ed-state electron-transfer rate, $k_f$, since it is expected that the reorganizational barrier for forward and back electron transfer should be similar and back electron transfer should occur in the Marcus "inverted" region. If both forward and back electron transfer occur via a through-bond (i.e., superexchange) mechanism, an explanation for the observed behavior may be that the forward electron transfer occurs via a superexchange path involving unoccupied orbitals of the bridge (electron transfer) while the back electron transfer occurs via hole transfer from occupied $\sigma$-bonding levels of the framework. Recently Waiselewski and co-workers used spectroscopic and electrochemical data to show that, for porphyrin–pentacene–quinone systems, forward electron transfer occurs via electron transfer while back electron transfer occurs via hole transfer and is faster than the forward electron transfer.[3h] Without further information it is not possible to distinguish which of the superexchange paths predominates in this case, but back electron transfer via hole transfer is not unreasonable since the requirement is that the energy gap between the metal d$\pi$ levels and the $\sigma$-bonding levels of the bridge be smaller than the gap between the diquat $\pi^*$ levels and the $\sigma^*$ levels of the bridge.

**Summary.** Intramolecular, photoinduced electron transfer from two ruthenium(II) diimine complex chromophores to a given diquat occurs with a variety of aliphatic tethers linking the chromophore and the diquat. The rate constant decreases sharply as the number of methylenes separating the donor and acceptor increases in straight chain alkyl bridged complexes. An odd–even alternation in the electron-transfer rate constant was observed in the straight chain series. Rate constants for electron transfer in a series of complexes bridged by a series of spacers having a fixed number of bonds but differing steric environments varied by only a factor of 2. On the basis of the data presented here, it is not possible to establish unambiguously whether or not there exists a significant superexchange contribution to the electron-transfer quenching process in these systems. Given the much weaker distance dependence expected for superexchange relative to through space coupling, superexchange would be expected to be most important for the longest linkages. The weight of the data presented here as well as data previously reported for similar systems tend to support a significant contribution of through-space electron transfer for the shortest chain linkages. For the longer linkages results are less clear; however, based on the results for the series of seven-bond-bridged complexes, through-bond interactions appear to contribute to the electron transfer.

**Acknowledgment.** R.H.S. thanks the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. C.M.E. acknowledges the National Science Foundation (Grant CHE 8821752) for support of this work. We thank Dr. Mark Sulkes for time-correlated single photon counting lifetime measurements and Professors David Kelley and George McLendon and the reviewers for valuable advice.

**Registry No.** *cis*-I, 137648-26-1; *trans*-I, 137648-27-2; II, 137648-28-3; III, 137648-29-4; *cis*-IVa, 137648-30-7; *trans*-IVa, 137648-31-8; $[(tmb)_2Ru(423\text{-}DQ^{2+})]^{4+}$, 96897-22-2; $[(tmb)_2Ru(433\text{-}DQ^{2+})]^{4+}$, 137648-32-9; $[(tmb)_2Ru(443\text{-}DQ^{2+})]^{4+}$, 137648-33-0; $[(tmb)_2Ru(453\text{-}DQ^{2+})]^{4+}$, 137648-34-1; $[(tmb)_2Ru(463\text{-}DQ^{2+})]^{4+}$, 137648-35-2; $[(tmb)_2Ru(473\text{-}DQ^{2+})]^{4+}$, 137648-36-3; $[(tmb)_2Ru(4123\text{-}DQ^{2+})]^{4+}$, 137648-37-4; $[(bpy)_2Ru(423\text{-}DQ^{2+})]^{4+}$, 96410-77-4; $[(bpy)_2Ru(433\text{-}DQ^{2+})]^{4+}$, 137648-38-5; $[(bpy)_2Ru(443\text{-}DQ^{2+})]^{4+}$, 137648-39-6; $[(bpy)_2Ru(453\text{-}DQ^{2+})]^{4+}$, 116595-54-1; $[(bpy)_2Ru(463\text{-}DQ^{2+})]^{4+}$, 137648-40-9; $[(bpy)_2Ru(473\text{-}DQ^{2+})]^{4+}$, 137648-41-0; $[(bpy)_2Ru(4123\text{-}DQ^{2+})]^{4+}$, 137648-42-1; $[(tmb)_2Ru(4ph3\text{-}DQ^{2+})]^{4+}$, 137648-43-2; $[(tmb)_2Ru(4cc3\text{-}DQ^{2+})]^{4+}$, 137648-44-3; $[(tmb)_2Ru(4tc3\text{-}DQ^{2+})]^{4+}$, 137764-34-2; $[(dmb)_2Ru(4tc3\text{-}DQ^{2+})]^{4+}$, 137648-45-4; $[(bpy)_2Ru(4ph3\text{-}DQ^{2+})]^{4+}$, 137648-46-5; $[(dmb)_2Ru(423\text{-}DQ^{2+})]^{4+}$, 96897-20-0; 4,4'-dimethyl-2,2'-bipyridine, 1134-35-6; 1,4-cyclohexanedione, 637-88-7.

**Supplementary Material Available:** Selected $^1H$ NMR spectral data (15 pages). Ordering information is given on any current masthead page.

# Spironaphthopyran Photochromism: Picosecond Time-Resolved Spectroscopy

**S. Aramaki[†] and G. H. Atkinson*[,‡]**

*Contribution from the Department of Chemistry and Optical Sciences Center, University of Arizona, Tucson, Arizona 85721.* *Received July 1, 1991. Revised Manuscript Received September 13, 1991*

**Abstract:** Photochromism of a spironaphthopyran (1'-(methoxyethyl)-3',3',5'-trimethyl-spiro[2*H*-1-naphthopyran-2,2'-indoline]) is studied with picosecond transient absorption and picosecond time-resolved resonance Raman spectroscopies. A photochromic reaction occurring within 50 ps after ultraviolet (287 nm) irradiation produces merocyanine species which absorb at 574 nm in both polar and nonpolar solvents. For as long as 1.5 ns, neither absorption nor resonance Raman spectroscopy reveals any changes in the merocyanine isomer(s) initially formed. In polar solvents, a second transient absorption (400–460 nm) appears both before the merocyanine isomer(s) is formed and whenever the merocyanine isomer(s) is excited at 574 nm. No back-reaction from the merocyanine isomer(s) to the spiro form is observed when the sample is irradiated at either 574 or 425 nm with delays of 100 ps to 1 ns after 287-nm excitation. A reaction mechanism describing spiropyran photochromism is suggested from these results.

## Introduction

Photochromism describes photolytic intramolecular reactions which proceed through the excited state(s) of the parent molecule and are characterized by a dramatic color change in the sample associated with the formation of products. Photochromism involving changes in the visible absorption spectrum, and thereby changes in the associated $\pi$-electron conjugation system, have drawn considerable attention.[1] For example, the photochromism observed in fulgides is derived from ring closure induced by the ultraviolet (UV) irradiation while spiro compounds undergo color

* To whom correspondence should be addressed.
[†] Present address: Mitsubishi Kasei Corp., Research Center, 1000 Kamoshida-cho, Midori-ku, Yokohama 227, Japan.
[‡] Lady Davis Professor, Technion, Israel, 1991.

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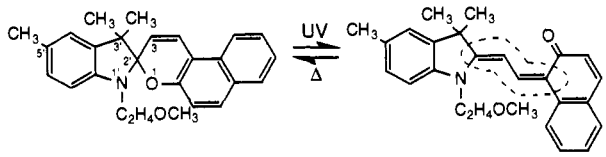

**Figure 1.** Molecular structure and photochromic reaction scheme of spironaphthopyran studied. The merocyanine product shown is only one of several isomers anticipated depending on the conformation in that part of the merocyanine molecule encompassed by a dashed line (i.e., bridge).

changes determined by a ring opening which form products, often with a variety of isomeric forms, having new $\pi$-electron conjugation.

Spiro compounds in general have been studied more extensively than other photochromic compounds not only as part of an expanding interest in the fundamental molecular properties underlying intramolecular excited-state dynamics, but also because spiro compounds have potentially important applications as functional dyes in photochromic glasses. When a spiro compound absorbs UV light, the C–O bond of the spiro moiety is broken and the ring is opened to form at least one merocyanine structure (Figure 1). The merocyanine isomer(s) produced absorbs in the visible (~600 nm) because of the newly formed delocalized $\pi$-electron conjugation. The merocyanine form thermally returns to the original spiro compound generally on the millisecond time scale.[2]

Spirobenzopyrans have been widely studied, with those compounds containing a nitro group at the 6-position attracting the most attention. From transient absorption studies,[3-6] it has been shown that the photolytic reactions in spiropyrans are strongly affected by oxygen and the polarity of the solvent and that the absorption spectra evolve over the nanosecond or longer time scale. Several different reaction schemes have been suggested,[3-6] but generally the reaction mechanism is based on the rapid formation of an open cisoid intermediate and the triplet state of the spiro form. After the rapid formation of these intermediates (8 or 270 ps), final photolytic products (open transoid isomers and their dimers) are generated in the nanosecond time regime. Nanosecond time-resolved Raman spectra of this type of spiro compounds also have been measured.[7-9]

The reaction dynamics of spiro compounds which do not contain nitro groups are known from several nanosecond and picosecond transient absorption studies to be significantly different.[2,10-12] The formation of merocyanine isomer(s) is faster ($\ll$1 ns), and the photolytic reaction is not affected by oxygen. This reaction, therefore, is considered to proceed via an excited singlet state. No intermediate of this type has been observed by transient absorption for this photolytic reaction at room temperature.

The striking differences in the room temperature photochromic reaction mechanisms between spiropyrans with a nitro group and those without have been discussed in terms of the relative energy positions of excited electronic states.[3] Apparently, the incorporation of a nitro group alters the relative energetic ordering of the excited electronic states and specifically the energy of the triplet n–$\pi^*$ state levels. These changes are proposed to control the rate

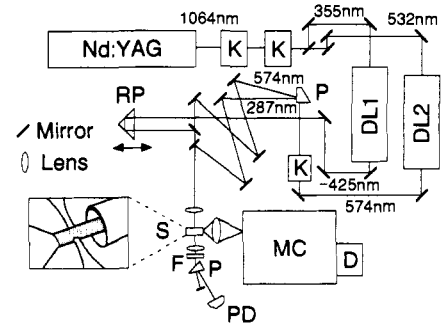


**Figure 2.** Experimental instrumentation: Nd:YAG, mode-locked, Q-switched Nd:YAG operating at 1064 nm; K, KDP crystals 532- or 355-nm generation; DL1/DL2, synchronously pumped dye lasers; P, prism; RP, retroprism in optical delay line; S, sample jet (inset illustrates spatial orientation of laser beams and liquid sample jet); F, color filter; PD, photodiode detector; MC, single monochromator; D, intensified photodiode array detector. Instrumentation for the measurement of two laser, pump (287 nm)/probe (574 nm) transient absorption utilizes only two beams, with the latter (574 nm) reflected through the optical delay line (not shown) and no monochromator. Measurements of transient absorption produced with two successive excitation pulses (287 and 574 nm) separated by a ~200-ps delay time utilize the third (~425 nm) beam in the optical configuration shown, but without a monochromator. The PTR[3] data are recorded with the 287-nm pump and 574-nm probe laser beams and use the monochromator/array detector combination shown.

of the intersystem crossing from the singlet excited state populated optically and thereby determine the photochromic reaction mechanism.

Photochromism in a frozen solution of the spironaphthopyran without a nitro group also has been studied by absorption spectroscopy.[13] Several merocyanine isomers have been shown to exist, and moreover, the formation of an intermediate state has been suggested. The species produced by photoexcitation returns to the initial spiro form when the photolytic product itself undergoes photoexcitation. This second intermediate is termed **X** and is assumed to be an open cisoid form.

The isomer distribution of the merocyanine form of spiro compounds has been detected and characterized, first with absorption spectroscopy in low temperature solutions[14] and recently with transient Raman and coherent anti-Stokes Raman spectroscopy (CARS).[15-18] The interpretation of these vibrational data from transient species and excited-state populations in terms of a general photochromic reaction mechanism remains unresolved. By measuring the Raman spectrum from the transient species in various solvents, it has been suggested that several different merocyanine isomers exist. In addition, the temperature dependence of features in these Raman spectra has been interpreted in terms of a change in the distribution of isomers.[15] These changes are considered to reflect different isomeric configurations around the bridge connecting the indoline and naphthalene (or benzene) moieties of the open merocyanine form (both cis and trans combinations). By means of picosecond time-resolved resonance Raman (PTR[3]) spectroscopy, the merocyanine isomers formed from the excitation of spironaphthoxazine recently have been observed in real time.[18] From this study, it is evident that the merocyanine isomers are produced directly from the excited singlet state populated by absorption and that no isomerization between the merocyanine isomers occurs during the 50 ps to 1.5 ns interval.

In this paper, the results of the picosecond transient absorption (PTA) and PTR[3] scattering measurements of a spironaphthopyran

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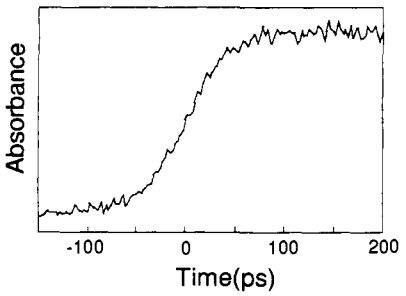


**Figure 3.** Picosecond time-resolved absorption at 574 nm of a cyclohexane solution of the merocyanine isomer(s) produced with 287-nm excitation. The 0 ps is determined from the midpoint of the 574-nm absorption rise time.

which does not have a nitro group are reported. Transient absorption which can be assigned to an intermediate of the photolytic reaction has been observed for the sample in several different solvents. PTR[3] spectra of the merocyanine isomer(s) formed also have been recorded, and on the basis of both types of observations, a reaction scheme describing the photochromism of spironaphthopyran is proposed.

## Experimental Section

The spironaphthopyran 1′-(methoxyethyl)-3′,3′,5′-trimethyl-spiro[2*H*-1-naphthopyran-2,2′-indoline] (denoted as SNP) whose molecular structure is shown in Figure 1 is supplied by Mitsubishi Kasei Corp. and is used without further purification. Its method of preparation has been described elsewhere.[19] Samples for measurements are prepared by dissolving SNP in methanol, acetonitrile, or cyclohexane (Fischer, spectro grade) with a typical concentration of $2 \times 10^{-3}$ M. A liquid jet of the sample is formed by circulating the solution through a 600-μm (i.d.) glass nozzle. The sample reservoir is cooled to ~10 °C by placing it in an ice–water bath. Sample degradation, as measured by changes in the UV absorption spectrum, is not observed during the measurements.

The basic experimental instrumentation is shown in Figure 2. The second harmonic output (532 nm) of a mode-locked, Q-switched Nd:YAG laser (Quantronix Model 416) is used to pump a Rhodamine 6G dye laser (Coherent Model 740) which produces 574-nm pulses at a repetition rate of 800 Hz. The 574-nm wavelength is in resonance with the absorption of the merocyanine products.[2] The third harmonic output (355 nm) of the mode-locked, Q-switched Nd:YAG laser is used separately to pump a Stilbene 420 dye laser which has an output in the 400–460-nm region. The 287-nm radiation used to initiate the photochromic reaction is obtained by passing the 574-nm laser pulses through a second KDP crystal to generate the second harmonic frequency. The laser pulse widths are determined from the autocorrelation measurements to be 50 ps for 574 nm and from the rise time of the fast photochromic reaction to be 35 ps at 287 nm and 25 ps in the 400–460-nm region.

For PTR[3] and PTA measurements with a two laser (287 and 574 nm), pump/probe configuration, only one of the synchronously pumped dye lasers is used. The pump and probe pulses are spatially separated by reflection after being generated in a KDP crystal, with the probe pulse (574 nm) traversing an optical delay line (optical path not shown in Figure 2) before arriving at the sample with a well-defined time delay relative to the 287-nm excitation pulse. The optical delay line is comprised of a retroreflective prism mounted on a computer-controlled translation stage. The pump and probe laser pulses are made collinear before being focused into a ~100-μm spot within the liquid sample jet of 600-μm diameter (inset, Figure 2). In absorption measurements, mechanical chopping of the laser beams is introduced in order to utilize lock-in detection. In PTR[3] measurements, Raman scattering at 90° to the plane formed by the liquid jet and the pump/probe laser beams is observed using a 1-m monochromator and a reticon array detector.

The transient absorption data recorded with two, successive excitation pulses requires the incorporation of a third laser pulse (400–460 nm). In this case, the 287- and 574-nm pulses are both used for pumping and the 400–460-nm pulse is used as an absorption probe. The optical configuration is shown schematically in Figure 2, and the three laser beams are aligned in the liquid jet by monitoring the transmitted and absorbed powers. To obtain good spatial overlap between the three laser beams, absorption at 400–460 nm is observed first with only 287-nm pumping. The 574-nm beam is then aligned in the sample in order to maximize 400–460-nm absorption. Mechanical chopping and lock-in detection also are used.

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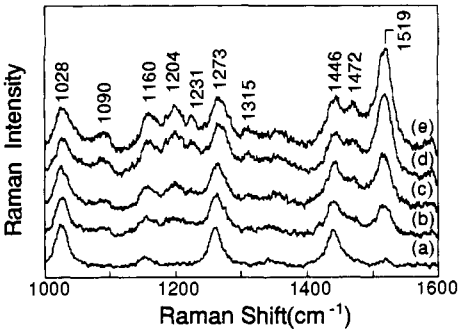


**Figure 4.** Resonance Raman (RR) spectra of the merocyanine isomer(s) in a cyclohexane solution (574-nm probe laser) obtained at a series of time delays after 287-nm pulsed excitation: (a) −100 ps, (b) 0 ps, (c) 25 ps, (d) 100 ps, (e) 500 ps. No significant differences are found in the positions of band maxima or relative band intensities in these RR spectra throughout the entire time range (1.5 ns) examined. The RR spectrum at −100 ps is identical to the Raman spectrum of cyclohexane solvent. To facilitate comparisons, each RR spectrum is normalized to the intensity of the 1028-$cm^{-1}$ band of cyclohexane.

## Results

**PTA and PTR[3] Scattering from Merocyanine Isomers.** The PTA at 574 nm over the initial 200 ps after 287-nm excitation of SNP in cyclohexane solution is presented in Figure 3. The 574-nm probe radiation is resonant with absorption from the merocyanine isomer(s), and since no other transient species or intermediate population is known to absorb in this spectral region,[2] the signal is relatively simple. Only a fast rise time is observed which can be attributed to the cross-correlation period defined by the pump and probe laser pulses (i.e., ~50 ps). Once the 574-nm absorption reaches a maximum, it does not change over the entire 1.5 ns measured. When these results are correlated with those from previous studies,[11] it is apparent that no change occurs during the initial 400 μs.

PTR[3] spectra of the merocyanine isomers produced by 287-nm excitation of the same SNP sample in cyclohexane are shown in Figure 4. PTR[3] spectra from other solvents (e.g., methanol and acetonitrile) are not readily measured due to the presence of large fluorescence backgrounds. The Raman spectra from the cyclohexane sample contain at least seven assignable features with a major band at 1519 $cm^{-1}$. The cyclohexane solvent Raman bands are evident in the −100-ps spectrum (i.e., the probe pulse arrives at the sample 100 ps before the pump pulse). The time evolution of RR band intensities in these PTR[3] spectra follows closely that observed in the PTA data (Figure 3). There is no evidence of changes in either the relative intensities or frequency displacements of RR bands after the cross-correlation period (~50 ps). A similar fast photochromic reaction also is observed in spirooxazine compounds which have a similar structure to that of SNP.[18]

**Transient Absorption in the 400–460-nm Region.** For specific probe wavelengths and solvents, a second type of transient absorption is observed in the 400–460-nm region. The time evolution of this 400–460-nm absorption is presented in Figure 5 for a probe wavelength of 435 nm. The 435-nm absorbance reaches a maximum within the ~50-ps cross-correlation time and then decreases to a plateau value which remains unchanged over the entire 1.5-ns interval monitored (data for delays longer than 200 ps are not shown in Figure 5).

These data can be analyzed kinetically by assuming that an intermediate (I) precedes the appearance of merocyanine isomer(s) (mi) and that it also absorbs at 400–460 nm:

spiro form + 287 nm → I (400–460 nm) →
mi (400–460 nm)

On the basis of the 400–460-nm data, the intermediate must appear in <50 ps and absorbs more strongly at 400–460 nm than the merocyanine isomers. This kinetic model, using Gaussian pulse

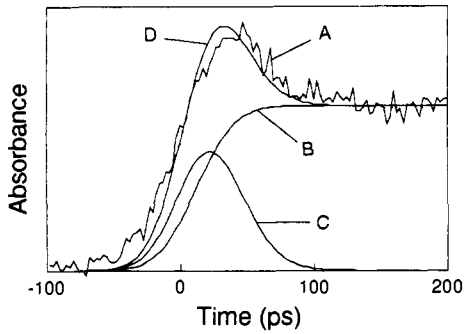


**Figure 5.** Transient absorption observed with 435-nm probe and 287-nm pump (A) and calculated transient absorption of the merocyanine form (B) and intermediate (C) which is assumed to be an excited electronic state of the merocyanine isomer(s). The total transient absorption (D = B + C) is also shown. Parameters used for the calculation include a decay time for the intermediate of 11 ps and an absorptivity for the intermediate that is 4 times larger than that of the merocyanine isomer(s). Since the time resolution of the measurement is limited by the cross-correlation of the two laser pulses, decay times shorter than 11 ps can be used if the absorptivity of the intermediate is permitted to increase correspondingly.

shapes to approximate the excitation process, provides the simulation shown in Figure 5. If the intermediate decays completely into the merocyanine isomer(s) with a lifetime of 11 ps (obtained from fit to data in Figure 5) and has a 435-nm molar absorptivity about 4 times larger than that of the merocyanine isomer(s), then the observed 435-nm kinetic data are well reproduced (Figure 5). Since the decay time is relatively short compared with the laser pulse widths, this analysis does not provide detailed kinetic parameters. From such an analysis, the plateau appearing for delays >100 ps can be assigned to absorption from the merocyanine isomer(s), and therefore, this part of the 400–460-nm signal parallels that observed at 574 nm (Figure 3). The 400–460-nm PTA feature appearing within the cross-correlation time can be assigned to the intermediate.

The 400–460-nm PTA signal also depends on the solvent used as shown in Figure 6 for methanol, acetonitrile, and cyclohexane. Three different probe laser wavelengths within the 400–460-nm region are used for each solvent. The distinct maximum appearing within <50 ps after 287-nm excitation (position A in Figure 6) is clearly present in methanol (Figure 6a) for 450- and 436-nm probe wavelengths, but cannot be seen at 412 nm. The PTA signal after 50 ps decreases to a level which remains unchanged for at least 1.5 ns (data beyond 350 ps not shown). The significance of feature B in these data is described below. Although it is more difficult to distinguish the <50-ps maximum in the acetonitrile data (Figure 6b), small maxima can be seen with low signal to noise ratios. Essentially no 400–460-nm absorption is observed in the cyclohexane solution (Figure 6c), indicating that in cyclohexane either the transient species is not formed effectively or the absorption of the intermediate is weaker and/or spectrally shifted relative to that in the other solvents.

The transient species can be characterized in greater detail through experiments using two excitation laser pulses, one to produce the merocyanine isomers (287 nm) and a second, delayed pulse (574 nm) to photolytically deplete the ground-state population of the merocyanine isomer(s). In these experiments, the 574-nm excitation pulse arrives at the sample at a fixed time delay after the initial 287-nm excitation. Absorption at 400–460 nm is measured over the initial 1.5-ns time period. When the 574-nm pulse is delayed by 200 ps (point B in Figure 6) in the polar solvents, a second 400–460-nm absorption maximum appears within the duration of the 574-nm pulse. It decays to the absorption level created by the initial 287 nm excitation (i.e., prior to 574-nm excitation). Changing the time delay between the 574- and 287-nm pulses over the 100 ps to 1.5 ns range gives the same results except, of course, that the second transient 400–460-nm absorption peak always appears coincident with the arrival of the 574-nm pulse. The 400–460-nm absorption signal always returns

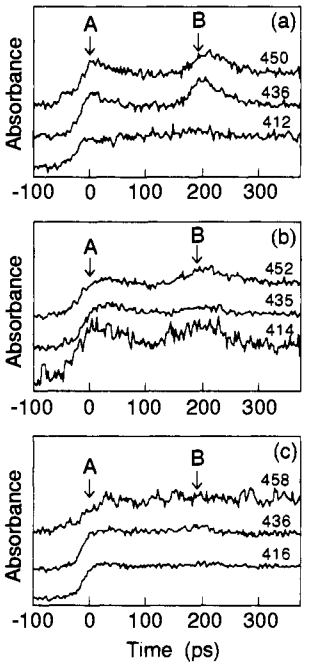


**Figure 6.** Transient absorption of the spironaphthopyran in three solvents (a, methanol; b, acetonitrile; and c, cyclohexane) obtained with two pump pulses separated by a delay time of 200 ps (287 nm at A and 574 nm at B) and a probe pulse. The wavelengths chosen for the probe laser are shown with each data trace. The laser powers of both 287- and 574-nm pumps are ~1 mW. The arrival time of the pump laser pulses at the sample is determined from the transient absorption profile assuming that the reaction rate is faster than the cross-correlation time defined by the pump and probe laser pulses. Signals are normalized so that the absorptions from the merocyanine isomer(s) are the same.

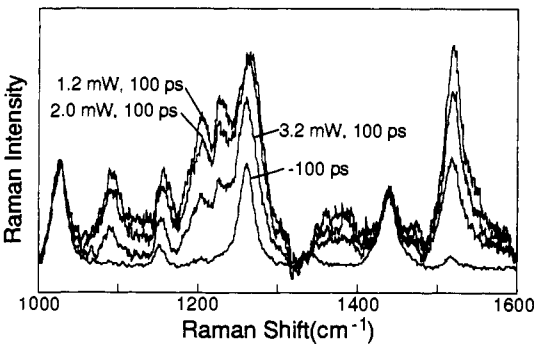


**Figure 7.** Resonance Raman (RR) spectra of SNP in cyclohexane with three different probe powers between 1.2 and 3.2 mW observed 100 ps after 287-nm excitation. The RR spectrum measured at −100 ps illustrates the influence of changing the excitation wavelength on the solvent bands. Each spectrum is normalized with respect to the intensity of the 1028-$cm^{-1}$ band of cyclohexane.

to the same level regardless of the time delay (up to 1.5 ns) between the 287- and 574-nm excitation pulses. The second transient absorptions also exhibit the same solvent dependence observed in the initial (<50 ps) absorptions, namely, significant values in polar solvents and very small (if any) signals in nonpolar solvents. It should be noted that the merocyanine isomers absorb strongly at 574 nm for all the solvents used.

**400–460-nm Transient Species and PTR[3] Scattering.** RR scattering from the transient species absorbing at 400–460 nm is not observed in these experiments, but its presence can be observed in 574-nm RR spectra of ground-state merocyanine isomer(s) recorded using the double excitation experiments described above (Figure 6). These PTR[3] spectra reveal a dependence of the merocyanine ground-state population on the power of the 574-nm laser pulse used (Figure 7). When low-energy (1.2 mW) 574-nm excitation probe pulses generate RR scattering 100 ps after 287-nm excitation, much larger merocyanine RR bands are

observed than when high-energy (3.3-mW) 574-nm probe pulses are used. Relative RR band intensities can be determined because the Raman bands from the solvent (cyclohexane) appear prominently in each spectrum and can be normalized to eliminate the influence of the changing laser intensities. The 574-nm Raman spectrum of the cyclohexane solvent is presented in Figure 7 to facilitate comparisons.

The decrease in the intensity of RR scattering as 574-nm power increases reflects a depleted ground-state population in the merocyanine isomer(s). Photolytic depletion does not result in new transient absorption near 574 nm since no new RR bands appear in the PTR$^3$ spectrum. Rather, only the intensities of all RR bands assigned to the merocyanine isomer(s) decreases as the 574-nm probe laser power increases. This is consistent with the formation of a kinetic intermediate during the pulse duration of the 574-nm excitation. Since the same RR bands appear in the spectra recorded at both 574-nm powers, the merocyanine isomer(s) remain photochemically unchanged. Furthermore, no other type of photochemistry is apparent.

Finally, the photochemistry of the merocyanine isomer(s) or the 400–460-nm intermediate, and specifically the presence of a back-reaction from the merocyanine isomer(s) even during the photochemical reaction to reform SNP, is studied directly by using ~425-nm radiation as the second pumping source. The merocyanine isomer(s) is produced by 287-nm excitation and then subsequently pumped, at variable time delays, with ~425-nm radiation while the transient absorption at 574 nm is monitored. Typically, pulsed laser pulses are 0.6 mW at 287 nm, 0.8 mW at 425 nm (~20-nm bandwidth), and 0.2 mW at 574 nm. The 574-nm absorption is monitored at a 750-ps delay. The signal is generated by chopping the 425-nm laser beam while the time delay between the 287- and 425-nm excitation pulses is scanned via an optical delay line. It can be anticipated that if ~425-nm excitation initiates a back-reaction to SNP, the 574-nm signal should decrease due to the decreased merocyanine concentration. Experimentally, no change in 574-nm absorbance is observed for any of the ~425-nm time delays from −100 to 750 ps. Thus, no evidence for a photolytic reaction involving the merocyanine isomer(s) or the 400–460-nm intermediate is found using either 574- or ~425-nm excitation. These results are in contrast to those reported previously involving back-reactions to reform SNP.[13]

## Discussion

**Merocyanine Formation.** It has been widely proposed that photochromism in spiro compounds produces several isomers primarily via conformational changes in the bridge region (Figure 1). Transient Raman and electronic absorption spectroscopies have been used to monitor such isomer formation (i.e., photochromism) in spiro compounds such as spirobenzopyrans,[15] spironaphthoxazines,[16-19] and spironaphthopyrans[2,12] dissolved in a variety of solvents. For example, it has been suggested from transient resonance Raman scattering that several different merocyanine isomers of spirobenzopyran are formed in different solvents,[15] but no complete vibrational assignments have been made by which the structures of different isomers can be identified. Vibrational spectra of the photochromism products in spironaphthoxazine compounds measured by PTR$^3$ scattering[18] and CARS[16,19] also have been used to suggest that at least two merocyanine isomers are formed, one of which is dominant in polar solvents and the other dominant in nonpolar solvents. Again, however, no specific isomeric structures have been identified. Molecular orbital calculations provide some additional insight by showing that two of the possible merocyanine isomers of spironaphthopyran are not stable due to steric hindrance between a hydrogen atom on the naphthalene ring and a hydrogen atom on the HC–CH bridge linking the indoline and naphthalene moieties. In spironaphthoxazines, the energy differences for similar steric instabilities have been estimated to be >2.5 kcal/mol using MNDO molecular orbital calculations.[20] In general, however, the number of isomers underlying photochromism in spiro compounds as well as their specific vibrational structures remains to be established experimentally.

On the basis of previous work, the spironaphthopyran compound examined here could be expected to produce more than one merocyanine isomer. The 574-nm PTA (Figure 2) and PTR$^3$ (Figure 4) data, however, provide no evidence by which to determine whether one or more isomer is present. These 574-nm absorption and PTR$^3$ spectra do demonstrate that the merocyanine isomer (or distribution of isomers) remains unchanged over the initial 1.5 ns after 287-nm excitation and that no changes in the merocyanine isomer(s) occur after their initial (50 ps) formation in all the solvents used. The same results have been reported for the merocyanine isomer(s) formed from spirooxazine compounds in which case photochromism occurs in <10 ps[16-18] and for spirobenzopyrans and spironaphthopyrans in *n*-pentane.[12] It is important to note, however, that none of the transient absorption or vibrational Raman data presented here or previously[12,16-18] directly establish whether more than one merocyanine isomer is present.

A more detailed understanding of the merocyanine isomeric structures requires a normal coordinate analysis of vibrational spectra from isotopically substituted SNP compounds. Only in the case of spirobenzopyrans has such a study with isotope substitution been reported.[21] Some assignments of the merocyanine RR spectra from SNP can be made by analogy with previous PTR$^3$ results on spiro compounds. Most of the RR bands can be assigned to the naphthalenic moiety and the bridge linking the two ring systems. The strongest RR band at 1519 cm$^{-1}$ (Figure 4) may be assigned to be C=C stretching mode connecting the indoline and naphthalene rings. The 1472-cm$^{-1}$ band observed in Figure 4 may be assignable to the C=C stretching mode in the naphthalene ring. The 1315- and 1273-cm$^{-1}$ RR bands can be assigned, respectively, to the C—C stretching mode in the bridge and to the C—N stretching mode in the indoline ring. RR bands near 1200 cm$^{-1}$ likely arise from the C—H bending mode in the bridge and naphthalene ring.

The dynamics underlying the formation of the merocyanine isomer(s) in SNP can be characterized from the 574-nm PTA and PTR$^3$ results. Photochromic dynamics in spirobenzopyrans without a nitro group occur within 1 ns and are not affected by oxygen and, therefore, are considered to proceed through an excited singlet state.[11,12] The same conclusion can be reached from the 574-nm PTA and PTR$^3$ results reported here. Absorption from the merocyanine isomer(s) occurs within the cross-correlation time of the PTA measurements (~50 ps) as does the appearance of the corresponding RR scattering. These results suggest that photochromism occurs from the excited singlet state(s) populated optically at 287 nm.

**Transient 400–460-nm Intermediate.** The relationship between the 400–460-nm transient absorption observed following 574-nm excitation and the merocyanine isomer(s) can be derived from the data in Figure 6. It is evident from the double excitation experiments in polar solvents that the new species absorbing at 400–460 nm is formed only when the merocyanine isomer(s) absorbs 574-nm radiation. It also is clear that the new species relaxes to the ground state of the merocyanine isomer(s) in <50 ps since the transient 400–460-nm absorbance returns to the same level as that measured prior to the 574-nm excitation (Figure 5). Thus, the concentration of the merocyanine ground state is the same before and after 574-nm excitation, and photochemical changes in the merocyanine isomer(s) caused by 574-nm excitation can be excluded (e.g., a back-reaction to the spiro form or photoisomerization in the merocyanine isomer(s)). PTR$^3$ data show that the merocyanine ground-state population is substantially depleted when 574-nm powers between 1.2 and 3.2 mW are used (Figure 7). Since these are the same conditions as those used for the 400–460-nm PTA measurements, it is evident that the 574-nm

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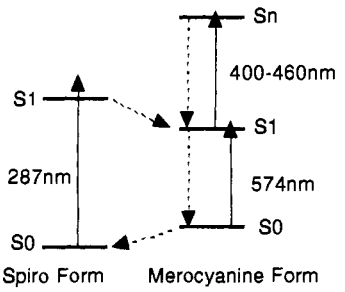


**Figure 8.** Suggested mechanism of the photochromic reaction of SNP. Dashed lines indicate nonradiative decay, and solid lines indicate the optical transitions used in these experiments.

laser power used to excite the merocyanines is strong enough to produce the 400–460-nm absorbing species directly from the merocyanine ground state. All of these characteristics suggest that absorption in the 400–460-nm range involves two excited electronic states of the merocyanine isomer(s) (e.g., $S_1 \rightarrow S_n$), the lowest energy one ($S_1$) of which decays with high efficiency to the merocyanine ground state ($S_0$). A representation of the reaction mechanism including the excited-state absorption is shown in Figure 8. Time-resolved experiments in which the recovery dynamics of the $S_0$ population is monitored could confirm this conclusion. These rates, however, are faster than the time resolution of the PTA measurements, and therefore, direct kinetic parameters cannot be determined from this study.

The 400–460-nm assignment of the $S_1 \rightarrow S_0$ absorption in the merocyanines is supported by the observation that PTA signals at both 574 and 400–460 nm exhibit the same solvent and wavelength dependencies (i.e., the solvent and spectral conditions which enhance or decrease one have the same effect on the other).

The PTR[3] data also support both this kinetic model and the assignment of the 400–460-nm absorption to an $S_1 \rightarrow S_n$ transition in the merocyanine isomer(s). No changes in the positions of RR features are observed over the initial 1.5 ns, but rather only time-dependent changes in the RR band intensities (Figures 4 and 6) which reflect the transient depletion and recovery of the merocyanine ground state. These PTR[3] data show conclusively that the merocyanine isomer(s) do not undergo any photochemistry initiated by 574-nm excitation. The excited electronic state of the merocyanine isomer(s) populated by 400–460-nm absorption, therefore, appears to be isolated from the excited states of SNP as well as from other merocyanine isomers.

A ground-state, cisoid intermediate might be considered as an alternative assignment for the 400–460-nm absorption. This possibility can be excluded, however, since a cisoid species would open a channel for reforming the spiro compound (i.e., a back-reaction). No back-reaction is observed for SNP (vide supra) although one is found in nitrospiropyrans.[22] In addition, the recovery time following 574-nm excitation of SNP is much faster (<50 ps, Figure 6) than the observed cisoid reaction (several nanoseconds in nitrospiropyrans[22]).

Studies of photochromism in other spiro compounds under a variety of experimental conditions have led to other conclusions concerning the photochemistry of merocyanine isomers. By contrast with the SNP case described here, photoexcitation of the merocyanine isomers of the 6-nitrospirobenzopyran derivative has been reported to initiate back-reactions (photodecoloring).[22] The population of an excited-state merocyanine may produce cisoid isomers which act as precursors for the re-formation of the original spiro form. Photochromism in low-temperature solutions of spironaphthopyrans also has been shown to involve photo-induced back-reactions from colored merocyanine isomers to the original spiro compounds.[13] An intermediate (X) which reacts to form either the merocyanine isomer(s) or the spironaphthopyran underlies the proposed mechanism. The double excitation (287 nm/574 nm) experiments monitored at 400–460 nm described here demonstrate the merocyanine isomer(s) from SNP does not photochemically re-form the spiro compound, and therefore, no analogous "X" intermediate is involved mechanistically. Transient absorption (616 nm) observed in a spirooxazine also has been assigned as an excited state of a cisoid intermediate.[16,17] If the analogous excited-state cisoid intermediate was formed by exciting the merocyanine isomer(s) of SNP, the 574-nm absorption observed in the double excitation experiments (Figure 6) would decrease (i.e., the 574-nm absorbance level would not return to the value measured prior to the second excitation). Since such a decrease is not found under any of the conditions studied here, an alternative interpretation of the 616-nm transient absorption in a nonpolar solution of spirooxazine is required, namely, that it corresponds to the 400–460-nm absorption transition from a merocyanine excited state observed here for SNP. Structural differences between the two spiro compounds and changes from a polar to a nonpolar solvent could underlie the shift in the absorption wavelengths between excited electronic states. The transient absorption observed in spirooxazines,[16,17] therefore, can be assigned to a transition between excited electronic states in one of the initially formed merocyanine isomers. Such variations in the photochemistries of the merocyanine products may reflect major differences in the excited-state potential surfaces accessible in each spiro compound and consequently distinguish the photochromism observed.

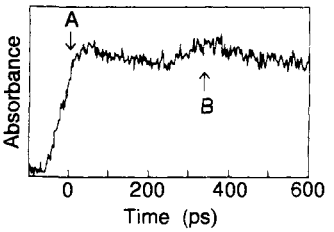


**Figure 9.** Transient absorption of SNP in cyclohexane obtained with two pump pulses separated by a time delay of 350 ps (287 nm at A and 574 nm at B) and a 435-nm probe. The power of the 287-nm pump pulse is 1 mW, and that of the 574-nm pump pulse is 2.1 mW.

Recently, transient absorption measurements with a time resolution of <1 ps have been reported for spirobenzopyran and spironaphthopyran without nitro groups.[12] A nonpolar solvent (*n*-pentane) was used for both compounds. On a time scale that was coincident with the pump pulse (<0.4 ps), absorption in the 400–460-nm region was observed. Due to the high peak laser powers used to overcome weak absorption cross sections, the 400–460-nm absorption feature was attributed in that work to a multiphoton transition in the solvent and not to a reaction intermediate associated with either the spiro compound or a merocyanine isomer(s). The merocyanine isomer(s) formation was reported to have a rise time of ~1 ps.[12]

In the results presented here, absorption signals assignable to reaction intermediates are not readily observed in a nonpolar solvent (Figure 6), and therefore, direct comparisons with the earlier data[12] are difficult. If the 574-nm laser powers are increased, however, small but definitive absorption features can be found in the transient 400–460-nm signals after 574-nm pumping of the merocyanine isomer(s) (Figure 9). The 400–460-nm absorption features in Figure 9, however, also are completely analogous with those described for polar solvents (Figure 6) and in that case assignable to an $S_1 \rightarrow S_n$ transition in the merocyanine isomer(s).

The influence of solvents on the strength of the 400–460-nm transient absorption signals also can be considered mechanistically. If the $S_1$ lifetime of the merocyanine isomer(s) shortens in nonpolar solvents, it would be more difficult to produce substantial transient $S_1$ populations, and therefore, the 400–460-nm absorption would decrease. Supporting this model is the observation that significantly less transient fluorescence appears from SNP in nonpolar solvents than in polar solvents. Furthermore, when sufficiently high laser power is used to cause substantial ground-state depletion

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(Figure 7), weak absorption can be observed (Figure 9). If this absorption is assigned to a $S_1 \rightarrow S_n$ transition in the merocyanine isomer(s), then its absence indicates that the $S_1$ lifetime in cyclohexane is so short that no significant $S_1$ population can be produced given the pumping conditions used. In general, this rationale suggests that a shortening of the $S_1$ lifetime in the merocyanine isomer(s) accounts for the weakening of the 400-460-nm absorption in nonpolar solvents.

**Concluding Remarks**

A reaction mechanism describing photochromism in SNP without a nitro group can be developed on the basis of the results presented here (Figure 8). This same mechanism also may have validity for other spiro compounds without a nitro group.

The initial ring opening appears unidirectional (i.e., irreversible) since the photolytic population of an excited electronic state in the merocyanine isomer(s) via double excitation experiments (Figure 6) does not result in any back-reaction to the SNP. Conversion from the merocyanine form to the original SNP seems to occur only thermally. The optical population of the $S_1$ state in the merocyanine isomer(s) by 574-nm excitation is confirmed through the 400-460-nm absorption observed by double excitation experiments (Figure 5). The effectiveness with which the merocyanine $S_1$ state is populated as well as its excited-state lifetime are strongly influenced by the solvent polarity (Figure 5), with polar solvents providing an environment in which the merocyanine $S_1$ state is more stable.

In a recent study, the merocyanine isomers produced from spirooxazines have been shown through PTR[3] data to equilibrate into different distributions (perhaps in some cases containing only one isomer) depending on the solvent.[18] These results suggest that the photochromism mechanism may involve several pathways which are influenced by interactions with the solvent. The observed changes in the 400-460-nm transient absorption reported here for SNP may reflect analogous solvent influences on the excited-state reaction mechanism. From such a perspective, the intermolecular interactions provided by the solvent environment may influence the excited-state relaxation properties and thereby change the photochemical reaction pathway and the merocyanine isomer(s) formed.

**Registry No.** SNP, 137668-57-6; merocyanine isomer, 137668-58-7.

# Unusual 1:2 Ligand:Metal Complex Formation between an Anthraquinone Cryptand and $Li^+$

**Zhihong Chen, Otto F. Schall, Mónica Alcalá, Yi Li, George W. Gokel,* and Luis Echegoyen***

*Contribution from the Department of Chemistry, University of Miami, Coral Gables, Florida 33124.* *Received July 22, 1991*

**Abstract:** A new cryptand containing an integral anthraquinone unit, **2**, has been synthesized. Electrochemical reduction of **2** in MeCN showed the two expected quasi-reversible waves at −1.03 and −1.40 V vs Ag/AgCl. Upon addition of 1 equiv of $Li^+$, a total of six reduction waves could clearly be seen at −0.44, −0.69, −0.97, −1.07, −1.31, and −1.48 V. The six waves correspond to the two electron reduction processes leading to the dianionic state of each of the three forms of the ligand: the free cryptand, the 1:1 complex, and 1:2 L:$Li^+$ complex. This is the first time that a 1:2 complex of this type has been detected by cyclic voltammetry. The existence of this 1:2 complex ($\mathbf{2}^{\bullet-}$:2$Li^+$) was confirmed by ESR spectroscopy and by a binding study using $^7$Li NMR. The binding constant for this 1:2 complex was found to be $1.7 \times 10^2$, but this value was increased to $1.0 \times 10^8$ upon one-electron reduction and to $1.3 \times 10^{13}$ upon two-electron reduction. Even in the presence of only 1 equiv of $Li^+$/equiv of $\mathbf{2}^{\bullet-}$, the ESR spectrum shows a hyperfine splitting from two equivalent $Li^+$ cations of 0.20 G. A possible structure for this 1:2 complex is proposed, in which the two cations interact with the same carbonyl group on the anthraquinone, while they are simultaneously solvated by the enveloping crown ether. 1:2 complex formation with $Na^+$ and $K^+$ has also been detected by using voltammetry and ESR. Since hyperfine coupling from only one cation is resolved, an unsymmetric complex is proposed. In this structure, the cation exhibiting the hyperfine splitting is inside the cryptand cavity. The other is assumed to be interacting with the external carbonyl and to be in relatively fast exchange with the solvent. While the $\mathbf{2}^{\bullet-}$:$Na^+$ complex can be dissociated by addition of cryptand [2.2.1], $\mathbf{2}^{\bullet-}$:$K^+$ complex cannot be fully dissociated by addition of cryptand [2.2.2]. This implies that reduced **2** is at least as good a $K^+$ binder as cryptand [2.2.2].

**Introduction**

For a number of years we have been interested in podands, macrocycles, and macrobicycles capable of exhibiting coupling between a redox reaction and a cation binding process.[1-5] The molecules are designed to show cation binding properties even in the absence of the redox process. Thus, they all have an acyclic (podand),[6] cyclic (crown),[7] or bicyclic (cryptand)[8] poly(oxyethylene) structure. An electroactive group is present in close to and in the proper geometrical orientation with respect to the cation binding center. Electrochemical (or chemical) reduction of the ligands then leads to excess negative charge which in turn enhances the binding of the cation. Binding enhancement values between

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