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Photochromism of 2*H*-Naphtho[1,2-b]pyrans: A Spectroscopic Investigation

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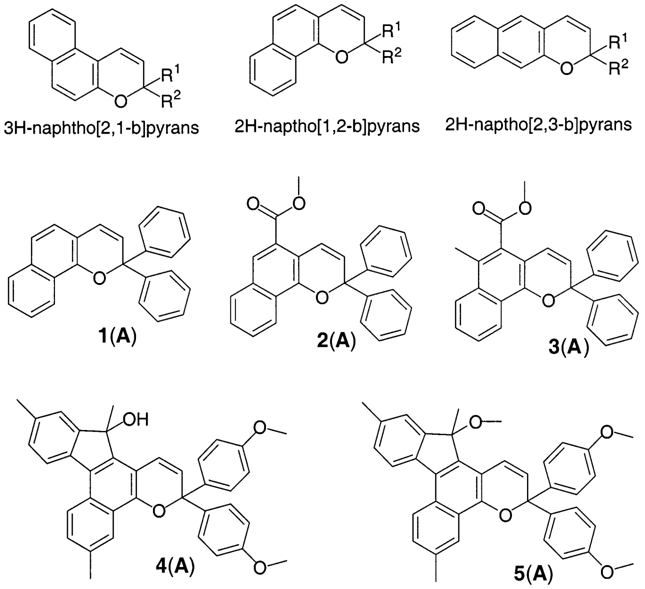
The photophysical and photochromic properties of 2,2-diphenyl-2H-naphtho[1,2-b]pyran and substituted derivatives were investigated by steady state and time-resolved optical absorption and emission spectroscopy in solution at room temperature and in a frozen matrix at 77 K. Fluorescence quantum yields, fluorescence lifetimes, and singlet energies depend strongly on the substitution patterns. Photoexcitation of the naphthopyrans (**A**) leads to efficient ring opening to produce the merocyanines (**B**) and (**C**). The optical absorption of the merocyanines can be tuned by the substituents and can cover most of the visible spectrum (400−700 nm). The decoloration kinetics of the open forms (merocyanines) **B** and **C** to produce naphthopyrans (**A**) depends strongly on the substituents. The ring closure rate constants ($k_{B\to A}$) range from 0.0009 to 0.04 s^{-1}.

Introduction

In the past few years, photochromic dyes, which show reversible photoisomerization, have attracted considerable attention because of their implications in a great number of practical applications including data storage, optical filters, displays, sensor protection, waveguides, and ophthalmic plastic lenses.[1−3] Chromenes, a class of photochromic compounds, have been studied in their photochromic properties in the pioneering work by Becker et al. more than 30 years ago.[4−11] Naphthopyran is a chromene derivative (benzochromene) and can be divided into three isomers, 3H-naphtho[2,1-b]pyrans, 2H-naphtho[1,2-b]pyrans, and 2H-naphtho[2,3-b]pyrans (Scheme 1). The photochemistry and photophysics of 3H-naphtho[2,1-b]pyrans were extensively studied.[9,10,12−18] Although, 2H-naphtho[1,2-b]pyrans are commercially used in plastic ophthalmic lenses,[19] systematic studies of the photophysics and photochemistry are surprisingly rare.[8,20,21] Most studies concentrated on synthetic aspects.[15,17,22,23] Therefore, we investigated in detail the photophysics and photochemistry of 2,2-diphenyl-2H-naphtho[1,2-b]pyran, **1**(**A**), and four of its derivatives, **2**(**A**)−**5**(**A**), (Scheme 1). The derivatives **2**(**A**)−**5**(**A**) were chosen to study influences of substituents on the properties.

Ottavi et al. showed that irradiation with UV light of 3,3-diphenyl-3H-naphtho[2,1-b]pyran produces two colored forms of ring opening products (cis−trans and trans−trans).[12] Applying this reaction mechanism to **1**(**A**) leads to Scheme 2 in which **A** is the (uncolored) closed form (pyran form) and **B** (cis−trans) and **C** (trans−trans) are open (colored) forms (merocyanine forms). For this investigation, the photophysical properties of the closed form (**A**) and the open forms (**B** and **C**) were determined separately, and afterward, the ring closure kinetics (**B** and **C** to **A**) were investigated.

SCHEME 1: Naphthopyrans



Experimental Section

The naphthopyrans **1**(**A**)−**5**(**A**) (PPG Industries, Inc.) were recrystallized from ethanol. Acetonitrile, ethanol, and methylcyclohexane (Aldrich, spectroscopic grade) were used as received.

The UV−vis spectra were recorded on a HP 8452A diode array spectrophotometer using quartz cells with path lengths of 1.0 cm. Steady-state fluorescence spectra were recorded on a Fluorolog 1680 0.22 m double spectrometer (SPEX). Fluorescence quantum yields were determined by using 9,10-diphenylanthracene as the standard ($\Phi_f = 0.95$)[24] and an excitation wavelength of 356 nm. For fluorescence measurements at low temperature (77 K), a liquid-nitrogen Dewar was employed. Time-resolved fluorescence measurements were performed by single-photon counting on an OB900 Fluorometer (Edinburgh

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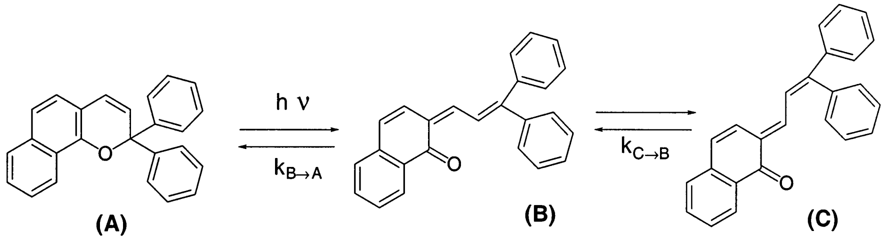
SCHEME 2: Photochromism of Naphthopyrans



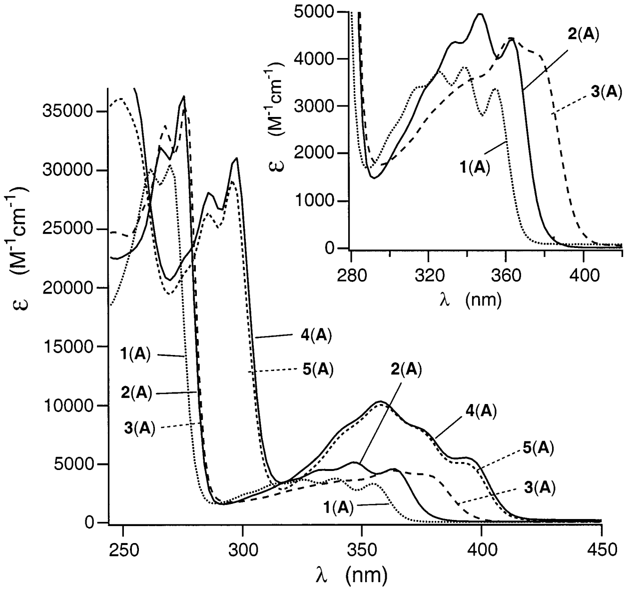


Figure 1. Optical absorption spectra of **1**(**A**)−**5**(**A**) in ethanol solution at 23 °C. The insert shows a magnification of the long wavelength absorbance of **1**(**A**)−**3**(**A**) for clarification.

Analytical Instruments) using a pulsed hydrogen lamp as excitation source.

Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150−30 Nd:YAG laser (355 nm, ca. 8 mJ/pulse, 5 ns) or from a Lambda Physik Lextra 50 excimer laser (308 nm, ca. 8 mJ/pulse, 20 ns) and a computer-controlled system that has been described elsewhere.[25] Solutions were prepared at concentrations of the chromophore such that the absorbance was ∼0.3 at the excitation wavelength employed. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells. Fresh solutions were prepared at each quencher concentration.

The thermal ring closure kinetics were measured as follows: after brief irradiation of naphthopyran (**A**) solutions with UV light ($\lambda_{irr} > 300$ nm) delivered from a xenon lamp (LX300UV; Varian) in conjunction with a WG-305 glass filter (CVI Laser Corporation), a series of absorption spectra were recorded using a diode array spectrometer (HP 8452A) to follow the decoloration kinetics. The temperature of the sample cell (25 °C) was controlled using a water circulating bath.

Results and Discussion

Closed Form of Naphthopyrans (A). The singlet excited states of a series of the naphthopyrans **1**(**A**)−**5**(**A**) (Scheme 1) were investigated by optical absorption and fluorescence spectroscopy. Figure 1 shows the optical absorption spectra of the naphthopyrans (**A**) in ethanol solution. All investigated naphthopyrans, **1**(**A**)−**5**(**A**), show absorbances in the UV spectral region but are transparent in the visible spectral region.

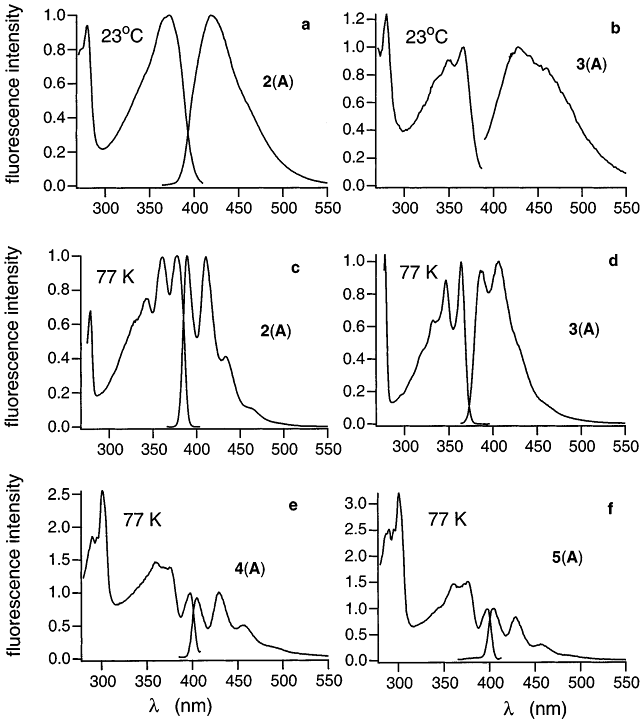


Figure 2. Fluorescence excitation (left spectra) and emission (right spectra) of **2**(**A**)−**5**(**A**) in ethanol solution at 23 °C (a and b) and ethanol glass at 77 K (c−f). Excitation wavelength $\lambda_{ex} = 356$ nm (a−f) for emission spectra.

Introduction of substituents into **1**(**A**), the simplest of the investigated naphthopyrans, causes some bathochromic shift of the $\pi\pi^*$ transition.

Figure 2a,b shows the fluorescence spectra of **2**(**A**) and **3**(**A**) in ethanol solution at room temperature. The fluorescence excitation spectra (Figure 2a,b, left spectra) matches well with the absorption spectra (Figure 1); therefore, it can be concluded that the fluorescence emissions (Figure 2a,b, right spectra) originate from the closed form **2**(**A**) and **3**(**A**). The fluorescence quantum yields ($\Phi_{f2(A)}{}^{23°C} = 0.008$, $\Phi_{f3(A)}{}^{23°C} \sim 0.0009$) were estimated by using 9,10-diphenylanthracene as the standard ($\Phi_f = 0.95$).[24] Consistent with the low fluorescence quantum yields, short fluorescence lifetimes were observed ($\tau_{f2(A)}{}^{23°C} = 0.18$ ns, $\tau_{f3(A)}{}^{23°C} \sim 0.06$ ns). The naphthopyrans **1**(**A**), **4**(**A**), and **5**(**A**) did not show a detectable fluorescence at room temperature.

Triplet states formed by intersystem crossing from excited singlet states show phosphorescence at low temperatures in organic glasses. No phosphorescence of **1**(**A**)−**5**(**A**) was observed in ethanol glass at 77 K. However, fluorescence of **2**(**A**)−**5**(**A**) was observed (Figur 2c−f), suggesting that the ring opening to produce the colored form **2**(**B**)−**5**(**B**) is slowed at low temperature. However, some coloration (ring opening) was still observed by eye upon prolonged irradiation with UV light at 77 K. The fluorescence quantum yields at 77 K were much higher than at 23 °C (Table 1). Consistent with higher

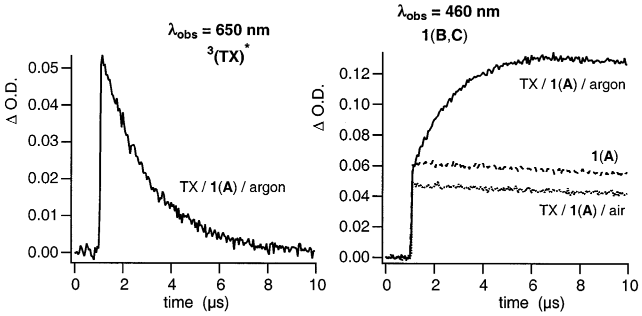


Figure 3. Kinetic traces observed at different wavelengths after laser flash photolysis (308 nm, 15 ns) of argon or air saturated acetonitrile solutions of TX and **1**(**A**) (0.05 mM) and air saturated solutions containing only **1**(**A**) (0.05 mM).

TABLE 1: Photophysical Properties of Naphthopyrans (A)

	ethanol solution		ethanol glass		
	$\Phi_f^{23°C}$	$\tau_f^{23°C}$ (ns)	Φ_f^{77K}	τ_f^{77K} (ns)	E^S (kJ/mol)
1(A)			< 0.001		
2(A)	0.008	0.18	0.34	6.4	311
3(A)	~0.0009	~0.06	0.04	6.3	321
4(A)	<0.0006		0.01	3	299
5(A)			0.004	3	299

fluorescence quantum yields, the fluorescence lifetimes are longer (Table 1). It is noteworthy that the fluorescence excitation and emission spectra at 77 K are more structured than at room temperature, which is commonly observed at low temperatures in frozen matrixes.

The unsubstituted naphthopyran, **1**(**A**), did not show a detectable fluorescence at room temperature and only a very weak fluorescence at 77 K ($\Phi_f^{77K} < 0.001$). Because the fluorescence excitation spectrum did not match the absorption spectrum and coloration was observed, probably because of ring opening, it was concluded that the observed emission does not originate from the closed form of **1**(**A**), and the true value of the fluorescence quantum yield of **1**(**A**) is much lower than 0.001.

Table 1 summarizes the photophysical properties of the closed form (**A**) of the naphthopyrans. The singlet energies, determined from the low-temperature fluorescence emission and excitation spectra, decrease with increasing substitution and are consistent with the optical absorption spectra. Surprisingly, **2**(**A**) showed the highest fluorescence quantum yield and lifetime.

Triplet Sensitization. Direct excitation of the investigated photochromic compounds did not show the presence of triplet states. Laser flash photolysis of the closed form (**A**) showed transient absorbances of the open forms (**B**) and (**C**) but no indication of triplet–triplet absorption. Furthermore, no phosphorescence at low temperature (77 K) was observed in polar (ethanol) or nonpolar (methylcyclohexane) glasses. The cause for the lack of detection of triplet states could be the following: (i) Low intersystem crossing quantum yield. This is consistent with fast ring opening from the singlet excited state. At room temperature, only very weak fluorescence (Table 1) attributed to the closed form was observed, which could be caused by fast ring opening. (ii) Short triplet lifetime. Fast ring opening or other deactivation mechanisms could cause a short triplet lifetime, which makes the observation of triplet states difficult.

To investigate the properties of the triplet states of the closed forms (**A**), the triplet states were generated by sensitization. Thioxanthone (TX) was chosen as the triplet sensitizer, because of its high intersystem crossing quantum yield, strong ground-state absorption at 308 nm, and strong triplet–triplet absorption at 650 nm. Laser excitation of TX in deoxygenated acetonitrile solution with 308 nm pulses yielded a strong transient absorption at 650 nm corresponding to the triplet–triplet absorption of TX[26] and decayed with a lifetime of approximately 17 µs. In the presence of **1**(**A**), the lifetime of TX triplets was reduced (Figure 3, left), suggesting quenching by triplet–triplet energy transfer (eq 1). The quenching rate constant was determined by pseudo-first-order treatment of the transient decay at 650 nm ($k_q = 8.8 \times 10^9$ M^{-1}s^{-1}; Figure 4). This rate constant, which is close to diffusion controlled limit, is typical for triplet–triplet energy transfer in acetonitrile solutions.[27]

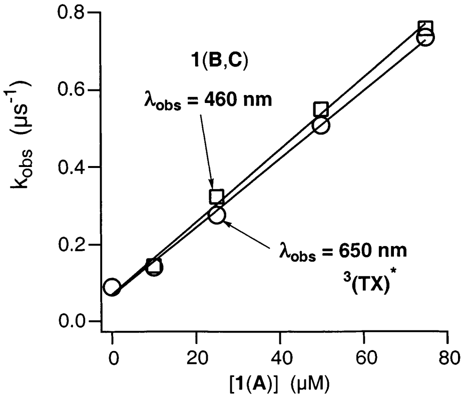
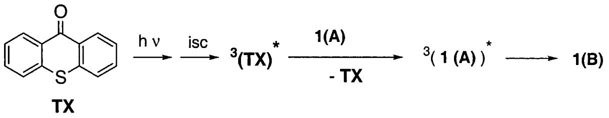


Figure 4. Pseudo-first-order rate constants of the TX triplet decay (monitored at 650 nm) and growth of **1**(**B**) (monitored at 460 nm) versus **1**(**A**) concentration; laser flash photolysis of argon-saturated acetonitrile solutions of TX (308 nm) in the presence of different concentrations of **1**(**A**) at 23 °C.



(1)

$$1(A) \xrightarrow{h\nu} 1(B) \qquad (2)$$

Laser flash photolysis of TX in the presence of **1**(**A**) showed, in addition to the transient absorption of ^{3}(TX)* at 650 nm (Figure 3, left), also a strong absorption centered at about 460 nm (Figure 3, right), which was attributed to the open forms **1**(**B**) and **1**(**C**) (see below). After an initial buildup in a time scale within the laser flash, this transient absorption continues to grow with a time scale synchronous to the decay of the ^{3}(TX)* observed at 650 nm. The initial buildup of the absorbance at 460 nm within the laser flash is caused by the laser light absorption of **1**(**A**) followed by fast ring opening from the excited singlet state (eq 2). This assignment was supported by laser flash photolysis of **1**(**A**) without TX. The initial buildup at 460 nm is almost as intense as that in the experiments containing both TX and **1**(**A**) (Figure 3, right). In addition, laser experiments of TX and **1**(**A**) in the presence of air supported this assignment. Oxygen does not influence the absorption of light by **1**(**A**) and production of singlet excited states of **1**(**A**) followed by ring opening to **1**(**B**), but it quenches the triplet states of TX. Because the triplet quenching of TX by oxygen in air saturated acetonitrile solutions ([O$_2$] = 1.9 mM)[28] is faster than the triplet energy transfer to **1**(**A**) (eq 1) at the used concentration of **1**(**A**) (0.05 mM), no slow buildup of transient absorption was observed (Figure 3, right).

The growth of the absorption of the open form **1**(**B**) (Figure 3, right) occurs simultaneously with the decay of ^{3}(TX)* (Figure 3, left), and plotting the pseudo-first-order growth constant

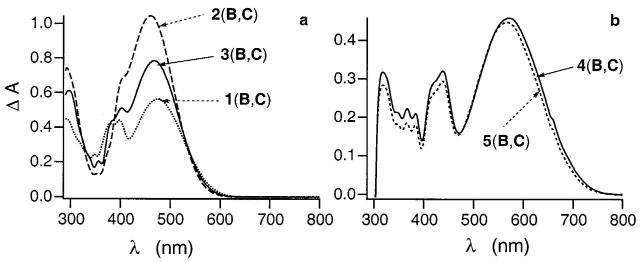


Figure 5. Optical absorption spectra after brief irradiation with UV light (λ_{irr} > 300 nm) of **1**(**A**)−**5**(**A**) in ethanol solution at 23 °C.

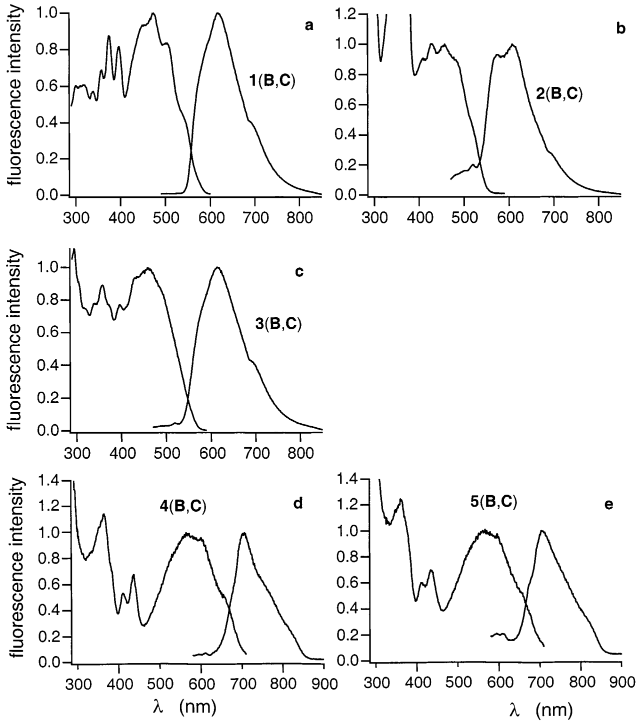


Figure 6. Fluorescence excitation (left spectra) and emission (right spectra) of **1**(**B** and **C**)−**5**(**B** and **C**) after brief irradiation with UV light (λ_{irr} > 300 nm) and then shock freezing in ethanol glass at 77 K.

TABLE 2: Photophysical Properties of Merocyanines (B) and (C)

	ethanol solution		ethanol glass		
	$k_{B\rightarrow A}{}^{25°C}$ (s^{-1})	$k_{C\rightarrow B}{}^{25°C}$ (s^{-1})	$\tau_f{}^{77K}$ (ns)	E^S (kJ/mol)	λ_{max} (nm)
1(B,C)	0.0009 0.002^a	$<10^{-4}$	0.36	215	474
2(B,C)	0.040	1.4×10^{-4}	0.76	224	460
3(B,C)	0.0022	$<10^{-4}$	0.75	218	468
4(B,C)	0.016	$\sim 5 \times 10^{-5}$	<0.1	180	570
5(B,C)	0.019	$\sim 5 \times 10^{-5}$	~0.08	179	568

[a] From ref 22.

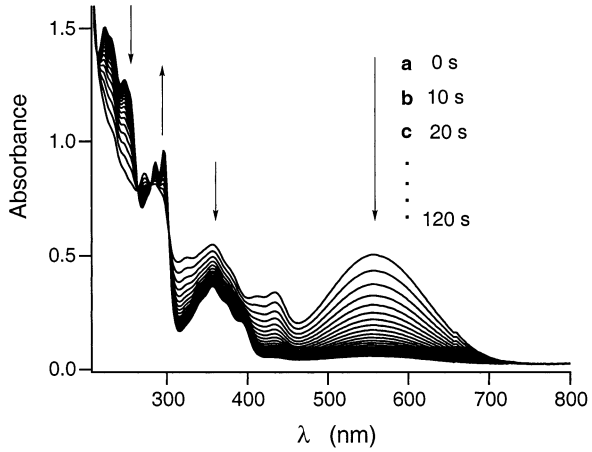


Figure 7. Absorption spectrum of **4**(**A**) in ethanol solution after irradiation with UV light (λ_{irr} > 300 nm, 10 s; spectrum a). The following spectra (b, c, d, ...) were recorded after 10 s each (at 25 °C).

versus the concentration of **1**(**A**) yielded an almost identical plot to the ^{3}(TX)* decay kinetics (Figure 4). This supports the notion that ring opening from the triplet state of **1**(**A**) is fast (ns time scale or faster).

Similar triplet sensitization experiments employing TX were also performed on **4**(**A**). The findings are similar to those in the case of **1**(**A**), and a similar rate constant of the quenching of TX triplets by **4**(**A**) was found ($k_q = 7.5 \times 10^9$ M^{-1} s^{-1}). The triplet sensitization experiments show that triplet states of **1**(**A**)−**5**(**A**) can be generated, and the triplet states undergo fast ring opening (ns time scale or faster) to form **1**(**B**)−**5**(**B**) (eq 1).

Singlet States of the Open Form (B and C). Photoexcitation of naphthopyrans (**A**) leads to ring opening to produce the merocyanines (**B**) and (**C**). Optical absorption spectra were recorded after brief irradiation of **1**(**A**)−**5**(**A**) in ethanol solutions with UV light (Figure 5). The merocyanines **1**(**B** and **C**), **2**(**B** and **C**), and **3**(**B** and **C**) possess strong optical absorption from 380 to 520 nm, and merocyanines **4**(**B** and **C**) and **5**(**B** and **C**) possess a bathochromically shifted absorption until 700 nm. At room temperature in fluid solutions, ring closing occurs fast (within several minutes) to regenerate (**A**). A detailed study of the kinetics will be discussed later. Because the lifetime of the open forms (**B**) and (**C**) at room temperature is too short for performing photophysical studies, the solutions were flash frozen at 77 K immediately after irradiation at room temperature to preserve the open forms (**B**) and (**C**). To study the singlet excited-state properties of the merocyanines, fluorescence experiments were performed. Figure 6 shows the emission spectra (right spectra) recorded after flash freezing of an ethanol solution of the naphthopyrans, which were irradiated with UV light prior to freezing. The excitation spectra (Figure 6; left spectra) show the origin of the emissions, which matches well with the absorption spectra of the open forms (**B**) and (**C**) (Figure 5). The singlet energy was estimated from the intersection of the normalized fluorescence emission and excitation spectra and are summarized in Table 2.

The singlet energies decrease in the order **2**(**B**) > **3**(**B**) > **1**(**B**) > **5**(**B**) > **4**(**B**), which is consistent with the expected effect of substituents and the increase of the absorption maxima at room temperature (Table 2). The fluorescence lifetimes of the open forms were estimated by single photon counting in ethanol glass at 77 K (Table 2). The yellow merocyanines [**2**(**B**), **3**(**B**), and **1**(**B**)] possess longer fluorescence lifetimes at 77 K ($\tau_f{}^{77K}$ = 0.76−0.36 ns) than do the blue merocyanines [**5**(**B**) and **4**(**B**); $\tau_f{}^{77K}$ < 0.1 ns].

Kinetics of Decoloration. The thermal ring closure of the open forms (**B**) and (**C**) in ethanol solution to produce naphthopyrans (**A**) was investigated at 25 °C (Scheme 2). Ethanol solutions of the naphthopyrans (**A**) were briefly irradiated with UV light (λ_{irr} > 300 nm) to produce the open forms (**B**) and (**C**), and a series of absorption spectra were recorded to follow the decoloration kinetics. Figure 7 shows an example of such a series of absorption spectra using solutions of **4**(**A**). The kinetics of the absorbance decrease of the open forms (**B**) and (**C**) were determined at the absorption maximum and are shown in Figure 8. The kinetic traces fit well to a

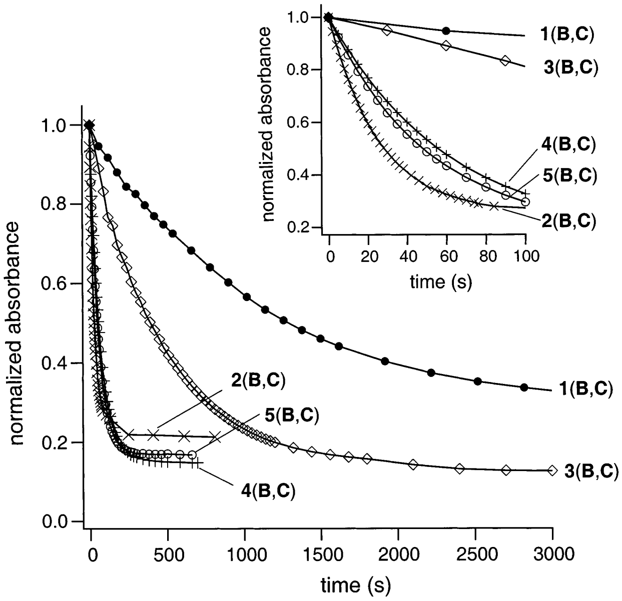


Figure 8. Decay of the absorbance at 474 nm (**1**(**B** and **C**)), 460 nm (**2**(**B** and **C**)), 468 nm (**3**(**B** and **C**)), 570 nm (**4**(**B** and **C**)), and 568 nm (**5**(**B** and **C**)) of ethanol solutions of naphthopyrans after brief irradiation with a lamp ($\lambda_{irr} > 300$ nm) at 25 °C.

monoexponential function and an offset, which accounts for the longer lived component (**C**). The rate constants $k_{B\to A}$ decrease in the order **2**(**B**) > **5**(**B**) ≈ **4**(**B**) ≫ **3**(**B**) ≫ **1**(**B**) (Table 2). Small changes in substitution can effect the kinetics dramatically. Introduction of a methyl ester function (**2**(**B**)) into the unsubstituted photochromics (**1**(**B**)) increases the rate constant by a factor of about 50. Introduction of a methyl group into **2**(**B**) to make **3**(**B**) decreases the rate constant by a factor of 18. The HO substituent in **4**(**B**) could influence the kinetics by hydrogen bond formation. Because the methyl ether derivative **5**(**B**) shows an almost identical $k_{B\to A}$, hydrogen bonding in **4**(**B**) probably does not play a role. In addition, most of the photophysical properties of the open and closed form of **4**(**A**, **B**, and **C**) and **5**(**A**, **B**, and **C**) are identical within the experimental error (Tables 1 and 2).

The trans–cis conversion kinetics (**C**) → (**B**) is orders of magnitudes slower than the ring closing kinetics (**B**) → (**A**) (Table 2). **2**(**C**) possesses the shortest lifetime ($\tau_C = 2$ h at 25 °C). The rate of trans–cis conversion (**C**) → (**B**) was increased by irradiation with light of 420–700 nm, showing that the cis–trans isomerization is photoreversible.

In the case of the isomeric 3,3-diphenyl-3H-naphtho[2,1-b]-pyran (Scheme 1), a 2 orders of magnitude faster cycloreversion, (**B**) → (**A**); $k_{B\to A} = 0.15$ s^{-1} (300 K)[12] and $k_{B\to A} = 0.12$ s^{-1} (298 K),[22] was reported compared to **1** ($k_{B\to A} = 0.0009$ s^{-1}). Consistently, the rate of trans–cis conversion (**C**) → (**B**) for 3,3-diphenyl-3H-naphtho[2,1-b]pyran, the isomer of **1**, was reported to be faster ($k_{C\to B} \sim 0.004$ s^{-1})[12] than for **1** ($k_{C\to B} < 10^{-4}$ s^{-1}). Conversely, the other isomer, 2,2-diphenyl-2H-naphtho[2,3-b]pyran (Scheme 1), shows a much faster cycloreversion, (**B**) → (**A**); $k_{B\to A} \sim 300$ s^{-1},[18] at room temperature. This shows that the isomeric structures of the naphthopyrans are dramatically different in their photochromic properties.

In our experiments, the decoloration kinetics was determined by employing a diode array spectrometer with a detector response time of about 0.2 s. With this experimental setup, it is not possible to observe any decoloration, which occurs at a time scale shorter than one second. Therefore, laser flash photolysis experiments were performed to observe any possible fast decoloration. Ethanol solutions of the naphthopyrans (**A**) were irradiated with a short laser pulse ($\lambda_{ex} = 355$ nm, 7 ns), and the formation of **B** was monitored by UV–vis spectroscopy. The buildup of the absorbance of **B** occurred within the response time of our instrument (20 ns) and remained constant over 8 orders of magnitude, until at least 1 s. This shows that no fast decoloration occurs within one second.

Summary and Conclusion

The photophysical properties of a series of naphthopyrans were investigated. The unsubstituted naphthopyran **1**(**A**) did not show a fluorescence at room temperature and in a frozen matrix at 77 K under our experimental conditions ($\Phi_f^{77K} < 0.001$), suggesting efficient ring opening. Introduction of substituents gave rise to a detectable fluorescence. The fluorescence lifetimes and quantum yields depend strongly on the substituents. Direct excitation of the closed form of the naphthopyrans (**A**) did not show any detectable triplet states. Triplet sensitization with thioxanthone generated triplet states of the naphthopyrans (**A**). The triplet states undergo fast ring opening to produce the open form (**B**) within several ns or shorter.

Photoexcitation of the naphthopyrans (**A**) leads to efficient ring opening to produce the merocyanines (**B**) and (**C**). The substituents shift the optical absorptions strongly bathochromically, **4**(**B**) and **5**(**B**), and hypsochromically, **2**(**B**) and **3**(**B**), as compared to the unsubstituted compound (**1**(**B**)). The yellow merocyanines, **1**(**B**), **2**(**B**), and **3**(**B**), possess longer fluorescence lifetimes at 77 K ($\tau_f^{77K} = 0.76-0.36$ ns) than do the blue merocyanines, **4**(**B**) and **5**(**B**) ($\tau_f^{77K} < 0.1$ ns).

The decoloration kinetics of the open forms (merocyanines) (**B**) and (**C**) to produce naphthopyrans (**A**) depends strongly on the substituents. The rate constants $k_{B\to A}$ decrease in the order **2**(**B**) > **5**(**B**) ≈ **4**(**B**) ≫ **3**(**B**) ≫ **1**(**B**). Small changes in substitution did effect the kinetics dramatically.

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