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Ultrafast Photo-Dynamics of a Reversible Photochromic Spiropyran[†]

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We report the first ultrafast ring closure kinetics of the merocyanine (**MC**) of a reverse photochromic spiropyran 1′,3′,3′-trimethyl-6,8-dinitrospiro[2H-1-benzopyran-2,2-indoline] (6,8-dinitro BIPS) and its 1′-(2-carboxyethyl) substituted derivative. The reaction is fast and essentially over in a few hundred picoseconds. The rate of **MC-S$_1$** state decay evaluated from transient absorbance can be correlated directly with the **MC-S$_1$** state lifetime as determined using stimulated and ordinary emission measurements. The recovery of the **MC-S$_0$** state from **MC-S$_1$** has a component with a lifetime of 60−78 ps in acetonitrile with a second component of 350−470 ps probably due to a metastable intermediate. We can further establish that the excited **MC-S$_1$** state takes on the order of 500 fs to form from higher-energy states after photoexcitation with 390 nm light.

1. Introduction

Fast and reproducible photoisomerization provides the potential for many optical switching processes from optical devices[1,2] to switchable molecular recognition and bioactivity.[3−6] Key compounds in this regard are the spiropyrans (**SP**s), which have been studied for many years using nanosecond, picosecond and steady-state irradiations as well as with X-ray and NMR techniques.[7−15]

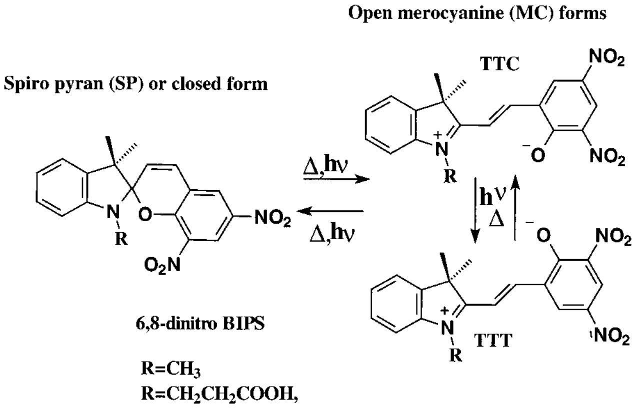
Scheme 1 shows the basic steady state (nontime resolved) mechanism by which **SP**s reversibly photoswitch between **SP** and merocyanine (**MC**) states under thermal and photochemical activation.[16,17] Because of their diverse futuristic applications,[1−6] a fundamental knowledge of the behavior of these compounds is required in order to steer this potential toward useful products.

The thermochemistry of the **SP MC** form is now relatively well understood,[15−17] as is the photochemistry of the ring opening reaction and the thermochemistry of the ring closure reaction.[18] In solution, the **SP MC** has been shown to be comprised mainly of a trans−trans−cis (**TTC**) configured isomer, with the trans−trans−trans isomer (**TTT**) also being a minor contributing form (see Scheme 1).[15−17] However, the photochemical ring closure reaction has not yet been investigated mechanistically on the picosecond to early nanosecond time scale. Also, it is apparent that the **SP-MC** often has a higher quantum yield for ring closure[19] than the related spiro oxazine **MC**[20,21] and chromene **MC**'s,[22,23] but no rationale has been applied to explain these findings, partly because the mechanism of ring closure is not yet well understood for any of these compounds and this is especially so for the **SP-MC**s.

Using nanosecond transient absorption spectroscopy, the **SP-MC** 3′,3′-dimethyl-1′-octadecyl-6,8-dinitrospiro[2H-1-benzopyran-2,2-indoline] ring closure reaction has been studied[24] with the conclusion that the reaction had three components for **MC** bleaching (<25 ns, 240 ns, and 3.4 μs) and two components for **SP** formation (620 ns and 4 μs). It was suggested that the transients with these time constants were consistent with a triplet pathway. Also with nanosecond spectroscopy a more rigorous study on several 1′,3′,3′-trimethyl spiro [2H-1-benzopyran-2,2-indoline] derivatives found that the nitro-substituted forms have a transient state (formed within the 15ns pulse) absorbing at 440 nm, which was assigned to a triplet **MC** isomer. A second transient absorbing at 430 and 635 nm was assigned to a longer lifetime cis **MC** isomer. This cis **MC** isomer was suggested to form from either the triplet or the singlet pathway, but these authors favoured a singlet route suggesting the triplet mechanism was essentially a side reaction. The transient assigned to the cis isomer had a lifetime of 2.1−8000 μs.

In the present work, we describe the subpicosecond to nanosecond time scales of the ring closure reaction for the **MC** of 1′,3′,3′-trimethyl-6,8-dinitrospiro[2H-1-benzopyran-2,2-indoline] (6,8-dinitro BIPS) and its 1′-(2-carboxyethyl) derivative and present a mechanism for this reaction via a purely singlet state manifold. We present evidence for a subpicosecond transient state in the photochemical reaction as well as a component due to either a metastable state on the pathway to the **SP** form or to the **S$_1$** state of the **TTT-MC** isomer.

SCHEME 1



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2. Experimental Section

Materials. The compound 6,8-dinitro BIPS was synthesized using the standard synthetic pathway.[18] The 1′-(2-carboxyethyl) derivative was synthesized from the same pathway, except a Fischer base with an 1′-(2-carboxyethyl) group was used. The structure and purity of this new photochromic spiropyran was established using H NMR (Bruker WP80/DS 80 MHz) and HPLC mass spectroscopy (PE-SCIEX API150EX using APCI, heated nebulizer 450 °C, positive ion mode in a 1:1 CH_3OH: water mixture). The principle peak in the mass spectrum was the MH^+ peak at 426.4 Daltons. The second highest peak was at 354.4, corresponding to the loss of the alkyl chain from the indoline nitrogen. This compound underwent thermal decomposition before its melting point at a temperature of 262 °C due to the strongly electron withdrawing nitro groups. The solvent used in spectroscopic experiments was Nacalai Tesque spectrophotometric grade acetonitrile, and this was used as supplied.

Steady-State Spectra. Static fluorescence measurements were made using a Hitachi F-4500 spectrofluorimeter and static absorbance measurements were made with a Shimadzu UV-3100PC spectrometer. No corrections were applied.

Transient Absorption Spectra. The initial form of the 6,8-dinitro BIPS and the 1′-(2-carboxyethyl) derivative used in these experiments was the **MC** form. The samples possessed a large flowing volume to prevent accumulation of photolysis products and **SP** form during data accumulation.

The apparatus used for transient absorption measurements consisted of a femtosecond Ti-sapphire laser (Coherent Mira 900) and a regenerative amplifier (Continuum TR70-10) with a fundamental of 780 nm, an energy of 3 mJ/pulse, a pulse duration of 170 fs, and a repetition rate of 10 Hz. The fundamental beam was doubled with a KDP crystal to produce 390 nm light, and this beam was split from the residual fundamental with a dichroic beam-splitter. The fundamental was then passed down an optical delay line and focused into a cell containing water to generate a white light continuum probe beam. This probe beam was further split, and one part was monitored with a multichannel photo detector attached to a monochromator to monitor the shot to shot probe spectral distribution. The remainder of the probe beam was directed into the sample. The frequency doubled (390 nm) portion of light (pump beam) was overlapped with the probe beam at the sample, and varying the optical delay between the pump and probe enabled time-resolved absorption measurements to be made by monitoring the probe beam intensity with a second monochromator and multichannel photo detector. All data was corrected for chirping of the probe pulse and for variation in the probe pulse spectral distribution.

Emission lifetimes were determined after excitation using the same Ti-sapphire laser frequency doubled with a KDP crystal. The time-resolved fluorescence was measured with a Hamamatsu C4334 streak camera.

Time-resolved Kinetic traces were fitted using commercially available “IgorPro Wavemetrics(Tm)” and “Photolumi” software.

3. Results and Discussion

Static measurements. Static absorption and fluorescent measurements are shown for 6,8-dinitro BIPS in acetonitrile in Figure 1. The main **MC** absorption maximum is at around 530 nm, whereas its main emission maximum is at around 605 nm. The **SP** form has little absorption above 400 nm. 6,8-Dinitro BIPS **MC** and its derivatives are highly zwitterionic, and as expected, their spectra shift to the blue in polar solvents.[15−17]

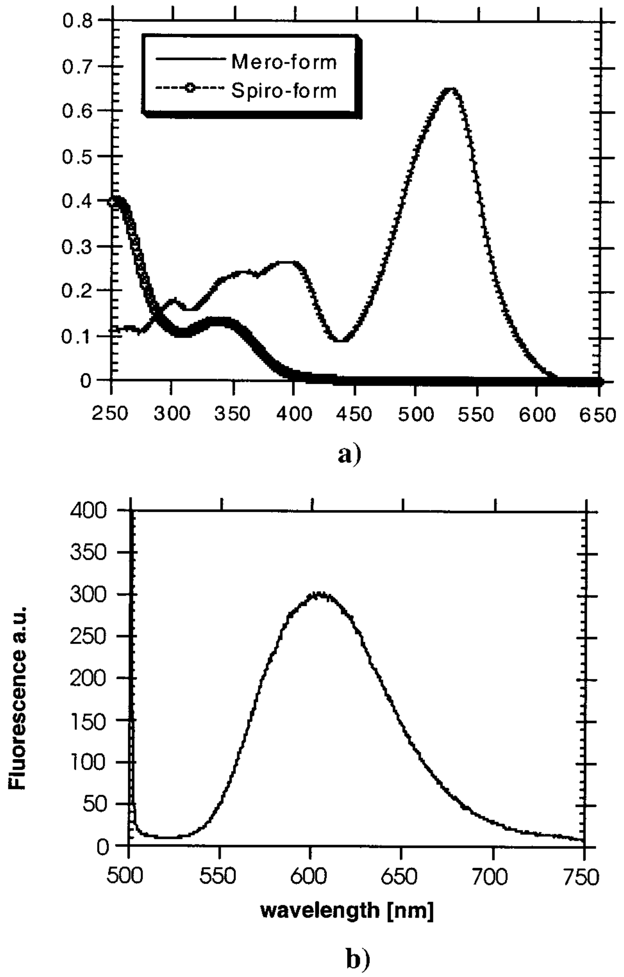


Figure 1. (a) Absorption and (b) emission spectra of 6,8-dinitro-BIPS in Acetonitrile, 3.1 × 10^{-6} M, λ_{ex} = 490 nm, λ_{max} = 605 nm.

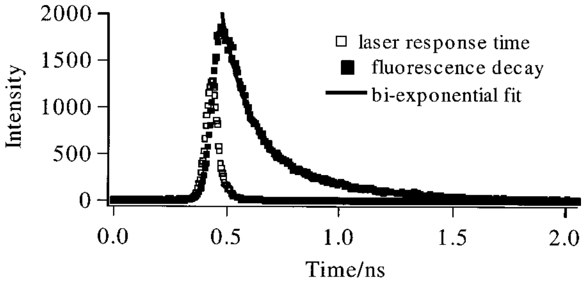
TABLE 1: Lifetimes of Transient States

solvent/compound/model for fit 6,8-dinitro BIPS	τ**1** [ps]	τ**2** [ps]
acetonitrile biexponential (emission)	(em) 75 ±15	(em) 350 ±20
biexponential (absorption)	(abs) 73 ± 10	(abs) 365 ± 20
1′-(2-carboxyethyl)−6,8-dinitro BIPS	τ1 [ps]	τ2 [ps]
acetonitrile biexponential (absorption)	78 ± 10	470 ± 15

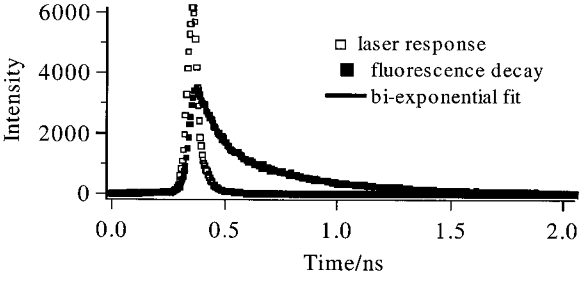
Fluorescence Lifetime Experiments. Kinetic traces from fluorescence lifetime measurements are shown in Figure 2, and the lifetime data are given in Table 1.

Time-resolved fluorescence of 6,8-dinitro BIPS in acetonitrile reveals two components to the decay of the excited **MC-S$_1$** state. The decay gives satisfactory fits to a biexponential decay function with short ($\tau1$ = 75 ps) and long ($\tau2$ = 350 ps) components. The ratio of ($\tau1$ amplitude):($\tau2$ amplitude) was 3.1:1.

Femtosecond Pump Probe Experiments. As shown in Figure 3, the transient absorption spectra can be split into three distinct regions. These are the **MC-S$_1$** state absorption region around 440 nm, the **MC-S$_0$** bleach and recovery region at 525 nm, and the region due to stimulated emission from the **MC-S$_1$** state at 630 nm. This stimulated emission is induced when the high-intensity 170 fs continuum probe beam’s photons encounter excited **MC-S$_1$** species in the solution inducing emission. The

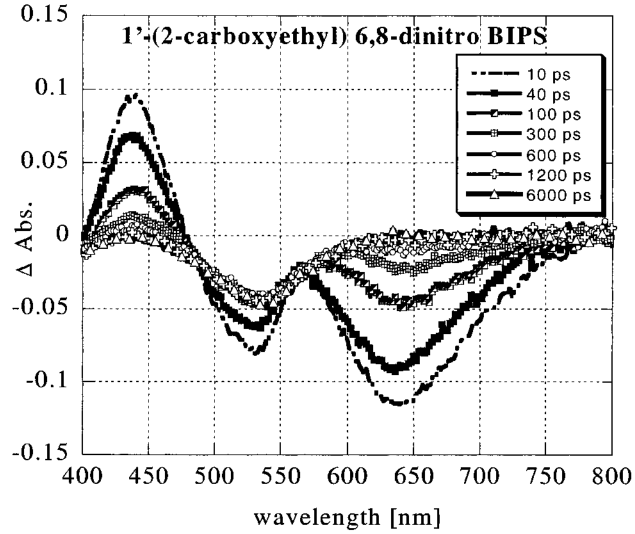


a) 6,8-dinitro BIPS



b) 1'-(2-carboxyethyl) 6,8-dinitro BIPS

Figure 2. Time-resolved fluorescence of (a) 6,8-dinitro BIPS and (b) 1′-(2-carboxyethyl) 6,8-dinitro BIPS in acetonitrrile.



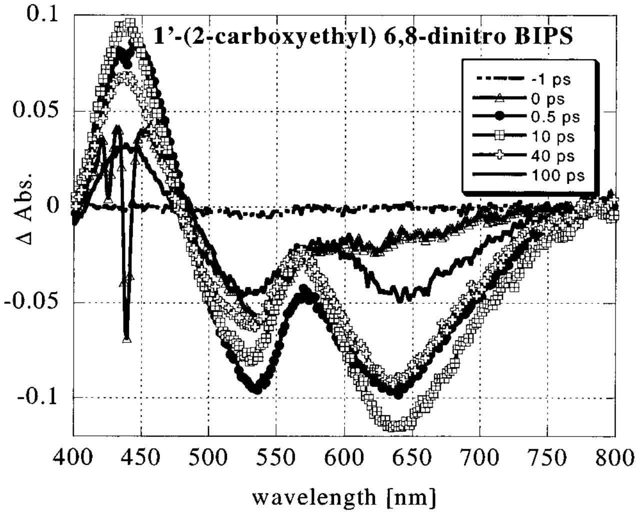


Figure 3. Transient absorption spectra for 1′-(2-carboxyethyl) 6,8-dinitro BIPS in acetonitrile.

stimulated emission region is handled theoretically in the same way as the rest of the absorption spectrum since it is the directly analogous reverse process to ordinary absorption. The spectral shape in the stimulated emission region may also contain a component of the **MC-S$_1$** state absorption spectrum since the maximum is at 630 nm rather than 605 nm, as measured in the static experiments although note that the static measurement is not corrected. The kinetics derived from the **MC-S$_1$** state absorption, ground-state recovery, and stimulated emission regions are intrinsically linked since they predominantly follow the lifetime of the excited **MC-S$_1$** state. None of the spectral regions studied will reliably follow the formation of the **SP** form.

The results of fitting to kinetic decays are summarized in Table 1. The simplest fit to the data was a biexponential, which adequately followed decays in all regions in the spectrum from times of 10−6000 ps. It is immediately apparent that there is good agreement between the fluorescence lifetime measurements and the biexponential decay lifetimes, $\tau 1$ and $\tau 2$. The **MC-S$_1$** state lifetime clearly has short and long components of lifetime on the order of $\tau 1 = 73-78$ ps and $\tau 2 = 350-470$ ps. Typical kinetic traces and fits to the data are given in Figure 4. Interestingly, at some wavelengths, the longer component $\tau 2$ was manifest as further bleaching. This is shown for a kinetic trace taken at 490 nm for the 1′-(2-carboxyethyl) 6,8-dinitro BIPS in acetonitrile. The positive amplitude of this $\tau 2$ decay necessitates the incorporation of an intermediate species other than the main **MC-S$_1$** state in any proposed mechanism. This is because if only a single **MC-S$_1$** state were responsible for the decay, then the amplitude of the decay would always be either positive or negative for a given wavelength but not both. To confirm this, we plotted the amplitude of the $\tau 1$ and $\tau 2$ decay as a function of wavelength. This is shown in Figure 5 for the 1′-(2-carboxyethyl) derivative, from which we can immediately see that there is spectral difference for the species having lifetimes of $\tau 1$ and $\tau 2$. The same spectral differences between $\tau 1$ and $\tau 2$ decays were found for 6,8-dinitro BIPS. We note that a component of stimulated emission is evident in the $\tau 2$ decay amplitude as is the **MC-S$_1$** state absorption at around 440 nm, indicating an intrinsic link to the **MC-S$_1$** state; however, for $\tau 2$, there is also positive absorption at around 540 nm that is not present in the $\tau 1$ amplitude spectral profile. Also in Figure 5, we compare the 0.5 and 10 ps spectra with the $\tau 2$ amplitude and note that significantly there is an increase in absorption in the ground-state depletion region at 540 nm in this time interval despite a corresponding increase in both stimulated emission and **S$_1$** state absorption.

We will examine two mechanisms to explain the above kinetic description and these are shown in Scheme 2 and Scheme 3.

Scheme 2 is described thus: Following femtosecond photolysis, an excited-state equilibrium is rapidly established (0.5−10 ps) between a transient that is twisted or cis about the central methine bond and the main **MC-S$_1$** state accounting for the absorption increase at 540 nm in this time interval. The central methine bond should have a low order close to 1 in the quinoidal excited state potential energy surface allowing the central bond to easily twist with low activation energy. This cis or twisted transient then slowly forms **SP** but, being metastable, can also re-form the **MC-S$_1$** state with a lifetime of $\tau 2$ as this state is depleted by recovery to the **MC-S$_0$** state with a lifetime of $\tau 1$. This mechanism adequately and simply explains the biexponential behavior and the $\tau 2$ bleach but does not account for the expected interplay from different isomers (**TTC** and **TTT**) known to exist in polar solutions.[15−17] The lack of evidence for any effect from the different isomeric forms that we know to

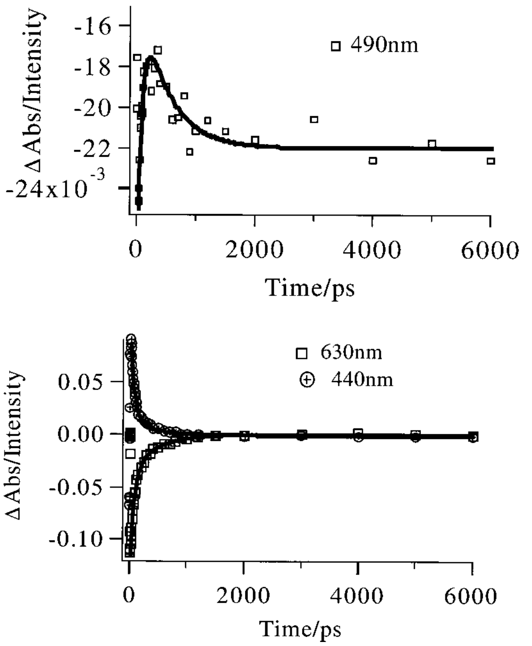


Figure 4. Time-dependent absorption changes for 1′-(2-carboxyethyl) 6,8-dinitro BIPS in acetonitrile at different wavelengths.

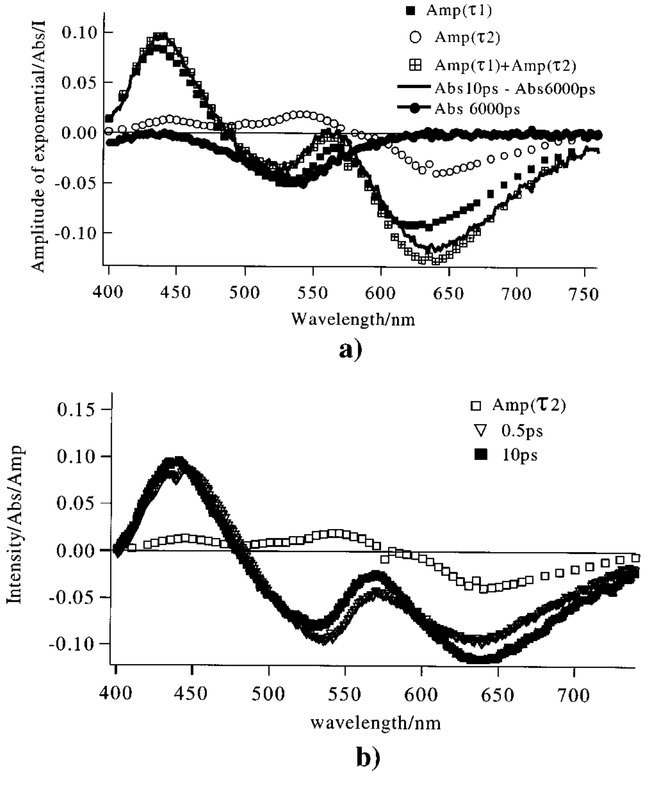


Figure 5. Amplitudes of components to the biexponential decays fitted at every wavelength (a) compared to the experimentally determined amplitude and (b) compared to the spectra at time intervals of 0.5−10 ps.

exist in solution may be because the **TTT** isomer is a minor contributor to the spectral envelope and the **TTC** isomer dominates the kinetics.

Another point of interest is the longer τ2 for the 1′-(2-carboxyethyl) derivative. This may suggest some H-bonding from the propanoic acid OH directed to the nitro group oxygens or the phenyl oxygen. Such an interaction is only favored in a twisted or cis type of conformation, as only in this form can interatomic distances be reduced sufficiently for close approach of these groups. This behavior supports the assignment of a twisted conformer being responsible for τ2.

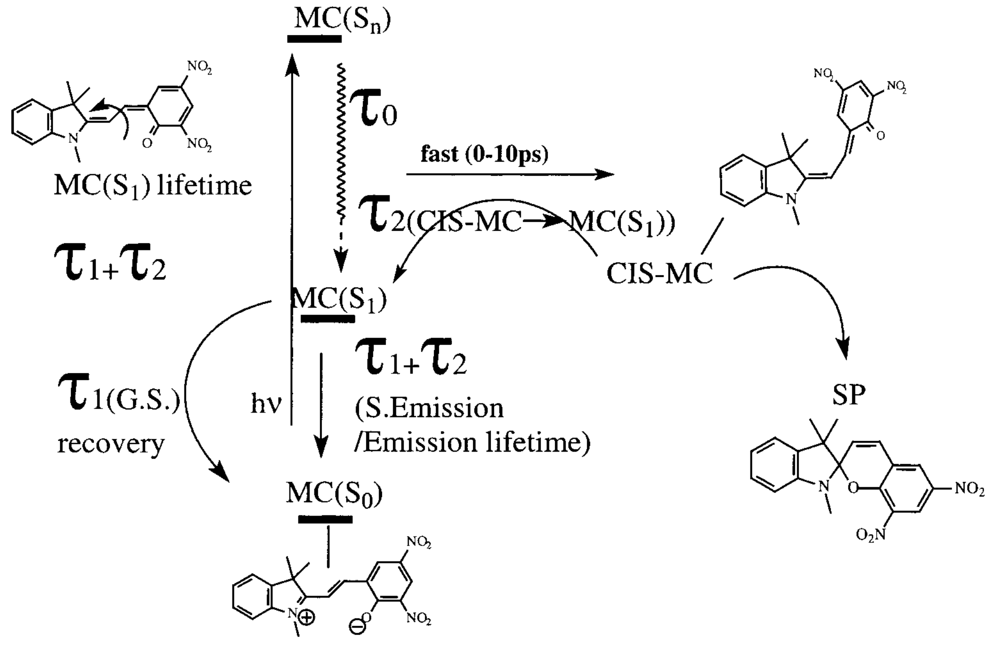
The second alternative mechanism is given in Scheme 3. This mechanism explains the biexponential behavior on the basis of two singlet states forming from the two **MC** isomers **TTC** and **TTT** that have been identified in equilibrium in solution.[15−17] In this equilibrium, the **TTC** isomer always dominates, and this can account for τ1, whereas the **TTT** isomer accounts for τ2.

However, from Figure 6, we can see that the spectral form of the bleached state at 4 ns is in good agreement with the steady-state difference spectrum obtained from static experiments. This spectral agreement is also good at 400 ps delay. This means that even after 400 ps and 4ns, apparently the same equilibrium distribution of isomeric forms is present in the solution as for infinite time and therefore the isomerization to the **SP** form appears to have occurred approximately equally from all species contributing to the **MC** absorption envelope. If different isomers with different spectra and photochemistries were responsible for the different kinetics of the two exponential decays (τ1 and τ2), then one would reasonably expect that one isomer should form **SP** more than the other leading to the relative depletion of one isomeric form more than the other in the excited state. This selective depletion should then be evident in the recovered ground-state spectrum unless (1) the spectral differences occurring due to two isomeric forms is too small to see, a possibility that can be ruled out in view of Figure 5a, or (2) the conversion to **SP** was equal from excited-state **TTC** and **TTT**, which is not likely in view of their different conformations and lifetimes, or (3) these isomeric species reequilibrate during internal conversion, vibrational cascade and the short time thereafter. Against this hypothesis is that the lifetime for **TTC**−**TTT** isomerization under normal thermal activation measured at 243K is 0.011 s, which is much slower than 400 ps to 4 ns[16] and the activation energy for this isomerization is 44 kJ mol^{-1}. We cannot rule out that a vibrationally hot molecule may isomerize many orders of magnitude faster as the molecule internally converts to the ground-state; however, such high temperatures would also be expected to shift the equilibrium between **TTT** and **TTC**, thereby altering the spectra. If the interchange of **TTC** and **TTT** were rapid enough in the excited state to lose spectral differentiation information before return to the ground state, then it would also lead to monoexponential decay behavior of the **MC-S$_1$** state, and we can therefore rule out such a scenario.

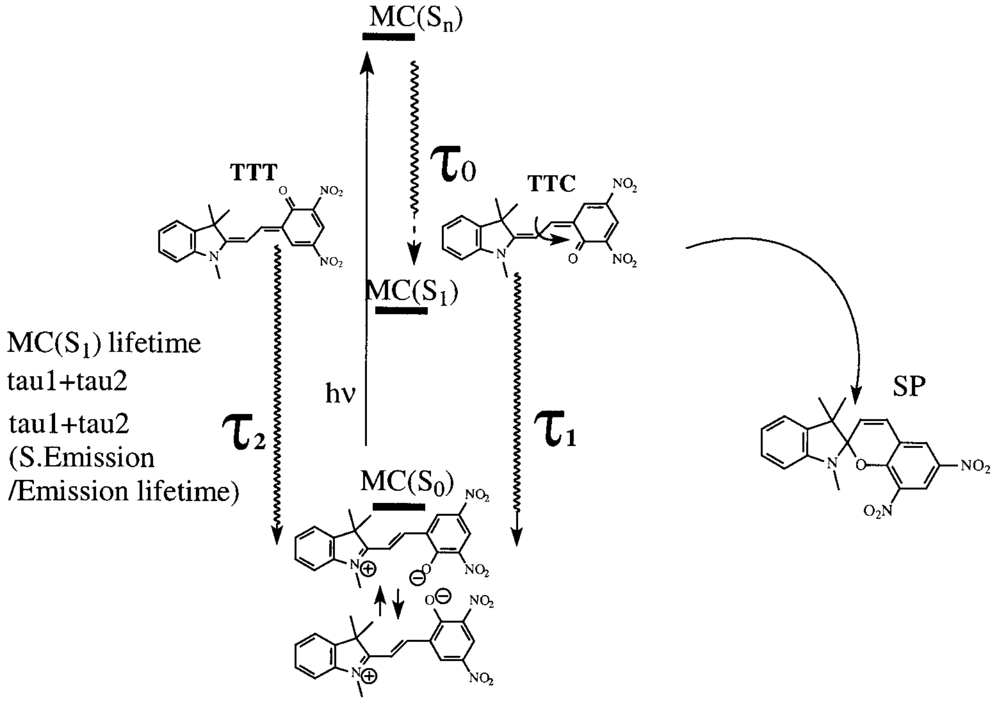
Both Scheme 1 and Scheme 2 are interesting models for the biexponential behavior that have individual merit, but both require that we somehow do not see the effect of the different isomers on one level or another and for one reason or another. The model that best accounts for all observations is that in Scheme 2, involving the twisted or cis intermediate, as this accounts for the obvious spectral difference seen in Figure 5a. The amplitude of the τ2 intermediate has an opposite sign to that of the τ1 state. This observed change of sign is unexpected if the TTT isomer were implicated. Further, the presence of a state distinct from the MC excited state is implied by the absorption increase in this same region between 0.5 and 10ps seen in Figure 5b.

In the shorter subpicosecond time scale shown in Figure 7, we note that the stimulated emission from the **MC-S$_1$** state lags behind the ground-state depletion monitored at 515 and 555 nm. Clearly it takes a measurable, although subpicosecond, lifetime for the lowest energy **MC-S$_1$** state to form from higher energy states. We denote this **MC-S$_1$** formation lifetime as τ0.

SCHEME 2



SCHEME 3



Further from Figure 7, we can see that the ground-state bleach at 555 nm also precedes the **MC-S$_1$** state rise measured at 450 nm. One explanation is that higher energy **MC-S$_n$** states do not give stimulated emission at 630 nm or as much absorption in the 450 nm region and the lifetime for relaxation from the upper excited states pumped with the excess energy from 390 nm light is about 500 fs (The **MC-S$_0$−S$_1$** transition is around 525 nm). An equally plausible alternative is that the **MC-S$_1$** state is vibrationally hot at times around time = 0 and exists in a conformation that is sufficiently distorted to reduce the efficiency of absorption or stimulated emission. We note the presence of some stimulated emission at $t = 0$ ps, but this is manifest as a lower intensity higher energy and broadened peak. The lifetime τ0 should depend on the amount of excess energy input. Note that good isosbestic points are maintained throughout the spectral evolution from >1 ps to 6 ns, indicating that rather simple two species processes are occurring thereafter; however at times of 1 ps and below, the isosbestic points deviate significantly in accord with the kinetic data shown in Figure 7.

Roughly, on the basis of the amount of ground-state bleach and recovery, we can estimate the quantum efficiency of formation of the **SP** form from the **MC** (ϕmc-sp) to be around 0.44 in acetonitrile. Of course, this estimate neglects the probable contribution of the **MC-S$_1$** state absorption and that of other species to the spectral envelope, but it gives a good ballpark guide. Judging by spectral shapes, this estimate should be an overestimate as the **MC-S$_1$** state absorption's contribution to the overall spectral form appears to eat into the bleached state

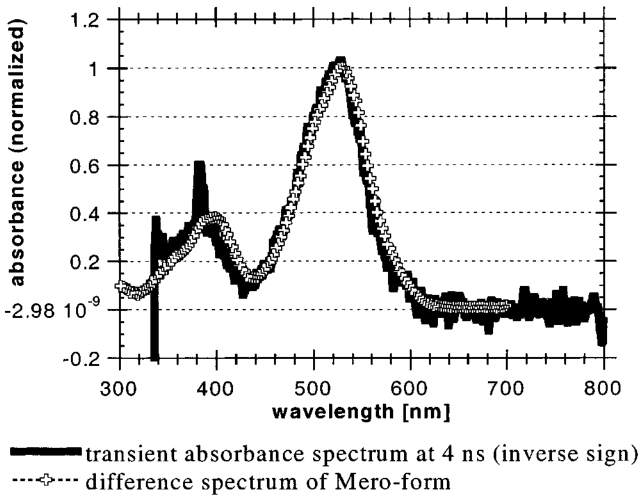


Figure 6. Comparison of steady-state bleaching and time-resolved bleaching at 4 ns.

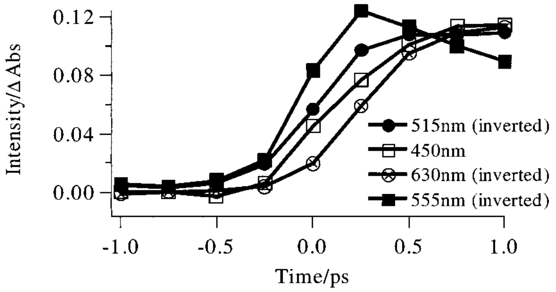


Figure 7. Ultrashort sub picosecond time-scale of the reaction.

spectral profile compared to the shape of the bleached **MC** spectrum obtained at long time scale and under steady state.

Summarizing the Transient Studies. We propose a singlet pathway to **MC** to **SP** isomerization also involving a twisted or cis intermediate. We see no transient states absorbing in the visible region after 400 ps when only bleached **MC** is seen. With reference to the nanosecond work of other authors,[7,24] we note that they used different compounds. In the case of ref 24, their N-octadecyl substituent should dramatically hinder isomerization, and in the case of ref 7, their triplet state was a minor pathway. However, we do not see any evidence for a longer lifetime cis isomer or its precursor during 6000 ps.

As to why the **SP-MC**s generally have a higher bleaching efficiencies than those of the spiro oxazine or the chromene **MC**s, we propose that it is the zwitterionic character that is the key to the issue. In the zwitterionic ground state of **SP-MC**s, bond rotation is favored around the less double bonded terminal bonds on the methine bridge,[16] whereas in the excited state, isomerization would be favored around the central methine bond which in the excited **MC-S$_1$** state will be the least double bonded after charge transfer from the phenyl oxygen to the indoline nitrogen. The reverse argument holds for the spirooxazine and chromene **MC**s, which are mainly quinoidal in the ground state (therefore zwitterions in the excited state). In that case, thermal isomerization is not favored in the ground state (although it does occur) due to steric hindrance of bond rotation for twisting around the central methine bond, and twisting around the high-order terminal methine bonds will be a high energy transition. For chromenes and spirooxazine, photochemical isomerization in the **MC-S$_1$** state will be favored about the terminal bonds on the methine bridge in these zwitterionic excited states.

4. Conclusions

We propose that the mechanism given in Scheme 2 is the most likely pathway for ring closure to the SP form. In both cases rapidly after photoexcitation with 390 nm light the **S$_1$** state forms from higher energy states with $\tau0$ of around 500 fs. In Scheme 2, the **S$_1$** state partitions between the recovery of the ground state of the MC and the formation of **SP** form via a metastable intermediate that is probably cis or twisted about the central methine bond. This intermediate rapidly forms in equilibrium with the **MC-S$_1$** state but can return to the **MC-S$_1$** state as ground-state recovery occurs. The singlet manifold is predominant, and no evidence for triplet state transients is seen.

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