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ARTICLES

Sequential Merocyanine Product Isomerization Following Femtosecond UV Excitation of a Spiropyran

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The ring-opening dynamics of the photochromic switch 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] in tetrachloroethene is studied with both femtosecond time-resolved ultraviolet (UV)/visible and UV/mid-infrared (IR) pump−probe spectroscopy. During the first picosecond we identify two new transient features in the UV/vis experiments, the first of which we assign to spiropyran $S_1 \rightarrow S_n$ absorption (lifetime ≤ 0.2 ps). The second feature (lifetime 0.5 ± 0.2 ps) we tentatively assign to the merocyanine T_2 state. After 1 ps both probing methods show biexponential merocyanine formation kinetics, with average time constants of 17 ± 3 and 350 ± 20 ps. In the UV/IR experiments, the initial dynamics show more dispersion in formation times than in the UV/vis measurements, whereas the slower time constant is the same in both. A weak transient IR signal at ∼1360 cm^{-1} demonstrates that this biexponentiality is caused by a sequential isomerization between two merocyanine species. Lifetimes provide evidence that the merocyanine S_1 state is not involved in the photochemical reaction.

1. Introduction

The photoinduced reversible conversion between spiropyran and merocyanine isomeric species has been the subject of numerous experimental and theoretical studies.[1−27] The main motivation for this research has been to attain the understanding of the photophysical behavior with the purpose of utilizing this photochromic pair in applications such as holographic data storage or functionalized molecular switches.[28,29] Exciting a spiropyran (SP) species in the near-ultraviolet (UV) to the first electronic singlet excited state leads to a ring-opening, involving cleavage of the C−O bond that connects the chromene and indoline parts, and results in the formation of merocyanine (MC) species, which have a strong $S_0 \rightarrow S_1$ band in the visible (vis) region, due to a larger conjugated π-electron system.[2,4,11,21,30] The electrocyclic reaction responsible for the photochromism of spiropyrans is shown in Figure 1. It is believed that the MC species can be transformed back to the SP form either thermally or photochemically [2,3,16]. The formation of several MC conformers has been considered, due to possible cis (C) to trans (T) isomerizations around the ethylenic bonds in the bridge segment that connects the indoline and the former chromene part.[2,8−10,15,20,25] Quantum mechanical calculations[23] for the SP 6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline], further abbreviated as 6-nitro-BIPS, have shown that in the MC electronic ground state the TTC isomer is the energetically most stable, while the other stable isomers, TTT, CTT, and CTC, lie at most about 1000 cm^{-1} higher in energy than the TTC isomer.

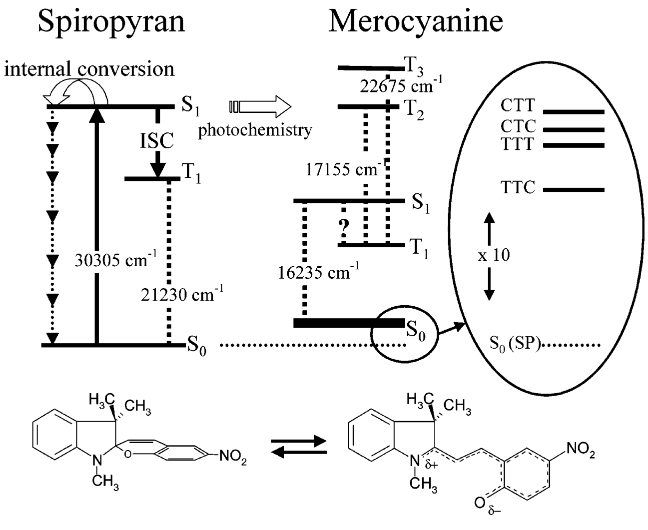

Figure 1. Molecular structures and energy level scheme of the spiropyran (SP) 6-nitro-BIPS and associated merocyanine (MC) in TCE. The energy level separations are based on absorption and emission data, except for the S_0(SP) − S_0(MC) separations, for all four stable ground-state cis−trans isomers. For these, results from calculations in vacuo are taken from ref 23.

Time-resolved spectroscopic studies have led to the conclusion that MC products appear on a picosecond time scale.[5,10,11,13,14,18] Transient electronic absorption bands, indica-

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tive of MC product, are observed in the range 500−650 nm, while for 6-nitro analogues an additional band is observed around 440 nm.[5,6,11,15,17,21] Equilibration of initially generated "hot" MC transient species toward a distribution of different MC configurations has been proposed.[11,14] For 6-hydroxy-BIPS a recombination channel for a transient MC species was mentioned, leading within 180 fs to the closed SP.[14] Several authors[5,7,16,17,21] have concluded that MC product formation follows a triplet excited-state channel for 6-nitro derivatives of BIPS, while it has been suggested that the reaction follows a singlet excited-state pathway for BIPS derivatives without the nitro group.[11,14] Nanosecond time-resolved Raman spectroscopy of 6-nitro-BIPS has led to conflicting conclusions on the number of existing transient MC isomers.[8,9,15,25]

For most spiropyran compounds the merocyanine isomers are thermally unstable, and in time a spontaneous "dark" reaction regenerates the closed SP isomer. A notable exception is 6,8-dinitro-BIPS, which is energetically most stable in an open MC form.[22] Recently an ultrafast time-resolved single color pump/probe study was performed with excitation at 620 nm of the MC form of 6-nitro-BIPS in acetone.[18] The data showed that excitation of MC to the S_1 state is followed by a complete recovery of the bleach, with an 84 ps time constant, which led to the suggestion that the reverse photochromic reaction (ring closing after optical excitation) does not occur for 6-nitro-BIPS in acetone.[18]

Most time-resolved investigations on spiropyrans have been performed with probing in the visible.[6,7,10,11,14−18,21,22] Following the photoinduced changes by monitoring molecular vibrations has been pursued as well.[13,24−26] Probing both in the visible and in the IR have merits and limitations. In the visible one can sensitively probe electronic transitions due to large cross sections. However, typically these electronic transitions have a large spectral broadening due to strong solute−solvent interactions. Therefore, there is a significant probability that different transient electronic absorption bands overlap. In addition, optical excitation often involves changes in charge distributions which can lead to substantial solvent reorganization, resulting in significant transient red-shifting of spectral bands (time-dependent Stokes shift), thereby further complicating the analysis. The SP → MC conversion presents a particularly complicated example, since several species/states appear to have electronic absorptions in the same spectral region. Vibrational spectroscopy can in principle provide a deeper insight into structural changes because specific molecular motifs are related to narrow vibrational absorption bands in relatively well-defined spectral regions. Time-resolved vibrational spectroscopy thus holds the promise of yielding detailed information on both kinetics and structural changes. Major disadvantages to IR spectroscopy are the inherent low extinction coefficients of vibrational transitions, and the frequent overlap of the absorptions bands with those of the solvent.

Recently, we have started investigating the ultrafast ring-opening dynamics of spiropyrans[24−26] using femtosecond infrared spectroscopy. For both BIPS and 6-nitro-BIPS internal conversion (IC) from the SP−S_1 state to the SP−S_0 state is a major relaxation channel. This pathway has not been identified before. From the solvent dependence of the IC quantum yield we demonstrated a deviation from standard "energy-gap law" behavior, that could be linked to large conformational changes upon optical excitation.[26] In perdeuterated acetonitrile vibrationally relaxed merocyanine product of 6-nitro-BIPS appears with a single-exponential time constant of 9.5 ps, while the dynamics in tetrachloroethene (TCE) exhibit more complicated multiexponential behavior, which suggests formation of additional MC isomers in TCE.[25,26]

Here we present the first comparative study of UV/vis and UV/IR pump−probe spectroscopy on the same spiropyran/solvent combination, namely 6-nitro-BIPS in TCE. Motivated by a noted discrepancy in results obtained by the two techniques on the same spiropyran compound in different solvents,[11,24] we wish to establish whether the two techniques give inherently different results. From our UV/vis experiments, we identify two intermediate states that disappear within the first picosecond. Our UV/IR measurements reveal the existence of a weak transient IR absorption band providing evidence of a sequential isomerization of MC products during the first nanosecond after UV excitation. Furthermore, we present emission lifetime measurements that, in combination with the pump−probe kinetics, provide solid proof that the MC excited S_1-state is not an intermediate in the photochemical formation of MC from SP.

2. Experimental Section

The photochromic compound 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (6-nitro-BIPS), and the solvent tetrachloroethene (TCE) (spectrophotometric grade), were both purchased from Sigma-Aldrich and used without further purification. Steady-state electronic absorption spectra were recorded with a Perkin-Elmer UV/vis absorption spectrometer. Steady-state IR spectra were taken with a Biorad FT-IR spectrometer.

The time correlated single photon counting (TCSPC) setup has been described elsewhere.[31] SP was excited with the frequency doubled 400 nm output from an amplified Ti:sapphire laser system, while the 550 nm excitation pulses for MC were generated using an optical parametric amplifier.

Transient UV/vis femtosecond measurements were performed with a 1 kHz amplified Ti:sapphire laser system, yielding 120 fs pulses at 790 nm, with ∼0.8 mJ pulse energy. The 790 nm pulsed output was divided by a 70/30 beam splitter to a pump and a probe/reference part. The pump light was passed through an optical parametric amplifier TOPAS (Light Conversion Ltd.) generating 660 nm pulses of about 20 μJ. Frequency doubling in a KDP crystal resulted in 2−3 μJ pump pulses of about 150 fs tuned to 330 nm, the electronic absorption maximum of 6-nitro-BIPS in TCE. White light continuum was generated in a moving CaF_2 window from the 790 nm probe/reference beam. A beam splitter divided the white light into a probe and a reference beam. The reference beam was used for correction of pulse-to-pulse intensity fluctuations. After spectral dispersion, the white light continuum probe and reference were detected by separate 512 pixel photodiode arrays, resulting in a spectral resolution of 0.65 nm. The transient UV/vis pump−probe measurements were performed on 0.3 mM solutions of 6-nitro-BIPS in TCE pumped through a home-built flow cell with CaF_2 windows separated by a 2 mm thick Teflon spacer. The absorbance at the pump wavelength was typically 0.6−0.7.

Time-resolved UV/IR-measurements were performed with a 1 kHz, 40 fs home-built amplified Ti:sapphire laser system, as described previously.[32] The 330 nm UV pump pulses, with 2−3 μJ energy and 70 fs pulse duration, were generated by sum frequency mixing of the fundamental 800 nm laser output and visible pulses tuned at 561 nm. The mid-IR probe pulses were generated by difference frequency mixing in a GaSe crystal of near-infrared signal and idler pulses generated in a double-pass collinear parametric amplifier pumped by the laser system. Complete IR spectra were recorded with spectrally dispersed

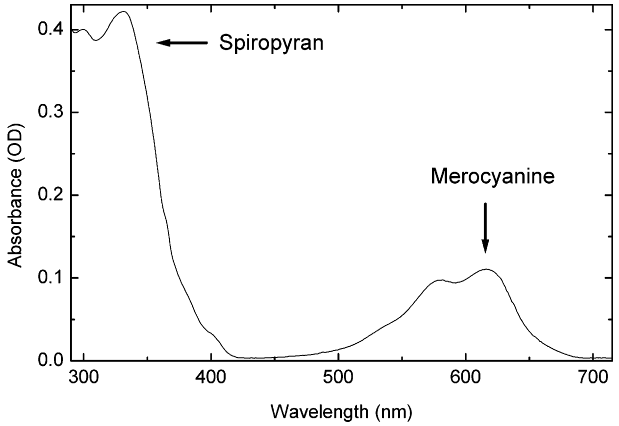

Figure 2. Steady-state UV/vis spectrum of a sample of 6-nitro-BIPS in TCE, several minutes exposed to 330 nm UV radiation. The spectrum shows the characteristic electronic absorption bands of both the spiropyran S_0 state and the merocyanine S_0 state.

100 fs IR probe pulses (~20 nJ/pulse), tunable between 1260 and 1600 cm^{-1}, using a HgCdTe detector array. In each measurement the detector covers 100−200 cm^{-1}, with a spectral resolution of 4−7 cm^{-1}. Zero pulse delay and the time resolution (~ 150 fs) were determined with a ZnSe crystal.

In the UV/IR pump−probe measurements, the photoinduced reaction was recorded on a 20 mM solution of 6-nitro-BIPS in TCE pumped through a free streaming jet with nominal thickness of 100 μm, ensuring that for every laser shot a fresh sample was excited, while the sample environment was continuously purged with nitrogen gas to avoid attenuation of the IR beams from absorption by water vapor. Streaming the large sample solution volume (about 0.4−0.5 l), together with the efficient thermal back-reaction sufficiently prevents MC aggregate formation.[33] No change was noticed in the electronic absorption spectra of our sample solutions during the time-resolved IR experiments. In addition, no noticeable spectral difference occurred between absorption spectra of the 0.3 mM solution used in the UV/vis experiments and the 20 mM solution used in the UV/IR experiments.

3. Results and Discussion

The spiropyran (SP) $S_0 \rightarrow S_1$ transition band of 6-nitro-BIPS in TCE is located in the near UV, with an absorption maximum at 330 nm. The merocyanine (MC) isomer(s) show prominent absorption in TCE between 500 and 700 nm, with a first absorption maximum at 616 nm. Figure 1 shows the energy level scheme for the involved isomers in TCE, based on quantum mechanical calculations found in the literature[23] and data presented here. In the nonpolar solvent TCE, the absorption spectrum in thermal equilibrium is dominated by SP, with at most 0.01% of the 6-nitro-BIPS compound present in the MC form. Figure 2 shows the absorption spectrum of a sample of 6-nitro-BIPS in TCE, which has been irradiated for a couple of minutes with lamplight of 330 nm, which results in a substantial concentration of MC, due to the relatively slow rate for the ring-closing reaction. The spectrum illustrates the characteristic absorption features of both MC and SP. In a previous report, the structure in the MC absorption spectrum was assigned to absorption maxima of different isomers.[12] However, we ascribe the structure to a vibronic progression. Support for this comes from Ernsting and Arthen-Engeland,[11] who concluded that a similar spectral structure for the parent compound BIPS in an argon matrix at 10 K is related to a single molecular species, and from Hobley and Malatesta, whose NMR experiments[20] on 6-nitro-8-bromo-BIPS indicated that one isomer dominates the mixture at thermal equilibrium at room temperature.

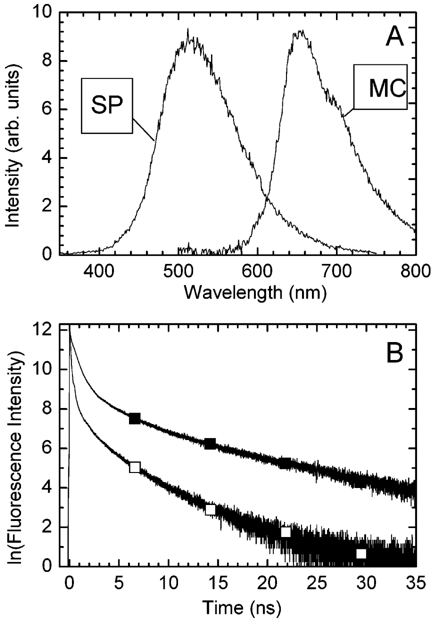

Figure 3. (A) Steady-state SP phosphorescence and MC fluorescence emission spectra. (B) TCSPC measurements of SP phosphorescence (■) and MC fluorescence (□). For the SP phosphorescence excitation is performed at 400 nm and detection at 500 nm. For the MC fluorescence excitation is at 550 nm and detection at 640 nm.

In the upper panel of Figure 3, steady-state emission spectra of the SP and the MC form of 6-nitro-BIPS in TCE are shown. The SP emission is phosphorescence from the SP triplet state T_1, with a maximum at 515 nm, while the MC emission is fluorescence from the MC S_1 state, peaking at 652 nm. We confirmed, on the basis of excitation spectra (not shown), the association of these emissions to absorption from the SP and MC ground state, respectively. Note that a fresh sample will typically exhibit MC fluorescence when excited in the SP absorption bands already after a single scan due to residual MC formed during the previous scan (MC absorbs even stronger than SP between 300 and 425 nm). The lower panel of Figure 3 shows TCSPC measurements for these two emission bands. For the SP phosphorescence (■) the sample was excited at 400 nm and the emission was selected using a 500 nm interference filter, resulting in a selected bandwidth of 10 nm. The MC fluorescence (□) was generated by excitation at 550 nm, and a 640 nm interference filter was used to select the detection wavelength. A three-exponential fit of the decay at 500 nm gave the following time constants (amplitudes; percentage of emitted photons): 55 ± 10 ps (0.535; 7.3%), 545 ± 30 ps (0.43, 58%), and 4.0 ± 0.4 ns (0.035; 34.7%). The decay is clearly nonexponential, and analysis of the decay between 10 and 35 ns indicates an even longer decay time of 8.8 ns over this interval. This latter value is rather close to the 11 ns decay constant reported in an experiment with 0.2 ns excitation pulses on 6-nitro-BIPS in oxygen-saturated acetonitrile by Lenoble and Becker.[7] Since we did not take any precautions to eliminate oxygen from our sample the nonexponential behavior is indicative of (mainly) diffusion-controlled quenching of the SP triplet state by oxygen. The MC fluorescence is fitted by the following parameters: 57 ± 6 ps (0.985; 73.2%), 600 ± 100 ps (0.011, 8.6%), and 3.5 ± 1.0 ns (0.004; 18.2%). Clearly the predominant fraction of emission decays with a 57 ps time constant, which we interpret to be the lifetime of the MC S_1 state. This is in good correspondence to previous pump−probe

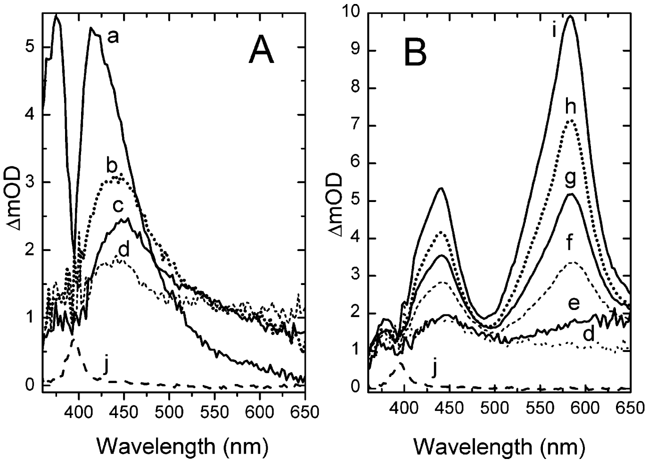

Figure 4. Transient UV/vis spectra illustrating the spectral evolution after excitation of 6-nitro-BIPS with 330 nm radiation. Frame A shows transient spectra 0 (a), 0.4 (b), 0.7 (c) and 1.0 ps (d) after UV excitation. Frame B shows transient spectra 1 (d), 2 (e), 15 (f), 30 (g), 100 (h), and 500 ps (i) after UV excitation. In both frames the dashed spectrum represents the spectrum at −5 ps (see the text).

measurements on 6-nitro-BIPS in acetone with excitation at 620 nm, where the bleach was found to recover completely with a 84 ps time constant.[18]

Figure 4 shows transient absorption spectra in the visible wavelength range obtained on 6-nitro-BIPS in TCE, after pumping at 330 nm and probing with a white light continuum. Transient absorption signals between 380 and 700 nm can be related to excited state absorption of SP, transient absorption of "hot" ground state SP molecules formed by internal conversion, or absorption of MC products either in an excited state or the ground state. Immediately after UV excitation, we observe a broad absorption band, over the range of 380−475 nm, with a tail extending to wavelengths as long as 600 nm. We ascribe this initial band to excited-state absorption from the SP S_1 state, i.e., $S_1 \rightarrow S_n$. The dip around 395 nm in this initial spectrum is due to interference of the white light probe beam with 790 nm stray light from the Ti:Sa laser. The peak at negative delay times at this wavelength confirms this conjecture.

The transient absorption below 400 nm, associated with SP $S_1 \rightarrow S_n$ absorption, is gone after 0.4 ps. This suggests a lifetime of at most a few hundred femtoseconds for the SP S_1 state in TCE. This compares well to a 180 fs decay component at 620 nm, observed by Zhang et al.[14] for 6-hydroxy-BIPS in 1-propanol, which they ascribed to absorption of either a metastable species X or the SP excited state.

Between 0.4 and 1 ps a band is seen at ∼445 nm, that decays during the first picosecond, and indicates the existence of a short-lived intermediate state or product, formed by relaxation from the SP S_1 state. A priori, this intermediate can originate from any of the following pathways for the excited 6-nitro-BIPS molecules: (a) direct internal conversion to the SP S_0 state, (b) intersystem crossing to the SP T_1 state, (c) formation of a cisoid intermediate species X,[1,2,5,14,18] or (d) a short-lived highly excited MC product state.

In a previous report, we demonstrated that in TCE 34% of the excited spiropyran molecules undergo $S_1 \rightarrow S_0$ internal conversion.[25] Initially these molecules possess about 30000 cm^{-1} vibrational energy in the SP S_0 state. From the recovery of bleached ground state vibrational absorption bands, we concluded that the cooling of these hot molecules, by dissipation to the surrounding solvent, is characterized by a 47 ps exponential time constant. When initially this excess energy is not dissipated to the solvent, the vibrational modes of the molecules are highly excited. "Hot" molecules often exhibit transient $S_0 \rightarrow S_1$ absorption, red-shifted from the room-temperature equilibrium electronic absorption spectrum.[34] During vibrational cooling, the electronic absorption should blue-shift back to the room-temperature spectrum. The transient band at ∼445 nm decays without blue-shifting, and in addition the subpicosecond decay time is extremely fast compared to the 47 ps overall cooling rate. Therefore, we exclude transient absorption of "hot" ground-state SP as the origin of the ∼445 nm transient absorption.

Absorption from the SP T_1 state we also consider unlikely to be responsible for this transient band. As shown above, the phosphorescence decay from the SP T_1 state of 6-nitro-BIPS in TCE is dominated by lifetimes of 545 ps and 4.0 ns, and thus the SP T_1 state lifetime is substantially longer than the subpicosecond lifetime of the ∼445 nm band. Therefore, we also exclude option b as the cause for this transient ∼445 nm band.

Several authors[1,2,5,14,18] have invoked the existence of an intermediate nonplanar cisoid species, typically designated as the species X, which is proposed to be close in molecular structure to the spiropyran and formed by breaking of the C−O bond. This species was first proposed by Heiligman-Rim et al.[1] based on the observation that only one of the species, identified in low-temperature steady-state absorption experiments, was capable of ring-closure under the influence of visible light; this species was labeled X. Recently Metelitsa et al.[35] observed absorption at 471 nm for a sterically crowded spiropyran at 77 K, related to a frozen-in cisoid species X. Quantum calculations have not found a local minimum in the potential energy surface around the cisoid conformation,[10,23] which does not lend credence to the cisoid intermediate proposal. However, these quantum calculations provide information on the ground state potential energy surface (PES), and the situation in the excited state PES might be different. In addition we mention that in quantum chemical calculations on the thermal ring-opening of closely related spirooxazines[36,37] evidence for a shallow local energy minimum at the cisoid conformation was found, indicating the possible existence of species X for these compounds. In time-resolved work on 6-nitro-substituted spiropyrans the appearance of a band at 430−450 nm[5−7] was ascribed to this cisoid species X as well. Krysanov and Alfimov[5] demonstrated that this band is already present 8 ps after UV excitation. This band has further been shown to decay more rapidly in the presence of oxygen,[7] which led to the conclusion that it is associated with a triplet state. Since we observe a band at ∼445 nm that decays during the first picosecond, it must belong to another state/species than the triplet state characterized by a band around 430−450 nm band that has a lifetime of tens of nanoseconds.[7] In our experiments the band at 430−450 nm, belonging to the triplet state, rises from 1 ps onward, simultaneously with an additional band at ∼583 nm (see Figures 4B and 5).

The MC T_2 state presents an interesting alternative assignment for the transient species observed at ∼445 nm during the first picosecond. On the basis of the MC $S_1 \rightarrow S_0$ fluorescence at 650 nm, the MC $T_1 \rightarrow T_2$ absorption at 583 nm (see below), and the 2000−3000 cm^{-1} energy difference between the SP and the MC S_0 states calculated by Futami,[23] the MC T_2 state could be approximately isoenergetic with the SP S_1 state. The exact location cannot be given, because it is unknown how far the MC T_1 state lies below the MC S_1 state nor have there been any reports of phosphorescence from the MC T_1 state. The 0.5

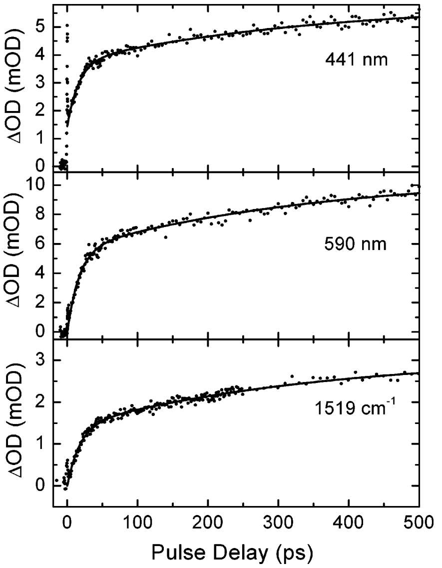

Figure 5. Transient absorbance changes recorded with probing in the visible at 441 and 590 nm, and in the mid-infrared at 1519 cm^{-1}. Fit parameters (offset, τ_1, A_1, τ_2, A_2) for the biexponential fits are as folows: 441 nm (1.5, 16.5 ps, 2.4, 350 ps, 4.4); 590 nm (0, 16.9 ps, 5.8, 350 ps, 10.7); 1519 cm^{-1} (0, 17.7 ps, 1.5, 354 ps, 3.1).

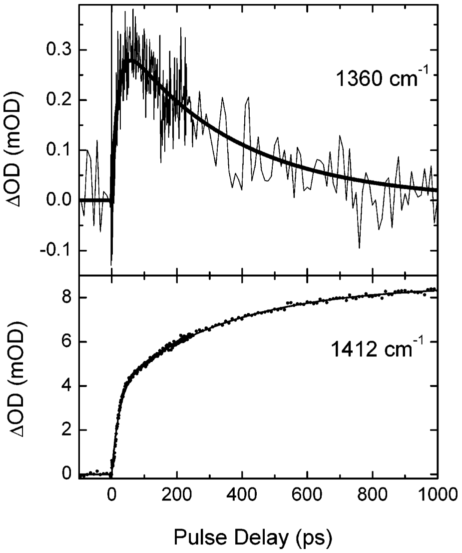

Figure 6. Transient response recorded at 1360 cm^{-1} showing the initial rise and subsequent decay (upper panel). The fit parameters (offset, τ_1, A_1, τ_2, A_2) are as follows: (0, 19.1 ps, 0.33, 350 ps, 0) at 1360 cm^{-1}. In contrast, the signal at 1412 cm^{-1} shows the typical bimodal rising behavior, with fitting parameters (offset, τ_1, A_1, τ_2, A_2) as follows: (0, 22.7 ps, 4.2, 350 ps, 8.6).

± 0.2 ps decay of the ~445 nm band can then be ascribed to the $T_2 \rightarrow T_1$ internal conversion process. Internal conversion between higher electronic states is generally ultrafast,[38,39] and this proposed process would be spin allowed. The merocyanine vibrational absorption bands show a dispersion in rise times from 5 to 28 ps.[25] The $T_2 \rightarrow T_1$ internal conversion provides a natural explanation for a dispersion in rise times accompanying the MC product formation in the T_1 state, because the vibrationally hot T_1* state resulting from this internal conversion would have to dissipate at least 15000 cm^{-1} of vibrational energy. We therefore tentatively assign the ~445 nm absorption band to an excited-state aborption from the merocyanine T_2 state.

We now turn our attention to the bands at 440 and 583 nm, emerging from 1 ps onward in Figure 4B, which previously have been discussed by several research groups.[5−7,11,15,17,21,22] Ernsting and Arthen-Engeland[11] showed for 6-nitro-BIPS in *n*-pentane, that during the first 75 ps after UV-excitation both these bands rise single exponentially, with the same time constant of 20 ps. In Figure 5, we show kinetics for 6-nitro-BIPS in TCE at both absorption bands during the first 500 ps. Although in our case the kinetics are clearly biexponential, it is worth noting that the kinetics are the same for both bands. This clearly indicates that the increased absorption bands at both 440 and 583 nm are associated with transitions from a common state. Nanosecond experiments established that the 440 nm band's decay rate is enhanced in the presence of oxygen,[7] and also formation of singlet oxygen was found in connection with this decay.[17] This supports the assignment of the 440 nm band to a triplet merocyanine species. From these studies, it was concluded that electronic excitation of 6-nitro-BIPS to the SP S_1 state leads to quantitative formation of MC in the triplet T_1 state within a nanosecond,[7,17] only to convert to MC in the electronic ground state on a microsecond time scale[7,15,17,21] (or faster if triplet quenchers such as oxygen are present). The formation time of this MC triplet state is now known to lie in the picosecond regime.[5,11,14,24−26] Considering the data in Figure 5, it is clear that both the 440 and 583 nm band must be excited state (triplet−triplet) absorptions from the same merocyanine T_1 triplet state.

In Figure 5, we also show the kinetics of the sharp 1519 cm^{-1} vibrational absorption band observed in our transient IR measurements. The overall similarity to the UV/vis data is apparent; however, some differences are found within the first 50 ps. Previously, we reported[25] IR measurements on 6-nitro-BIPS in TCE only up to 150 ps, due to experimental limitations at the time. This allowed us to detect the multiexponentiality in the kinetics, but it rendered a legible interpretation of the data impossible. Here the IR investigations are extended to the nanosecond time-delay regime. From biexponential fits to the transients displayed in Figures 5 and 6, we determine a value of 350 ± 20 ps for the slower time constant. The faster time constant is 17 ± 3 ps in the UV/vis experiments. For the IR measurements, however, the fast component varies from 5 to 28 ps, depending on the position within an IR band, with faster time constants at the lower frequency side of the IR absorption bands. This behavior indicates cooling of vibrationally hot merocyanine product. Note that with this interpretation the rise times of both electronic absorption bands (here at 441 and 583 nm) and the MC vibrational absorption bands do not fully characterize the MC formation kinetics. Instead the observed rise times are better considered the approximate formation time of a vibrationally cooled MC product in the T_1 state. Figure 5 demonstrates clearly that the 1519 cm^{-1} IR band is related to the same state(s) and species as the 440 and 583 nm band observed in the visible. The good agreement between the kinetics observed in the UV/vis and the UV/IR experiments illustrated in Figure 5, despite the factor 50 difference in concentration used in these experiments, proves that there is negligible influence on the data from aggregation.

The strong similarity of the 583 nm band in Figure 4 with the ground state merocyanine absorption shown in Figure 2 may lead to the conclusion that ground-state merocyanine absorption is already formed on the picosecond time scale. However, closer inspection of our case reveals that the 583 nm band is still clearly blue-shifted compared to the merocyanine ground-state absorption spectrum. For 6-nitro-BIPS in cyclohexane, Takahashi and co-workers[15] demonstrated that the 0.33 μs decay of the MC-(T_1) state, as evidenced by disappearance of the 435 nm band, leads only to modest intensity and shape changes of the band around 580 nm. The transient spectrum showed a further intensity increase with little spectral changes between 1 and 100 μs. High UV excitation powers, as well as the presence of oxygen were found to further affect the precise position of the MC absorption maximum after 100 μs. Observations such as these indicate that carefulness should be exerted in making assignments of specific absorption bands, as different electronic states and isomeric species clearly can give rise to fairly similar absorption features.

The biexponential rise of the merocyanine absorptions in the IR and the visible suggests either the formation of merocyanine product by two different pathways or formation of two different isomers. We have identified a very weak IR absorption band at $\sim$1360 cm^{-1}, for which the transient signal is shown in Figure 6, that rises with a time constant of 19 ± 5 ps, followed by a decay of the transient absorbance to zero with a time constant of 350 ± 70 ps. This signal proves that the initially formed merocyanine product, associated with the faster 5−28 ps time constants, is quantitatively and completely converted at a rate of 2.9×10^9 s^{-1} into another merocyanine product with *almost the same* IR and visible absorption spectral characteristics. It is relevant to point out that the $\sim$17 ps formation time of the first MC isomer is much faster than the 57 ps lifetime of the MC S_1 state, while at the same time the 350 ps formation time of the second isomer is much slower than this fluorescence lifetime. This provides solid evidence that the MC S_1 state is *not* an intermediate in the formation of MC from SP (following optical excitation).

We can summarize the kinetics of 6-nitro-BIPS in TCE during the first nanosecond after UV excitation in the following scheme:

$$\mathrm{SP(S_1)} \xrightarrow{\leq 0.2\ \mathrm{ps}} \left\{ \begin{array}{l} \mathrm{MC_1(T_2)} \xrightarrow{\approx 0.5\ \mathrm{ps}} \mathrm{MC_1(T_1{*})} \xrightarrow{\tau \approx 17\ \mathrm{ps}} \\ \qquad\qquad\qquad \mathrm{MC_1(T_1)} \xrightarrow{\tau_2 = 350\ \mathrm{ps}} \mathrm{MC_2(T_1)} \\ \mathrm{SP(S_0{*})} \xrightarrow{47\ \mathrm{ps},\ 34\%} \mathrm{SP(S_0)} \\ \mathrm{SP(T_1)} \xrightarrow{545\ \mathrm{ps} - 8.8\ \mathrm{ns}} \mathrm{SP(S_0)} \end{array} \right. \tag{1}$$

The asterisk indicates a vibrationally hot electronic state. On the basis of this scheme the signals in Figures 5 and 6 are fitted with the following expression:

$$A(t) = A_1\left[\left(\frac{\tau_2}{\tau_2 - \tau_1}\right)(\mathrm{e}^{-t/\tau_2} - \mathrm{e}^{-t/\tau_1})\right] + A_2\left[1 + \left(\frac{\tau_1}{\tau_2 - \tau_1}\right)\mathrm{e}^{-t/\tau_1} - \left(\frac{\tau_2}{\tau_2 - \tau_2}\right)\mathrm{e}^{-t/\tau_2}\right] \tag{2}$$

In this biexponential expression the terms between rectangular brackets are normalized terms characterizing the rise and decay of the first MC isomer ($\mathrm{MC_1(T_1)}$), and the rise of the second isomer ($\mathrm{MC_2(T_1)}$), respectively. The amplitudes A_1 and A_2 are proportional to the extinction coefficients of the visible or IR bands for the two species. For practical purposes we can regard the intermediate created after the 0.5 ps relaxation as the starting situation for fits with eq 2, because the subpicosecond formation of the intermediate leading to the $\mathrm{MC(T_1)}$ product is completed long before any substantial $\mathrm{MC(T_1)}$ product is created, given that the time constants τ_1 and τ_2 are much slower. Therefore, the subpicosecond processes are not incorporated in eq 2. The data and fits indicate that the main spectral difference between the two MC products is that the extinction coefficients are considerably larger for the second merocyanine product species, for both the 440 and 583 nm band the extinction coefficient increases by a factor 1.8, while the 1519 cm^{-1} IR band increases by a factor 2.1. Note that the IR band at $\sim$1360 cm^{-1} is only associated with $\mathrm{MC_1}$; therefore, $A_2 = 0$ in the fit for this band in Figure 6.

Geometric rearrangement by cis−trans isomerization around the ethylenic bonds of the bridge segment is a frequently suggested explanation for observations in spiropyran photochemistry.[1,2,8,9,15,20,21,40] Recent quantum mechanical calculations of the IR spectra of the four metastable merocyanine isomers in the electronic ground state[23] (TTC, CTC, CTT, and TTT), demonstrate only modest differences in their IR spectra. It seems reasonable to expect similar results for these isomers in the T_1 state. Sequential isomerization of one MC isomer into another seems therefore a viable interpretation.

4. Conclusions

We have investigated the spiropyran ring-opening reaction of 6-nitro-BIPS in TCE, following UV excitation, and probing both with white-light (visible) and IR femtosecond pulses. The results reveal new kinetic details on the reaction during the first nanosecond. In the UV/vis experiments we identify during the first picosecond two new transient features. The first of these features, which disappears within less than 0.4 ps, we assign to spiropyran excited-state $S_1 \rightarrow S_n$ absorption. The second feature, with a lifetime of 0.5 ± 0.2 ps, we ascribe to a higher triplet state (T_2) of MC. Return to the SP S_0 ground state, by internal conversion[25,26] and vibrational cooling, is the fate for 34% of the 6-nitro-BIPS molecules, with an overal time-constant of 47 ± 10 ps. Both probing methods demonstrate comparable biexponential merocyanine product formation kinetics, typically characterized by a 17 ± 3 ps and a 350 ± 20 ps time constant. This proofs that the rising new IR vibrational absorption bands are associated with the same merocyanine products (in the excited T_1 triplet state) as the well-known electronic absorption bands at 440 and 583 nm. The faster picosecond time constant in the IR experiments varies from 5 to 28 ps from the red to the blue edge of the IR absorption bands, due to vibrational cooling. A weak transient IR signal at $\sim$1360 cm^{-1} demonstrates that the biexponentiality is the result of the sequential conversion of the one merocyanine species into another. Combining the pump−probe results with emission lifetime measurements, we prove that the MC S_1-state is not a reaction intermediate.

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