Excited-State Dynamics of Spiropyran-Derived Merocyanine Isomers

Christopher J. Wohl and Darius Kuciauskas*

Department of Chemistry, Virginia Commonwealth University, 1001 West Main Street, Richmond, Virginia 23284-2006

Received: July 9, 2005; In Final Form: October 3, 2005

Merocyanine (MC) isomers that are formed after absorption of a UV photon by 1′,3′-dihydro-1′,3′-3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2′,2′-(2*H*)-indole] were studied. Several, predominantly TTC and TTT, merocyanine isomers are present in toluene solution ("T" and "C" indicate trans and cis conformations of the C−C bonds in the methine bridge). Excitation in the MC visible absorption band (at 490, 550, and 630 nm) with 100 fs laser pulses was used to study MC excited-state dynamics. Internal conversion on the picosecond time scale was found to be the dominant relaxation pathway. Excited-state isomerization reactions were also observed. Excitation at 630 nm (assigned to TTC isomer excitation) leads to formation of a third isomer (either CTC or CTT). Excitation at 490 nm (assigned to TTT isomer excitation) leads to more complex excited-state relaxation, including formation of two isomers: TTC (absorption at 600 nm) and CTC or CTT (absorption at 650 nm).

Introduction

Photochromic molecules have been used in a broad array of both applied and fundamental studies. This is a consequence of their unique optical properties. Investigations of photochromic reactions have contributed to an improved understanding of twisted internal charge transfer (TICT), conical intersections of potential energy surfaces, and other effects.[1,2] New technologies such as optical switching,[3] optical data storage,[4] and molecular logic gates[5] have benefited from the incorporation of photochromic materials. Biological applications are also pursued due to the often dramatic changes in molecular structure, polarity, and volume occurring in photochromic reactions.[6−10]

Perhaps the most extensively studied photochromic compound is 1′,3′-dihydro-1′,3′-3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2′,2′-(2*H*)-indole] (6-nitroBIPS spiropyran) (Scheme 1).[11,12] It consists of weakly interacting substituted indole and benzopyran moieties connected orthogonally at a spiro carbon atom. Spiropyran converts to a planar form, merocyanine (MC), upon absorption of a UV photon. This reaction results in an increased dipole moment (from 4.3 to 17.7 D),[13] a larger molecular volume, and the onset of absorbance in the visible region. This new absorption band is indicative of increased conjugation in the MC form. The photochemistry of the spiropyran ring-opening reaction has been reviewed.[11,14] The reaction is both thermally and photochemically reversible.

Merocyanine contains a methine bridge consisting of three conjugated C−C bonds. Three dihedral angles (labeled α, β, and γ for the TTC isomer in Scheme 1) can be altered to form several isomers.[15] It has been suggested that the TTC form is the most stable ground-state isomer due to hydrogen-bonding interactions;[16,17] however, the relative energies of the remaining isomers are still unclear. ^{1}H and ^{13}C NMR studies[17−19] and density functional theory calculations[20,21] suggest that the TTT isomer is the second most stable isomer. The relative MC isomer energies determined from quantum chemical calculations and NMR line broadening studies are given in Scheme 1.[19−21] The activation barrier for isomerization in the ground state is ∼40 kJ mol^{-1}.[19]

The presence of multiple merocyanine isomers has been implicated in photoinitiated ring-opening[22,23] and thermal decoloration reactions.[24,25] Few studies, however, have been conducted with direct excitation of specific merocyanine isomers.[26,27] Hobley et al. studied the excited-state dynamics for a merocyanine possessing nitro substituents at the 6- and 8-positions of the benzopyran moiety (6,8-dinitroBIPS).[26] They found that excitation at 390 nm did not result in selective MC isomer excitation.[26]

In this paper, we show that transient absorption spectra and kinetics measured using several excitation wavelengths in the visible absorption band region indicate the presence of multiple MC isomers. Using ultrafast pump−probe experiments, we selectively excited these isomers to determine their excited-state relaxation pathways.

Experimental Section

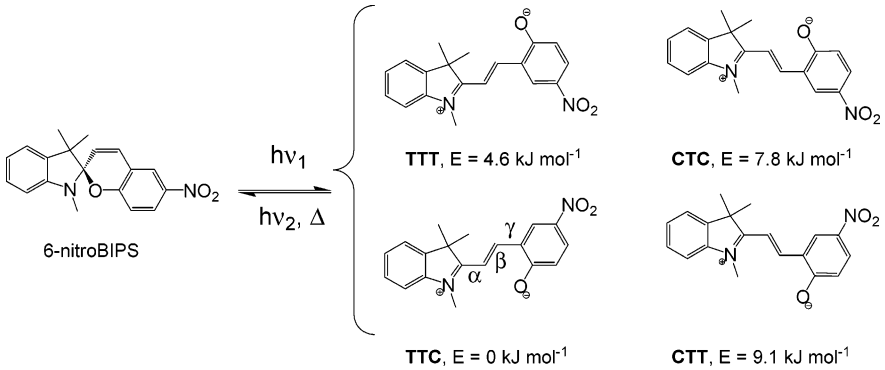
Materials and Methods. 1′,3′-Dihydro-1′,3′-3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2′,2′-(2*H*)-indole] (6-nitroBIPS) was purchased from Aldrich and used as received. Solvents were high-performance liquid chromatography grade and used without further purification. Absorption spectra were obtained using a HP8452A diode-array spectrometer. Fluorescence measurements were conducted with a Varian Cary-Eclipse fluorimeter. Merocyanine formation was induced using a low-power Entela UV lamp (central irradiation wavelength of 364 nm).

Ultrafast Transient Absorption Spectroscopy. The optical scheme of the pump−probe transient absorption spectrometer is shown in Scheme 2. A regeneratively amplified Ti:sapphire laser system (Spectra Physics) provided 100 fs, 0.7 mJ pulses at 780 nm and a 1 kHz repetition rate. Excitation pulses were obtained using an optical parametric amplifier (TOPAS, Quantronix/Light Conversion). A white-light continuum was generated from focused probe pulses incident on a sapphire window. A stable continuum was generated by controlling probe light

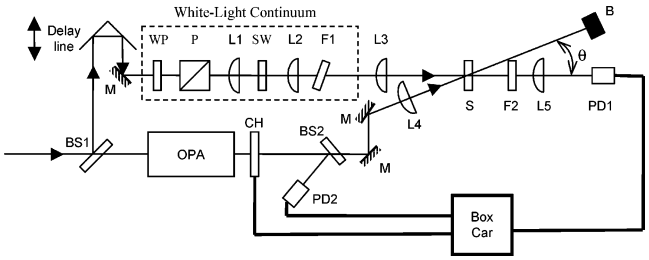
* Author to whom correspondence should be addressed. Phone: (804)828-8551. Fax: (804)828-8599. E-mail: dkuciauskas@vcu.edu.

10.1021/jp053782x CCC: $30.25
Published on Web 11/05/2005

SCHEME 1: Spiropyran-Derived Merocyanine Isomers



SCHEME 2: Optical Scheme of a Pump−Probe Spectrometer[a]



[a] OPA = optical parametric amplifier; BS1 and BS2 = beam splitters (90% T); M = mirrors; WP = $\lambda/2$ waveplate; P = polarizer; L = plano-convex lenses (L1 f = 100 mm, L2 f = 50 mm, L3 f = 250 mm, L4 f = 350 mm, L5 f = 75 mm); SW = sapphire window; F1 = low-pass filter; F2 = interference filter (10 nm bandwidth); B = beam block; S = sample; PD1 and PD2 = photodiodes; CH = chopper. The angle between the pump and probe beams is $\Theta = 4°$.

intensity with a $\lambda/2$ waveplate and a Glan−Taylor polarizer and by translating a 2-mm-thick sapphire plate in the beam waist region using a micrometer stage. The relative polarizations of pump and probe beams were adjusted to 54° (the "magic angle"). Kinetics measurements from 100 fs to 3 ns were made by varying the probe beam time delay with a computer-controlled linear translational stage. Electrical signals from Si photodiodes were gated with a boxcar. To improve the signal-to-noise ratio, an optical chopper blocked every other pump pulse, and computer software (developed using LabView, National Instruments) was used to take the difference of signals measured with and without excitation.

6-NitroBIPS solutions in toluene (2.5 mM) were measured in a 1 mm optical path length flow cell connected to a peristaltic pump equipped with Viton tubing. The temperature was 25 °C for all experiments. Preparation of samples containing a substantial merocyanine concentration was achieved using a UV lamp (364 nm) to illuminate the sample reservoir and the volume of the flow cell immediately preceding the pump and probe beams. The peristaltic pumping rate was approximately 1.7 mL/min. Variation of the repetition rate of the laser indicated no change in the transient absorption characteristics.

Results

Merocyanine Steady-State Absorption and Fluorescence Properties. In toluene, the ring-closed form of 6-nitroBIPS predominates. Upon UV excitation, ring-opening and subsequent isomerization results in the appearance of a new absorption band with the maximum of absorption at 579 nm (Figure 1A). The emission spectrum of the MC form (maximum at 625 nm) is shown in Figure 1B.

It is well established that multiple MC isomers can be formed in the SP → MC reaction, but absorption (and emission) properties of these various isomers have not been identified. The presence of multiple MC isomers in toluene solution is suggested by the fluorescence excitation spectra shown in Figure 1C. Depending on the wavelength at which fluorescence emission is measured (620 or 700 nm), the maximum of the excitation spectrum shifts from 567 to 600 nm. Several fluorescence excitation spectra were obtained when the detection wavelength was varied between 600 and 700 nm. At wavelengths below 610 nm, the maximum of the excitation spectrum was at 562 nm. As the detection wavelength is increased from 620 to 650 nm, the maximum of the excitation spectrum shifted from 569 to 593 nm. The maximum was at 598 nm for experiments with the emission measured above 660 nm.

These data could be interpreted by assuming the presence of at least two MC isomers in toluene solution, where emission between 600 and 610 nm is due to the first isomer and emission between 660 and 700 nm is due to a second isomer. (At 610−660 nm, the overlapping emission of both isomers leads to a 36 nm shift of the excitation spectrum maximum depending on the detection wavelength.) Further evidence for this model was obtained in the time-resolved studies.

Merocyanine Transient Absorption Difference Spectra. To further characterize the MC isomers, we used 100 fs laser pulses to excite the MC absorption band at 490, 550, and 630 nm (inset in Figure 1A). Figure 2A shows the transient absorption difference spectrum measured at 1 ps time delay after 550 nm excitation. The negative signal with a minimum at ∼575 nm is assigned to MC ground-state bleaching, as it overlaps with the normalized MC steady-state absorption spectrum. The positive signal at 460−500 nm is assigned to the MC excited-state absorption.[26] The negative signals at 650−690 nm could have contributions from stimulated emission, as MC steady-state emission is observed at these wavelengths (Figure 1B).

Different results are obtained when 1 ps transient absorption spectra are measured with 490 and 630 nm excitation (Figure 2B). While the major features (bleaching, excited-state absorption, and stimulated emission) are also evident in these spectra, the bleaching minima shift from ∼575 nm for 550 nm excitation to ∼568 nm for 490 nm excitation and ∼600 nm for 630 nm excitation. The dependence of the bleaching minimum on the excitation wavelength supports the presence of multiple MC isomers in toluene solution.

Since the excitation of the "red" (630 nm) and "blue" (490 mm) sides of the MC absorption band are most likely to excite different isomers, we proceed to an analysis of ΔA spectra measured using these excitation wavelengths (Figures 3A and 3B). The decrease of the bleach and excited-state absorption signal amplitudes at longer time delays indicates that excited-

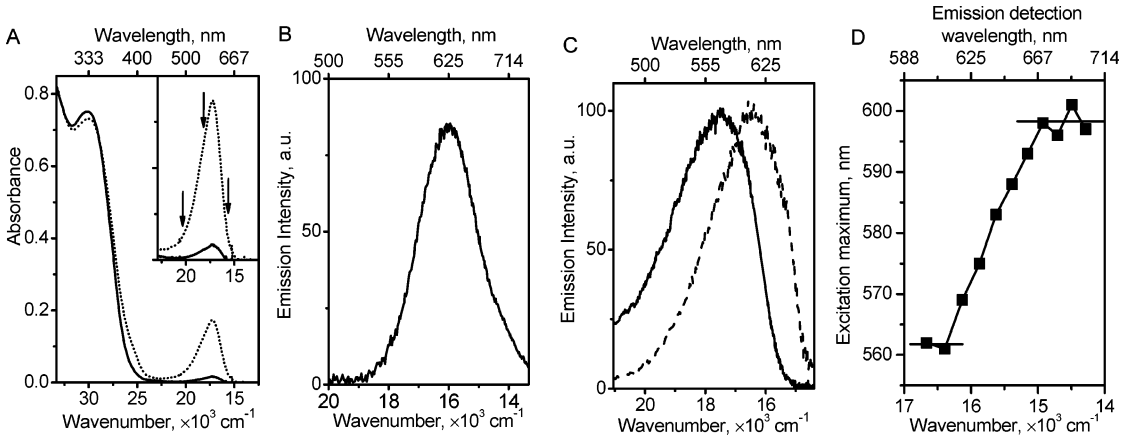


Figure 1. (A) 6-NitroBIPS absorption spectra in toluene before (—) and after UV irradiation (---). The inset shows the expansion of the MC visible absorption band region. The wavelengths used for excitation in ultrafast experiments are indicated with arrows. (B) Fluorescence emission spectrum measured in toluene with excitation at 490 nm. (C) Fluorescence excitation spectra measured in toluene at 620 nm (—) and 700 nm (---). (D) Shift of the maximum of the fluorescence excitation spectrum with variation of the emission detection wavelength.

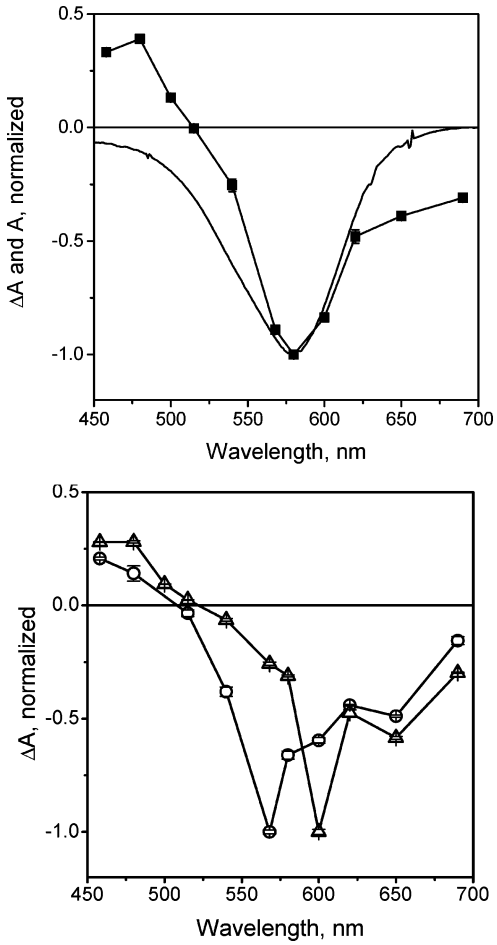


Figure 2. Transient absorption difference spectra in toluene solution measured 1 ps after excitation with 100 fs laser pulses at 550 nm (■, A), 490 nm (○, B), and 630 nm (△, B). In part A, the normalized and inverted steady-state absorption spectrum of MC in toluene is also shown (—). Error bars are indicated in the transient absorption spectra.

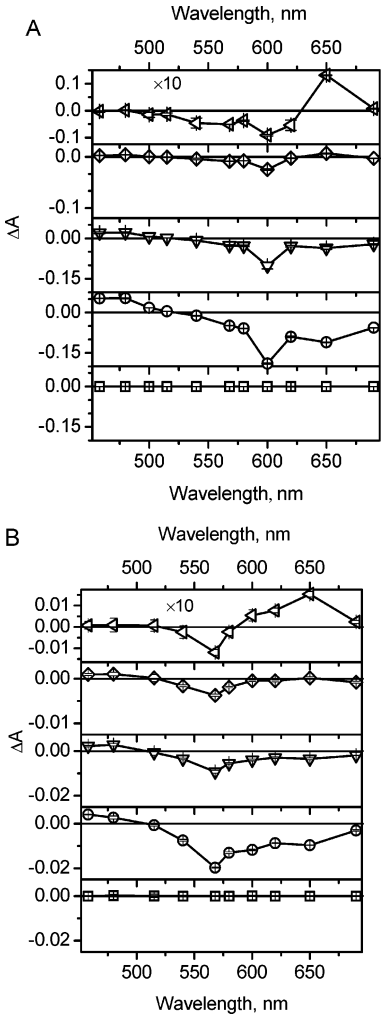


Figure 3. Transient absorption spectra in toluene solution collected with λ_{exc} = 630 nm (A) and λ_{exc} = 490 nm (B). Time delays: 0 ps (□), 1 ps (○), 50 ps (▽), 200 ps (◇), and 2000 ps (△). Error bars are indicated for each measurement, and 2000 ps spectra are multiplied 10 times for clarity.

state reactions are occurring on a picosecond time scale. Interestingly, the differences in the 2 ns time delay spectra shown in Figures 3A and 3B and Figure 4 suggest that MC isomers do not follow the same excited-state relaxation pathways.

Figure 4 compares the long-time (2 ns) difference spectra. The minima at 568 and 600 nm (measured with λ_{exc} = 490 nm and λ_{exc} = 630 nm, respectively) correspond to ground-state bleaching. The positive absorption at 650 nm seen in both spectra suggests that following either "red" (630 nm) or "blue" (490 nm) excitation a new isomer was formed in an excited-state reaction. In addition, the λ_{exc} = 490 nm spectrum has a positive amplitude at 600 nm. The simplest model that is

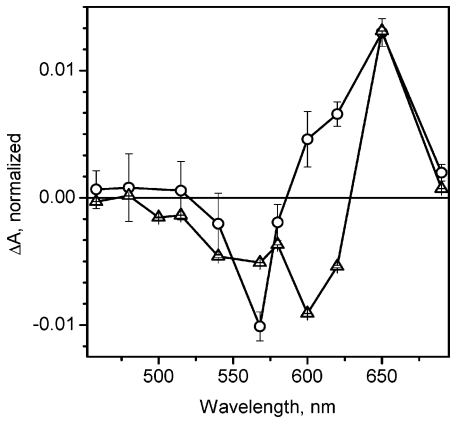


Figure 4. The 2 ns time delay transient absorption difference spectra for $\lambda_{exc} = 490$ nm (○) and $\lambda_{exc} = 630$ nm (△). The spectra have been normalized at the maxima. Absorption at 650 nm in both spectra indicates formation of a third isomer.

consistent with these data is the presence of three MC isomers in toluene solution. Two isomers would correspond to bleaching minima at 568 and 600 nm, while the third isomer would have absorption at 650 nm. Because the 650 nm absorption signal amplitude is small, the quantum yield of the third isomer is low (Discussion).

This model is consistent with the identification of TTC and TTT isomers in acetonitrile solutions of merocyanine formed from 6,8-dinitroBIPS. (NMR line shape analysis was used in these studies.[18]) In experiments with nanosecond time resolution, a positive absorption signal with a maximum at 635 nm was also attributed to a new MC isomer.[28] The amplitudes of the bleaching and positive 650 nm signals in Figure 4 are similar to the results obtained by Görner et al.[28] One important new finding in the current experiments is the unambiguous demonstration that the 650 nm signal amplitude is small in comparison to the initial bleaching amplitude. (The amplitude at 2 ns time delay is about 10% of the initial amplitude; see Figures 3 and 5.) Therefore, the isomerization yield is low, and the major MC excited-state relaxation pathway is internal conversion. The same conclusion was recently reached for the "closed-form" 6-nitroBIPS spiropyran.[22]

Excited-State Dynamics. Figure 5 shows the transient absorption kinetics measured at 480 nm, at the MC ground-state bleaching minimum and at 650 nm. The excitation wavelengths were 490 and 630 nm.

Excited-State Absorption. The positive signal at 480 nm is assigned to excited-state absorption in agreement with earlier studies.[26] For $\lambda_{exc} = 630$ nm, signal rise is faster than 100 fs and is followed by a 1.5 ± 0.5 ps lifetime decay. In marked contrast, $\lambda_{exc} = 490$ nm leads to biexponential rise, where the smaller amplitude second rise component has a 2 ± 0.5 ps lifetime. These 1.5−2 ps lifetime components could reflect vibrational relaxation or electronic relaxation from S_n to S_1 states. The difference in amplitudes (positive or negative) could reflect different excited-state absorption properties of MC isomers. On the longer time scale (data not shown in Figure 5A), 480 nm excited-state absorption kinetics decay with the same lifetimes as the bleach recovery signals described below.

TABLE 1: Excited-State Lifetimes and MC Isomer Spectral Assignments

λ_{exc} (nm)	τ_1 (ps)	τ_2 (ps)	bleach amplitude at $t > 2000$ ps	bleaching minimum (nm)	MC isomer[b]
630	67 ± 5		$10 \pm 3\%$	600	TTC
490	36 ± 4 (60%)[a]	270 ± 25 (28%)[a]	$12 \pm 4\%$	568	TTT

[a] Amplitudes of τ_1 and τ_2 components. [b] Assignments based on isomer relative energies determined in refs 19−21.

Bleaching. Figure 5B shows the bleaching kinetics at 568 nm ($\lambda_{exc} = 490$ nm) and at 600 nm ($\lambda_{exc} = 630$ nm). These wavelengths represent measured bleaching minima for the respective excitation wavelengths. Excitation at $\lambda_{exc} = 630$ nm results in faster bleach recovery than excitation at $\lambda_{exc} = 490$ nm. At $t > 10$ ps, all kinetics were fit to exponential functions, and the results are summarized in Table 1. The ground-state recovery measured with $\lambda_{exc} = 630$ nm can be described by a 67 ± 5 ps lifetime single-exponential decay. The $\lambda_{exc} = 490$ nm ground-state recovery yielded more complex kinetics that required a biexponential fit with $\tau_1 = 36 \pm 4$ ps and $\tau_2 = 270 \pm 25$ ps. Bleach recovery is incomplete for both kinetics in Figure 5B; the persistent bleach amplitudes are 10−12% (Table 1).

Stimulated Emission/Isomerization. At $t < 10$ ps, signals at 650 nm (Figure 5C) exhibit similar characteristics to the excited-state absorption signals in Figure 5A. Excitation at $\lambda_{exc} = 630$ nm results in the appearance of a negative amplitude signal within 100 fs followed by decay with a 1.5 ± 0.5 ps lifetime. The kinetics measured with $\lambda_{exc} = 490$ nm required biexponential fitting with $\tau_1 = 100$ fs and $\tau_2 = 2 \pm 0.5$ ps. At intermediate time delays (10 ps $< t <$ 500 ps), the 650 nm kinetics behave in a manner similar to the bleaching signals. Excitation with $\lambda_{exc} = 630$ nm resulted in a single-exponential decay ($\tau_1 = 67 \pm 5$ ps) whereas excitation at $\lambda_{exc} = 490$ nm yielded biexponential decay kinetics with $\tau_1 = 36 \pm 4$ ps and $\tau_2 = 270 \pm 25$ ps. At $t > 500$ ps, positive transient absorption signals were observed at this wavelength; this absorption band (Figure 4) was assigned to formation of the third MC isomer.

Thus, measurements at the excited-state absorption, bleaching, and stimulated emission/new isomer absorption wavelengths can be consistently explained using one rate constant for $\lambda_{exc} = 630$ nm and two rate constants for $\lambda_{exc} = 490$ nm.

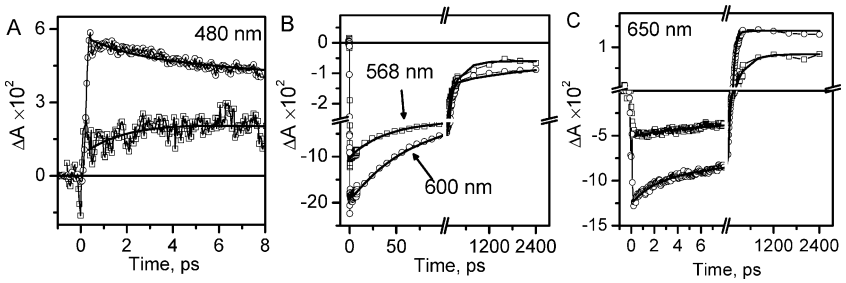


Figure 5. Transient absorption kinetics measured at 480 nm (A), 568 nm/600 nm (B), and 650 nm (C): $\lambda_{exc} = 490$ (□); $\lambda_{exc} = 630$ nm (○). Note the breaks in both axes in parts B and C. Solid lines are fitting results. Kinetics were measured at equal MC concentrations in toluene solution; 490 nm excitation kinetics have been multiplied 5 times for clarity.

Discussion

MC Isomers and Excited-State Relaxation Pathways. The excited-state lifetime dependence on the excitation wavelength (Table 1) and shifts of the bleaching minima (Figure 2) suggest the presence of multiple MC isomers in toluene solution. Transient absorption difference spectra in Figure 4 (albeit measured with low resolution) 2 ns after excitation indicate the presence of at least three MC isomers with absorption at 568, 600, and 650 nm, respectively. The bleaching signals at 568 and 600 nm indicate that the corresponding MC isomers are present in the ground state. The two predominant ground-state isomers are likely to be TTC and TTT, as they have the lowest ground-state energies (Scheme 1). The third isomer could be either CTC or CTT. An NMR line shape analysis also indicated the presence of TTT and TTC isomers in solutions of a related merocyanine.[18]

The positive 650 nm signal (Figures 4 and 5C) suggests that this isomer is formed in excited-state isomerization reactions but is not significantly populated in the ground state. This assignment is consistent with results obtained by Görner and co-workers, who, in experiments with nanosecond time resolution, have observed positive signals with maxima at 635 nm that have been attributed to formation of "cis" isomers.[28]

The difference spectra in Figure 4 also suggest that TTC and TTT isomers follow different excited-state relaxation pathways. Excitation of the isomer with absorption (bleaching) at 600 nm leads to absorption at 650 nm, while excitation of the isomer with absorption at 568 nm leads to formation of both 600 and 650 nm absorbing isomers.

It is possible to assign TTC/TTT isomers to the 600/568 nm absorption bands if we assume that MC photochemical reactions take place on the singlet excited-state potential energy surface and estimate excited-state energies from the absorption and emission spectra. A singlet excited-state isomerization pathway was proposed by Sheng et al., who theoretically analyzed merocyanine isomerization and decoloration reactions.[21] They found that the isomerization energy barrier in the excited singlet state is much lower than barriers determined in the triplet and ground states (2.8 kJ mol^{-1} in the S_1 state, 12.0 kJ mol^{-1} in the T_1 state, and 25.1 kJ mol^{-1} in the ground state).[21] Another possibility would be fast internal conversion to hot vibrational energy levels of the ground state and isomerization due to this excess vibrational energy in the ground state. (In equilibrium, isomerization between TTC/TTT isomers would be slow, as the energy barrier for ground-state isomerization is ~40 kJ mol^{-1} for 6-nitro-8-bromo-BIPS-derived merocyanine.[19])

Our results are consistent with excited-state isomerization. Figure 6 shows that excited-state absorption kinetics at 480 nm decay with a 67 ps lifetime. (Transient absorption signals in this spectral region were assigned to excited-state absorption by Hobley et al.[26]) Formation of the CTC/CTT isomer (kinetics at 650 nm at longer time delay) can also be described by the same lifetime. Decay of the excited states with the same lifetime as product (CTC/CTT isomer) formation reflects an excited-state isomerization reaction.

Scheme 3 shows a state diagram constructed to explain the transient absorption results. After excitation of the TTC (600 nm) isomer, isomerization is possible to only CTC/CTT conformers (absorption at 650 nm, rate constant k_{iso1}). In contrast, excitation of the TTT isomer (568 nm) leads to TTC and CTC/CTT formation (absorption at 600 and 650 nm, rate constants k_{iso3} and k_{iso2}, respectively). Experiments with nanosecond time resolution are required to determine further dynamics of the CTC/CTT (650 nm) isomers and in particular to estimate the quantum yield of the "ring-closed" 6-nitroBIPS spiropyran (Scheme 1). While 6-nitroBIPS spiropyran is perhaps the most extensively investigated photochromic compound, to our knowledge no studies have addressed complete femtosecond to microsecond dynamics for the same system (same temperature, solvent, excitation wavelength). Because of the complex potential energy surface of this reaction (conical intersections of the ground- and excited-state potential energy surfaces,[2] excited singlet and triplet state reactions,[28] and unusual intersystem crossing properties[1] reported for spiropyrans) such studies are required to obtain a full description of 6-nitroBIPS ↔ merocyanine photophysical and photochemical reaction pathways.

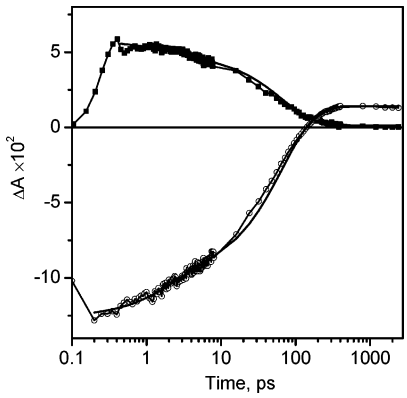
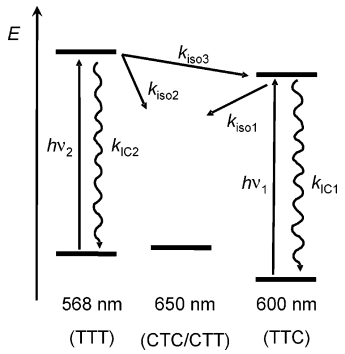


Figure 6. Comparison of 480 nm (■) and 650 nm (○) kinetics measured with 630 nm excitation in toluene solution. The solid lines are fitting results. The same lifetime (τ = 67 ps) describes the 0.5−2000 ps data at both probe wavelengths.

SCHEME 3: Reaction Pathways upon Selective MC Isomer Excitation



Rate Constants and Quantum Yields of the Excited-State Reactions. Scheme 3 indicates that excited states of the TTC isomer decay due to the internal conversion (rate constant k_{IC1}) and isomerization (rate constant k_{iso1}) to CTC/CTT forms. Internal conversion is the dominant relaxation pathway. (The 650 nm absorption amplitude is only ~10% of the initial 600 nm bleach amplitude; see Table 1 and Figure 4.) Internal conversion was also found to be the dominant excited-state relaxation pathway for "closed-form" 6-nitroBIPS spiropyran in tetrachloroethylene and perdeuterated acetonitrile solutions.[1,22]

MC isomerization can be followed by a photochemical decoloration (or "ring-closing") reaction. In experiments on 6,8-dinitroBIPS-derived merocyanines, an estimate for the ring-closing reaction yield was obtained by comparing the initial and final bleach amplitudes.[26] Using a similar method, we can estimate the quantum yields of isomerization, Φ_{iso}, and ring-closing, Φ_{RC}. Such an estimate yields $\Phi_{iso} + \Phi_{RC} \approx 10\%$. Assuming that the extinction coefficients are similar for all isomers, Φ_{iso} is higher than Φ_{RC}. (Persistent bleaching and

positive absorption at 650 nm have approximately equal amplitudes.) Therefore, we see no evidence for ring-closing on a <2.5 ns time scale. The difference between our results and those obtained on 6,8-dinitroBIPS could be related to solvent polarity. Hobley et al. studied MC dynamics in acetonitrile, while our experiments were carried out in toluene. Spiropyran photochemical reactions are generally faster in polar solvents.[29−31] In addition, spiropyran photochemical reaction yields depend on solvent polarity.[29−31] This sensitivity could be related to the unusual internal conversion properties of spiropyran compounds.[1]

From the data in Table 1, $k_{IC1} + k_{iso1} = (67\ ps)^{-1} = 1.49 \times 10^{10}\ s^{-1}$. Because the yield of the new isomer is low, $k_{IC1} > k_{iso1}$, and $k_{IC1} \approx 1.49 \times 10^{10}\ s^{-1}$. Assuming $\Phi_{iso1} = 10\%$ yields $k_{IC1} = 1.34 \times 10^{10}\ s^{-1}$. Kasha's rule describes internal conversion as being relatively inefficient and occurring on a nanosecond to microsecond time scale for the S_1 state of many organic compounds.[32] Fast internal conversion from the spiropyran S_1 state was recently found and attributed to large conformational changes upon excitation.[1,22,23] The same mechanism could be important for spiropyran-derived merocyanines and lead to picosecond internal conversion for the MC isomers.

Excited-state relaxation processes observed with 490 nm excitation are more complex (Scheme 3). In addition to internal conversion (rate constant k_{IC2}), isomerization to the TTC form (rate constant k_{iso2}) and to the third isomer (CTC/CTT, rate constant k_{iso3}) are observed. The origin of the biexponential TTT isomer excited-state relaxation is ambiguous. Biexponential kinetics could be observed if the excited states of several isomers were in equilibrium. Biexponential kinetics could also reflect excitation of multiple isomers at 490 nm. In this case, τ_1^{-1} and τ_2^{-1} components in Table 1 would represent internal conversion and isomerization rate constants, $k_{IC} + k_{iso}$, for these isomers. It has been suggested that differences in solvent stabilization for MC isomers could lead to different excited-state lifetimes for these isomers.[28] This argument supports the presence of two isomers with absorption at 490 nm, but more detailed studies are required to assign the kinetic components observed with 490 nm excitation. The average excited-state relaxation rate constant obtained with 490 nm excitation is $k_{av} = (a_1\tau_1^{-1} + a_2\tau_2^{-1})/(a_1 + a_2) = 2 \times 10^{10}\ s^{-1}$, which is somewhat faster than the TTC isomer excited-state decay rate constant of $1.5 \times 10^{10}\ s^{-1}$. When using 490 nm excitation, the 650 nm absorption signal amplitude is about 10% of the initial bleaching amplitude; therefore internal conversion is more efficient than isomerization, $k_{IC2} > k_{iso2}$, k_{iso3}, for all MC isomers.

Conclusions

Several merocyanine isomers are formed after UV excitation of 6-nitroBIPS spiropyran; these isomers include the TTC and TTT forms. Variable excitation wavelength ultrafast pump−probe spectroscopy was used to determine MC isomer excited-state relaxation pathways. We find that internal conversion is the dominant relaxation pathway, and it occurs on the picosecond time scale. In addition, isomerization reactions in excited singlet states were studied. After TTC isomer excitation at 630 nm, a third isomer (with absorption at 650 nm, either CTC or CTT) is formed. In contrast, after excitation at 490 nm, isomerization to both TTC and CTC/CTT forms is observed. Determination of the isomeric distribution, excited-state photochemical reaction pathways, and relaxation dynamics for photochromic spiropyran/merocyanine molecules may contribute to the development of novel molecular materials and photonic devices. In particular, the properties of multiple merocyanine isomers should be considered when designing molecular switches that incorporate spiropyran compounds.

Acknowledgment. This work was supported by the Jeffress Memorial Trust and startup funds from Virginia Commonwealth University.

References and Notes

(1) Fidder, H.; Rini, M.; Nibbering, E. T. J. *J. Am. Chem. Soc.* **2004**, *126*, 3789.
(2) Celani, P.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 10815.
(3) Straight, S. D.; Andreasson, J.; Kodis, G.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2005**, *127*, 2717.
(4) Kinoshita, T. *J. Photochem. Photobiol., B* **1998**, *42*, 12.
(5) Raymo, F. M.; Giordani, S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4941.
(6) Pfeifer, U.; Fukumura, H.; Misawa, H.; Kitamura, N.; Masuhara, H. *J. Am. Chem. Soc.* **1992**, *114*, 4417.
(7) Willner, I.; Rubin, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 367.
(8) Khairutdinov, R. F.; Hurst, J. K. *Langmuir* **2001**, *17*, 6881.
(9) Pieroni, O.; Fissi, A.; Angelini, N.; Lenci, F. *Acc. Chem. Res.* **2001**, *34*, 9.
(10) Kocer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. *Science* **2005**, *309*, 755.
(11) Minkin, V. I. *Chem. Rev.* **2004**, *104*, 2751.
(12) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741.
(13) Bletz, M.; Pfeifer-Fukumura, U.; Kolb, U.; Baumann, W. *J. Phys. Chem. A* **2002**, *106*, 2232.
(14) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875.
(15) Ernsting, N. E., T. *J. Phys. Chem.* **1991**, *95*, 5502.
(16) Futami, Y.; Chin, M. L. S.; Kudoh, S.; Takayanagi, M.; Nakata, M. *Chem. Phys. Lett.* **2003**, *370*, 460.
(17) Hobley, J.; Malatesta, V.; Giroldini, W.; Stringo, W. *Phys. Chem. Chem. Phys.* **2000**, *2*, 53.
(18) Hobley, J.; Malatesta, V.; Millini, R.; Montanari, L.; Parker, W. O. N., Jr. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3259.
(19) Hobley, J.; Malatesta, V. *Phys. Chem. Chem. Phys.* **2000**, *2*, 57.
(20) Cottone, G.; Noto, R.; La Manna, G. *Chem. Phys. Lett.* **2004**, *388*, 218.
(21) Sheng, Y.; Leszczynski, J.; Garcia, A. A.; Rosario, R.; Gust, D.; Springer, J. *J. Phys. Chem. B* **2004**, *108*, 16233.
(22) Holm, A.-K.; Rini, M.; Nibbering, E. T. J.; Fidder, H. *Chem. Phys. Lett.* **2003**, *376*, 214.
(23) Rini, M.; Holm, A. K.; Nibbering, E. T. J.; Fidder, H. *J. Am. Chem. Soc.* **2003**, *125*, 3028.
(24) Sciaini, G.; Wetzler, D. E.; Alvarez, J.; Fernandez-Prini, R.; Laura Japas, M. *J. Photochem. Photobiol., A* **2002**, *153*, 25.
(25) Wojtyk, J. T. C.; Kazmaier, P. M.; Buncel, E. *Chem. Commun.* **1998**, 1703.
(26) Hobley, J.; Pfeifer-Fukumura, U.; Bletz, M.; Asahi, T.; Masuhara, H.; Fukumura, H. *J. Phys. Chem. A* **2002**, *106*, 2265.
(27) Minami, T.; Tamai, N.; Yamazaki, T.; Yamazaki, I. *J. Phys. Chem.* **1991**, *95*, 3988.
(28) Gorner, H.; Atabekyan, L. S.; Chibisov, A. K. *Chem. Phys. Lett.* **1996**, *260*, 59.
(29) Chibisov, A.; Gorner, H. *J. Phys. Chem. A* **1997**, *101*, 4305.
(30) Gorner, H. *Phys. Chem. Chem. Phys.* **2001**, *3*, 416.
(31) Chibisov, A. K.; Gorner, H. *Phys. Chem. Chem. Phys.* **2001**, *3*, 424.
(32) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991.