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ARTICLES

The Competitive Effect of Intramolecular Charge Transfer on the Photochromism of Spiro[cyclohexadiene-indolines] Studied by ps-Spectroscopy

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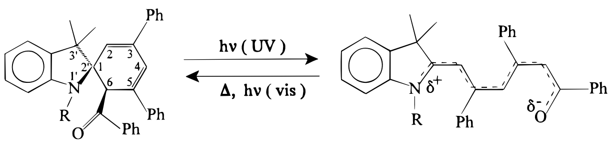
The photochromism of spiro[cyclohexadiene-indolines], the reversible bond cleavage at the spiro-carbon resulting in a colored merocyanine, is affected by solvent polarity. Photoexcited intramolecular charge transfer within the preserved spiro form of the molecule is favored in polar solvents, explaining the drop in merocyanine yield (less than 1% in acetonitrile compared to 18% in cyclohexane). Charge transfer is expressed by a strongly solvatochromic fluorescence corresponding to an increase of the dipole moment of more than 20 D in the excited state with respect to a charge separation over a distance of 4 Å. Picosecond-resolved measurements of the fluorescence and the transient absorption confirm the picture of photoisomerization via the first excited singlet state and a vibronically hot ground state of the merocyanine. The time constant (∼100 ps) for the merocyanine formation is hardly sensitive to the solvent polarity and is independent of the lifetime of the charge transfer state of the spiro[cyclohexadiene-indoline] (5 ps to 1.4 ns, increasing with solvent polarity).

Introduction

Photochromic spiro compounds are promising objects of research,[1] since reversible isomerization into a merocyanine dye holds the prospect of usage in optical devices, including storage and switches. The most intensively studied compounds are the spirobenzopyrans, whose process of photochemical ring-opening has been examined[2−7] by comparing the results of ultrafast spectroscopy experiments with quantum chemical considerations. The excited-state species of the spirobenzopyran decays, breaking the C−O bond to produce a vibronically hot merocyanine (200 fs) that forms the colored photoproduct after cooling within about 100 ps. This process is thermal or partially photochemical (irradiation with visible light) reversible.

A new class of spiro compounds has been introduced consisting of an aroylcyclohexadiene moiety instead of the benzopyran ring, and which isomerizes under UV-excitation.[8−12] One of the two possible enantiomers of the spiro[cylohexadiene-indoline] is shown in Scheme 1. The quantum yield of the merocyanine is observed to be solvent dependent. Fluorescence spectroscopy indicates that intramolecular charge transfer, which is favored in polar media, maintains the orthogonality between the indoline and cyclohexadiene parts and reduces the yield of C_1-C_6 bond cleavage. Similar behavior has been observed for rhodamine 101, where charge transfer in the lactone form prevents C−O dissociation.[13] The present paper studies the picosecond dynamics of the photoisomerization of spiro[cyclohexadiene-indoline] and the competing intramolecular charge transfer by means of time-resolved absorption and emission experiments in solutions of different polarity. It also examines the impact of various substitutions at the nitrogen atom of the indoline moiety.

SCHEME 1



SI-R spiro[cyclohexadiene-indoline]

M-R merocyanine

R = Me, Ph

Experimental Section

The absorption spectra were taken with the UV−vis spectrometer (Shimadsu UV-2101).

The fluorescence spectra recorded (ISA Instruments Fluoromax-2) were corrected by subtraction of the background due to the solvent (Raman line, trace impurities) and by the wavelength-dependent detector sensitivity. Fluorescence quantum yields were determined using diphenylhexatriene in cyclohexane as reference[14] ($\Phi_{fl} = 0.78$ [15]). The excitation lamp of the same spectrometer was used to perform the photolysis of the spiro[cyclohexadiene-indoline] solution, which causes the coloration due to merocyanine formation.

The following served as excitation source for the time-resolved measurements:

(a) second and third harmonic (380/253 nm, 5/1.5 mJ/pulse, 200 fs pulse duration, 10 Hz repetition rate) of the Ti:sapphire laser radiation (chirped pulse amplified, BMI Alpha 10, our

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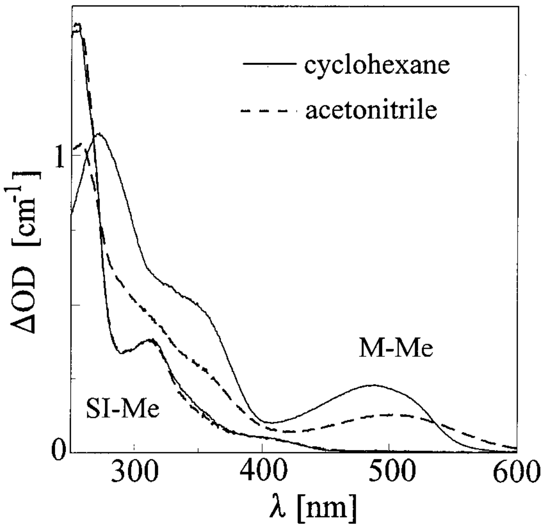

Figure 1. UV-vis absorption spectra of pure SI−Me and merocyanine-colored (M−Me) solution (cyclohexane−solid lines; acetonitrile−dashed lines).

laboratory [16]) and (b) a frequency-tripled Nd:YAG laser at 355 nm (pulse duration 18 ps, 1.5 mJ/pulse, 10 Hz repetition rate, Radiation Laboratory of the University of Notre Dame[17]).

For the pump−probe measurement of the transient absorption, a white light continuum pulse was generated by focusing the basic radiation of the laser systems (760 nm Ti:sapphire, 1064 nm Nd:YAG) in a water cell. The spectra were recorded with an OMA system. Extinction coefficients and products of quantum yield and extinction coefficient were determined by relative actinometry using the triplet of benzophenone in acetonitrile as reference ($\Phi_T = 1$, $\epsilon_T(525\text{ nm}) = 6250$ L mol^{-1} cm^{-1} [18]).

Only a few μJ per pulse were used to generate the fluorescence, which was recorded on a highly sensitive streak camera (Hamamatsu Photonics C5680/M5676). The time resolution of fluorescence detection was increased up to 1 ps.[19] Unless otherwise stated the measurements were carried out at room temperature.

The solvents used (cyclohexane = c-C_6H_{12}, dibutyl ether = $^nBu_2O$, diethyl ether = Et_2O, tetrahydrofuran = THF, dimethyl sulfoxide = DMSO, acetonitrile = CH_3CN) were of spectroscopic quality (Merck). Aprotic solvents were chosen to exclude the influence of hydrogen bonding on the electronic spectra.

SI−Me = 6-benzoyl-1′3′,3′-trimethyl-3,5-diphenyl-spiro-[cyclohexa-2,4-diene-1,2′-indoline] and **SI−Ph** = 6-benzoyl-3′,3′-dimethyl-3,5,1′-triphenyl-spiro[cyclohexa-2,4-diene-1,2′-indoline] have been synthesized as previously described.[8]

Results and Discussion

Electronic Absorption and Emission Spectra. The UV−vis spectra of spiro[cyclohexadiene-indoline] solutions show a weak low-energy absorption at 410 nm and a stronger absorption at 320 nm. The latter is responsible for the photoisomerization to the colored merocyanine. The absorption spectra of the spiro-[cyclohexadiene-indolines] are not affected by the solvent polarity. In Figure 1 the spectra of SI−Me in cyclohexane and acetonitrile are compared. UV-irradiation causes an absorption in the visible range owing to the conjugation of the formerly isolated π systems in the merocyanine (M−Me) formed. A photokinetic analysis of the photochromic equilibrium under continuous UV- and vis-irradiation has been done earlier.[10] There is a slight bathochromic shift (490 nm in cyclohexane, 503 nm in acetonitrile) due to a partial charge separation along the cyanine chain.

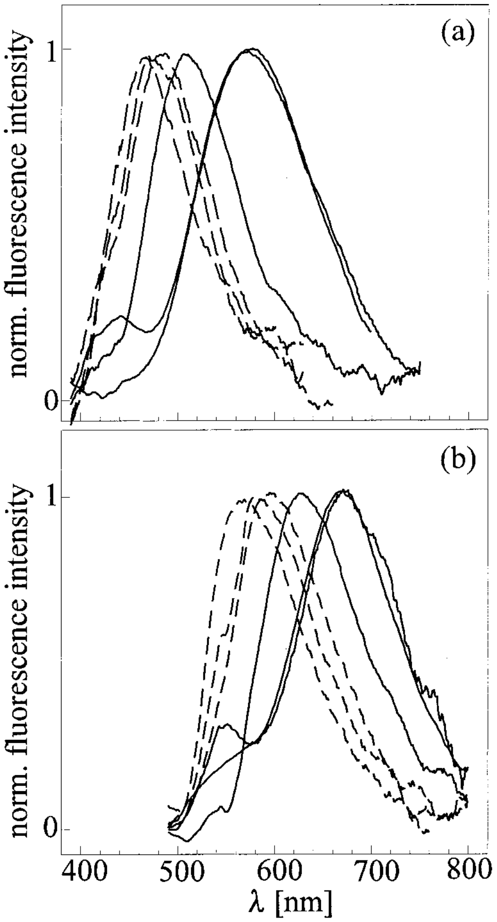

Figure 2. Fluorescence spectra in c−C_6H_{12}, $^nBu_2O$, Et_2O (dashed lines), THF, DMSO, and CH_3CN (solid lines) in the order of their polarity (red-shift) (a) of SI−Ph excited at 380 nm and (b) of the merocyanine M−Ph excited at 480 nm.

The emission spectra of both the spiro[cyclohexadiene-indoline] and the merocyanine exhibit a more significant solvent effect (see Figure 2). The positive solvatochromism indicates the stabilization of a very polar excited species in polar solvents.The Stokes shifts (see Table 1) are analyzed by their dependence on the dielectric parameters of the solvent[20−22]

$$\Delta\tilde{\nu} = \Delta\tilde{\nu}_0 + \frac{2|\Delta\mu|^2}{4\pi\epsilon_0\, h\, c\, a_w^3}\Delta f$$

with

$$\Delta f = \frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

where $\Delta\tilde{\nu}$ is the difference of the wavenumbers of absorption and fluorescence maxima (with subscript 0 for the gas phase), $\Delta\mu$ the difference of the dipole moments in the first excited singlet and the ground state, h Planck's constant, c the velocity of light, and a_w the Onsager radius, taken as 6 Å. The values for the dielectric constant ϵ_r and the refractive index n listed in Table 1 were taken from ref 23. The change of the dipole moment could only be calculated as a rough approximation because of a certain arbitrariness in the choice of a_w. However, the values found may help to determine the nature of the

TABLE 1: Solvent-Dependent Optical Properties of SI−Me (6-benzoyl-1′,3′,3′-trimethyl-3,5-diphenyl-spiro[Cyclohexa-2,4-diene-1,2′-indoline) and SI−Ph (6-benzoyl-3′,3′-dimethyl-1′,3,5-triphenyl-spiro[Cyclohexa-2,4-diene-1,2′-indoline) and the Merocyanine-Colored Solutions

	c−C_6H_{12}	^{n}Bu_2O	Et_2O	THF	DMSO	CH_3CN
solvent						
n [13]	1.4262	1.3992	1.3524	1.4072	1.4793	1.3441
ϵ_r [13]	2.02	3.08	4.20	7.58	46.45	35.94
Δf	0	0.096	0.162	0.210	0.263	0.305
SI−Me						
λ_{abs} [nm]	410	410	410	410	420	410
λ_{fl} [nm]	505	525	535	560	625	620
$\Delta\nu$[cm^{-1}]	4580	5340	5700	6530	7810	8260
τ_{fl} [ps]	5	29	69	270	325	580
$10^3 \times \Phi_{fl}$	0.3	0.7	1.4	2.4	2.0	1.8
M−Me						
λ_{abs} [nm]	490	490	495	500	518	503
λ_{fl} [nm]	575	600	620	645	700	690
$\Delta\tilde{\nu}$ [cm^{-1}]	3020	3740	4070	4500	5020	5390
τ_{fl} [ps]	7	23	51	140	63	35
$10^3 \times \Phi_{fl}$	0.3	0.5	0.5	1.2	5.8	2.0
E_a [kcal/mol]	2.1					3.1
SI−Ph						
λ_{abs} [nm]	390	390	390	390	395	390
λ_{fl} [nm]	469	480	480	513	573	573
$\Delta\tilde{\nu}$ [cm^{-1}]	4320	4800	4800	6150	7550	8200
τ_{fl} [ps]	∼10	30	32	73	1440	1120
$10^3 \times \Phi_{fl}$	0.2	0.3	0.3	0.5	2.9	2.1
M−Ph						
λ_{abs} [nm]	472	474	474	481	498	485
λ_{fl} [nm]	572	590	590	590	663	673
$\Delta\tilde{\nu}$ [cm^{-1}]	3700	4150	4150	4700	5000	5760
τ_{fl} [ps]	11	16	16	46	75	30
$10^3 \times \Phi_{fl}$	0.2	0.3	0.3	0.6	5.5	1.4
E_a [kcal/mol]	1.2					

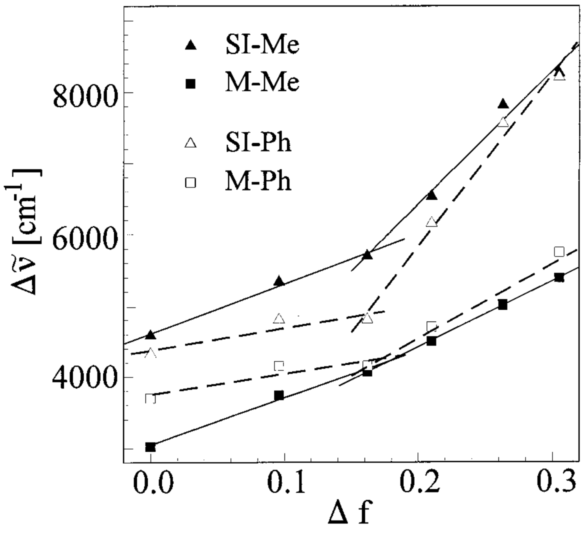

Figure 3. Stokes-shift ($\Delta\tilde{\nu}$) vs solvent polarity (Δf) for SI−Me (full triangles), M−Me (full squares), SI−Ph (open triangles), and M−Ph (open squares).

emitting state. Figure 3 illustrates a sharp deviation from the linear relationship for the fluorescence of the spiro compounds, SI−Me and SI−Ph.

Concerning the merocyanine fluorescence (M_1, λ_{exc} = 480 nm) of the methyl-substituted compound, the solvatochromic shift follows a linear dependence on Δf corresponding to a change of the dipole moment of 13 D. This indicates a partial shift of charge along the merocyanine chain toward the oxygen atom ($N^{\delta+}\cdot\cdot O^{\delta-}$). The fluorescence of the excited SI−Me (S_1), however, exhibits a stronger increase of the Stokes shift for more polar solvents (THF, DMSO, CH_3CN). The change of the dipole moment was calculated to be 20.2 D, while for less polar solvents (c−C_6H_{12}, ^{n}Bu_2O, Et_2O) it is similar to that of M−Me (12.3 D). This means that charge transfer occurs in the excited state (S_{CT}) between the indoline, where the nitrogen with its electron pair is the donor, and the aroylcyclohexadiene moiety, where the keto group is the acceptor. The charge of one electron is separated over a distance of more than 4 Å.

More significantly, the charge transfer character of emission in polar solvents was found for the fluorescence of the phenyl-substituted compound SI−Ph. Both the fluorescence of the spiro and the merocyanine form show a much sharper increase in the Stokes shift for the polar solvents compared to the nonpolar solvents. Therefore, solvent-assisted charge transfer even occurs in the excited merocyanine M_1. This is also indicated by the dual fluorescence spectra for both, SI−Ph and M−Ph, in DMSO and acetonitrile (Figure 2). The change of the slopes of the solvent-dependent Stokes shift does not disappear when the different polarizabilities of the ground state and the excited state are taken into account. The same nonlinear behavior, observed for instance for dimethylaminophenylphenanthrene,[24] where charge transfer is accompanied by the twisting of the *N*,*N*-dimethylamino group, has been explained by an equilibrium between two excited states and a solvent-induced level crossing.

Table 1 also contains the values for the fluorescence quantum yields of the spiro and the merocyanine form (SI−Me, M−Me, SI−Ph, M−Ph). In general, the fluorescence yield ranges from 10^{-4} to 10^{-3} and increases with solvent polarity. The low quantum yield of the merocyanine fluorescence leads us to assume that isomerization is the main channel of radiationless deactivation. Intersystem crossing has not been observed for the excited merocyanine. This would allow the activation barrier to be estimated from the temperature dependence of the fluorescence quantum yield.[25] The ratio of the radiative rate constant k_r and the overall rate constant yields the fluorescence quantum yield Φ_{fl}.

$$\Phi_{fl} = k_r/(k_r + k_{nr})$$

The main distribution to the nonradiative rate constant k_{nr} is the photoisomerization rate k_{iso} ($k_{nr} \approx k_{iso}$).

From the Arrhenius equation

$$k_{nr} = A \exp(-E_a/RT)$$

follows

$$(1/\Phi_{fl})-1 \sim \exp(-E_a/RT)$$

The linear regression of ln[$(1/\Phi_{fl})-1$] vs 1/T (shown in Figure 4) yields a solvent specific activation energy E_a. The E_a values for M−Me range from 2.1 kcal mol^{-1} in cyclohexane to 3.1 kcal mol^{-1} in acetonitrile. For M−Ph in cyclohexane the activation barrier for isomerization is even lower (1.2 kcal mol^{-1}).

Time-Resolved Fluorescence. Different individual lifetimes were determined when the fluorescence decay was recorded with a streak camera for the excited states of spiro[cyclohexadiene-indoline] (S_{CT}) and merocyanine (M_1, Table 1).[11] The stabilization of the intramolecular charge transfer within the excited spiro[cyclohexadiene-indoline] (S_{CT}) confirms the increase of lifetime with increasing solvent polarity, amounting to 2 magnitudes between nonpolar cyclohexane (5 ps) and polar acetonitrile (580 ps for SI−Me, 1.12 ns for SI−Ph). Rapid

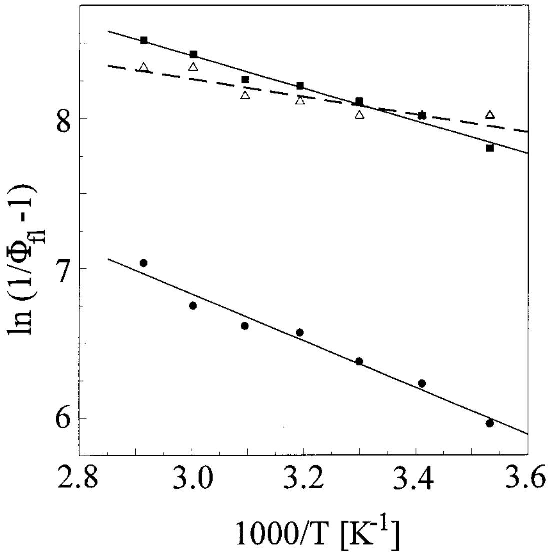

Figure 4. Arrhenius plots of $(1/\Phi_{fl})-1$ vs $1/T$ for M−Me in c-C_6H_{12} (full squares, $E_a = 2.1 \pm 0.2$ kcal mol^{-1}) and in CH_3CN (full circles, $E_a = 3.1 \pm 0.1$ kcal mol^{-1}), and for M−Ph in c-C_6H_{12} (open triangles, $E_a = 1.2 \pm 0.3$ kcal mol^{-1}).

change occurs for most polar solvents, DMSO and acetonitrile. The quantum yield of fluorescence obeys the same tendency only in the less polar solvents (e.g., SI−Me: $0 < \Delta f < 0.162$, $3 \times 10^{-4} < \Phi_{fl} < 1.4 \times 10^{-3}$), while for the polar solvents the quantum yield ($\Phi_{fl} \sim 2 \times 10^{-3}$) is lower, compared to the increased lifetimes, than expected concerning the Strickler−Berg equation.[26] Transient absorption measurements[10] show intersystem crossing to be the main channel of charge transfer deactivation.

The lifetime of M_1 is always shorter than of S_{CT}, remaining in the order of several tens of picoseconds, increases sligthly with the solvent polarity, but is again reduced for the polar solvents DMSO and acetonitrile. As mentioned above, this is due to isomerization, which is assumed to be the main deactivation process. The fluorescence lifetime is determined by not only the polarity but also the viscosity, and thus the temperature, of the medium.

Picosecond Transient Absorption. Photoisomerization, resulting in the merocyanine, and intersystem crossing are solvent-dependent processes that have been studied by means of transient absorption spectroscopy. Typical transient absorption spectra are shown in Figure 5. They were taken in the two cases of nonpolar cyclohexane (5a: SI−Ph, 5c: SI−Me) and polar acetonitrile (5b: SI−Ph, 5d: SI−Me). Immediately after the excitation with the 355-nm pulse of the frequency-tripled Nd:YAG laser, the excited singlet state of the spiro[cyclohexadiene-indoline] absorbs. These spectra always decay with the same time constant as their fluorescence (S_1 in cyclohexane $\tau < 10$ ps, S_{CT} in acetonitrile τ(SI−Ph) = 1.12 ps, τ(SI−Me) = 580 ps). The insets to Figure 5 contain the time profiles of the

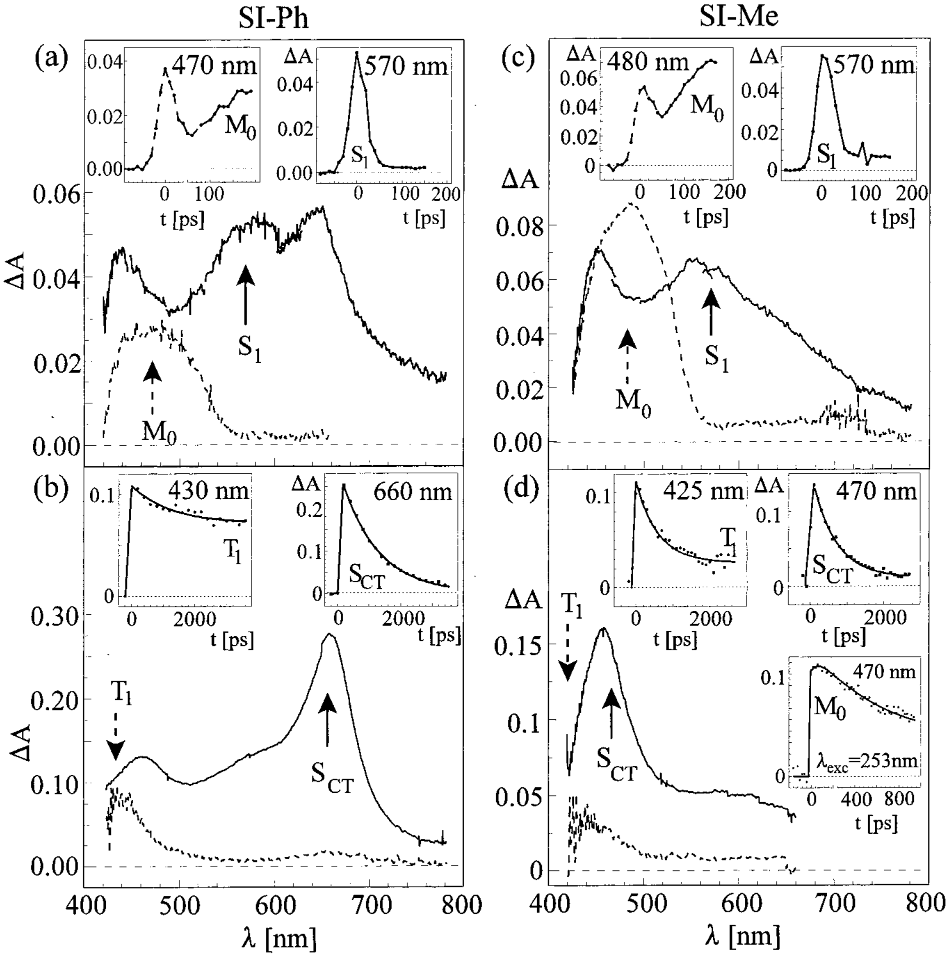

Figure 5. Transient absorption spectra of SI−Ph in c-C_6H_{12} (a) and in CH_3CN (b), as well as SI−Me in c-C_6H_{12} (c) and in CH_3CN (d) excited at 355 nm, taken at delay 0 (solid line) and 200 ps (dashed line) in c-C_6H_{12} (a,c), at delay 0 (solid line) and 3000 ps (dashed line) in CH_3CN (b,d). Insets show the time profiles at the given probe wavelengths for the marked transients. The third profile with higher time resolution in (d) illustrates the decay of the charge transfer band overlain by the growth of M−Ph under excitation at 253 nm.

TABLE 2: ps-Transient Absorption of the Spiro[cyclohexadiene-indolines] Excited at 355 nm

spiro (Fig.)	solvent	transient (λ_{abs} [nm])	τ [ps]	$\Phi\ \epsilon(\lambda_{abs})$ [L M^{-1}cm^{-1}]	$\epsilon(\lambda_{abs})$ [L M^{-1}cm^{-1}]	Φ
SI−Ph	c-C_6H_{12}	decay				
(5a)		S_1 (420)	<10	900		
		S_1 (650)	<10	1050		
		growth				
		M_0 (480)	50‥100	500	5500[a]	0.09
SI−Me	c-C_6H_{12}	decay				
(5b)		S_1 (450)	4[c]	1100		
		S_1 (570)	7[c]	1000		
		growth				
		M_0 (490)	50‥100	1400	7600[a]	0.18
SI−Ph	CH_3CN	decay				
(5c)		S_{CT} (460)	1120	2800		
		S_{CT} (660)	1120	6400		
		growth				
		T_1 (425)	∼1100	1400	2350[a]	0.60
		M_0 (500)	∼30	100	5500[a]	0.015
SI-Me	CH_3CN	decay				
(5d)		S_{CT} (460)	580	3500		
		S_{CT} (570)	580	1000		
		growth				
		T_1 (430)	500‥600	500	2550[a]	0.20
		M_0 (500)	30‥110[c]	<50	6600[b]	<0.01

[a] Values taken from ref 10. [b] Determined as in ref 10 by separation of the UV-vis spectra of SI−Me and M−Me in HPLC. [c] Derived from the subpicosecond pump probe experiment, $\lambda_{exc} = 253$ nm.

different transients. The spectra at delay 0 between pump and probe pulse consist of three bands for the excited singlet of SI−Ph (440 nm, 570 nm, 640 nm in cyclohexane (5a), red-shifted by ca. 20 nm in acetonitrile (5c)) and of two bands for SI−Me (450 nm, 570 nm in cyclohexane (5b), red-shifted by ca. 10 nm in acetonitrile (5d)). The charge transfer bands at 460 nm (and additionally at 660 nm for SI−Ph) are increased up to 6 times in acetonitrile compared to cyclohexane (see Table 2). Although the strength of the absorption around 570 nm is less affected by the solvent and could differ from the charge transfer nature, its decay time could not be distinguished from that of the charge transfer absorption (S_{CT}).

The dashed spectra in Figure 5 taken after the relaxation of the excited singlet (200 ps for cyclohexane, 3 ns for acetonitrile) belong to different species depending on the solvent. In cyclohexane a strong absorption band at 490 nm corresponds to the expected formation of the merocyanine (M_0). Its quantum yield is higher for the sterically less hindered M−Me ($\Phi_M = 0.18$) compared to M−Ph ($\Phi_M = 0.09$). This tallies closely with the results of former ns-photolysis experiments[10] ($\Phi_M = 0.15/0.05$). The growth proceeds within 50 to 100 ps, slower for the red components of the merocyanine spectrum, corresponding to a red-shift of the visible absorption. This formation time is much slower than the lifetime of the excited singlet state (S_1, $\tau < 10$ ps) in cyclohexane. That means the isomerization to form the colored merocyanine (M_0) proceeds in the ground state of the relaxed structure with a broken C_1−C_6 bond at the former spiro carbon.

In acetonitrile the yield of merocyanine (M_0) is less than 10^{-2} after excitation of spiro[cyclohexadiene-indoline] with 355 nm. Another absorption at 420 nm grows within the same time as the excited singlet state decays (S_{CT}, $\tau \sim 600$ ps for SI−Me, $\tau \sim 1100$ ps for SI−Ph). This absorption has been identified as the triplet state (T_1) of the ring-closed molecule by means of nanosecond photolysis.[10] The yield of the triplet is much higher for the phenyl-substituted compound SI−Ph ($\Phi_T = 0.6$) than for SI−Me ($\Phi_T = 0.2$), reflecting the proportion of their charge transfer absorption bands (S_{CT}).

Higher energy excitation at 253 nm increases the yield of merocyanine, as is shown by the measurements with the higher time resolution of the Ti:sapphire system. Merocyanine absorption at 500 nm appears in a similar manner as in cyclohexane within 30−110 ps, increasing with absorption wavelength. The third time profile in Figure 5d shows the superposition of charge transfer decay (S_{CT}) and merocyanine formation (M_0) at 470 nm. The kinetics of the photoisomerization does not depend on the lifetime of the excited singlet state of the spiro[cyclohexadiene-indoline], and no influence of the solvent polarity was found. The activation barrier for the isomerization of the hexatriene is the decisive property. This ought to be in the order of 1−3 kcal mol^{-1}, as concluded from the temperature-dependent measurement of the merocyanine fluorescence. Similar values for the time of merocyanine formation (30−110 ps) and lifetimes of the excited merocyanine confirm this consideration.

Discussion of the Mechanism. The mechanism of photoinduced isomerization gleaned from the results of different experiments is depicted in Figure 6. Investigations of optical spectra of spiro compounds with respect to the orthogonality of the noninteracting π systems at the spiro carbon[28] suggest that the aroylhexadiene moiety is the chromophore of the spiro[cyclohexadiene-indoline] (320 nm, 410 nm). From the vibronically excited Franck−Condon state (S^*), apart from degradation, there are two relaxation channels of the first excited singlet.

The first one is a charge transfer within the spiro form between the indoline and the aroylcyclohexadiene moiety (S_{CT}, **1**). Changing into a zwitterionic state, the donor of the molecule takes on the character of an aminyl radical cation, the acceptor that of a ketyl radical anion. Their spatial vicinity, confirmed by the X-ray structure determination for the spiro molecule,[8] and the Coulomb attraction prevent isomerization. This is possible because of the noncyclic acceptor, the aroyl group in the 6-position of the cyclohexadiene, and therefore is not observed in different photochromic molecules, such as spirobenzopyrans. The second process is the C_1−C_6 bond cleavage and the rapid radiationless relaxation toward a vibronically hot ground state of the merocyanine, obeying the Woodward−Hoffmann rules[29] of electrocyclic, conrotatory reactions in the first excited singlet state (**2**). Both processes proceed in the subpicosecond range.[5]

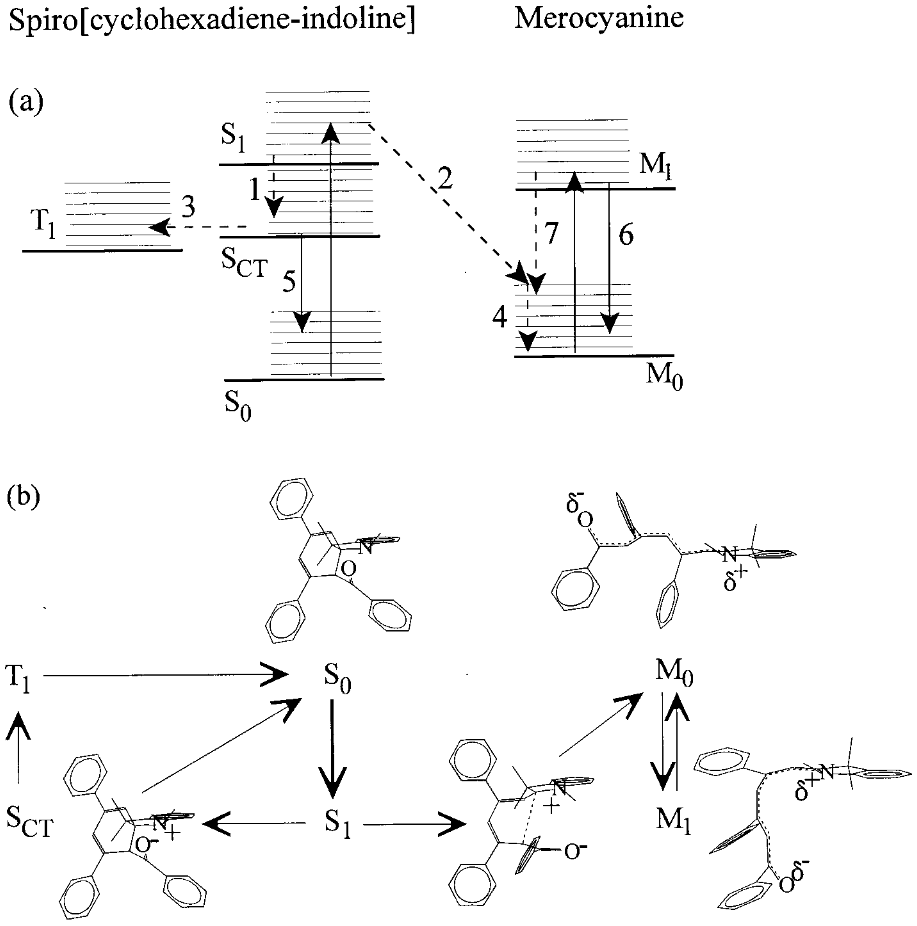

Figure 6. (a) Jablonski diagram of the photoisomerization of spiro[cyclohexadiene-indoline]: **1.** charge transfer, **2.** C_1-C_6 bond cleavage, **3.** intersystem crossing, **4.** relaxation of the vibronically hot ground state, **5.** spiro fluorescence, **6.** merocyanine fluorescence, **7.** hexatriene isomerization; radiative transitions (full lines) and nonradiative transitions (dashed lines) (b) reaction scheme including geometry-optimized structures[27] (PM3).

The deactivation of the charge transfer state (S_{CT}) mainly proceeds via intersystem crossing (**3**). Its lifetime was derived from the time-resolved measurement of the weak fluorescence (**5**). The formation of the merocyanine (M_0) was observed by the time-resolved measurement of the growth of the visible absorption. As it was found to be independent of the lifetime of the excited singlet state of the spiro molecule, we attribute the growth of the merocyanine absorption (M_0) to the relaxation of a vibronically hot ground state (**4**), which is confirmed by its red-shift during the first 100 ps. The fluorescence of the excited merocyanine (M_1, **6**) has a similar lifetime ($<$100 ps), which is temperature dependent because of the deactivation by isomerization of the hexatriene. Similar activation energies (1−3 kcal mol^{-1}) are expected for the conrotatory ring opening of the excited spiro[cyclohexadiene-indoline] (S_1).

Once the merocyanine has been formed (M_0) it is unable to return thermally to the spiro form in the ground state level.[10] Photoexcited ring closure is difficult to quantify because of degradation. In acetonitrile, no back reaction to the spiro form could be observed in the HPLC analysis of the products of the irradiation with visible light.[30] The charge transfer character of the excited states of both the spiro form and the merocyanine form prevents the rearrangement of the spiro[cyclohexadiene-indoline].

Conclusion

Studying the photoisomerization of spiroindolines using time-resolved spectroscopy supports the hypothesis of ring opening within the first excited singlet state. The occurrence of intramolecular charge separation (S_{CT}) in polar solvents, obtained by the solvatochromism of the fluorescence, retains the spiro form of the molecule. The excited state is then deactivated within the relatively long lifetime of several hundred picoseconds, mainly as a result of intersystem crossing. In nonpolar solvents the yield of isomerization to the merocyanine increases up to 18% for the sterically less hindered SI−Me. Picosecond-resolved transient absorption shows that the visible absorption band of the merocyanine grows within 100 ps, which is determined by the activation energy for the isomerization of the hexatriene. In the polar solvent acetonitrile, even the excited merocyanine has charge transfer nature. This prevents the back reaction to the spiro conformation, and thus the photoisomerization is no longer photochromic.

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