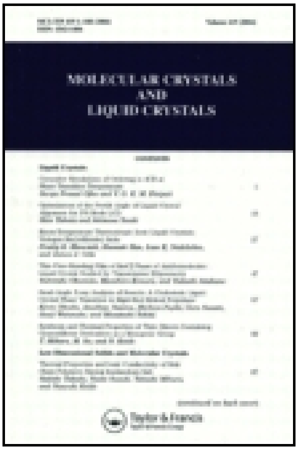

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Femto/Picosecond Transient Absorption Spectroscopy of Photochromic 3,3-Diphenylnaphtho[2,1-b]pyran

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Femto/Picosecond Transient Absorption Spectroscopy of Photochromic 3,3-Diphenylnaphtho[2,1-b]pyran

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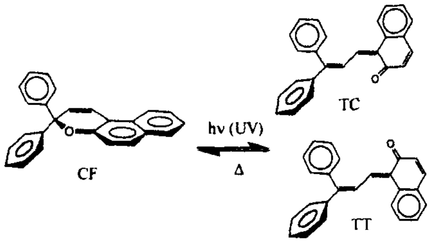
Transient absorption spectroscopy with femtosecond time resolution was used to probe the photochemical ring opening process of 3,3-diphenylnaphtho[2,1-b] pyran in solution. Analysis of the temporal evolution of the spectra from 0.4 ps to 100 ps has allowed us to detect and identify some of the intermediates involved in the photochemical formation of colored photomerocyanine isomers. From these data and those of recent *ab initio* and semi-empirical calculations on related photochromic systems, a simple mechanistic model was proposed for the ring opening/closing reaction in room temperature solution.

Keywords: fs spectroscopy; diphenylnaphthopyran; opening mechanism

I - INTRODUCTION

The increasing interest in diarylnaphthopyran series comes mainly from the new spectral features of these compounds complementary to those of the classical spiropyrans and spirooxazines [1]. By analogy with the spiropyrans, the photochromism of 3,3-diphenylnaphtho[2,1-b]pyran is believed to involve the breaking of the C-O bond of the pyran ring leading to colored metastable photomerocyanine isomers (open forms), absorbing in the blue/purple region of the visible spectrum (scheme 1). The similarity of this photochromic compound with the naphthopyran moiety in the parent spiro-compounds suggests that the opening process in diphenylnaphthopyran should be very close to that found for spironaphthopyran [2].

In this paper we report high quality transient absorption spectra (300-700 nm) following the UV irradiation of the diphenylnaphthopyran by 266 nm femtosecond pump pulse. The analysis of the temporal evolution of the absorption spectra from 0.4 ps to 100 ps along with the spectrokinetic data obtained on the ms to seconds time range have allowed us to detect and identify some of the intermediates involved in the course of the photochromic reaction. On the basis of these results and those obtained from *ab initio* and semi-empirical calculations on the fundamental and excited reaction pathways, it was possible to propose a detailed mechanism for the ring-opening/closing reaction in room temperature solution.



SCHEME 1. Schematic representation of diphenylnaphthopyran photochromic reaction. CF (closed form); TC and TT are the most stable trans photomerocyanine isomers.

II - EXPERIMENTAL SECTION

Synthesis and purification of 3,3-diphenylnaphtho[2,1-b]pyran (scheme 1) were reported previously [3]. Transient absorption spectra were obtained using a pump/probe spectrometer based on a Ti-Sapphire femtosecond laser system [4]. This system provides at 800 nm, 1 mJ, 90 fs pulses with 1 KHz repetition rate. Frequency tripling, using BBO crystals, produces pump pulses at 266 nm with an efficiency of 8%. The white light probe continuum is generated in a thin UV-transparent material using part of the 800 nm amplified pulses ; it covers a spectral range from 300 to 700 nm and its time dispersion is *ca.* 500 fs in the experiments reported here. The sample solution (concentration *ca.* 1mM) circulates in a calcium fluoride flow cell of 2-mm optical path length. The white light continuum probe pulse is time-delayed with respect to the 266 nm pump pulse using a computerized translation stage with a minimum step of 1 μm.

III - RESULTS AND DISCUSSION

The time evolution of the diphenylnaphthopyran absorption spectra in the range 300-700 nm, following 266 nm femtosecond pump pulse, were recorded in acetonitrile and n-hexane. A typical example is shown in figure 1, where the absorption spectra in acetonitrile recorded from 0.4 ps to 100 ps, are given. Except at very short time-delays (< 0.6 - 0.8 ps), the temporal evolution of the spectra was similar in the two solvents. Spectra obtained at times before 0.6 - 0.8 ps contain a contribution from two photon absorption of the solvent, from both the pump and probe pulses [4], which may interfer with the solute signal within this time range (Fig. 1). Since, on one hand, this effect is smaller in acetonitrile than in n-hexane and, on the other hand, spectra in acetonitrile present higher signal to noise ratios, the spectrokinetic analysis, presented further on, was performed on the data obtained in this solvent. However, the conclusions drawn in this case could be easily generalized to other solvents.

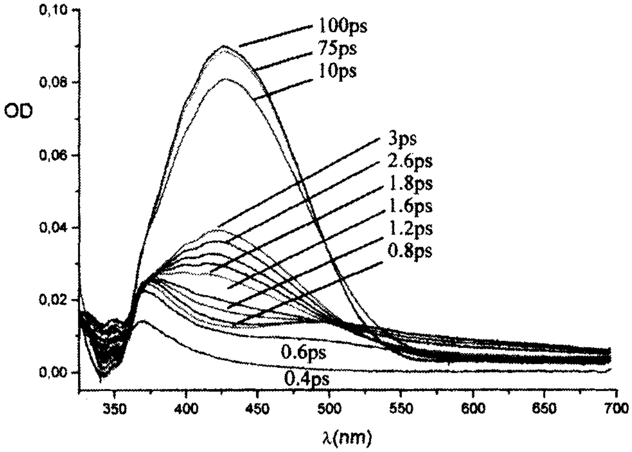


FIGURE 1. Time evolution of the absorption spectra, following the 266 nm femtosecond pulse, of 3,3-diphenyl-3H-naphtho[2,1-b]pyran.

The detailed analysis of the spectral variations in Fig. 1 leads to the following results. At short time, i.e. 0.8 ps after UV excitation, a broad absorption spectrum lying in the whole white light continuum spectral range (300-700 nm) is observed with the presence of three more or less resolved maxima respectively, 360-370 nm, 500 nm and *ca.* 650 nm. Within the time range of observation of this broad spectrum, i.e. 0.8ps - 1.6 ps, the presence of an isosbestic point at *ca.* 495 nm is revealed. Further time evolution shows that the spectra rapidly change and from 1.8 ps to 3 ps a well-defined band centered at 425 nm definitively appears with the presence of a new isosbestic point at 530 nm. While the time constant of the decay of the broad spectrum, as measured at 530 nm, was estimated to *ca.* 450 fs, the rise of the 425 nm band which follows this event was of the order of 1.8 ps (assuming in both case a single exponential function). At longer times (10 ps - 100 ps), this band only slightly develops showing a small rise in OD (ca 10^{-2} unit) and a concomitant decrease of its width. Above *ca.* 75-100 ps spectra do not evolve any more. In this last series of transient absorption spectra a third isosbestic point at *ca.* 500 nm is also observed and the rise in optical density measured at 425 nm, was estimated to be *ca.* 21 ps, assuming again a simple exponential function.

The above experimental results highlight three important observations : i) three isosbestic points are detected thus indicating that four species are involved in the time course of the experiments; ii) from 1.8 ps the rise in absorption falls within a spectral range typical of diphenylnaphthopyran open forms in polar solvents [5] ; iii) from 75 ps and beyond the transient spectra do not develop any longer and closely resemble to the spectra recorded in the µs-ms range and to the open form spectrum obtained under stationary regime [5].

Let's call A the starting product (closed form) and B_i the various photomerocyanine isomers (open forms) consecutive to the ring-opening reaction. The experimental results indicate that from 1.8 ps and beyond, transient spectra are typical of transoid open forms. Thus, the corresponding species which is the third appearing one in the kinetics (appearance time *ca.* 1.8 ps), must be a trans photomerocyanine isomer in its ground electronic state. Theoretical approaches (*vide infra*) suggest that a transition state and an intermediate species, B_1, (a cisoid isomer) could be involved in the reaction pathway. This species could occur within 0.8-1.6 ps but with different spectral characteristics which could be masked by the development, in this time range, of the 425 nm band. In these conditions we propose to ascribe the first appearing short-lived species to the lower excited singlet state of the closed form, $^1A^*$, and the following one (appearance time 450 fs) to the intermediate species, B_1. Although the 266 nm excitation wavelength promotes A to higher excited levels than $^1A^*$, electronic relaxation leads to $^1A^*$ through an unmeasurable ultra fast decay (< 100 fs).

Subsequent evolutions of the transient spectra indicate that photomerocyanine further isomerizes to reach a final state at *ca.* 100 ps which could be related to a thermal equilibrium between two trans photomerocyanine isomers [5]. This hypothesis, of the existence of two trans stereoisomers, B_2 and B_3, in thermal equilibrium at the longest times measured here (*ca.* 100 ps) is supported by the observation, on a time scale of tens of seconds, of a thermal ring closure kinetics which shows a biphasic behaviour [5]. This is currently interpreted as arising from the ring closure process of the most stable trans photomerocyanine isomers, TC and TT (scheme 1) and confirmed by a recent

NMR study [6]. The complete reaction kinetics, corresponding to the above observations, is summarized below :

$$^{1}A^{*} \xrightarrow{450fs} B_1 \xrightarrow{1.8ps} B_2 \xrightarrow{21ps} B_3$$

Theoretical support for ring-opening/closing mechanism

Recent calculations, *ab initio* for the ground state on the 1,3,3-trimethylspiro[indoline-naphthoxazine] and semi-empirical for the first excited singlet state on spiro[indoline-benzoxazine], led to the following assumptions for the ring opening reaction [7].

For the fundamental pathway, the reaction was found to follow a two-steps mechanism. The first step, which is rate determining with a barrier of 19.8 kcal/mol, involves the formation of a cisoid isomer followed by conformational rearrangements, leading to trans isomers [7]. While the cis-trans isomerization barrier was low (11.2 kcal/mol), trans isomerization occur with a barrier of 30.5 kcal/mol. In the first excited singlet state, the ring-opening occurs without any barrier of activation, corresponding to a dissociative state. During the C-O bond cleavage the S_1 and S_0 potential surfaces come closer suggesting a conical intersection (CI) in the region of the fundamental ring-opening transition state.

These theoretical approaches, obtained for photochromic systems closely related to the studied compound, are consistent with the reaction kinetics above. A schematic model for the ring-opening/closing mechanism is depicted in Fig. 2. In summary, excitation at 266 nm of the closed form, A, in its ground electronic state, promotes the molecule to one of its singlet excited states, $^{n}A^{*}$, which decays through an unmeasurable electronic relaxation process to the first excited singlet state, $^{1}A^{*}$. The molecule dissociates directly

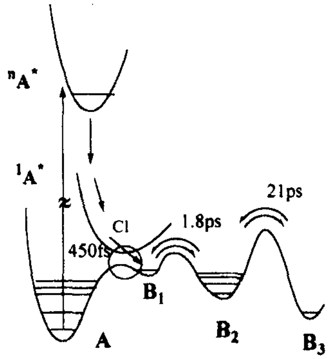


FIGURE 2. Schematic representation of the ring opening/closing reaction pathway in the fundamental and first singlet excited states.

in less than 500 fs to a primary isomer, B_1, through a conical intersection in the region of the ring opening transition state. Further isomerization in *ca.* 2 ps leads from this primary isomer to one of the trans-isomers, B_2. Subsequent conformational relaxation in *ca.* 20 ps, results in the observed thermal equilibrium between the two trans photomerocyanine isomers B_2 and B_3, which are stable on the time scale of tens of seconds.

IV - CONCLUSION

In this work, the photochemical ring-opening reaction of 3,3 diphenylnaphtho[2,1-b]pyran has been probed with femtosecond time resolution. These first results indicate, that a primary photomerocyanine isomer, B_1, is already present *ca.* 1ps after the 266 nm excitation and that thermal equilibrium between the most stable TC and TT photomerocyanine isomers is established within 20 ps. On the basis of recent *ab initio* and semi-empirical calculations, on related photochromic systems, we have been able to propose a mechanistic picture consistent with the experimental data. However, neither this model nor transient absorption measurements have allowed us to clarify definitely the nature of B_1

Acknowledgments

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