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Sub-picosecond transient absorption spectroscopy of substituted photochromic spironaphthoxazine compounds

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ABSTRACT

The photochromic reaction dynamics of spiroindolinenaphthoxazine 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 S_1 state potential energy surface of the ring-closed form. The observed kinetics suggest that the production of OF (photocoloraton reaction) is controlled by the efficiency of the competing process rather than by an s-cis – trans isomerisation energy barrier.

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]. Spironaphthoxazine molecules combine indoline and naphthoxazine moieties linked in a perpendicular and electronically uncoupled configuration via a common sp^3 (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. ^{1}H 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 spironaphthoxazines 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 spironaphthoxazine (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

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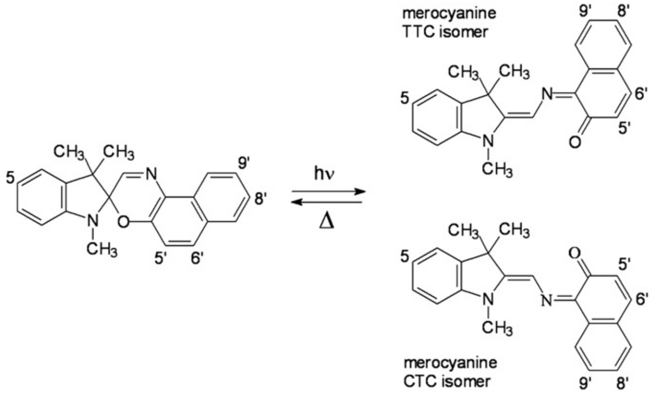


Scheme 1. Representation of the photochromic transformation between the ring-closed form (left) and main ring-open forms (right) of SNO.

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 spironaphthoxazine compound (6′CN–SNO) in acetonirile 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 ($\Phi_{col} = 0.41$ in methylcyclohexane, 0.32 in ethanol) but notably smaller for 6′CN–SNO ($\Phi_{col} = 0.17$ 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 ($\Phi_{col} = 0.35$ in toluene) and to that of 6′CN–SNO in polar solvents ($\Phi_{col} = 0.13$ 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

Spironaphthoxazines 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

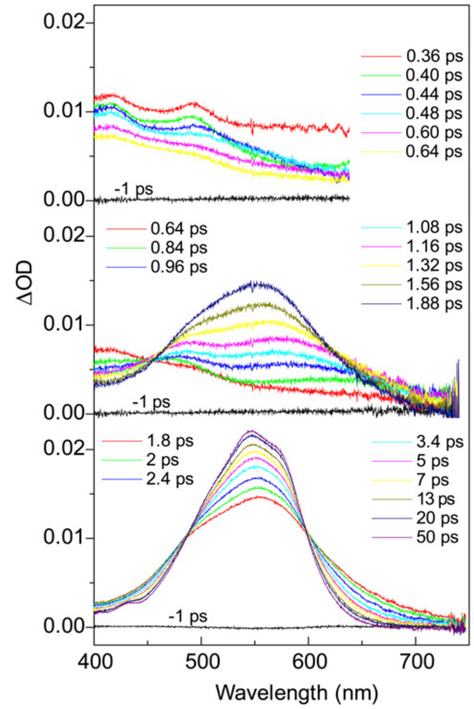


Fig. 1. Transient absorption spectra of SNO (10^{-3} M) in n-hexane after excitation at 377 nm. For clarity, the spectral evolution is separated into 3 time domains 0–0.64 ps (top), 0.64–1.88 ps (middle), and 1.8–50 ps (bottom). Spectra below and above 1.8 ps are recorded with the flowing jet and the flow cell systems, respectively. The pump-probe time delays are given. The −1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

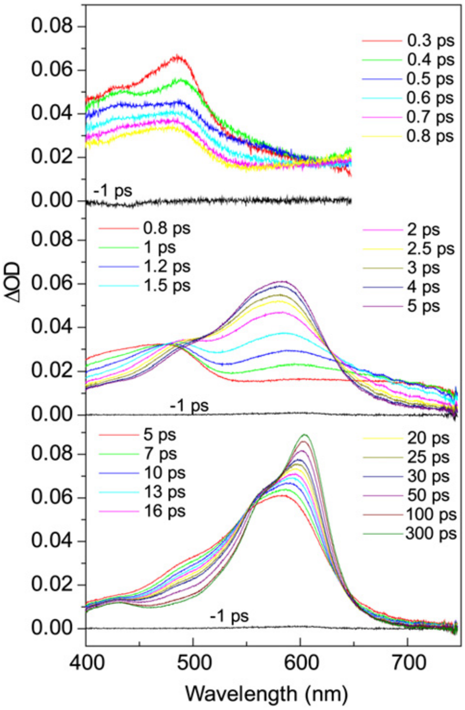


Fig. 2. Transient absorption spectra of SNO (10^{-3} M) in acetonitrile after excitation at 377 nm. For clarity, the spectral evolution is separated into 3 time domains 0–0.8 ps (top), 0.8–5 ps (middle), and 5–300 ps (bottom). Spectra below and above 0.8 ps are recorded with the flowing jet and the flow cell systems, respectively. The pump-probe time delays are given. The −1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

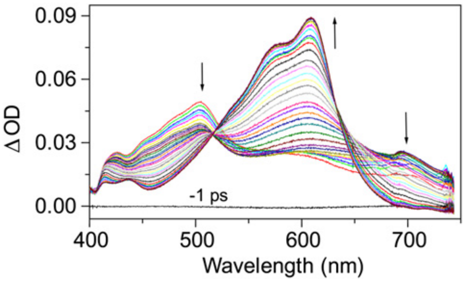


Fig. 3. Transient absorption spectra of 5′CHO–SNO (10^{-3} M) in n-hexane at different pump-probe time delays in the 0–500 ps range after excitation at 377 nm. The −1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

differ mainly by their kinetic parameters. The spectra of 6′CN–SNO in toluene resemble those recorded for this compound in n-hexane. As a general rule, in all solvents, these transient spectra are characterized by two main absorption components exhibiting opposite time evolutions (λ_{max} given in Table 1). On one hand, a “red” band peaking at 550–650 nm is rising with time and corresponds unambiguously to the coloured merocyanine (open form, OF) by analogy with steady-state spectra previously reported for this species [3]. As can be seen in Table 1, its peak position decreases in energy upon substitution of the SNO skeleton and also on going from nonpolar to polar solvents, in agreement with steady-state measurements [3]. On the other hand, a “blue” band lying in the 400–550 nm region is formed within the pump excitation pulse width and decays with time. The relative initial intensity of this band, as compared to the final intensity of the OF band, varies strongly from one compound to the other and upon the changing of the solvent: whereas it is high in the cases of 6′CN–SNO in all

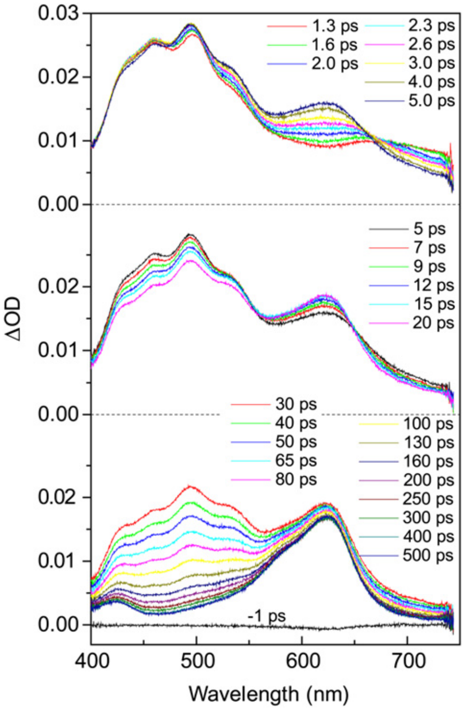


Fig. 4. Transient absorption spectra of 5′CHO–SNO (10^{-3} M) in acetonitrile after excitation at 377 nm. For clarity, the spectral evolution is separated in 3 time domains 0–5 ps (top), 5–20 ps (middle), and 30–500 ps (bottom). The pump-probe time delays are given. The −1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

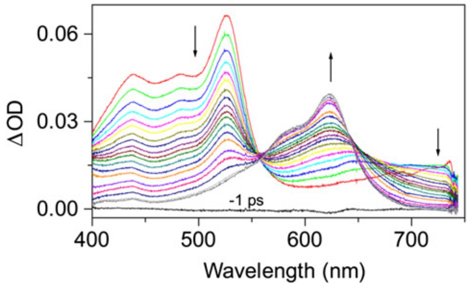


Fig. 5. Transient absorption spectra of 6′CN–SNO (10^{-3} M) in n-hexane at different pump-probe time delays in the 0–500 ps range after excitation at 377 nm. The −1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

solvents (Figs. 5 and 6) and of 5′CHO–SNO in acetonitrile (Fig. 4) and ethanol, it is much weaker in the cases of 5′CHO–SNO in n-hexane (Fig. 3) and of SNO (Figs. 1 and 2). For all compounds, the final intensity of the OF band relative to the initial intensity of the blue band appears systematically increased upon changing the pump excitation from 377 to 252 nm, although the spectral evolution remains unaffected.

In addition to the two absorption components mentioned above, a decay of absorption is observed for all compounds above 700 nm, suggesting the presence in this region of the edge of a third “near-IR” band. Spectra recorded in the 770–975 nm region for 6′CN–SNO in n-hexane, ethanol, and acetonitrile confirmed the presence of a broad absorption band peaking around 880 nm (see λ_{max} in Table 1), characterized by similar decay kinetics (discussion below) as the blue band but about three times less intense. The near-IR and blue bands are thus likely to characterize the same transient species.

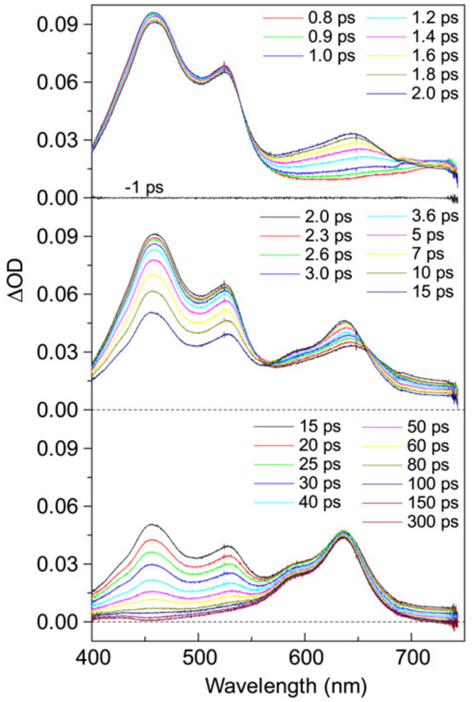


Fig. 6. Transient absorption spectra of 6′CN–SNO (10^{-3} M) in acetonitrile after excitation at 377 nm. For clarity, the spectral evolution is separated in 3 time domains 0–2 ps (top), 2–15 ps (middle), and 15–300 ps (bottom). The pump-probe time delays are given. The −1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

Some spectral modifications accompany the decay of the blue band and the growth of the OF band. These modifications are solvent dependent and include band shifts and changes in band shape. For example, the OF band maximum of SNO in acetonitrile (Fig. 2) undergoes a 610–575 nm blue shift from 2 to 3 ps, then a 575–595 nm from 3 to 100 ps. In parallel, the bandwidth decreases from 20 to 100 ps whereas a shoulder appears at 565 nm. These changes can have several origins, as already suggested [17–21,28,32]. Firstly, is the probable presence, for any species involved in the reaction pathway (excited states and ground state intermediates, final OF form), of molecular relaxation processes such as cooling or solvation. A second cause of band shape variation can be the inhomogeneous character of the population of molecules due to the possible existence, at each step of the reaction, of a distribution of conformers evolving with specific kinetic characteristics. This is particularly expected for the merocyanine form for which 8 ground state OF isomers arising from rotation about the three central bonds can exist, at least transiently, and which evolve toward the most stable ones, TTC and CTC [10–12]. The effect of ground state cis–trans conformational rearrangement on the OF absorption band shape and intensity has been well predicted in the case of SNO from theoretical calculations [28].

In the case of SNO, the observed spectral evolution is consistent with the most recently reported results [17–20]. For pump-probe delays longer than 1 ps, the evolution resembles that observed for the 6′CN and 5′CHO substituted compounds: a broad and structureless blue band (~1 ps spectrum in Figs. 1 and 2) declines and a red band typical of the OF species develops. In addition, a sub-picosecond spectral evolution, not observed for the substituted compounds, is noticed in the case of SNO. A very short-lived band (0.3–0.4 ps spectra in Figs. 1 and 2), lying at the same position as the blue band but showing a sharper structure, disappears within 1 ps.

3.2. *Kinetic analysis*

The kinetic evolution is complex and differs noticeably for the three compounds. It is also strongly dependent on the solvent. As discussed above, this complexity can be accounted for by the cumulative effect of molecular relaxation processes arising in the picosecond time domain and solvent-dependent distribution of conformers. Examples of plots extracted from the spectra and monitored at the maxima of the blue and red bands are shown for 5′CHO–SNO and 6′CN–SNO in Figs. 7 and 8, respectively. Approximate fits with 2 or 3 exponential components were generally satisfying and the corresponding time constants are listed in Table 1. Curiously, for 5′CHO–SNO in ethanol and acetonitrile, the blue band absorption decay is well fitted by a single-exponential kinetics. On the contrary, in the case of SNO, a supplementary very short decay component (about 0.2 ps) is necessary to characterize the transition from the initially produced blue absorption band to the less structured one. Although some isosbestic points seem more or less apparent during the decay of the blue and near-IR bands and the rise of the OF band, the blue band decay and OF band rising kinetics are never really matching. In some cases, they are even completely different. This is particularly evident for 6′CN–SNO: in n-hexane a main time constant of about 1 ps characterizes both the OF absorption growth and blue band decay (Fig. 8, part A), leading to the observation of a quasi-isosbestic point at 610 nm (Fig. 5) and suggesting that the blue-absorbing intermediate is the precursor of the OF species; in contrast, in acetonitrile, the blue band decay is much slower than the OF band growth (Fig. 8, part B), which excludes unambiguously the hypothesis that the blue-absorbing intermediate is the precursor of the OF. The isosbestic point noticed in n-hexane is

Table 1
Wavelength of maximum absorption (nm) and main time constants (ps) measured by pump-probe absorption for the blue and OF absorption bands of 6′CN–SNO, 5′CHO–SNO, and SNO, and for the near-IR band of 6′CN–SNO (pump excitation at 377 nm).

Compounds	Band type	n-hexane		Toluene		Ethanol		Acetonitrile	
		λ	τ (%)	λ	τ (%)	λ	τ (%)	λ	τ (%)
6′CN–SNO	blue band	526	1.0 (72) 26 (28)	529	1.9 (70) 94 (30)	527	1.7 (33) 39 (67)	458	6.8 (15) 30 (85)
	NIR band	878	1.5 (70) 24 (30)	[a]		875	1.7 (40) 38 (60)	880	8.2 (10) 34 (90)
	OF band	623	1.2 (68) 13 (32)	635	1.5 (69) 15 (31)	642	0.8 (60) 6.5 (40)	637	0.9 (70) 8.5 (30)
5′CHO–SNO	blue band	505	0.5 (60) 7.5 (40)			501	28 (100)	494	78 (100)
	OF band	608	3.3 (63) 14 (37)			630	1.8 (20) 7.5 (80)	623	2.4 (66) 12.5 (34)
SNO	blue band	485	0.17 0.65 (67) 9.9 (33)			488	0.25 0.45 (50) 4.1 (27) 43 (23)	489	0.25 0.5 (24) 2.2 (42) 62 (34)
	OF band	550	0.75 (75) 10.5 (25)			604	1.1 (35) 8.5 (45) 40 (20)	595	0.96 (73) 11.6 (27)

[a] Not measured.

thus fortuitous. In the case of 5′CHO–SNO, the blue band decay kinetics is much shorter than the OF band rise kinetics in n-hexane (Fig. 7, part A) but much longer in acetonitrile (Fig. 7, part B). The fact that, in acetonitrile, the OF band reaches its maximum intensity well before the full decay of the blue band is clearly visible in the 15–300 ps spectral evolution observed for 6′CN–SNO (bottom of Fig. 6) and in the 50–500 ps spectral evolution recorded for 5′CHO–SNO (bottom of Fig. 4). In Fig. 7, part B, the fast rise that precedes the main decay kinetics of the blue band (494 nm trace) is due to the presence of a weak contribution of the OF absorption band overlapping the blue band. Similarly, we ascribe the slight decay that follows the fast rise of the OF band (623 nm trace) to the presence of a weak contribution of the blue band's foot overlapping the OF signal. As a matter of fact, a three-exponential kinetic model involving the two OF band growth components and the blue band decay component leads to an excellent fit of the experimental kinetic plot at all wavelengths.

3.3. Discussion of the photoinduced processes and photocoloration quantum yield

Previous interpretations of the femtosecond transient absorption spectra of SNO proposed that the first transient observed around 490 nm corresponds to the excited S_1 state that deactivates in less than 1 ps by ring-opening following the spiro carbon-oxygen bond cleavage to yield a primary photoproduct of cisoid structure, the so-called X intermediate, also absorbing in the blue region [17–19]. The cisoid X intermediate is believed to belong to either the ground state surface [17,18] or to the S_1 state surface [19]. It is assumed to be a precursor of the final, solvent dependent distribution of transoid OF isomers. The evolution between the X species and the stable OF mixture at equilibrium arises in several tens of picoseconds with multiexponential kinetics.

From a theoretical point of view, Maurel et al. recently reported quantum mechanical results on the photocoloration reaction in the

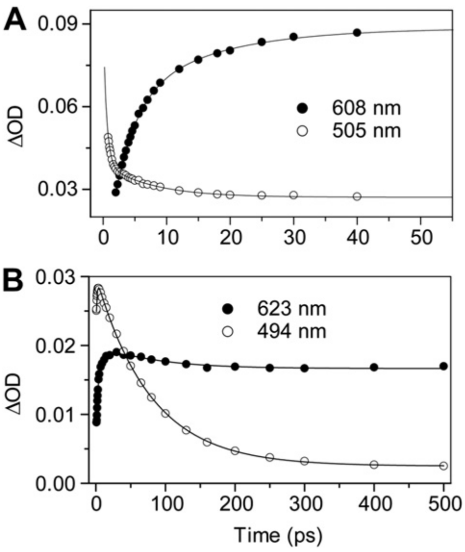


Fig. 7. Kinetic traces for 5′CHO–SNO in (A) n-hexane at 505 nm (○) and 608 nm (●) and (B) acetonitrile at 494 nm (○) and 623 nm (●). The solid lines are the best fits to the data (time constants in Table 1).

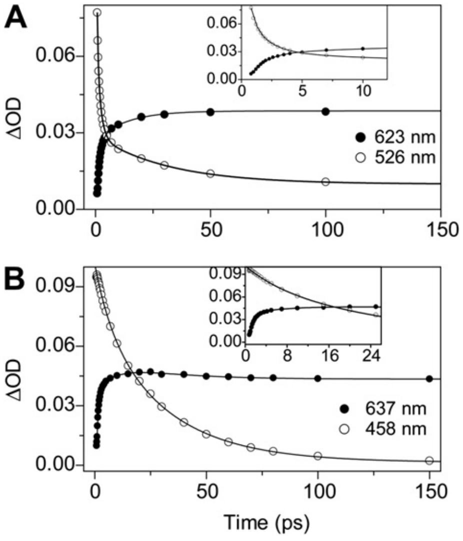
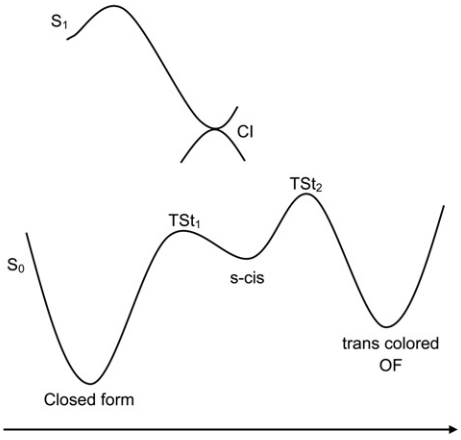


Fig. 8. Kinetic traces for 6′CN–SNO in (A) n-hexane at 526 nm (○) and 623 nm (●) and (B) acetonitrile at 458 nm (○) and 637 nm (●). The solid lines are the best fits to the data (time constants in Table 1). The insets show enlargements of the early time domain kinetics.



Scheme 2. Representation of the ground and first excited potential energy surfaces for the ring-opening reaction of SNO based on the reaction scheme established from theoretical calculations (Fig. 9 in ref. [28]).

Table 2
Ratio ($R^{OF/blue}$) of the final intensity of the OF absorption band (band surface measured at 500 ps) and of the initial intensity of the blue absorption band (band surface measured at 1 ps) for 6′CN–SNO, 5′CHO–SNO, and SNO in n-hexane, toluene, ethanol, and acetonitrile, and quantum yield of photocoloration (Φ_{col}) in nonpolar and polar solvents.

	$R^{OF/blue}$				Φ_{col}[a]	
	Hex	Tol	EtOH	Aceto	Nonpolar	Polar
6′CN–SNO	0.42	0.43	0.32	0.35	0.17[c]	0.11[e]
5′CHO–SNO	2.0	[b]	1.0	0.38	0.35[c]	0.13[e]
SNO	2.5	[b]	2.0	1.9	0.41[d]	0.32[f]

[a] From Ref. [2].
[b] Not measured.
[c] In toluene.
[d] In methylcyclohexane.
[e] In methanol.
[f] In ethanol.

SNO family [28] that were consistent with the picture of an ultrafast ring-opening process on the excited S_1 state surface followed by a near barrierless deactivation to the ground state surface through a conical intersection (CI), yielding both an s-cis opened intermediate and the initial closed form with a distribution ratio of about 1:1 (Scheme 2). This predicted s-cis opened form could correspond to the X intermediate observed experimentally. Then, the s-cis form is expected to evolve via cis–trans isomerization toward the trans forms (transition state TSt_2) in competition with the back ring-closure process (transition state TSt_1) with the partition ratio governed by the relative heights of the respective energy barriers. Indeed a good correlation was found between experimental quantum yields of photocoloration (Φ_{col}) reported for a series of substituted SNO derivatives and the calculated cis–trans isomerization barriers $E(TSt_2)$, suggesting that this barrier is an important parameter in controlling the photocoloration reaction [28].

On the other hand Metelitsa et al. found, for a series of 17 substituted SNO compounds, that the quantum yield of photocoloration is systematically higher in toluene than in methanol [3]. This effect has been interpreted, with reference to the assumption that an intermediate X is involved in the reaction mechanism, by supposing a better stabilization by solvation of X and thus a structure closer to the initial ring-closed reactant in the polar solvent. In this configuration, a weak energy barrier between X and the closed form would favor the ring-closure back reaction. On the contrary, in toluene, the less solvated X species would have a structure closer to the final OF photoproduct, lowering the energy barrier toward the OF form and thus favoring its formation. This interpretation is consistent with the conclusion of Maurel et al. stating from quantum chemical results that the $E(TSt_2)$ reaction barrier between a cisoid intermediate and the stable trans OF species is a crucial parameter governing the photocoloration reaction [28].

Confronting the transient absorption results obtained for the 6′CN–SNO, 5′CHO–SNO, and SNO compounds with the corresponding quantum yield of photocoloration is expected to provide very complementary information on the influence of the nature of the substituent and the solvent on the reaction mechanism. A key issue for this task is certainly the assignment of the transient absorption blue band that evidently plays a determinant role in the photophysics of these compounds. In this regard, three major conclusions can be stated from the analysis of the spectral and kinetic evolution observed after excitation for 6′CN–SNO, 5′CHO–SNO, and SNO. The first point concerns the dissimilar kinetics of the appearance of the OF species (red band) and the decay of the blue band, which points out the important result that the blue-absorbing intermediate, previously named X, cannot be the precursor of the OF product. The analogy of the blue band decay kinetics and OF band rising kinetics observed for some SNO derivatives is thus probably fortuitous. The second point is the surprising constancy of the OF band growth kinetics. For almost all compounds and all solvents, the appearance of this band can be acceptably fitted by a two-exponential kinetic model with a main component of time constant around 1 ps and a lower one of time constant of about 10 ps (see Table 1). Such constancy in the OF formation kinetics contrasts with the strongly substituent- and solvent-dependent efficiency of OF production measured by the coloration quantum yields (see Φ_{col} values in Table 2). For instance, in nonpolar solvents, the Φ_{col} value doubles on going from 6′CN–SNO to 5′CHO–SNO or SNO but the time constants of OF appearance in n-hexane are not significantly different in the 3 compounds. On the other hand, for 6′CN–SNO as well as for 5′CHO–SNO, Φ_{col} is notably enhanced on going from nonpolar to polar solvents but the OF appearance time constants do not decrease and are even slightly higher in n-hexane than in ethanol or acetonitrile. The nearly constant value of the rate constants of formation of OF is not consistent with the previous statements that the substitution and solvent effects on the efficiency of this reaction, measured by Φ_{col}, results from variations of the associated barrier height [3,28]. Therefore, it must be assumed that a parallel photoinduced process is competing with the formation of the OF species and arises with an efficiency strongly dependent on the substituent and solvent, thus controlling the Φ_{col} value.

The third important piece of information arising from the time-resolved data concerns the influence of the nature of the substituent and the solvent on the relative intensity of the blue and OF absorption bands. The ratio $R^{OF/blue}$ of the final intensity of the OF absorption band, as measured by the band surface in the 500 ps spectrum, to the initial intensity of the blue absorption band, as measured by the band surface at 1 ps, for 6′CN–SNO, 5′CHO–SNO, and SNO in the different solvents is given in Table 2, together with the Φ_{col} values reported for these compounds in polar and nonpolar solvents [2]. There is an apparent correlation between the $R^{OF/blue}$ and Φ_{col} variations. On one hand, in a given solvent, both parameters increase on going from 6′CN–SNO to 5′CHO–SNO and SNO. On the other hand, for a given spironaphthoxazine compound, both parameters increase on going from polar to nonpolar solvents. The strongest effect is observed for 5′CHO–SNO, for which both the $R^{OF/blue}$ and Φ_{col} factors are somewhat similar to those found for SNO in nonpolar solvents but rather comparable to those of 6′CN–SNO in polar solvents. This correlation suggests that an increase of the blue-absorbing species yield parallels a decrease of the OF yield, i.e. both species are formed via competing pathways. This result corroborates the above conclusion that the blue-absorbing species is not the precursor of OF and reveals that it is, instead, the product of the photoinduced process that competes with the formation of OF and controls its efficiency.

With regards to these results, the exact nature of this blue-absorbing species cannot be identified with certainty but two hypotheses can be proposed on the basis of the schematic representation of the ring-opening reaction path (Scheme 2) derived from that proposed by Maurel et al. for SNO from quantum chemical predictions [28]. A first possibility is an assignment to the ground state s-cis form, as proposed by some authors for X [17,18,28], but with the further restriction that the s-cis form is not the precursor of OF. To take this constraint into account, it can be envisaged that ultrafast (sub-picosecond) excited state relaxation through the S_1/S_0 conical intersection (CI) leads to an unsolvated and vibrationally hot ring-opened cisoid species, which can either relax by cooling/solvation toward a vibrationally relaxed s-cis form at equilibrium geometry or evolve via cis–trans isomerisation to the trans OF species (passage above the TSt_2 barrier). The observed growth and band shape evolution of the OF band can be due to structural relaxation and thermal equilibration of the distribution of OF conformers after the barrier crossing. Moreover, it must be assumed that the barrier between the relaxed s-cis form and the trans form (transition state TSt_2) is too large to be surpassed so that (i) hot s-cis molecules can cross the TSt_2 barrier but vibrationally relaxed s-cis molecules cannot and (ii) the only possible deactivation of vibrationally relaxed s-cis is to cross the barrier of reformation of the closed form (transition state TSt_1). In support to this assumption, the theoretical calculation performed by Maurel et al. predict systematically, for various substituted SNO derivatives, that the TSt_2 barrier is one order of magnitude higher than the TSt_1 barrier [28]. A low TSt_1 barrier implies that fast ring-closure reaction must yield back the CF molecule, which is consistent with the fast decay observed for the blue-absorbing species. In this hypothesis, the OF growth and relaxed s-cis form decay kinetics are effectively unrelated, as found experimentally. As discussed above, a near-IR band maximizing in the 800–900 nm region is associated with the blue band and is thus also attributed to the s-cis species. Both spectral features are consistent with the theoretical vertical excitation wavelengths predicted, in the case of SNO, for the s-cis species with the CS-INDO-CIPSI method [28]. The fact that the formation of the OF product and s-cis isomer are competing processes is easy to understand but the substitution and solvent effects on the partitioning ratio is more difficult to rationalize. A strong dependence of the position of the S_1/S_0 CI on the substituent nature and solvent is probably determinant in these effects. In any case, the observation that the formation of OF is favored upon switching the pump excitation wavelength from 377 nm to 252 nm can be understood as the effect of a much larger excess of vibrational energy given to the system. After fast S_1/S_0 relaxation through the CI, this excess energy contained in the hot s-cis molecules is logically expected to promote the TSt_2 barrier crossing to the detriment of vibrational cooling, thus enhancing the formation of the trans OF form and reducing the production of the blue-absorbing relaxed s-cis form. To summarize, this mechanism assumes that both the final trans OF and relaxed s-cis form (blue-absorbing species) arise simultaneously and concurrently from a vibrationally hot cisoid population produced from ultrafast excited state relaxation through a S_1/S_0 CI.

An alternative interpretation is to assign the blue band to a metastable minimum of the excited S_1 state potential energy surface distant from the S_1/S_0 CI leading to the ring-opened cisoid species. No prediction of such excited state minima was reported in the theoretical investigation by Maurel et al. which was focused on the ring-opening reaction route and did not explore relaxation processes other than that driving the system to the CI [28]. However, it is not excluded that, in such complex molecules, relaxation of the excited Franck–Condon geometry toward the S_1/S_0 CI is competing with relaxation along other valleys of the excited state potential energy surface. In this case, it must be assumed that another S_1/S_0 CI allows fast deexcitation of the metastable S_1 state minimum to account for the fast decay observed for the blue absorption band. This interpretation corresponds to that already proposed in a previous report on 6′CN–SNO excited at 377 nm [32], where a competing excited state deactivation route was assumed to involve a blue-absorbing chemical intermediate called Y. In this previous work it was suggested that both Y and a short-lived intermediate species X, precursor of the OF product, were contributing to the transient blue absorption band. However this point remains to establish. In fact, in the hypothesis that a blue-absorbing excited state metastable minimum is populated in parallel to the ring-opening deactivation route, it is not clear whether or not another blue-absorbing species X precedes the formation of OF.

4. Conclusion

We have presented an analysis of the photochromic reaction dynamics of spiroindolinenaphthoxazine and its 6′CN and 5′CHO substituted compounds in different solvents by femtosecond transient absorption spectroscopy. In addition to the formation of the merocyanine coloured form (ring-opened trans form, OF), we have undeniably demonstrated the presence of another metastable species, which can be attributed to either a relaxed ground state s-cis ring-opened isomer or to a metastable minimum of the excited S_1 state potential energy surface of the ring-closed form, the formation of which is competing with that of merocyanine. The relative yields of these two concurrent processes appear strongly dependent on the nature of the substituent and on the solvent and their variation parallels the changes in quantum yield of photocoloration observed for these compounds [2]. On the basis of the observed kinetics, it is concluded that, at least in the case of the molecules investigated in this work, the production of OF (photocoloraton reaction) is controlled by the efficiency of the competing process rather than by an s-cis – trans isomerisation energy barrier. This result asserting the existence of a branching into two parallel and competing excited-state deactivation processes is certainly a key aspect of the photoreactivity of spirooxazines.

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