



Sub-picosecond transient absorption spectroscopy of substituted photochromic spironaphthoxazine compounds

Guy Buntinx^a, Olivier Poizat^{a,*}, Sarah Foley^{a,1}, Michel Sliwa^a, Stéphane Aloïse^a, Vladimir Lokshin^b, André Samat^b

^aLaboratoire de Spectrochimie Infrarouge et Raman (UMR 8516 du CNRS), Centre d'études et de recherches Lasers et Applications (FR 2416 du CNRS), Université de Sciences et Technologies de Lille, Bat C5, 59655 Villeneuve d'Ascq Cedex, France

^bCentre Interdisciplinaire de Nanoscience de Marseille (UPR 3118), Universités d'Aix-Marseille, Campus de Luminy, Case 901, 13288 Marseille Cedex 9, France

ARTICLE INFO

Article history:

Received 22 December 2009

Received in revised form

22 April 2010

Accepted 15 May 2010

Available online 24 May 2010

Keywords:

Photochromism

Spirooxazine

Spiro-naphthoxazine

Femtochemistry

Time-resolved absorption

Transient spectroscopy

ABSTRACT

The photochromic reaction dynamics of spiroindolenaphthoxazine and its 6'CN and 5'CHO substituted compounds is investigated in different solvents by femtosecond transient absorption spectroscopy. In addition to the formation of the merocyanine coloured form (ring-opened trans form, OF), another short-lived intermediate species is produced upon photoexcitation, which is not a precursor to the OF product but which is formed in parallel to it via a competing relaxation process. This species is ascribable to either a relaxed *s-cis* ring-opened isomer on the ground state potential energy surface or to a metastable minimum of the excited S₁ state potential energy surface of the ring-closed form. The observed kinetics suggest that the production of OF (photocoloration reaction) is controlled by the efficiency of the competing process rather than by an *s-cis* – trans isomerisation energy barrier.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Photochromic spirooxazine derivatives are the object of considerable efforts of synthesis [1–5] motivated by their widespread use in the commercial manufacture of ophthalmic lenses for adjustable sunlight-protection glasses or in other applications requiring the transparency of an object to vary according to surrounding light intensity. They are also promising compounds for a wide range of potential applications in photonics such as memories and switches [6]. Spiro-naphthoxazine molecules combine indoline and naphthoxazine moieties linked in a perpendicular and electronically uncoupled configuration via a common sp³ (spiro) carbon (ring-closed form, CF). Accordingly, their absorption spectrum is roughly the superposition of the UV absorption features of both moieties. The photochromic transformation (Scheme 1) induced by UV irradiation proceeds via the ultrafast cleavage of the spiro carbon-oxygen single bond followed by isomerisation [7–9]

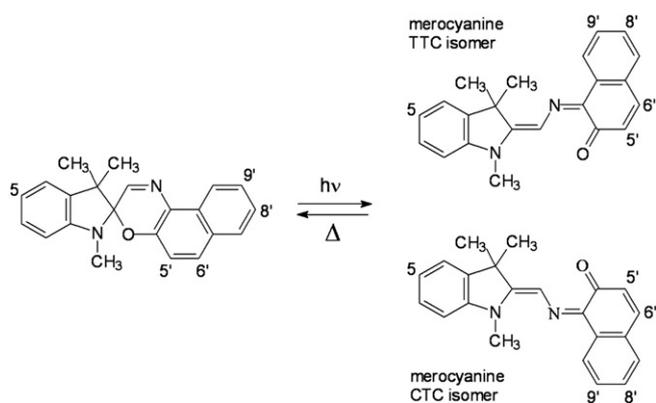
and leads to a mixture of coloured, ring-opened merocyanine isomers (open forms, OF) with extended π conjugation, which absorb in the 500–700 nm range. ¹H NMR [10] and resonance Raman [11] measurements, in agreement with theoretical predictions [12], have shown that only the two most stable OF isomers, TTC and CTC, are formed. The merocyanine isomers undergo thermal back reaction in the seconds to minutes time domain at room temperature [13].

A major purpose of recent experimental [2–5] and theoretical [14] work on spiro-naphthoxazines in view of the applications is the design of new structures with well-controlled and tunable optical properties. In this regard, Metelitsa et al. showed that modifying the spiro-naphthoxazine (SNO) parent molecule by substitution so as to form *push-pull* type compounds leads to a notable red-shift of the merocyanine absorption but simultaneously reduces the quantum yield of photocoloration, Φ_{col} (CF → OF reaction yield) [3]. To understand the parameters that control the efficiency of the photochromic process, it is essential to be able to describe in detail, at the molecular level, the photoinduced reaction pathway. The ring-opening reaction mechanism and dynamics have been studied by ultrafast time-resolved spectroscopy for SNO in solution [15–21] and in the microcrystalline powder phase [22–26]. This reaction has also been investigated theoretically by using quantum chemical

* Corresponding author. Fax: +33 3 20 33 63 54.

E-mail address: olivier.poizat@univ-lille1.fr (O. Poizat).

¹ Present address: Université de Franche-Comté, Laboratoire de Chimie Physique et Rayonnement (UMR CEA E4), 16 route de Gray, 25030, Besançon, France.



Scheme 1. Representation of the photochromic transformation between the ring-closed form (left) and main ring-open forms (right) of SNO.

calculations [12,27,28]. However, the detailed ring-opening mechanism remains unclear. In particular the nature of the primary transient species precursor of the merocyanine form is still questioned. The C–O bond cleavage is generally assumed to occur in the excited S_1 state in the sub-picosecond to picosecond time scale. The growth of the strong red absorption band of the ring-opened merocyanine ground state product takes place in a few picoseconds and is accompanied by a spectral evolution (red-shift, band narrowing, and notable increase in intensity) which has been explained by the cumulative effects of solvation, vibrational cooling, and cis–trans conformational rearrangement [17–21,28]. Absorption components observed in the 400–550 nm region and decaying in the sub-picosecond time scale were tentatively attributed to a species belonging to the excited S_1 state surface with contributions from the closed form [17,19] and also a cisoid ring-opened form (so-called X primary photoproduct) [19], preceding the formation of the ground state merocyanine form. On the other hand, combined ab initio and semi-empirical quantum mechanical calculations recently performed by Maurel et al. for SNO were consistent with the picture of an ultrafast ring-opening process on the excited S_1 state surface followed by a quasi-instantaneous barrierless deactivation through a conical intersection to a ground state s-cis opened intermediate considered as the first photoproduct along the ring-opening pathway [28]. It was concluded that the only significant barrier to the photoinduced formation of the final merocyanine form is that of cis–trans isomerization and, consequently, the time–evolution of the UV–vis absorption spectra is probably essentially characterizing this ground state isomerization process.

Although the nature and position of the substituents greatly influence the macroscopic properties of spirooxazines (colourability for instance), thus reflecting a strong influence of substitution upon the photophysical and photochemical characteristics [3,29–31], very few substituted derivatives of spirooxazines have been concerned by such ultrafast time-resolved spectroscopic investigations. There is thus almost no report in the literature on the influence of substitution on the reaction pathway at the microscopic level. Recently, we investigated the photophysics of the 6′-cyano substituted spirooxazine compound (6′CN–SNO) in acetonitrile solution by femtosecond transient absorption spectroscopy [32]. Besides the growth of the typical merocyanine absorption spectrum, a strong band covering the 400–550 nm region was tentatively assigned to a new, unidentified metastable species formed concurrently to the merocyanine product, which suggested the existence of an additional excited-state deactivation process concurrent to the photochromic reaction and which could explain the 50% reduction of the photocoloration quantum yield

(Φ_{col}) on going from SNO to 6′CN–SNO. To better characterize the influence of substitution on the complex photophysics of this class of molecules, we have thus undertaken an extensive investigation by transient absorption spectroscopy of the photoinduced reactivity of a series of substituted derivatives of SNO.

We present here a comparative analysis of the results obtained in various solvents for the parent SNO molecule and its 6′CN and 5′CHO substituted compounds, for which the experimental Φ_{col} values have been determined [2]. Whereas the efficiency of the photochromic transformation is rather good for SNO ($\Phi_{\text{col}} = 0.41$ in methylcyclohexane, 0.32 in ethanol) but notably smaller for 6′CN–SNO ($\Phi_{\text{col}} = 0.17$ in toluene, 0.11 in methanol), the behavior of 5′CHO–SNO is intermediate and can be compared to that of SNO in nonpolar solvents ($\Phi_{\text{col}} = 0.35$ in toluene) and to that of 6′CN–SNO in polar solvents ($\Phi_{\text{col}} = 0.13$ in methanol) [2]. These three representative compounds are thus interesting since they may be able to provide precious information on the influence of substituents and of the solvent on the reaction mechanism.

2. Experimental

Spirooxazines have been synthesized by reaction of 2-methylene-1,3,3-trimethylindoline (Fischer's base) with the corresponding nitroso (or amino) naphthols. Detailed synthesis has already been reported for the parent SNO molecule [2] and the 6′CN [1] and 5′CHO [33] substituted compounds. Spectrophotometric grade acetonitrile, ethanol, toluene, and n-hexane solvents were obtained from Aldrich. Most of the measurements were performed on 10^{-3} M solutions circulating in a 2 mm thick flow cell (equipped with 200 μm thick CaF_2 windows). In addition, for some detailed measurements of the early time dynamics (0–1.8 ps), the flowing jet sampling technique was adopted (200 μm thick jet, 10^{-2} M solutions). The apparatus used for obtaining the femtosecond transient absorption measurements has been described previously [34]. In the present investigation, 377 and 252 nm pump pulses (100 fs, 1 kHz) were obtained by frequency doubling and tripling, respectively, the output of the amplified Ti:Sapphire laser tuned at 756 nm in 300 μm thick BBO crystals. The pump power was limited to 10–20 μJ per pulse (1.0–2.0 mJ/cm^2). The broadband white light continuum probe pulses were generated by focussing 756 nm, 1 μJ pulses in a CaF_2 plate. In order to avoid rotational diffusion effects on the absorption spectra, the pump polarization was set at the magic angle (54.7°) relative to the probe. Spectra were recorded over the 400–740 nm and 770–975 nm spectral ranges and were corrected from group-velocity dispersion (GVD) effects. The time resolution was better than 300 fs with the flow cell and 180 fs with the flowing jet configuration.

3. Results and discussion

3.1. Spectral evolution

Pump-probe transient absorption spectra have been recorded for n-hexane, acetonitrile, and ethanol solutions of SNO, 5′CHO–SNO, and 6′CN–SNO in the 400–740 nm range and in the 0–2 ns time domain following pump excitations at 377 and 252 nm. 6′CN–SNO has also been studied in toluene solution. Typical transient absorption spectra of SNO (10^{-3} M) excited at 377 nm and recorded in the 400–740 nm spectral range are shown in Figs. 1 and 2 for solutions in n-hexane and acetonitrile, respectively. The 377 nm excitation corresponds to the low energy edge of the $S_0 \rightarrow S_1$ transition [35]. Similar spectra obtained in n-hexane and acetonitrile are shown in Figs. 3 and 4 for 5′CHO–SNO and in Figs. 5 and 6 for 6′CN–SNO. For all compounds, the spectra obtained in ethanol (not shown) are somewhat comparable to those in acetonitrile and

Download English Version:

<https://daneshyari.com/en/article/177257>

Download Persian Version:

<https://daneshyari.com/article/177257>

[Daneshyari.com](https://daneshyari.com)