theory (DFT) methods have made *ab initio* calculations feasible for large organic compounds of

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practically any size. Besides the increase in computer power, the development of the so-called time-dependent density functional method (TD-DFT) have been decisive for the description of excited states. Different DFT-based computational approaches are now available and have shown to be both efficient and precise for performing molecular simulation of many complex systems. A fruitful collaboration between theoreticians and experimentalists is an essential requirement to propose rigorous and simple conceptual framework and to discuss the structure and photochemistry properties of large conjugated molecules.

In this contribution, from theoretical approach, we discuss the photochromic properties in spirooxazine series and this provides a real dialogue between theoreticians and experimentalists. The study was focused on the reference compound, namely the spiroindoline naphthoxazine (SNO) [1] for which many experimental data are available [2–7]. The capability of DFT calculations to reproduce the experimental results is illustrated from NMR, UV-Visible absorption spectra and quantum yield of photocoloration.

## COMPUTATIONAL DETAILS

Quantum-chemical calculations were performed using Gaussian 98 suite of programs [8]. The characterization of stationary point on the ground state surface could be easily carried out at the density functional theory level. For such purpose, the ground state potential surface for ring opening was studied by using the hybrid B3LYP functional with the 6-31G(d) basis set. Owning to the size of the studied system, the description of excited state potential surface at *ab initio* level is beyond the capability of calculations. The vertical excitation energies were calculated using the time-dependent DFT method (TD-DFT). Isotropic NMR chemical shielding was evaluated by means of the GIAO (Gauge-Independent Atomic Orbital) method as implemented in Gaussian 98. Chemical shifts $\delta_\mathrm{i}$ were calculated by subtracting the appropriate isotropic part $\sigma_\mathrm{i}$ of the shielding tensor from that of standard compound $\sigma_\mathrm{st}$: $\delta_\mathrm{i} = \sigma_\mathrm{st} - \sigma_\mathrm{i}$ (ppm). The standard TMS was calculated using the same methods and basis set. The $^1$H nuclei isotropic shielding constants values for TMS were calculated using B3LYP/6-31G(d) calculations (32.18 ppm).

## RESULTS AND DISCUSSION

### NMR Calculations

Under UV irradiation, colorless spirooxazines undergo reversible photochemical transformation to colored open forms, photomerocyanines.

**TABLE 1** Calculated and Experimental $^1$H Chemical Shifts of Closed form and Photomerocyanines

| | CF | TTC | CTC | Average (CTC and TTC) | Exptl(Ref. 7) |
|---|---|---|---|---|---|
| $C(CH_3)_2$ | 1,45 | 1,84 | 1,53 | 1.68 | 1.89 |
| $N-CH_3$ | 2,46 | 3,24 | 3,75 | 3.49 | 3.63 |
| 4 | 6,95 | 7,20 | 7,17 | 7.18 | 7.57 |
| 5 | 6,79 | 6,90 | 6,93 | 6.92 | 7.28 |
| 6 | 7,09 | 7,17 | 7,22 | 7.19 | 7.45 |
| 7 | 6,21 | 6,62 | 6,64 | 6.63 | 7.32 |
| 2′ | 7,71 | 9,88 | 10,07 | 9.97 | 10.09 |
| 5′ | 6,83 | 6,18 | 6,20 | 6.19 | 6.53 |
| 6′ | 7,51 | 7,00 | 6,99 | 6.99 | 7.58 |
| 7′ | 7,50 | 7,03 | 7,04 | 7.03 | 7.55 |
| 8′ | 7,29 | 7,037 | 7,02 | 7.03 | 7.34 |
| 9′ | 7,47 | 7,21 | 7,16 | 7.19 | 7.54 |
| 10′ | 8,65 | 8,21 | 7,72 | 7.97 | 8.36 |

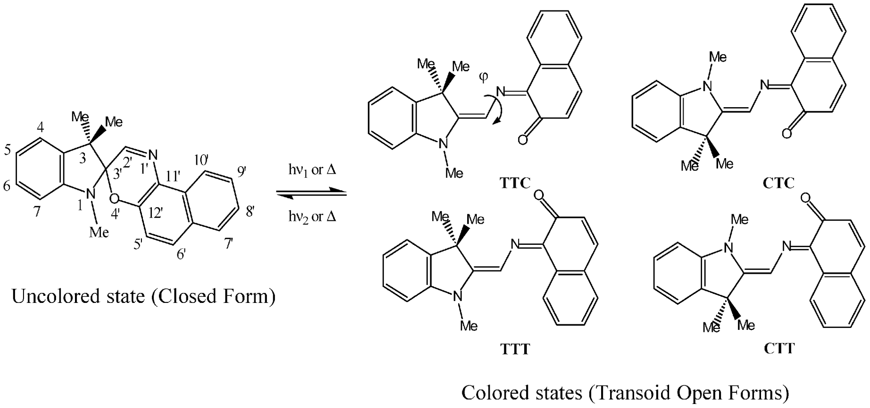
Although eigth photomerocyanine isomers are theoretically possible, only four transoid isomers contribute to the equilibrium mixture [9]. In recent $^1$H NMR experiments, it was concluded that only two transoid isomers, *i.e.* CTC and TTC, are favored [7].

The calculated $^1$H NMR chemical shifts for closed form and for the most stable photomerocyanines isomers, *i.e.* TTC and CTC, are gathered in Table 1.

Comparison of the calculated and measured $^1$H NMR chemical shifts shows that the theoretical method used reproduces the $\delta^1_{\mathrm{H}}$values quite well. However, it should be noted that the experimental values were obtained in solution, whereas in theoretical approach it is assumed that the molecule is isolated. Nevertheless, the shifts of indoline proton (H4, H5 and H6), naphthalene proton (H5′–H9′) are in the same range than the experimental values. The chemical shift of H2′ and H10′ protons are particularly interesting. The H2′ proton is localized on the pyran ring in the closed form and belongs to the conjugate bridge between indoline and naphthalene moieties in open forms. Therefore, its chemical environment strongly changes during the ring opening from the closed to open forms. The calculations agree with this prediction since H2′ becomes the most downfield shifted signal at 9.97 ppm in good agreement with the experimental result (10.09).

## UV-Vis Spectroscopy

It is well known that the first step of the photocoloration process, *i.e.* C–O bond cleavage, is very fast (less than a few hundred of



**SCHEME 1**

femtoseconds). This primary process leads to the *s-cis* isomer, probably CCC, in the ground state [9]. Therefore, the time evolution of UV-visible absorption spectra following the UV irradiation, mainly arises from the relaxation of this transient intermediate. From a previous study [9], it was shown that the CCC undergoes a *cis–trans* isomerization to give the corresponding photomerocyanines CTC. In order, to reproduce the time evolution of the absorption spectra we calculate the lowest excitation energies using TD-DFT as a function of the rotation angle $\varphi$ (Scheme 1), *i.e.* the reaction coordinate of the *cis–trans* isomerization step (Fig. 1a).

For small dihedral angle, a maximum absorption is calculated near 450 nm. There is a red shift in the absorption spectrum as the molecule rotates around the C2′-N1′ bond until 90°. From this value, when the dihedral angle increases up to 180°, the molecule becomes more planar and the maximum absorption smoothly undergoes a red shift while the intensity strongly increases. Although the cis–trans isomerization cannot explain the whole complexity of the experimental spectra, these evolutions are in good agreement with those observed in transient absorption performed in hexadecane (Fig. 1b). Thus, the results of calculation suggest that the time evolution of spectra, *i.e.* the red shift, the strong increase absorption intensity and decrease of the bandwidth are consistent with conformational rearrangement during cis–trans isomerization.

## Quantum Yield of Photocoloration

The mechanism of ring-opening deduced from theoretical calculations have shown that the first photoproduct formed along the ring-opening

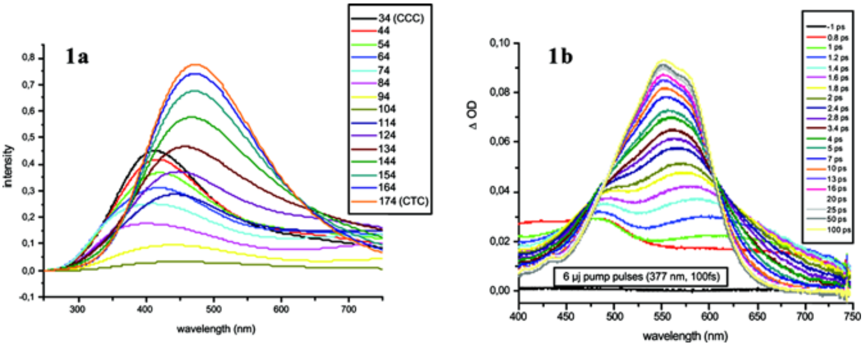


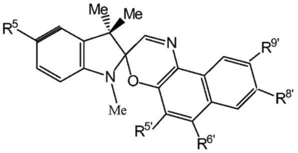
**FIGURE 1** (a) UV-Vis spectra of SNO as a function of the torsional angle $\varphi$ from CCC to CTC; (b) transient absorption spectra from 0.8 ps to 1000 ps after UV irradiation (experiments provided by G. Buntinx, LASIR, UMR 8516, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France).

process should be a CCC or TCC intermediate [9]. This species can rearrange through *cis–trans* isomerization leading to photomerocyanine or to initial closed form via ring-closure back reaction.

Therefore, when the CCC (TCC) region is populated, the quantum yield efficiency of photocoloration should depend on the ability of the system to overcome the energy barrier between the CCC (TCC) and CTC (TTC). It is expected that the presence of substituents should affect the energy barrier and may influence the quantum yield. To test the validity of this hypothesis, we carried out calculations of the

| | $R^5$ | $R^{5'}$ | $R^{6'}$ | $R^{8'}$ | $R^{9'}$ |
|---|---|---|---|---|---|
| 1 | -H | -H | -H | -H | -H |
| 2 | -H | -$C_2H_2$-CN | -H | -H | -H |
| 3 | -H | -H | -$NC_5H_{10}$[a] | -H | -H |
| 4 | -H | -H | -CN | -H | -H |
| 5 | -$OCH_3$ | -H | -CN | -H | -H |
| 6 | -$OCH_3$ | -H | -H | -CN | -H |
| 7 | -H | -H | -H | -H | -$OCH_3$ |

[a] piperidino substituent



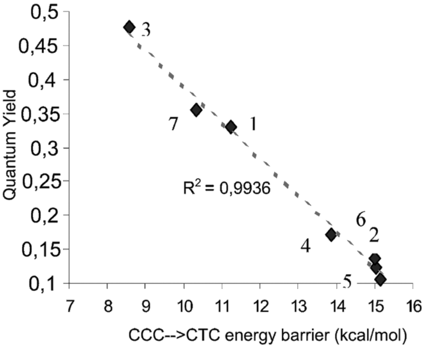


**FIGURE 2** Correlation of the experimental quantum yield of photocoloration (determined in toluene, see Ref. 10) with the calculated CCC → CTC energy barrier (kcal/mol).

energy barrier for *cis–trans* isomerization (B3LYP/6-31G(d)// B3LYP/3-21G calculations) for various derivatives for which experimental quantum yields of photocoloration, $\phi_{\mathrm{col}}$, are known. The calculations were conducted only for the CCC → CTC process. As clearly seen in Fig. 2, a very good correlation between the quantum yield of photocoloration and the magnitude of CCC → CTC energy barrier is obtained, this suggests that the *cis–trans* isomerization is an important parameter that controls the photocoloration process.

## CONCLUSION

In this contribution, a comparison between theoretical and experimental results for three different physical properties of SNO is presented. Recent progress in ground and excited states calculations have made it possible to use the theoretical tools (like Density Functional Theory) with a certain reliability. Moreover, the present results highlight the important contribution of DFT calculations to improve our knowledge in photochromic reactions.

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