Chapter 7

Ultrafast Photophysics of Photochromic Spiropyrans

Structure:
- electronic state coupling
- large displacement of vibrational modes
- anharmonic coupling between vibrational modes

Dynamics:
- internal conversion
- intramolecular vibrational redistribution
- vibrational energy dissipation
- ring-opening
- cis-trans isomerisation

Published as:
Abstract: We present a femtosecond UV-mid-IR pump–probe study of the photochemical ring-opening reaction of the spiropyran \(1',3',3',3'\text{-trimethylspiro[2H-1-benzopyran-2,2' indoline]}\) (also known as BIPS) in tetrachloroethene, using 70 fs UV excitation pulses and probing with 100 fs mid-IR pulses. The time evolution of the transient IR absorption spectrum was monitored over the first 100 ps after UV excitation. We conclude that the merocyanine product is formed with a 28 ps time constant, contrasting with a 0.9 ps time constant obtained in previous investigations where the rise of absorption bands at visible wavelengths were associated with product formation. We deduce from the observed strong recovery of the spiropyran IR absorption bleaches that, in tetrachloroethene, the main decay channel for the \(S_1\) excited state of the spiropyran BIPS, is internal conversion to the spiropyran \(S_0\) state with a quantum yield of \(\geq 0.9\). This puts an upper limit of 0.1 to the quantum yield of the photochemical ring-opening reaction.
Ring Opening of a Photochromic Spiropyran

**Figure 1.** Reactant and product structures for the photochromic reaction of BIPS.

**Figure 2.** Absorption spectrum of 1 mM BIPS in tetrachloroethene. The insert illustrates the nearly complete absence of merocyanine absorption around 540 nm.

the enormous research effort on these systems it is remarkable that up to now only a handful of studies have been performed with subnanosecond time-resolution.5–11 The molecule we investigated is 1',3',3',-trimethylspiro-[2H-1-benzopyran-2,2'-indoline, commonly referred to as BIPS, dissolved in tetrachloroethene. The spiropyran compound can to first approximation be regarded as two nearly independent orthogonal halves: 12 a chromene and an indoline. The BIPS molecule does not absorb in the visible (cf. Figure 2). Upon absorption of a UV photon a ring opening and cis–trans isomerizations take place, resulting in a more or less planar molecule with a strong broad absorption around 540 nm. The huge shift in absorption wavelength can easily be understood from the fact that now the delocalized \( \pi \)-system extends over the entire molecule. In the literature, it has been concluded that if the chromene part contains an NO\(_2\) substituent, then the ring opening reaction of spiropyrans will (at least to some extent) involve triplet states.13 For spiropyran compounds without this NO\(_2\) substituent, such as the one we investigate here, it has been stated\(^6\) that the reaction involves only singlet states. In principle, eight isomers can be formed of the merocyanine compound, due to cis–trans configurations at the three double bonds of the bridge segment. Theoretical calculations have indicated, however, that due to steric hindrance only isomers with a trans configuration around the second bond are stable.7

Femtosecond UV-pump/white-light probe experiments have been performed at room temperature on BIPS in ethanol\(^6\) and \( n \)-pentane,\(^6,7\) and on the naphthopyran analogue\(^6\) naphtho-BIPS and 6-nitro-BIPS\(^8\) in \( n \)-pentane. These data demonstrated the appearance after about a picosecond of a broad nearly featureless absorption, covering the entire probing range of 380–680 nm. At the wavelengths of the merocyanine product absorption band, the rise\(^6\) in \( n \)-pentane was 0.9 ps for BIPS (at 540 nm) and 1.4 ps for naphtho-BIPS (at 520 nm). During the following 6 ps, the absorption at the maximum did not change drastically; however, the featureless initial spectrum did evolve toward sharper spectral features that more closely resemble the product spectra observed on \( \mu s \) time-scales.\(^6,7\) The broad initial absorption and subsequent sharpening was ascribed to transitions from the spiropyran excited state to higher electronic states, and to transitions from vibrationally hot merocyanine in the electronic ground state.\(^6\) For the 6-nitro-BIPS compound the initial spectrum was similar. However, at later times, two absorption bands, at 430 and 575 nm, increased in intensity with a 20 ps time constant.\(^6\) Room-temperature experiments with femtosecond UV-pump and probing at diverse wavelengths in the visible have been performed on 6-hydroxy-BIPS in 1-propanol, methanol, and 1-hexanol.\(^8\) Pumping at 310 nm and probing at 620 nm an exponential rise of the signal with \( \approx 2 \) ps was identified in 1-propanol. The general conclusion from these experiments seems therefore that the merocyanine product is formed with a 1–2 ps time constant in the compounds without a nitro-group, and with a 20 ps time constant for 6-nitro-BIPS.

The nearly featureless absorption after 1 ps, covering at least the range of 380–680 nm,\(^6\) motivated us to undertake the present UV pump-mid-IR probe studies. Electronic transitions of molecules in solutions are typically significantly broadened by optical dephasing and inhomogeneity effects. Therefore, at every wavelength, several different vibronic and/or electronic states contribute to the absorption, resulting in smooth broad spectral features. Consequently, the question can be raised if UV–vis investigations are ideal for unravelling the details of such a complex chemical reaction. In contrast, vibrational IR absorption lines are typically very narrow and without much inhomogeneous broadening. Although the large number of vibrations for larger molecules can also be complicating, there are still good chances of finding regions with relatively few IR absorption lines. In addition, no time-resolved single color UV experiment has yet been reported to directly determine whether any recovery of the spiropyran (closed form) absorption occurs. Such a measurement is essential for obtaining quantitative information on the quantum yield of this photochemical reaction. In the present study, we will extract this information from the time evolution of bleaches related to the IR vibrational absorption spectrum of the spiropyran compound. We believe therefore that the present method of investigation can increase the insight into the possible existence and structure of reaction intermediates, the time scale(s) of product formation, and whether different isomers are being formed on femtosecond and picosecond time scales. The FT-IR spectrum of BIPS in tetrachloroethene, and existing resonance Raman spectra on the photo-products of BIPS in different solvents,\(^9\) taken 200 ns after UV excitation, are used to support the analysis.

**Experimental Section**

The absorption spectrum of 1 mM BIPS in a 1 mm quartz cuvette was recorded in a Perkin-Elmer UV–vis spectrometer. Below 280 nm strong absorption from tetrachloroethene (\( C_2\)Cl\(_2\)) prevents an accurate determination of the absorption spectrum. Steady-state FT-IR spectra were recorded with 2 cm\(^{-1}\) resolution, using a Biorad FT-IR spectrometer. The 50 mM
sample of BIPS in C₂Cl₄ was injected in a home-built cell with CaF₂ windows and a spacer of approximately 100 μm. For the femtosecond pump–probe experiments, 400 ml solution of 21 mM BIPS in C₂Cl₄ was made, and pumped through a free streaming jet with a nominal thickness of 100 μm. No noticeable degradation of the solution was observed after the measurements.

The near-UV pulses for electronic excitation were generated by sum frequency mixing of the fundamental of a home-built 1-kHz amplified Ti:sapphire laser and visible pulses obtained by a noncollinear optical parametric amplifier, as described elsewhere. The excitation wavelength was tuned to 316 nm, the pulse energy was 2.5 μJ and the pulse duration around 70 fs. The pump pulses could be variably delayed and were focused with a concave mirror on the sample with a spot diameter of approximately 150 μm. The mid-infrared probe pulses were generated using double-pass collinear optical parametric amplification, followed by difference frequency mixing of signal and idler, as described in detail in ref 18. The center frequency was tuned to 1530 cm⁻¹ and the output energy was about 700 nJ. Probe and reference pulses were formed using reflections from a BaF₂ wedge, and were both focused in the sample with off-axis parabolic mirrors (spot size 100 μm). The entire pump–probe setup was purged with nitrogen gas to prevent spectral water vapor in air. Probe and reference pulses were dispensed in a grating spectrometer after passing the sample, and complete spectra were recorded simultaneously for each shot using a liquid nitrogen cooled 2 × 31 HgCdTe detector array. Normalization of probe and reference signal on a single shot basis provided highly reliable transient absorption spectra: allowing at best the detection of absorption changes ΔOD as small as 0.10 mOD, with an accuracy of ±0.05 mOD. The experimental curves presented here are the average of 15–25 time delay scans, with each scan averaging 400 shots per data point. The time-resolution (fwhm ≈ 130 fs) and the zero time delay point were determined by a cross-correlation experiment performed in a polished ZnSe window.

Results and Discussion

Transient Changes in the IR Absorption Spectrum. The spectral evolution of the transient changes in optical density (OD) of the IR absorptions between 1430 and 1620 cm⁻¹ during the first 100 ps after excitation of BIPS at 316 nm is illustrated in the upper panel of Figure 3. For comparison the IR absorption spectrum of BIPS in the electronic ground state, at a concentration of 50 mM in tetrachloroethene, is depicted in the lower panel of Figure 3 over the same frequency range. We have investigated the entire spectral range from 1200 to 1800 cm⁻¹. The other ranges did not provide additional information. The presented range contains the strongest IR band, as well as the most isolated IR band. Note furthermore that the merocyanine compound does not exhibit a true carbonyl stretching mode in the range 1600–1800 cm⁻¹, probably because it is part of the delocalized π-system.

The spectrum after 2 ps is dominated by strong bleaches of the ground-state IR absorption bands at 1458, 1486, and 1610 cm⁻¹. For the data in Figure 3 each detector pixel integrates signal over a range of 6 cm⁻¹. This implies that for vibrational bands broader than 6 cm⁻¹ the peak position of bands can be determined within ~4 cm⁻¹. The calibration of the grating spectrometer was checked by comparing the positions of the bleaches to those observed in the steady-state FT-IR spectrum. In addition, weak transient (increased) absorption is seen at most other frequencies. Between 1535 and 1585 cm⁻¹ most of this absorption (amplitude ranging from 0.1 to 0.4 mOD) disappears with time constants ranging from 2 to 22 ps, leaving a residual change in absorbance (ΔOD) varying between 0.06 and 0.20 mOD (accuracy ±0.05 mOD). The height of this residual offset was found to depend clearly on the pulse duration of the UV pulse and is ascribed to minor undesirable multiphoton contributions from BIPS molecules and the solvent. After 100 ps, the strong bleaches have nearly entirely recovered, indicating that the majority (~90%) of the BIPS molecules have by that time returned to the vibrational and electronic ground state of the closed spiropyran form. At this time delay, product vibrational absorption bands can clearly be identified at 1461 cm⁻¹ (0.6 mOD), 1489 cm⁻¹ (0.6 mOD), and 1591 cm⁻¹ (0.6 mOD).

Kinetic Scheme for Analysis of the Time-Resolved Data. The following kinetic scheme is used for the data analysis. The assignments are defined in the discussion below.

![Figure 3](image)

**Figure 3.** Upper panel: Transient changes in the IR absorption spectrum between 1430 and 1620 cm⁻¹ at, from bottom to top, 2, 10, 20, 51, and 100 ps after UV excitation at 316 nm. For representation purposes the signals are displayed with the offset at consecutive delay times increased in steps of 0.8 mOD. The dashed lines indicate the zero signal level for the different traces. Lower panel: Steady-state IR spectrum of 50 mM BIPS (closed form) in tetrachloroethene.
This scheme assumes the following: the initial species generated by UV photoexcitation is the excited singlet state of spiropyran, SP(S1). This either decays through internal conversion to form hot spiropyran in the electronic ground state, (S0) designates the vibrational manifold), or decays to other intermediate states which eventually may lead to merocyanine product formation. The SP(S1) decays with time t according to

\[ A e^{-\frac{t}{\tau_1} + \frac{t}{\tau_2}} \]

where A is the amplitude at delay time \( t = 0 \).

The time constant \( \tau_1 \) does not represent the true internal conversion time constant in our analysis. A complete characterization of the cooling process from the initial hot vibrational distribution to the thermally equilibrated vibrational distribution in the electronic ground state, requires knowledge about many more parameters than the data give access to. Therefore, we have chosen to fit the data related to vibrational cooling using an effective description involving only two time constants: \( \tau_1 \), which characterizes the average arrival time at the vibrational levels within the frequency interval covered by the relevant detection diode, and the time constant \( \tau_2 \), which characterizes the effective average departure time from this frequency interval. Note that the signals are the nett difference between (increased) absorption from \( \nu \rightarrow \nu + 1 \) and stimulated emission from \( \nu + 1 \rightarrow \nu \). The signals related to transient passage of vibrational levels other than \( \nu = 0 \), are now described by

\[ B \left( \frac{\tau_2}{\tau_2 - \tau_1} \right) e^{\frac{-t}{\tau_2}} \left( e^{\frac{-t}{\tau_2}} - e^{\frac{-t}{\tau_1}} \right) \]

The recovery of the thermally equilibrated electronic ground state, using the effective parameters \( \tau_1 \) and \( \tau_2 \), as evidenced by the refilling of the bleached IR absorptions, is described by

\[ C \left[ \left( \frac{\tau_1}{\tau_2 - \tau_1} \right) e^{\frac{-t}{\tau_1}} - \left( \frac{\tau_2}{\tau_2 - \tau_1} \right) e^{\frac{-t}{\tau_2}} \right] \]

Amplitude C divided by the amplitude of the bleach at \( t = 0 \), in principle equals the internal conversion quantum yield (disregarding solvent and multiphoton contributions).

The rise of the main product absorption bands can be described by

\[ D (1 - e^{-\frac{t}{\tau_1}}) \]

This equation is valid if formation of intermediates from the SP(S1) state, governed by \( (1/\tau_0 + 1/\tau_1)^{-1} \), is very fast compared to the time constant \( \tau_3 \) that governs formation of merocyanine product from these intermediates. The amplitude D gives the final signal strength of the product band.

**Kinetic Behavior at Vibrational Frequencies of the (Closed) Spiropyran Form of BIPS.** We first address the recovery of the bleaches in more detail. Figure 4 shows kinetic traces measured at the IR absorption maxima at 1486 and 1610 cm\(^{-1}\), and, in both cases, at slightly lower frequencies. The observed kinetics is consistent with rapid internal conversion followed by vibrational cooling. Note that during the first 20 ps the recovery of the bleaches occurs clearly at a slower pace than in the following 80 ps. This can easily be understood because the relaxation from the excited state created by the UV pulse passes through other intermediate vibronic states with \( \nu > 0 \) before returning to the vibrational and electronic ground state (\( \nu = 0 \)). Stimulated emission from \( \nu = 1 \rightarrow \nu = 0 \) presents an additional reason for an initially slower recovery of the bleaches at the fundamental frequencies. Due to anharmonicity, lower frequencies correspond to IR transitions between increasingly higher consecutive levels \( \nu \) of the vibrational ladder. Signals at frequencies below the fundamental frequencies are the difference between (increased) absorption from \( \nu \rightarrow \nu + 1 \) and stimulated emission from \( \nu + 1 \rightarrow \nu \). Nett increased absorption can be taken as an indication that the wave function amplitude for the level \( \nu \) is larger than for the level with \( \nu + 1 \). After internal conversion from the S1 electronic state to the S0 electronic state, the initial distribution is expected to be dominated by states with relatively high vibrational quantum numbers \( \nu \). Note that the 316 nm light contains sufficient energy for about 20 quanta of the 1486 or the 1610 cm\(^{-1}\) mode (disregarding anharmonicity). The rapid rise of the signal at 1467 cm\(^{-1}\) immediately after the spike (see Figure 4 and Table 1) therefore indicates that the internal conversion probably occurs on a subpicosecond time-scale. In accordance with a stepwise downward relaxation on the vibrational ladder,\(^{19}\) the increased absorption rises slower the

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**Table 1.** Fit Results for the Data Displayed in Figures 4–6

<table>
<thead>
<tr>
<th>( \nu ) (cm(^{-1}))</th>
<th>constant</th>
<th>B (mOD)</th>
<th>( \tau_1 ) (ps)</th>
<th>( \tau_2 ) (ps)</th>
<th>C (mOD)</th>
<th>D (mOD)</th>
<th>( \tau_3 ) (ps)</th>
</tr>
</thead>
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<tr>
<td>1461</td>
<td>0.41</td>
<td>0.26</td>
<td>85</td>
<td></td>
<td>0.38</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>1474</td>
<td>0.18</td>
<td>0.62</td>
<td>1 8</td>
<td>21</td>
<td>0.31</td>
<td>28 (F)</td>
<td></td>
</tr>
<tr>
<td>1492</td>
<td>0.02</td>
<td>0.56</td>
<td>28</td>
<td></td>
<td>0.64</td>
<td>28 (F)</td>
<td></td>
</tr>
<tr>
<td>1591</td>
<td>0.13</td>
<td>0.46</td>
<td>28</td>
<td></td>
<td>0.13</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>1597</td>
<td>0.22</td>
<td>0.40</td>
<td>14 14</td>
<td></td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1604</td>
<td>1.01</td>
<td>25</td>
<td>25</td>
<td>0.71</td>
<td>0.38</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>1610</td>
<td>0.05</td>
<td>25</td>
<td>25</td>
<td></td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
nearer the frequency is to that of the \( \nu = 0 \rightarrow \nu = 1 \) transition, as is clearly illustrated in Figure 4. Finally the red-shifted increased absorption of the higher-lying vibrational quantum levels \( \nu \) disappears, while simultaneously the bleach of the ground-state vibration is filled up.

Fit results for the displayed transients based on eqs 1–4, are summarized in Table 1. It appears that fits with expressions 2 and 3 have a strong tendency to make \( t_1 \) and \( t_2 \) nearly equal if they do not differ very much (naturally the numbers cannot be exactly equal since this would make the factor \( 1/(t_2 - t_1) \) infinite). Only for the data at 1467 and 1474 cm\(^{-1} \) this does not occur. A single-exponential fit for the 1486 cm\(^{-1} \) data resulted in a value of 37 ps for the bleach recovery, comparable to the sum of \( t_1 \) and \( t_2 \) (both 17 ps) obtained from fitting with eq 3. The values for \( t_1 \) and \( t_2 \) obtained at 1610 cm\(^{-1} \) are slightly longer than at 1486 cm\(^{-1} \), i.e., both 25 ps instead of 17 ps. In principle, there is no reason the recovery should not be very different for different vibrational modes. First of all, the internal conversion may favor specific vibrational modes for the conversion of electronic to vibrational energy. Second, the quantum number \( \nu \) of the levels populated by the internal conversion can vary considerably (differences in anharmonicity, fundamental frequency, and population of combinatorial bands). Third and last, the relaxation rates along different vibrational ladders may strongly depend on the capacity of the solvent to accept vibrational energy quanta of different frequencies, and on the efficiency of intramolecular vibrational redistribution (IVR) to other modes with lower fundamental frequencies.

Although at 1610 cm\(^{-1} \), the signal is only related to the bleached spiropyran IR absorption, at 1486 cm\(^{-1} \) the bleach appears to overlap with the IR band at 1489 cm\(^{-1} \) of a merocyanine product (open form), and therefore, eventually, the bleach turns into an increased absorption. The kinetics at both of these bands indicate that the dominating fraction that underwent internal conversion contributes very little to the signals after 100 ps. Because, as illustrated by the data in Figures 3 and 4, the bleach of the 1610 cm\(^{-1} \) IR absorption band has already recovered by 90% after 100 ps, the quantum yield for the internal conversion has to be \( \geq 0.9 \). Consequently, the quantum yield for the photochemical conversion can maximally be 0.1. This value compares well to a photocoloration quantum yield of 0.055 mole/einstein at \(-120^\circ\)C in a 1-propanol/2-propanol mixture reported\(^{16,15} \) for BIPS irradiated at 313 nm.

**Kinetics at Vibrational Frequencies of the Merocyanine Product.** As mentioned before we identify the peaks in the spectrum after 100 ps at 1461, 1489, and 1591 cm\(^{-1} \) as product bands. Because the open merocyanine form fairly quickly converts back to the spiropyran form (within seconds, because no coloration of the streaming solution was noticed), steady-state IR spectra of the merocyanine compound are not available. Further support for the assignment can however be derived from published time-resolved resonance Raman data\(^6 \), generated 200 ns after UV irradiation, in a variety of solvents. Unfortunately, tetrachloroethene is not one of the solvents used in these studies. We propose that the data in benzene should be closest in comparison, since tetrachloroethene and benzene both do not form hydrogen bonds, are without a permanent dipole moment but slightly polarizable, and have the same dielectric constant \((\varepsilon_r = 2.28)\). Naturally, vibrational modes that are Raman active need not be active in IR absorption, and vice versa. Many modes are nevertheless active in both and should then appear at the same frequencies, albeit with probably very different peak intensity patterns. The 1461, 1489, and 1591 cm\(^{-1} \) bands obtained from our data correspond reasonably well with the lines at 1447, 1493, and 1577 cm\(^{-1} \), observed in the resonance Raman spectrum of merocyanine species\(^6 \). The difference in these numbers could very well be accounted for by the resolution and signal/noise in both measurements. Note in ref 16 that the resonance Raman signals do not drop to zero inbetween the vibrational peaks, perhaps due to nonresonant Raman contributions.

Figures 5 and 6 show the time dependent behavior during the first 100 ps at frequencies we identify as product related. In Figure 5, it is shown that the signals at both 1461 and 1591 cm\(^{-1} \) jump within a few hundred femtoseconds to about 0.4–0.5 mOD, to be followed by a modest increase to about 0.6 mOD in the next 100 ps. Only on the high frequency side of the fairly broad product band at 1489 cm\(^{-1} \) clear product formation transients, well exceeding the noise level (about ±0.05 mOD) are observed. We postulate that the rise time extracted from the data in Figure 6 best characterizes the formation rate

\[(\nu_1 = 2.28)\]

FIGURE 5. Transient signal behavior at the 1461 and 1591 cm\(^{-1} \) product bands.

FIGURE 6. Product formation kinetics of the 1489 cm\(^{-1} \) IR absorption band, together with fits indicating a rise time of 28 ps.
of merocyanine product(s). A look at the IR absorption spectrum of the closed form in Figure 3b illustrates that both at 1461 and 1591 cm\(^{-1}\) we should expect complication of the dynamical behavior due to transient signals related to vibrational cooling of the large fraction of spiropyran molecules that underwent the internal conversion \(S_1 \rightarrow S_0\). In addition, at 1461 cm\(^{-1}\) recovery of bleached spiropyran vibrational absorptions will also contribute to the signals. On the other hand the traces in Figure 6 at 1492 and 1498 cm\(^{-1}\) are fairly free of such contributions, since the first vibrational mode which could noticeable contribute through hot band absorption has its fundamental frequency more than 100 cm\(^{-1}\) higher at 1610 cm\(^{-1}\). Only a minor bleach recovery contribution from the tail of the bleached IR absorption at 1486 cm\(^{-1}\) can complicate these signals. We therefore conclude that only at 1492 and 1498 cm\(^{-1}\) interpretation of the data results in a reliable product formation time constant. We extract a product formation time constant of 28 ps from these data (see Table 1). This is drastically slower than the 0.9 ps time constant previously concluded from UV-pump/white-light probe measurements on BIPS in n-pentane.\(^6\) Can these vastly different numbers be reconciled with each other?

In our opinion, the 0.9 ps rise time of the broad absorption band peaking at 540 nm after UV irradiation of BIPS does not characterize the merocyanine product formation rate, but instead is an indication of how fast the \(S_1 \rightarrow S_0\) internal conversion rate is for the spiropyran form. The additional absorption, which makes the spectrum after 1 ps nearly featureless between 380 and 680 nm, was assigned by Ernsting and Arthen-Engeland\(^6\) to absorption from the \(S_1\) excited state of the spiropyran form to higher electronic states of the closed form and absorption from vibrationally hot merocyanine products. In view of the rapid and efficient internal conversion indicated by the data in Figure 4, we prefer to assign this featureless spectrum to absorption from a mixture of vibrationally hot levels of the spiropyran \(S_0\) state to vibrational levels of the spiropyran \(S_1\) state. The sharpening of the 540 nm band between 1.1 and 7.5 ps, accompanied by about 50% increase in increased absorption, as reported by Ernsting and Arthen-Engeland, would then be the result of a gradual replacement of absorption from vibrationally hot spiropyran, which disappears due to vibrational cooling, by merocyanine absorption which is formed with a 28 ps time constant according to our data. Unfortunately, the published UV pump/white-light probe transients for BIPS do not exceed beyond 8 ps, and as mentioned previously, no single color UV pump—probe measurements have been reported yet that could confirm the nearly complete ground-state recovery of the closed spiropyran form. Further support for our interpretation can be derived from combining quantum yield information for photocoloration of BIPS and 6-nitro-BIPS, with the UV/white-light pump—probe data for these two compounds. At \(-120^\circ\)C in a 1-propanol/2-propanol mixture a photocoloration quantum yield of 0.055 mole/einstein has been reported for BIPS, whereas for 6-nitro-BIPS this yield is 0.3 mole/einstein, both with irradiation at 313 nm.\(^1,15\) The generally much higher photocoloration quantum yield for 6-nitro-BIPS compared to BIPS is well established and has been brought in connection with involvement of triplet states\(^3,14\) in the photochemical reaction route for 6-nitro-BIPS. In addition, preliminary results of measurements performed by us on 6-nitro-BIPS in tetrachloroethene indicate a much higher quantum yield for photochemistry and a lower yield for internal conversion. Although based on the above numbers the photocoloration quantum yield for 6-nitro-BIPS is expected to be about 5 times higher than for BIPS, the UV-white light pump—probe data\(^6\) show spectra with comparable peak intensities during the first 7.5 ps, and even after 70 ps the 6-nitro-BIPS signal is only about twice that of BIPS after 7.5 ps. Notice that for 6-nitro-BIPS a 20 ps merocyanine formation time constant has been reported.\(^6\) Clearly, the difference in visible absorption at the product wavelength is less than the quantum yield data suggest, but this could be accounted for by additional absorption for BIPS from vibrationally hot molecules formed by internal conversion. As mentioned above, the energy of the 316 nm radiation is equivalent to about 20 quanta of the fundamental frequency of the 1486 or 1610 cm\(^{-1}\) modes. Absorption at 680 nm could, for instance, correspond to transitions for these from \(v = 10 \rightarrow v' = 0\), and at 380 nm to transitions \(v = 3 \rightarrow v' = 0\) (the accent indicates vibrational levels of the electronic excited state).

**Intermediate States to Product Formation and Different Isomers.** Given the fact that we could determine the product formation rate undisputably only at the 1489 cm\(^{-1}\) IR absorption band, it is clear that we cannot make any statements about the possibility of formation of several different isomers for the merocyanine form of BIPS. Because the ring opening and closing reactions can both occur thermally as well as photochemically, it seems worth to raise the question whether the product is formed from the vibrationally hot states created by internal conversion, or from other intermediates (not involving the spiropyran \(S_0\) state). In any case, it is clear that the product is not directly formed from the \(S_1\) state of spiropyran. Direct competition between the internal conversion process and the ring-opening reaction from the \(S_1\) state of spiropyran should lead to a subpicosecond product formation rate, which is clearly not observed.

The perhaps somewhat puzzling aspect is the absence of a clear distinct signature of an intermediate species/state that itself is decaying with a 28 ps time constant. Ways to explain this rely on the proposal that there are many intermediates rather than a single one. This still leaves two possibilities:

1. A large number of intermediates (spiropyran-like, merocyanine-like, and/or neither), each with distinct vibrational signatures, could be involved. This could simply lead to a diffuse background absorption in the transient IR spectrum, similar to the signal we assigned to multphonon and solvent effects. (2) If photochemistry takes place from vibrationally hot \(S_0\) states, a distribution over several vibronic levels of the vibrational manifold (including combinatorial bands), would make absorption of the transient species diffuse. Our preference lies with the first scenario, since it seems highly likely that in the last scenario the photochemistry efficiency would strongly depend on the vibrational quantum number \(v\). This should lead to nonexponentiality in the formation dynamics, which was not observed here. Also the formation time is then expected to be considerably faster than the bleach recovery time, whereas the observed 28 ps is still fairly close to the 37 ps single-exponential fit result for the bleach recovery at 1486 cm\(^{-1}\). The signals in Figure 6 strongly suggest that the intermediate(s) are formed in less than a picosecond, without any additional feeding occurring at later times.
Conclusions

We studied the photochemical ring-opening reaction of the spiropyran BIPS in tetrachloroethene, by probing the evolution of the transient IR absorption spectrum with a time resolution of 130 fs. The merocyanine product is probably formed from intermediates other than the initially created excited state of the spiropyran, which are populated on a subpicosecond time-scale in competition with a very efficient and rapid internal conversion process. From these intermediates a single exponential formation of a merocyanine form with a 28 ps time constant is concluded, which is in sharp contrast to previous conclusions of a 0.9 ps formation time constant, derived from femtosecond UV pump/white-light probe measurements. This illustrates that care has to be taken with conclusions based on optical pump–probe spectroscopy only. From the recovery of the spiropyran IR absorption bleaches we conclude that the main decay channel for the spiropyran S\textsubscript{1} excited state is internal conversion to the spiropyran S\textsubscript{0} state with a yield of 90% or more. The quantum yield for the photochemical reaction is therefore ≤0.1. The present results demonstrate the usefulness of direct femtosecond IR probing as an alternative means of obtaining information on photochemical reactions.

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Femtosecond UV/mid-IR study of photochromism of the spiropyran 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro-[2H-1-benzopyran-2,2′-(2H)-indole] in solution

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Abstract

The ring-opening reaction of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] is investigated in two solvents, by probing the evolution of the vibrational absorption spectrum with 130 fs time-resolution. Competition between internal conversion and photochemistry is found to depend on the solvent. The internal conversion quantum yield is determined to be 0.63 in perdeuterated acetonitrile and 0.34 in tetrachloroethene. Based on spectral features and biexponential kinetics, the formation of an additional merocyanine isomer in tetrachloroethene is concluded.

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1. Introduction

Photochromism is the property that a substance can undergo reversible colour changes by exposure to light of specific wavelengths. Photochromism has met with a longstanding scientific and industrial interest [1–17], with visions of applying this phenomenon in optical data storage [2], and optically controlled molecular switching [3]. Here, we investigate the spiropyran–merocyanine photochemical ring opening/closure (Fig. 1) of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (6-nitroBIPS) in two solvents: tetrachloroethene (TCE) and perdeuterated acetonitrile (ACN-d3).

Scientifically this simple reaction already presents a rather complex puzzle. Not only is there the issue whether singlet and triplet states both are involved [4–7], but also the product can appear as eight different cis–trans isomers [8–13]. On top of that the merocyanine product can aggregate [14]. A wide range of experiments has been performed on 6-nitroBIPS, including low temperature absorption [8], triplet sensitization [6], femto- [12,15] and nanosecond [7] time-resolved UV–vis pump–probe spectroscopy, and time-resolved resonance

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Raman spectroscopy [9,10]. Nevertheless, the number of investigations on the femto- and pico- second timescale is still relatively limited.

Recently, we started femtosecond UV/mid-IR investigations on photochromism of spiropyans, focussing on the time evolution of the vibrational absorption spectrum. In a first publication [16] on the compound 1,3-dihydro-1,3,3-trimethylspirotetrahydrobenzopyran-2,2(2H)-indole (BIPS) in TCE, we concluded that the photochemistry quantum yield was maximally 0.1 due to a very fast and efficient internal conversion process. Moreover, appearance of the merocyanine product seemed to involve a 28 ps time constant, much slower than the 0.9 ps rise time concluded from UV–vis experiments [12]. Here, we extend our investigations to 6-nitroBIPS. We find that internal conversion competes with the photochemical conversion pathways, although less efficient than for BIPS. In addition, the efficiency of this process appears to be solvent dependent. Data acquired over a wider frequency range are presented and comparisons are made to results from investigations on 6-nitroBIPS with other techniques [7–13].

2. Experimental

Tetrachloroethene (TCE) and 6-nitroBIPS were purchased from Sigma–Aldrich. Perdeuterated acetonitrile (ACN-d3; deuteration grade 99.8%) was purchased from Deutero GmbH. The compounds were used without further purification. These solvents have limited IR absorption in the investigated frequency range. Steady-state FT-IR spectra of 6-nitroBIPS in TCE and ACN-d3 were recorded with 1 cm⁻¹ resolution, using a Bio-Rad FT-IR spectrometer. Time-resolved measurements were performed on 20 mM solutions of 6-nitro-BIPS in TCE and ACN-d3. The photochromic reaction was initiated by 70 fs pulses at 330 nm (2 µJ/pulse), and the evolution of the vibrational absorption spectrum was probed with 100 fs IR pulses (~20 nJ/pulse), with the centre frequency varying from 1260 to 1600 cm⁻¹. In each measurement the detector covers 100–200 cm⁻¹, with a spectral resolution of 4–7 cm⁻¹. More extensive experimental details can be found in [16].

3. Results

Fig. 2 shows the steady-state IR absorption spectra of 6-nitroBIPS in ACN-d3 and TCE at room temperature, corrected for solvent contributions, in the range probed in our time-resolved measurements. Electronic absorption spectra (not shown) indicate that the compound is almost exclusively in the closed spiropyran form in both solutions. We estimate that at most 1% is in a merocyanine form in ACN-d3 and 0.01% in TCE. The IR spectra in Fig. 2 clearly illustrate that the peak intensities of IR absorption bands can vary quite considerably in different solvents. For instance, the ratio of the peak intensities at ~1342 cm⁻¹ divided by that at ~1524 cm⁻¹ differs by 40% for these two solvents. Solvent dependence of IR
absorption intensities and frequencies is a known effect [18].

Fig. 3 demonstrates overall transient differential spectra created from our data for 6-nitroBIPS in TCE (Fig. 3, upper panel) and ACN-d3 (Fig. 3, lower panel), 2 ps after UV excitation, and at long delay. For comparison with the bleaches at early delays the steady-state IR absorption spectrum is also plotted. The initial spectra resemble the steady-state IR spectra well, indicating removal of ground state (closed) spiropyran species by the femtosecond UV excitation pulse. Note further that in TCE not a single sharp increased absorption feature is found at early times. In ACN-d3 the initial spectrum shows a few positive features (marked *), that we assign to vibrational hot bands of the spiropyran species in the electronic ground state formed after internal conversion. The kinetics in ACN-d3 at 1264 cm⁻¹ depicted in Fig. 4c, illustrate the vibrational cooling dynamics for hot spiropyran [16].

Spectra at long delay times show for both solvents (residual) bleaches as well as a number of peaks related to photoproducts. First we point out that in TCE the bleaches have recovered by ~34% in TCE after 150 ps, and ~63% in ACN-d3 after 60 ps. Note also the strong lines at 1297 and 1519 cm⁻¹ (marked O) in TCE, which appear nearly absent in ACN-d3. These lines we associate with the formation of an additional merocyanine isomer in TCE.

4. Discussion

4.1. Bleach recovery and internal conversion

The kinetic behaviour related to the spiropyran form of 6-nitroBIPS is illustrated in Fig. 4 at two bleached vibrational absorption bands: at 1342 and 1612 cm⁻¹. These data show that both in TCE (Fig. 4a) and in ACN-d3 (Fig. 4b) the bleaches
partially recover. This recovery has to be due to regeneration of the spiropyran ground state, and therefore indicates the occurrence of internal conversion. The data demonstrate that the quantum yield for internal conversion is solvent dependent: about 34% in TCE, and 63% in ACN-d$_3$. (Error margin: 5%). Previous investigations had not identified this apparently rather influential decay channel. It may well be that the efficiency of internal conversion is a key factor in determining the overall photochemistry quantum yield. Given the observed bleach recovery the maximum quantum yield for photochemistry of 6-nitroBIPS is 0.66 in TCE, and 0.37 in ACN-d$_3$. (Absolute [1,17] and relative [4,5] photochemistry quantum yields have been reported for 6-nitroBIPS in various solvents.) The refill rate of the bleach, after internal conversion and subsequent vibrational cooling, is also different for these two solvents: 47 (±10) ps in TCE, and 14 (±2) ps in ACN-d$_3$.

4.2. Existence of different merocyanine isomers

Based on the spectra at long delays shown in Fig. 3, combined with observed kinetics at different frequencies, we identify with certainty product bands in ACN-d$_3$ around 1245, 1299, 1355, 1417 and 1551 cm$^{-1}$. In TCE bands are identified at the similar frequencies 1251, 1297, 1351, 1413 cm$^{-1}$ and in the range 1537–1556 cm$^{-1}$. In addition, in TCE we observe bands at 1263, 1318, 1439, 1463 and 1519 cm$^{-1}$. Note that, in general, the signals in TCE are much stronger than in ACN-d$_3$. Therefore some of the weaker bands in TCE could be below the detection threshold in ACN-d$_3$. The bands at 1297, 1413 and 1519 cm$^{-1}$ are much more intense in TCE than in ACN-d$_3$ (about an order of magnitude or more). As the difference in internal conversion efficiency can only justify a factor two in photochemistry quantum yield, we conclude that these three peaks constitute reliable evidence for the existence of an additional different merocyanine isomer in TCE, that is not present in ACN-d$_3$. Because all product bands in ACN-d$_3$ are also observed in TCE, the isomer that is formed in ACN-d$_3$ is likely to be present in TCE as well. These conclusions are further supported by the product formation kinetics discussed below.

Takahashi and co-workers have concluded the existence of five isomeric species [9] from time-resolved Raman spectra of 6-nitroBIPS, taken from 200 ns to 2 ms after UV excitation in three different solvents. These assignments were mainly based on intensity variations with solvent of different Raman lines, and analogy to a similar study on the parent compound BIPS [11]. Two species were brought in connection with only a single Raman line. As we demonstrated for spiropyran in Fig. 2, IR absorption intensities of the same species can already vary considerably from solvent to solvent. Clearly, moderate intensity variations alone are a poor basis for the identification of different isomeric species. In a later investigation on 6-nitroBIPS in cyclohexane, they followed the time evolution of the Raman spectrum between 20 ns and 100 μs after UV excitation [10]. This time only three transient species were invoked in the interpretation. The species identified at earliest times was ascribed to a merocyanine triplet state. A convincing correlation between the decay of the 1409 cm$^{-1}$ Raman intensity (0.33 μs time constant), and the increase of the 1525 cm$^{-1}$ Raman intensity, led to assignment of the second species as ground state merocyanine. On the microsecond timescale a third species is identified as a dimeric species. As none of these re-assignments require the existence of different isomers, the previous claim of five existing isomers should at least be reduced to maximally three. Several other inconsistencies can be noted in their Raman assignments. For example, the 20 ns data in [10] clearly illustrate that assigning both the 1550 and 1523 cm$^{-1}$ lines to the same initial cisoid 1523 cm$^{-1}$ species in [9] was incorrect.

About half of the observed resonance Raman peaks correspond to lines we observe in IR absorption: for 6-nitroBIPS in ACN (after 2 ms, [9]) these are at 1358 and 1411 cm$^{-1}$. Data in TCE are probably best compared to the 20 ns Raman data in cyclohexane [10], that show related peaks at 1297, 1350, 1409 and 1552 cm$^{-1}$. Recall that Raman and IR absorption yield complementary information.

Recently, density-functional-theory calculations on the spiropyran form of 6-nitroBIPS and the four most stable merocyanine isomers were
presented, and compared to IR absorption spectra in an argon matrix at 8 K [13]. Reasonable agreement was obtained between experiment and calculations, although insufficient to unequivocally identify the isomers. More specific, we point at the intense experimental line at 1529 cm$^{-1}$, which corresponds to a calculated line at 1551 cm$^{-1}$. This experimental 1529 cm$^{-1}$ line could be associated with the extra isomer in our TCE data, whereas the calculated 1551 cm$^{-1}$ line agrees with both isomers observed by us.

Altogether we are convinced that existing experimental results provide insufficient evidence for claiming formation of five isomers. It seems therefore prudent to limit our conclusion to strong indications for existence of a second isomeric species in TCE, not formed in ACN-d$_3$.

4.3. Product formation kinetics

Kinetics at selected wavelengths is depicted in Fig. 5. In Fig. 5b the product formation kinetics in ACN-d$_3$ are shown at 1418 (●) and 1551 cm$^{-1}$ (○). Single exponential fits of these two traces indicate a single exponential formation time of 9.5 ± 1.5 ps. No further change in product absorption was observed between 30 and 100 ps. However, there seems to be some variation in rise time over the bands; e.g., at 1413 cm$^{-1}$ we obtain 7.1 ps. This behaviour is observed even more clearly in TCE, where the overall product formation in TCE is considerably slower. As an illustration Fig. 5a shows the product related signals at 1551 (□) and 1556 cm$^{-1}$ (■). Clearly the signal rises much faster at 1551 cm$^{-1}$ during the first 50 ps. Single exponential fits at different product bands produce rise times in the range of 35 to 60 ps for 6-nitroBIPS in TCE. As indicated by the data in Fig. 5b the kinetics require at least a biexponential fitting approach. For the strongest band (around 1413 cm$^{-1}$) this procedure resulted in a faster component increasing from about 5 ps at 1397 cm$^{-1}$ to 28 ps at 1413 and 1418 cm$^{-1}$, and a second component typically >100 ps. Because the data are only up to 150 ps, the time constant of the slow component cannot be extracted reliably. The most likely source for the observed frequency dependence of the faster component is vibrational cooling dynamics of the merocyanine products.

Absorption change studies on 6-nitroBIPS in hexane and acetonitrile by Lenoble and Becker [7], with 1 ns time resolution, indicated that in acetonitrile the rise of the 570 nm product related band was complete within 1 ns. Our measurements lower the upper limit for the product formation time in (perdeuterated) acetonitrile to about 9.5 ps. The fast component in TCE (∼5–28 ps), and the time constant in ACN-d$_3$ (∼7–10 ps), are in line with a 20 ps time constant found by Ernsting and Arthen-Engeland [12] in a femtosecond UV/white-light investigation of 6-nitroBIPS in n-pentane.

Based on solvent polarity one may suspect that the kinetic behaviour in hexane, n-pentane, and tetrachloroethene should be rather similar. This seems true for our measurements compared to those of Ernsting and Arthen-Engeland [12]. However, in hexane the fastest rise time identified by Lenoble and Becker was 4 ns at 430 nm [7]. Whether the slow >100 ps component in TCE can be reconciled with their nanosecond result in hexane remains an open question.

Fig. 5. (a) Merocyanine product formation kinetics for 6-nitroBIPS in TCE at 1551 (□) and 1556 cm$^{-1}$ (■). (b) Product formation kinetics for 6-nitroBIPS in ACN-d$_3$ at 1418 (●) and 1551 cm$^{-1}$ (○).
The biexponentiality of the product formation in TCE, versus single exponential kinetics in ACN-d₃, clearly corroborates the conclusion drawn above on formation of a second isomeric species in TCE. This biexponentiality also implies that these species cannot be formed in direct competition from a mutual precursor state, since this would lead to the same formation constant for both. Note that published conclusions on different isomers was based on data obtained 20 ns or more after UV irradiation of a sample. These data therefore constitute the first time-resolved evidence that a second isomer already appears within 100 ps.

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References

The Role of Large Conformational Changes in Efficient Ultrafast Internal Conversion: Deviations from the Energy Gap Law

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Abstract: Conversion of electronic excitation energy into vibrational energy was investigated for photochromic spiropyran molecules, using femtosecond UV–mid-IR pump–probe spectroscopy. We observe a weaker energy gap dependence than demanded by the “energy gap law”. We demonstrate that large conformational changes accompanying the optical excitation can explain the observed time scale and energy gap dependence of ultrafast $S_1 \rightarrow S_0$ internal conversion processes. The possibility of dramatic deviations from standard energy gap law behavior is predicted. We conclude that controlling molecular conformations by rigid environments can have a substantial impact on photophysical and (bio)chemical processes.

Introduction

Internal conversion (IC) is a process through which electronic excitation energy is converted into vibrational excitation energy.1,2 (see Figure 1). Internal conversion plays a crucial role in many photoinduced and biological processes. For instance, it enables photostabilization of polymers3 and expands the energy harvesting range in photosynthesis with the help of carotenoids.4 Efficient internal conversion also occurs in DNA and RNA nucleosides5 and is believed to be an important factor in increasing genomic stability and preventing photodamage, and thus suppresses the possibility of skin cancer.

Usually IC is ultrafast from highly excited states to the lowest electronic excited state,1,2,4,5 that is, $S_n \rightarrow S_0$. Relaxation from the lowest electronic excited state, on the other hand, tends to be dominated by fluorescence and intersystem crossing. This is known as Kasha’s rule, with azulene as the textbook exception.1 According to conventional wisdom, $S_1 \rightarrow S_0$ internal conversion is inefficient, with typical time constants in the nanosecond to microsecond range.1,2 During the 1960s, Robinson and Frosch developed a theory that predicts a linear relationship between internal conversion rates and the Franck-Condon factor.7,8 Supporting this idea, Siebrand established from experimental data on the $T_1 \rightarrow S_0$ transition for a series of hydrocarbons that the decrease in IC efficiency with increasing energy gap between the involved consecutive electronic states can be traced back to an exponential drop of the Franck-Condon overlap for the displacement $D = \sqrt{39}$ (see text).

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IR pulses. Optical pumping of spiropyran molecules from the absorption spectrum in the fingerprint region with temperature, by monitoring the time-evolution of the vibrational energy of the spiropyran ground state was followed, at room initiate the photophysical and photochemical processes (see section with UV light, in various solvents. The spiropyran theoretical analysis, that the physical mechanisms behind the (13) Zimmer, M. J. AM. CHEM. SOC. 1998, 120, 759.

Recently, we started a time-resolved exploration of photochromic spiropyran-merocyanine molecular switches. (16,17) We observed that internal conversion and vibrational cooling back to the spiropyran ground state is a dominant fate for the spiropyran S1 state. (16,17) This inspired us to investigate the influence that solvents have on the IC process. To this end, we studied the recovery of the vibrational absorption spectrum of the molecule 6-nitro-1,3,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline], further abbreviated as 6-nitro-BIPS, after excitation with UV light, in various solvents. The spiropyran compound is excited by 70 fs UV pulses (λ ≈ 325–330 nm) to initiate the photophysical and photochemical processes (see Figure 2). Formation of merocyanine photoproducts and recovery of the spiropyran ground state was followed, at room temperature, by monitoring the time-evolution of the vibrational absorption spectrum in the fingerprint region with ~100 fs mid-IR pulses. Optical pumping of spiropyran molecules from the electronic ground state (S0) to the electronic excited state (S1) results in an increased transmission (lower optical density) for the infrared probe pulse at vibrational frequencies of the spiropyran ground state. The time scale of the overall cooling process is reflected in the recovery kinetics of the transmission, and the S1 → S0 IC quantum yields determine the final extent of the recovery.

Furthermore, we demonstrate, on the basis of an elementary theoretical analysis, that the physical mechanisms behind the energy gap law7–11 can account for ultrafast internal conversion as well, but do not necessarily lead to the standard energy gap dependence. (5,10) In particular, we advance the idea that efficient S1 → S0 internal conversion is related to large conformational changes upon optical excitation. This resembles conclusions of previous investigations, that identified the importance of structural rigidity in enhancing fluorescence quantum yields, and established promotion of internal conversion by flexible side-groups, known as “loose bolt” and “free rotor” effects. (1,19) As large conformational changes seem inherent to chemical reactions, fast internal conversion could be a rather common side-effect in many photochemical reactions. Our results also give further insight into the relevance of (conical) intersections for ultrafast internal conversion.

Experimental Section

Femtosecond UV pump/mid-infrared probe experiments were performed on 6-nitro-BIPS molecules in a number of solvents, selected to minimize solvent absorption in the investigated IR spectral range. The following solvents were used: tetrachloroethene (C2 Cl4), chloroform (CHCl3), n-hexane, and perdeuterated acetonitrile (CD3CN), dimethyl sulfoxide ((CD3)2SO), and methanol (CD3OD). The compound 6-nitro-BIPS and the solvents C6H6 and CHCl3 were purchased from Sigma-Aldrich. The deuterated solvents (deuterium grade 99.9%) were purchased from Deutero GmbH. Steady-state emission spectra and excitation spectra were recorded on an SPEX Fluorolog2 system, using spectroscopic grade nondeuterated solvents purchased from Sigma-Aldrich.

The femtosecond pump–probe setup, based on a 1 kHz, 40 fs home-built amplified Ti:sapphire laser, has been described in detail previously. (18) The UV pump pulses for the electronic excitation are generated by sum frequency mixing of the Ti:sapphire fundamental and visible pulses coming from a noncollinear optical parametric amplifier. The pulse energy was 2–3 μJ, and the pulse duration was about 70 fs, as determined by self-diffraction autocorrelation. The probing mid-infrared pulses were generated by difference frequency mixing in a GaSe crystal of near-infrared signal and idler pulses coming from a double-pass collinear parametric amplifier pumped by the Ti:sapphire fundamental. Probe and reference pulses, derived using reflections from a BaF2 wedge, were focused in the sample with a diameter of 150 μm and then dispersed in a grating spectrometer. Complete spectra were recorded for each shot using a nitrogen-cooled double HgCdTe detector array (2 × 32 elements). The delay zero and the time resolution (about 150 fs) were determined in a frequency-resolved cross-correlation measurement in a thin ZnSe crystal. The 6-nitro-BIPS molecule was dissolved in various solvents with a concentration of 0.01–0.02 M and pumped through a free streaming jet of nominal thickness 100 μm.

Results and Discussion

As a typical example of the absorption recovery kinetics of a spiropyran vibration, we show in Figure 3A the kinetics of the ~1340 cm−1 IR band, in CHCl3 and (CD3)2SO. This IR absorption band is related to the symmetric stretching mode of the NO2 substituent of 6-nitro-BIPS. (19) Identical behavior is observed for the ~1610 cm−1 vibration. The fraction of absorption recovery is taken as the IC quantum yield, φIC, which is found to vary from 34% in C6H6 to 80% in (CD3)2SO. Emission measurements (see below) demonstrate that the spiropyran triplet state is significantly populated only in C6H6. As a consequence, the spiropyran triplet state does not influence the dynamics in Figure 3A. Because the same kinetics is
observed at different bleached spiropyran vibrational absorption bands, we can exclude that the kinetics is related to coincidental overlap with vibrational bands of the merocyanine isomers. In addition, merocyanine product formation (not shown), determined at ~1415 cm⁻¹ where the spiropyran has no IR band, occurs with different time constants. The data in Figure 3A lead to vibrational cooling time constants, after internal conversion, of 23 ps in CHCl₃ and 11 ps in (CD₃)₂SO. The merocyanine product formation time constants are 14 ps in CHCl₃, and 15 ps in (CD₃)₂SO, respectively. Nitro-groups are known to enhance internal conversion through the “loose bolt” effect.¹⁹

We stress that in the present case the ultrafast internal conversion is not related to the nitro-group, as a previous investigation¹⁶ by us on the related compound BIPS (6-nitro-BIPS without the nitro-group) in C₂Cl₄ also demonstrated ultrafast IC for this compound, with an even higher IC quantum yield of electronic state. In Figure 3B, we show increased transient nitro-group) in C₂Cl₄ also demonstrated ultrafast IC for this.

In Figure 4A, the IC data for 6-nitro-BIPS are plotted against the compound, with an even higher IC quantum yield of electronic state. In Figure 3B, we show increased transient nitro-group) in C₂Cl₄ also demonstrated ultrafast IC for this.

We stress that in the present case the ultrafast internal conversion rate that is affected by the change in energy gap with solvent. Figure 4B shows a plot of kIC rel versus the energy gap. The variation of kIC rel with energy gap is still modest, although somewhat stronger than that for the IC quantum yield. In support of the above-mentioned assumption underlying eq 1, we point out the following: If the drop in φIC with increasing energy gap instead stems from an enhancement of either the intersystem crossing rate or the rate of the photochemistry, the responsible process would actually exhibit a trend opposite to that of the energy gap law. Recall that experimental verification of the energy gap law was in fact performed on data related to an intersystem crossing transition: T₁ → S₀. In addition, we introduce additional anharmonicities, and as a result the ν = 0 → ν = 1 transition energy of a mode changes if other vibrational modes become highly excited.¹⁸ Consequently, the data in Figure 3B do not automatically imply that the vibrational relaxation occurs (exclusively) through the ~1340 cm⁻¹ mode. However, the rise times of the signals in Figure 3B do provide an upper limit to the IC time constant, which is 3.6 ps in (CD₃)₂SO and 6.4 ps in CHCl₃.

The IC quantum yield, φIC, apparently increases very modestly with decreasing energy gap (Figure 4A). In our case, the energy gap (more precisely: the S₁ → S₀ absorption maximum) of a single molecular species is modified by solvent–solvent interactions, while Siebrand analyzed data where variation of the energy gap was obtained by comparing a series of related different molecular species.⁷–¹¹ Figures 3 and 4 illustrate two aspects that are not within the conventional understanding of the energy gap law: [2,3] extremely efficient internal conversion can take place (1) on picosecond or even subpicosecond time scales, and (2) even at rather large energy gaps where Franck–Condon factors are thought to be very small.

Relative internal conversion rates, kIC rel, are calculated from the φIC data in Figure 4A using the equation

\[ k_{IC \text{ rel}} \propto \frac{\phi_{IC}}{(1 - \phi_{IC})} \]  

This equation assumes that it is predominantly the internal conversion rate that is affected by the change in energy gap with solvent. Figure 4B shows a plot of kIC rel versus the energy gap. The variation of kIC rel with energy gap is still modest, although somewhat stronger than that for the IC quantum yield. In support of the above-mentioned assumption underlying eq 1, we point out the following: If the drop in φIC with increasing energy gap instead stems from an enhancement of either the intersystem crossing rate or the rate of the photochemistry, the responsible process would actually exhibit a trend opposite to that of the energy gap law. Recall that experimental verification of the energy gap law was in fact performed on data related to an intersystem crossing transition: T₁ → S₀. In addition, we

Figure 3. (A) Absorption recovery kinetics at the ~1340 cm⁻¹ IR band of 6-nitro-BIPS in CHCl₃ (●) and (CD₃)₂SO (○). (B) Transient kinetics related to vibrational cooling in CHCl₃ (●) and (CD₃)₂SO (○) at ~1320 cm⁻¹. Signals in CHCl₃ are raised by 1 mOD for representation purposes.

Figure 4. (A) Internal conversion quantum yield (■) versus the position of the spiropyran S₁ → S₀; absorption maximum in various solvents. (B) Relative IC rates (■) derived from the data in (A) using eq 1. The lines illustrate the behavior of the Franck–Condon factor for transitions ν′ = 0 → ν = n, for three vibrational energies. These energies hν and the corresponding displacements D are as follows: hν = 1250 cm⁻¹, D = 5.4 (- -); hν = 2500 cm⁻¹, D = 3.3 (- -); and hν = 3750 cm⁻¹, D = 2.4 (- -). The inset illustrates for the second combination the expected behavior over a larger energy gap range.

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mention that the combination of higher IC quantum yield and a faster vibrational hot band rise time in (CD$_3$)$_2$SO as compared to CHCl$_3$, as illustrated in Figures 4A and 3B, confirms the conclusion that the higher IC quantum yield is caused by an increase in internal conversion rate.

Only the data point for the solvent C$_2$Cl$_4$ deviates significantly from the general trend in Figure 4. We investigated the emission properties of 6-nitro-BIPS in all solvents. While at 77 K we detected spiropyran phosphorescence in all solvents, with peaks at ~471 and ~508 nm, we observed at room temperature phosphorescence only in C$_2$Cl$_4$; now broadened and peaking around 510 nm. Room-temperature emission spectra after excitation at 330 nm of 6-nitro-BIPS in some of the solvents are shown in Figure 5. The deviation of C$_2$Cl$_4$ from the observed trend is therefore most likely the result of a much more efficient intersystem crossing in this solvent. In the other solvents, intersystem crossing seems to be a negligible channel. The increased intersystem crossing yield in C$_2$Cl$_4$ cannot be attributed to a heavy atom effect, as no phosphorescence is detected spiropyran phosphorescence in all solvents, with peaks around 510 nm. Room-temperature emission spectra after excitation at ~471 nm, related to excitation of the tiny fraction of the molecules which is present in this form. Emission excitation spectra (performed by $\chi$) confirm that the 510 nm band in C$_2$Cl$_4$ is related to excitation of the first electronic absorption band of the spiropyran, whereas the ~650 nm fluorescence band is related to excitation of the merocyanine.

The clue to understanding the weak energy gap dependence and high IC efficiency is found by examining the effect of changes in equilibrium conformation (coordinate) upon optical excitation. A simple illustrative model situation is sketched in Figure 1. We assume harmonic oscillator potential energy surfaces (PES), and the effect of conformation changes is approximated by introducing a displacement along a single distorting vibrational mode. In Figure 1, the displacement $D$ is $\sqrt{39}$ (~6.2) in units of the vibrational coordinate $y = (\hbar/kT)^{1/2}x$, where $k$ is the vibrational force constant and $x$ is the vibrational frequency. Our displacement parameter $D$ is linear in the vibrational coordinate and is related to Siebrand’s displacement parameter$^{10}$ $y$ by $y = 1/2 \sqrt{D}$. The harmonic potential energy function $V = \frac{1}{2}kx^2$ becomes $V = \frac{1}{2}\hbar \nu y^2$, upon substitution of $x$ by $y$. In Figure 1, the excited-state PES is elevated by 20 vibrational quanta, which for the energy gaps observed for 6-nitro-BIPS would correspond to a vibrational ladder with vibrational quanta of about 1250 cm$^{-1}$. In Figure 6A, we illustrate how the Franck–Condon factor of the excited-state $\nu = 0$ vibrational wave function with the ground-state vibrational wave functions changes with vibrational quantum number and increasing displacement of the excited-state PES. The main features to be noted are as follows: (1) The Franck–Condon factor peaks at increasingly higher vibrational quantum numbers with increasing displacement. (2) Sizable Franck–Condon factors are obtained over increasingly larger ranges of this quantum number for larger displacements.

Figure 6B plots the same data in the manner done by Siebrand$^{10}$ for displacements $D = 1, \sqrt{2}, 2$, and for $\nu = 0–7$. For $D = 1–5$, Figure 6B illustrates at higher values of $\nu$ the type of behavior expected according to the energy gap law. Note that the slope decreases for higher values of $\nu$. Plots for higher values than $D = 2$ are not found in the literature. Figure 6B also demonstrates that for higher values of $D$ the behavior (depicted here up to $\nu = 25$) can even become more or less opposite to the traditional energy gap law prediction. Consequently, these calculations indicate that the energy gap law is not valid for transitions between electronic states for which the molecule has a very different structure.

Now, we demonstrate that the data in Figure 6 can account for the observed weak energy gap dependence. The lines in Figure 6B illustrate that many combinations of vibrational energy and displacement are in accordance with the observed trend. These lines are linear interpolations of consecutive Franck–Condon factors for the following combinations: $\hbar \nu = 1250$ cm$^{-1}$, $D = 5.4$ (–); $\hbar \nu = 2500$ cm$^{-1}$, $D = 3.3$ (–); and $\hbar \nu = 3750$ cm$^{-1}$, $D = 2.4$ (–). The inset depicts the trend of the FC-factor over a wider energy range for the combination $\hbar \nu = 2500$ cm$^{-1}$ and $D = 3.3$. The trend established by these fits indicates that fitting the data with displacements smaller

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than about 2.4 calls for unrealistic vibrational frequencies, as typically vibrational frequencies do not exceed 4000 cm\(^{-1}\). To quantify the weak energy gap dependence, we have examined the derivative of plots as in Figure 6B for the combinations of displacement and vibrational energy that fitted the data in Figure 4B. For both \(D = 2.4\) and \(D = 3.3\), the first derivative of the logarithmic plots appears to be about 2.1 times higher at \(v = 24.5\) than in the energy range covering our experimental data. Plots of the first derivative further indicate that for both \(D = 2.4\) and \(D = 3.3\), true energy gap law behavior, exemplified by a constant value for the derivative, has not been reached yet at \(v = 25\). In the case of the fit with \(D = 5.4\), the experimental data fall in the high end of our calculated range: \(v = 23 - 25\).

Experimental information on the displacement is in principle attainable from the intensity pattern of the vibronic progression in the absorption spectrum. However, large displacements are expected if the excited-state structure of the molecule differs significantly from the electronic ground-state structure. The excited-state PES will then not only be displaced, but also have a different shape (and associated force constant \(k\)). As a consequence, the vibronic structure of the progression \(v = 0 \rightarrow v'\) will in practice not be representative for that of \(v \rightarrow v' = 0\). Another complication is that inhomogeneous and lifetime broadening (due to ultrafast IC) often results in very little discernible vibronic structure in absorption spectra of these molecules, as is the case for 6-nitro-BIPS. On the other hand, low-temperature spectra of merocyanine isomers of spiropyrans do have clear vibronic progressions in nonpolar media. On the basis of such spectra, we derive for the merocyanine of BIPS discernible vibronic structure in absorption spectra of these molecules; as is the case for 6-nitro-BIPS. On the other hand, low-temperature spectra of merocyanine isomers of spiropyrans do have clear vibronic progressions in nonpolar media. On the basis of such spectra, we derive for the merocyanine of BIPS at 10 K in argon\(^{21}\) a displacement \(D = 1.9\), and for the merocyanine of 6-nitro-BIPS in methycyclohexane at 77 K \(D = 1.5\). These numbers suggest that certainly displacements of about \(D = 2 - 3\), as encountered in fitting the data in Figure 4B, are not beyond reason.

The concept of large conformational changes upon optical excitation, forwarded here, even provides a further rationale to the relevance of conical intersections for ultrafast internal conversion.\(^{14,15}\) Analysis of the data in Figure 6A reveals the following relation between the vibrational quantum number with maximum Franck–Condon factor and the displacement:

\[
v_{\text{FCmax}} = \frac{1}{2}(D^2 - 1) \quad D \geq 1
\]

and

\[
v_{\text{FCmax}} = 0 \quad D \leq 1
\]

The condition of energy conservation during the actual internal conversion process then requires that the excited-state PES is raised above the ground-state PES by \(hv_{\text{FCmax}}\). Graphically, this always corresponds to a situation as depicted in Figure 1, where the ground-state PES exactly crosses through the bottom of the excited-state PES. Coupling of PESs at crossings can lead to conical intersections.\(^{24}\) Our result indicates that internal conversion from \(v' = 0\) will be most efficient at such intersections\(^{25}\) and thereby unites perturbation theory-based approaches and quantum theoretical calculation methods. Note that IC from levels other than \(v' = 0\) could present an additional source for deviations from standard energy gap law behavior.\(^{25}\)

Initially, the electronic energy should predominantly be converted into vibrational energy of those vibrational coordinates along which such (conical) intersections occur. This opens up the possibility of identifying the modes most active in the internal conversion process by performing picosecond time-resolved resonance Raman scattering experiments.\(^{26}\) Quantum theoretical modeling of ultrafast IC aimed at identifying a coupling mode and tuning modes\(^{15}\) is therefore supported by our analysis.

Finally, one may wonder if the results in Figure 4 justify pico- and femtosecond time scales for internal conversion processes. For this, we return to Siebrand and Williams’ work\(^{9-11,27}\) on \(T_1 \rightarrow S_0\) and \(S_1 \rightarrow S_0\) internal conversion in hydrocarbons. They introduced the parameter \(\alpha(E_0)\),\(^{11,27}\) which can be interpreted as the maximum IC rate that is reached for a Franck–Condon factor of 1. Their analysis on hydrocarbons\(^{27}\) led to a value \(\alpha(E_0) \approx 10^{13} - 10^{14}\) s\(^{-1}\). The FC-factors at 30 000 cm\(^{-1}\) for the plots in Figure 4B are 0.0066 (\(D = 2.4\)), 0.0061 (\(D = 3.3\)), and 0.0064 (\(D = 5.4\)). Although the value of \(\alpha(E_0)\) may not be a universal constant for all types of molecules, combining these two pieces of information indicates that for the spiropyran molecule IC time constants in the order of 1–10 ps are fully in line with expectations. Clearly, large conformational differences between the excited and the ground state can explain ultrafast IC, within the theoretical framework of the “energy gap law”. On the other hand, we predict that these molecules will typically not exhibit the standard energy gap law behavior.

Our findings have important implications for many chemical processes, as chemical reactions by definition involve conformational and structural changes. For instance, it opens interesting avenues in the design of efficient photochromic switches. Depending on the exact conformational changes that accompany different electronic transitions, a tradeoff could be achieved between ultrafast IC and rapid “internal” conversion to photoproducts. This is illustrated by efficient subpicosecond photoproduction formation in the dihydroazulene/vinylheptafurfure photochromic switch, which has been ascribed to a conical intersection of the reactant excited electronic state and the photoproduction electronic ground state.\(^{28}\) Enhancing photochemistry quantum yields over IC, or vice versa, could also be an important function of protein structures in biochemistry. As a prime example, we mention the GFP system,\(^{12,13,25}\) Quantum mechanical calculations led to the conclusion that the two halves of the free GFP chromophore are planar in the \(S_0\) electronic state, while they are perpendicular in the \(S_1\) state.\(^{29}\) The high fluorescence quantum yield of the GFP chromophore in the

\(^{22}\) So-called “mirror symmetry” of absorption and fluorescence requires the same force constant for excited- and ground-state PESs, as well as symmetrical PESs around the coordinate \(y_0\) where \(V\) is minimum, that is: \(V_{y=0-y} = V_{y=0+y}\).


\(^{24}\) Yarkony, D. R. Acc. Chem. Res. 1998, 31, 511. This paper points out that for molecules of three atoms or more, even states of the same symmetry are permitted to intersect, instead of resulting in an avoided crossing (“noncrossing rule”).

\(^{25}\) Reference 14 mentions the question whether IC takes place at the absolute minimum of the PES or also at other “points” as an important issue in research on conical intersections.\(^{26}\) Kozich, V.; Werncke, W.; Vodchits, A. I.; Dreyer, J. J. Chem. Phys. 2003, 118, 1808.


protein has been suggested to originate from blocking this conformational change, thereby allowing proton transfer to take place from the excited chromophore to an extensive hydrogen-bonding network formed by the protein binding pocket. Controlling chemical conformations by rigid matrices or protein environments could therefore be an important aspect in nature’s way to alter the efficiency of (photo)chemical events.

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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[2H-1-benzopyran-2,2′-(2H)-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 S₁ → S₀ absorption (lifetime ≤ 0.2 ps). The second feature (lifetime 0.5 ± 0.2 ps) we tentatively assign to the merocyanine T₂ 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 S₁ 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 S₀ → S₁ 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.²,³,¹⁰ 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 calculations²³ for the SP 6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indole], further abbreviated as 6-nitro-BIPS, have shown that in the MC

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 S₀(SP) − S₀(MC) separations, for all stable ground-state cis–trans isomers. For these, results from calculations in vacuo are taken from ref 23. 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. Time-resolved spectroscopic studies have led to the conclusion that MC products appear on a picosecond time scale.⁵,⁷,¹⁰,¹¹,¹³,¹⁴,¹⁸ 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.1,5,6,11,14,17,21 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 authors5,7,16,17,21 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 the MC to the S1 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 spiropyran24–26 using femtosecond infrared spectroscopy. For both BIPS and 6-nitro-BIPS internal conversion (IC) from the SP→S1 state to the SP→S0 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 multieponential 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 S1-state is not an intermediate in the photochemical formation of MC from SP.

2. Experimental Section

The photochromic compound 1′,3′-dihydro-1′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-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/referenc beam. 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 CaF2 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 CaF2 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-m 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
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 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. However, we ascribe the structure to a vibronic progression. Support for this comes from Ernsting and Arthen-Engeland, 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 on 6-nitro-8-bromo-BIPS indicated that one isomer dominates the mixture at thermal equilibrium at room temperature.

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. 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
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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.1,2

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 S1 state, i.e., S1 → S0. 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 S1 → S0 absorption, is gone after 0.4 ps. This suggests a lifetime of at most a few hundred femtoseconds for the SP S1 state in TCE. This compares well to a 180 fs decay component at 620 nm, observed by Zhang et al.34 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 S1 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 S0 state, (b) intersystem crossing to the SP T1 state, (c) formation of a cisoid intermediate species X1,2,5,14,18 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 S1 → S0 internal conversion.25 Initially these molecules possess about 30000 cm−1 vibrational energy in the SP S0 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 S0 → S1 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 T1 state we also consider unlikely to be responsible for this transient band. As shown above, the phosphorescence decay from the SP T1 state of 6-nitro-BIPS in TCE is dominated by lifetimes of 545 ps and 4.0 ns, and thus the SP T1 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 authors1,2,5,14,18 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 Heiligerman-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 spirooxazines36,37 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 spiroerythrons the appearance of a band at 430−450 nm7 was ascribed to this cisoid species X as well. Krusanov and Alifimov2 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,2 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 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 T2 state presents an interesting alternative assignment for the transient species observed at ~445 nm during the first picosecond. On the basis of the MC S1 → S0 fluorescence at 650 nm, the MC T1 → T2 absorption at 583 nm (see below), and the 2000−3000 cm−1 energy difference between the SP and the MC S0 states calculated by Futami,23 the MC T1 state could be approximately isoenergetic with the SP S1 state. The exact location cannot be given, because it is unknown how far the MC T1 state lies below the MC S1 state nor have there been any reports of phosphorescence from the MC T1 state. The 0.5
state within a nanosecond, only to convert to MC in the T state. Nano- 
second experiments established that the 440 nm band is still clearly 
visible at 441 and 590 nm, and in the mid-infrared at 1519 cm
-
¹. From these studies, it was 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 demonstrated that the 0.33 μs decay of the MC (T1) state, as evidenced by disappearance of the 435 nm band, leads only to modest intensity and shape changes of the band.

\( \text{rise times are better considered the approximate formation time of a vibrationally cooled MC product in the T1 state.} \)

In contrast, the signal at 1412 cm
-
¹ shows the typical bimodal rising behavior, with fitting parameters (offset, \( r_1, A_1, r_2, A_2 \)) as follows: (0, 22.7 ps, 4.2, 350 ps, 8.6).

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 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 multieponentiality 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 T1 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.

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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 care 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 ~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 \(2.9 \times 10^8\) s\(^{-1}\) into another merocyanine product with almost the same IR and visible absorption spectral characteristics. It is relevant to point out that the ~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:

\[
\begin{align*}
\text{SP}(S_0^\ast) & \rightarrow [MC(T_2)] \xrightarrow{\text{MC}(T_1^\ast), \tau \approx 17\text{ ps}} [MC(T_1)] \rightarrow \text{MC}(T_1^\ast) + \text{SP}(S_0) \\
[MC(T_2)] & \rightarrow [MC(T_1)] \xrightarrow{\text{MC}(T_2^\ast), \tau \approx 0.2\text{ ps}} \text{SP}(S_0) \xrightarrow{\text{MC}(T_2^\ast), \tau \approx 0.5\text{ ps}} \text{MC}(T_1^\ast)
\end{align*}
\]

(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:

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

(2)

In this biexponential expression the terms between rectangular brackets are normalized terms characterizing the rise and decay of the first MC isomer \([MC(T_1^\ast)]\), and the rise of the second isomer \([MC(T_2^\ast)]\), 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 point mission fellowship of the Egyptian government (O.F.M.), and travel support by the LIMANS Cluster of Large Scale Laser Facilities (Project Nr. MBl000237), support through a long-term mission fellowship of the Egyptian government (O.F.M.), and travel support for M.R. by the “Femtochemistry and Femtobiology” ULTRA Program of the European Science Foundation.

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References and Notes