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A Search for Chiral Photochromic Optical Triggers for Liquid Crystals: Photoracemization of 1,1′-Binaphthylpyran through a Transient Biaryl Quinone Methide Intermediate

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Abstract: The photochromic pair 1,1′-binaphthylpyran (**1**) and 2-hydroxy-2′-hydroxymethyl-[1,1′]-binaphthylene (**2**) was examined to assess suitability as optical triggers in a liquid crystal switch. Both **1** and **2** are chiral and they were resolved into enantiomers by HPLC. The absorption and circular dichroism spectra of optically active **1** and **2** were recorded and the Kuhn anisotropy factors (g_λ) were calculated. The photochemistry of **1** and **2** was studied. Irradiation of optically active **1** in an CH_3CN/H_2O solution leads to its racemization and the formation of optically active **2**. Irradiation of optically active **2** under these conditions gives optically active **1** but no racemization of **2**. Time-resolved absorption spectroscopy shows that irradiation of **1** generates an intermediate assigned to a 1,1′-biaryl quinone methide (**3**). Analysis of the mechanism for photoracemization and photochromism reveals that **3** is the key intermediate in both processes. This system is not well-suited for development as an optical trigger for a liquid crystal switch because the magnitude of g_λ is too small in the useful spectral region.

Introduction

The first observation of the formation of an optically active liquid crystal by the addition of a chiral dopant was reported more than 60 years ago.[1] It was found that inclusion of small amounts of optically active cholesteryl benzoate in a normally nematic liquid crystal converts it into a cholesteric phase. This observation led to the development of electrooptic liquid crystal switches and, eventually, to extraordinarily useful display devices.[2] We have been searching for an all-optical analogue to electrooptical liquid crystal switches. In this approach, a liquid crystal is reversibly switched by light between cholesteric and nematic forms and the form of the liquid crystal is detected optically.[3−7] Materials having these properties might find application as memory elements, displays, or coatings for waveguides.[8]

In one approach to the development of these materials, a racemic "trigger" compound dissolved in a liquid crystal is irradiated with circularly polarized light (CPL). Since the enantiomers of the trigger absorb CPL with different probability (circular dichroism), photoresolution is possible in carefully chosen cases. Two classes of photoresolution mechanisms are identified by us as chiroptical and as reversible photodestruction.[3−7] In a chiroptical system, irradiation of the trigger causes no structural change other than conversion of one enantiomer into its mirror image (photoracemization of an optically pure reagent). In this system, the ultimate obtainable optical purity of the trigger at the photostationary state (γ_{pss}) by irradiation with CPL is determined by the Kuhn anisotropy factor ($g_\lambda = \Delta\epsilon/\epsilon$) according to $\gamma_{pss} = g_\lambda/2$. Very few potential triggers are capable of providing a γ_{pss} large enough to be useful for switching a liquid crystal.[9−12]

Resolution by reversible photodestruction is based on photochromism.[13] Selective irradiation of a photochromic compound generates a product having an absorption spectrum that is different than its precursor. Selective irradiation of the product (or in some cases, spontaneous thermal reaction) reforms the original compound. If either, or both, compound in this pair is chiral, then its irradiation with CPL will cause photoresolution where the optical purity (γ_{EOC}) depends on the extent of conversion (x) according to eq 1. The magnitude of the Kuhn asymmetry factor is still crucial to finding suitable triggers, but the reversible photodestruction route provides additional control parameters since the enantiomeric excess of the trigger increases with the extent of conversion.[14]

$$\gamma_{EOC} = {}^1/_2\{[(1 + x)/(1 - x)\}^{(1/2)-(1/g)} + [(1 + x)/(1 - x)]^{(-1/2)-(1/g)}\} \quad (1)$$

Our continuing search for photochromic compounds suitable for use as photodestruction triggers led us to consider the 1,1′-binaphthylpyran system reported recently by Wan, eq 2.

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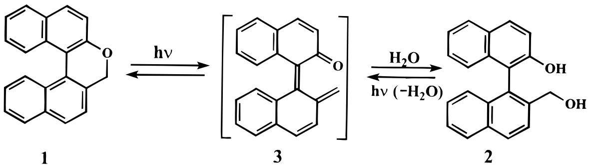

(2)

Irradiation (λ > 350 nm) of pyran **1** in an CH_3CN/H_2O solution leads to the exclusive formation of diol **2** (eq 2).[15] Similarly, irradiation of **2** at 254 nm leads to the reformation of **1**.[15] Of course, both **1** and **2** are chiral and potentially resolvable if the barrier to rotation about the inter-naphthalene bond is sufficiently high. If the enantiomers can be resolved, this system is suitable for exploration as a reversible photochromic trigger for liquid crystals.

Herein, we report the resolution of **1** and **2** and the investigation of their photoracemization mechanism. We obtained circular dichroism spectra and followed the reaction dynamics by laser flash photolysis. These results indicate that racemization proceeds thermally through an intermediate 1,1′-biaryl quinone methide (**3**) formed photochemically. Although the magnitude of g_λ for **1** in the useful spectral region is too small to be effectual as a trigger for a liquid crystal switch, this study reveals important details about the mechanism of this photochromic reaction.

Results

(1) Resolution and Circular Dichroism Spectra of 1 and 2. Binaphthylpyran (**1**) and binaphthyl diol (**2**) were prepared in racemic form according to previously described procedures.[16−19] Resolution of **1** and **2** into enantiomers was achieved by HPLC using a chiral stationary phase. The details of the resolution and isolation procedures are presented in the Experimental Section.

The CD and absorption spectra of the first-eluted enantiomers of **1** and **2** are shown in Figure 1. The CD spectra of the other enantiomer for each compound is, as expected, identical but opposite in sign. The CD spectra of both **1** and **2** exhibit unusually intense Cotton bands in the ^1L_a and ^1B_b transition regions of the naphthalene chromophore as a result of exciton interaction between the two nearly identical aromatic groups.[20] The Kuhn anisotropy factors, g_λ, are also plotted in Figure 1 for **1** and **2**. The maximum value found is $|g_{259}| = 0.03$. This value is large enough for **1** to function as a photoreversible trigger for a liquid crystal switch if it can be efficiently resolved by irradiation with CPL since we determined that its twisting power, $\beta_M = 77\ \mu m^{-1}\ M^{-1}$, is large.[21]

(2) Racemization of 1 and 2. The observation that optically active **1** and **2** can be isolated by HPLC indicates at least a moderate barrier to thermal racemization in both cases. We analyzed rate constants and activation barriers for thermal racemization of **1** and **2** to allow the unambiguous separation of the light driven and thermal processes.

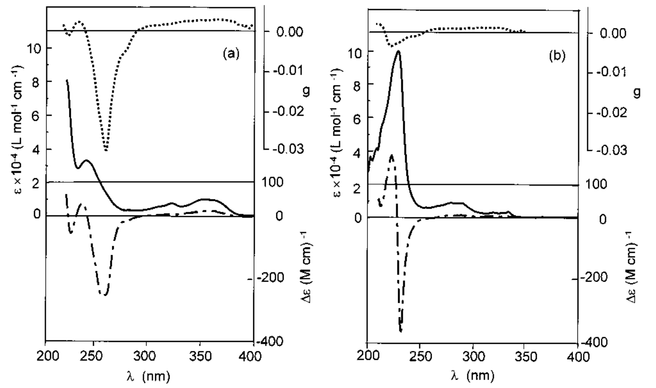

Figure 1. Absorption (solid line) and circular dichroism (broken line) spectra of the first-eluted enantiomers of (a) binaphthylpyran **1** and (b) binaphthyl diol **2** in a 1:1 CH_3CN/H_2O solution at room temperature. The dotted line is the Kuhn anisotropy (g) value.

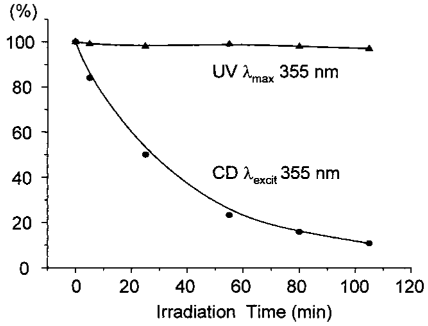

Figure 2. Plot of the effect of irradiation (λ > 350 nm) of the first-eluted enantiomer of **1** on its UV spectrum (triangles) and CD spectrum (circles) in cyclohexane solution at 11 °C. There is no decomposition, but photoracemization is apparent.

The change in CD intensity at 351 nm for resolved **1** was monitored as a measure of its optical purity over time at various temperatures. The decrease of CD intensity for **1** in cyclohexane solution follows a clean first-order kinetic law. The total concentration of **1** in solution measured by its ultraviolet absorption remains constant during the experiment and no side products are detected by GC/MS or by HPLC. This finding shows that racemization of **1** is the exclusive reaction under these conditions. Rate constants for racemization were determined at several temperatures between 25 and 55 °C and the activation energy for racemization of **1** was calculated to be 26 ± 1 kcal/mol. No change in the CD intensity of resolved **2** was detected after 3 h at 85 °C in sodium phosphate solution buffered at pH 7.0. The activation barrier reported for 1,1′-binaphthyl diol, closely related to **2** structurally, is 37.5 kcal/mol.[21] A similar value for **2** would make racemization too slow to detect under the experimental conditions. On the basis of these observations, we conclude that the enantiomers of pyran **1** and diol **2** will be thermally stable under our irradiation and analytical conditions (see below).

A solution of resolved **1** in cyclohexane solution was irradiated (λ > 350 nm) at 11 °C while its CD spectrum was monitored at intervals to determine if **1** racemizes photochemically. In the absence of nucleophiles, the irradiation of **1** should not lead to its destruction. This was confirmed by measuring the total concentration of **1** in solution by absorption spectroscopy and by GC/MS or HPLC. The decrease of the CD intensity for **1** (Figure 2) reveals racemization. Control experiments show that this is not a thermal process. The quantum yield for the photoracemization (Φ_{rac}) of **1** in cyclohexane solution was determined to be 0.0025 by comparison with a

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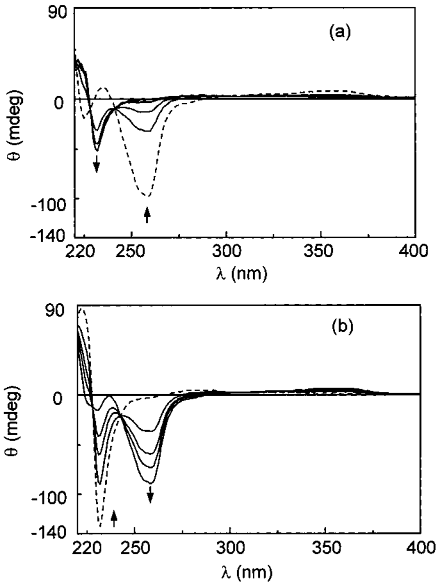

Figure 3. The change in the CD spectra of the reaction mixture resulting from irradiation of a solution of optically active **1** at $\lambda > 350$ nm (Panel a, the dashed line is the CD spectrum before irradiation) and **2** at 254 nm (Panel b).

trans-azobenzene actinometer. Unfortunately, for its application as a trigger, photoracemization of **1** is an inefficient process.

The photoracemization of **2** was investigated in a 1:1 solution of CH_3CN/H_2O. Irradiation of an optically active sample of **2** (99.5% ee, 2.0×10^{-4} M, $\lambda = 254$ nm) at 11 °C was carried out to 20% conversion. There was no measurable racemization of the residual **2** and the ee of the pyran **1** generated in this reaction is 96%. This experiment indicates that racemization of **2** does not occur in its excited state.

(3) Attempt To Photoresolve 1 by Irradiation with Circularly Polarized Light. In principle, irradiation of racemic **1** with CPL at a wavelength where **2** does not absorb will result in its enantiomeric enrichment by converting one enantiomer preferentially to **2**. For **1**, all values of g_λ at wavelengths greater than 360 nm (where it absorbs uniquely) are very small ($g_{max} \approx 0.002$). Consequently, calculation from eq 1 indicates that 98% conversion of **1** will result in only a 0.4% ee. Experimentally, no enantiomeric enrichment is found when a 1×10^{-4} M solution of **1** is irradiated with CPL at $\lambda > 360$ nm in a 1:1 H_2O/CH_3CN solution up to 90% conversion. The g value for **1** is 0.03 at 259 nm and irradiation with CPL at this wavelength would give a reasonable enantiomeric enrichment, but **2** also absorbs at this wavelength and so do nearly all liquid crystalline materials. These facts limit opportunities for development of the photochromic reactions of **1** or **2** as reversible photodestruction triggers for optical liquid crystal switches.

(4) Mechanism of Photoracemization. The photoracemization of **1** and **2** is an intriguing process that might proceed through excited states or through ground-state intermediates. We examined the time course of the racemization process, studied the photophysics and photochemistry of **1** and **2**, and probed the reaction by time-resolved absorption spectroscopy. These experiments led to a well-supported mechanism for reaction.

Photochromism of Optically Active 1 and 2. Irradiation of optically active **1** (> 95% ee, 4.1×10^{-5} M) in an CH_3CN/H_2O solution ($\lambda > 350$ nm) gives optically active **2** ($\Phi_{1\rightarrow 2} = 0.007$) as shown by the appearance of a negative Cotton band at 232 nm in the CD spectrum of the reaction mixture, Figure 3a. Similarly, when optically active **2** (>95% ee, 2.7×10^{-5} M) is irradiated at 254 nm the growth of a negative Cotton band at 256 nm (Figure 3b) reveals that optically active **1** is being formed (72% ee at 99% conversion of **2**). Clearly, the mechanism for interconversion of **1** and **2** must be complex with the outcome dependent on the rates of several competing processes.

Table 1. Optical Activity of **1** and **2** during Phototransformation[a]

irradiation time (min)	conversion[b] (%)	total concn (M)	ee_1[c] (%)	ee_2[c] (%)
0	0.0	9.6×10^{-5}	97.0	
736	19.9	9.7×10^{-5}	76.7	91.9
1050	26.9	9.8×10^{-5}	61.6	75.2
1400	37.0	9.8×10^{-5}	60.0	74.0
2101	45.2	9.8×10^{-5}	21.7	37.9

[a] Optically active **1** was irradiated at $\lambda > 390$ nm at 11 °C. [b] Determined by UV/vis spectra and chiral HPLC. [c] Determined by chiral HPLC.

The optical activities of **1** and **2** were monitored by HPLC when **1** was irradiated at $\lambda > 390$ nm (where it absorbs uniquely) up to 45% conversion of **1**. The results are shown in Table 1. The ee of the pyran drops from 97% at the start to 22% at 45% conversion. The diol that is formed is optically active and, surprisingly, at all conversions the ee of residual **1** in the reaction mixture is less than the ee of the **2** that is produced. No byproducts are detected by HPLC and the concentration of the sample [**1** + **2**] remains constant throughout the experiment. These findings suggest that the photoracemization of **1** can occur independently of its conversion to **2**. We probed the excited-state behavior of **1** and **2** to assess this possibility.

Fluorescence Spectra and Lifetimes. It is feasible that the excited singlet state of **1** is trapped by water to form **2** in competition with other processes such as intersystem crossing to a triplet or formation of an intermediate that leads to its racemization. We studied the fluorescence of **1** to probe this possibility.

The fluorescence of **1** in a cyclohexane solution (ca. 10^{-4} M, $\lambda_{excit} = 352$ nm) at room temperature is a weak, structureless band centered at 400 nm with no significant Stokes shift. If the excited singlet state of **1** reacts with water, its fluorescence intensity should be less in an CH_3CN/H_2O solution than it is in cyclohexane. It is not. The fluorescence quantum yield of **1** is essentially the same ($\Phi_{fl} = 0.03$) in cyclohexane as it is in CH_3CN/H_2O mixtures. In a frozen methylcyclohexane glass at 77 K, the fluorescence of **1** is more intense ($\Phi_{fl} \approx 0.3$) and more structured than it is at room temperature, but it occurs in exactly the same spectral position. The increase of Φ_{fl} at low temperature indicates that fluorescence competes with a thermally activated process such as chemical reaction (k_r), intersystem crossing (k_{isc}), or internal conversion (k_{ic}). We determined that the fluorescence lifetime of **1** at room temperature is less than 0.4 ns, the instrument resolution limit. At 77 K, there is a monoexponential fluorescence decay for **1** with a lifetime of 1.6 ns. There is no measurable phosphorescence emission from **1** under any conditions we examined. From Φ_{fl} and the natural radiative lifetime (τ_o, determined from the integrated absorption spectrum), the singlet lifetime (τ_s) at room temperature for **1** is calculated to be 0.3 ns. This value is in good agreement with the estimate (0.2 ns) from the low-temperature experiments according to eq 3.[22]

$$\tau_{s(RT)} = \tau_{s(77K)}\Phi_{fl(RT)}/\Phi_{fl(77K)} \qquad (3)$$

The temperature dependence of Φ_{fl} for **1** shows a linear

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[22] Gross, H.; Dúrr, H. *J. Photochem.* **1984**, *26*, 165.

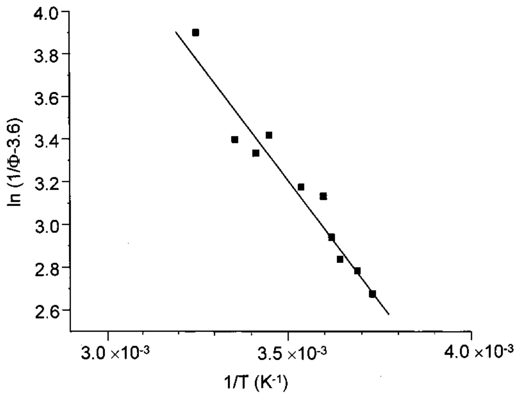

Figure 4. Temperature dependence of the quantum yield for fluorescence of **1** in methyltetrahydrofuran solution plotted according to eq 4.

relationship (Figure 4) from −5 to 35 °C when plotted according to eq 4.[23] This indicates that there is one predominant temperature-dependent reaction from the excited singlet state of **1** with an apparent activation energy of ca. 4.8 kcal/mol.

$$\ln[1/\Phi_{\mathrm{fl}} - (k_{\mathrm{fl}} + k_{\mathrm{ic}})/k_{\mathrm{fl}}] = E_{\mathrm{a}}/\mathrm{RT} + \ln(A/k_{\mathrm{fl}}) \qquad (4)$$

Intersystem Crossing and Racemization of Triplet 1. A second possibility is that the racemization of **1** occurs through its triplet state as is the case for other binaphthol derivatives.[24−27] The absence of phosphorescence from **1**, even at 77 K, and no observable triplet−triplet absorption in time-resolved experiments (see below) suggest that intersystem crossing is slow and that no triplet **1** is formed by direct irradiation. Nevertheless, we carried out sensitization and quenching experiments to probe the role of the triplet state in photoracemization of **1**.

The triplet energy of **1** is expected to be similar to that of 1,1′-binaphthyl ($E_{\mathrm{T}} = 59$ kcal/mol). On that basis, we selected dimethylaminobenzophenone (Michler's ketone), which has a triplet energy of 64 kcal/mol, as a sensitizer for **1**.[28] Irradiation of a cyclohexane solution of optically active **1** and Michler's ketone at $\lambda > 390$ nm (only the sensitizer absorbs) results in the loss of optical activity. Clearly, the triplet state of **1** will racemize. However, in the direct irradiation of **1**, triplet quenchers *trans*-stilbene ($E_{\mathrm{T}} = 49$ kcal/mol)[29] or acridine ($E_{\mathrm{T}} = 45$ kcal/mol)[29] have no effect on the rate of its photoracemization. Evidently, while the triplet state of **1** will racemize, this state is not formed in significant yield by direct irradiation.

Time-Resolved Absorption Spectroscopy. The conclusion that direct irradiation of **1** does not lead to racemization from the excited singlet or triplet state suggests the formation and reaction of an intermediate. Wan and others[30] have proposed that the irradiation of hydroxy-substituted benzyl alcohols generates quinone methides which can cyclize thermally. The 1,1′-biaryl quinone methide could be the common intermediate formed from irradiation of **1** or **2** that is responsible for photoracemization, eq 2. We carried out a series of time-resolved absorption experiments to address this question.

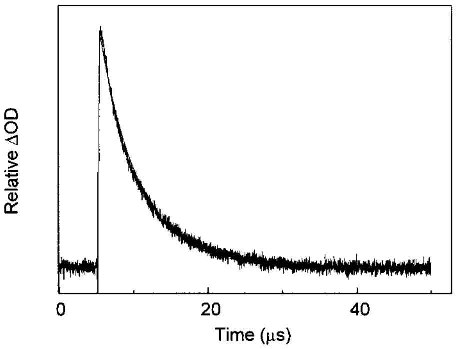

Figure 5. Time-resolved decay ($\tau = 5.02$ μs) of transient absorption monitored at 560 nm following irradiation of **1** in a cyclohexane solution at 355 nm with the output of a Q-Switched Nd:YAG laser.

Nanosecond laser flash photolysis (355 nm; Nd:YAG laser; 50 mJ; 25 °C) of **1** in a N_2-saturated cyclohexane solution reveals a transient species rising immediately with an absorption centered at 560 nm[31] and a well-defined first-order decay with a lifetime of 5 μs, Figure 5. Molecular oxygen has no effect on either the intensity of the transient absorption or the rate of its decay. Thus, this species cannot be a triplet state. The decay of the transient is apparently unaffected also by added nucleophiles such as water and methyl alcohol (0.6 M). Irradiation of **1** in a water-containing solution gives **2**, but the quantum yield for reaction of **1** (Φ_{disapp}) is only 0.02 ± 0.005. This shows that the rate for consumption of the intermediate is considerably greater than that for its reaction with water. Consequently, there should be little effect on the lifetime of the intermediate when water is present in the reaction solution. On the basis of these experiments, we assign the transient spectrum we observe to **3**.

Discussion

The motivation for examination of the reversible photochromism of binaphthylpyran **1** and binaphthyl diol **2** was its potential utility as an optical trigger in a "reversible photodestruction" liquid crystal switch. This application requires, first, that either partner (since both are chiral in this case) have a g_λ sufficiently large at a wavelength absorbed uniquely to generate a γ_{EOC} that induces a measurable pitch in a nematic liquid material. This system does not meet that criterion. The value of g_λ for **1** is too small at all wavelengths. For **2**, sufficiently large values of g_λ occur only at wavelengths absorbed by both **1** and **2**. A second requirement for development of a reversible photodestruction trigger is a reaction mechanism that permits efficient interconversion of photochromic partners. The resolution of **1** and **2** into enantiomers allows the detailed study of this mechanism and provides further insight into the photochemistry of these compounds.

The Mechanism of Photochromism and Photoracemization. Our investigation supports the reaction mechanism outlined in Scheme 1 for interconversion of **1** and **2** and their racemization. The mechanism for photoracemization of binaphthyl derivatives has been carefully studied by several research groups. Irie and co-workers concluded that an increase in bond order in the intra-annular carbon−carbon bond of the triplet excited state causes rotation of the binaphthyl rings to a smaller equilibrium dihedral angle with a concomitant reduction

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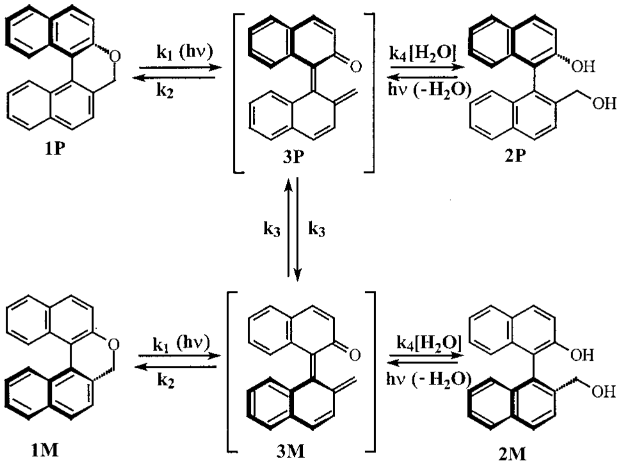
(31) Related species with similar spectra in the visible region have been reported: Shi, Y.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1217. The transient we detect absorbs broadly from 520 to 620 nm with an apparent maximum at 560 nm.

Scheme 1



in the activation barrier for racemization.[24] Tétreau and co-workers suggested an alternative process in which bond cleavage in the triplet state of a binaphthyl acetal formed a biradical that was the species responsible for racemization.[26] Our work ruled out the bond cleavage mechanism in that case and showed that single-bond rotation (atropisomerism) in the excited triplet state is the applicable mechanism.[27]

Examination of Scheme 1 indicates that there are at least three pairs of enantiomers that might racemize in the ground state or an excited state. For example, excitation of either **1** or **2** could lead to racemization from their excited singlet or triplet states. Alternatively, excitation of **1** or **2** could generate **3** which can racemize and then reform **1** or **2** in their racemic forms. Our results indicate that the latter process operates in this system.

Irradiation of optically active **2** in an CH_3CN/H_2O solution leads to the formation of partially racemized **1** but does not cause any measurable racemization of residual **2**. This observation rules out racemization of **2** through its excited singlet or triplet state. Irradiation of optically active **1** results in its partial racemization and in the formation of optically active **2**. The singlet state of **1** is short-lived and consequently it is not likely to photoracemize. A similar conclusion was reached in the examination of 9,10-dihydrodibenzophenanthrene,[32] which is an all-carbon analogue of **1**. Further, the excited singlet state of **1** is not quenched by water and thus it is not directly converted to **2**. Sensitization experiments show that the triplet state of **1** does racemize, but quenching experiments reveal that the direct irradiation of **1** generates little or no triplet. Thus, we conclude that irradiation of **1** generates an intermediate that is responsible for its racemization and its conversion to **2**. We detect an intermediate in the time-resolved experiments that is assigned to 1,1′-biaryl quinone methide **3**.

1,1′-Biaryl quinone methides are species of special interest but all attempts to isolate them have so far been unsuccessful. The spectroscopic and chemical properties of related ortho quinone methides have been examined.[30,31,33−35] 1,1′-Biaryl quinone methides undergo electrocyclic ring closure and can be trapped by nucleophiles. Wan and co-workers identified an *o,o′*-biphenyl quinone methide as an intermediate in the photocyclization of 2-(2′-hydroxyphenyl)benzyl alcohol.[30] However, we are aware of no previous assessment of the optical activity and racemization of 1,1′-biaryl quinone methides. In the present case, racemization of **3** could be either a thermal or a photochemical process since it absorbs light where **1** is being irradiated. The thermal route seems far more likely because the concentration of **3** is always low in a steady-state irradiation. Further, the thermal racemization of related helicenes,[32] 9,10-phenanthrenequiones,[40] and a biphenanthrylidene[41] has been reported.

The Dynamics of Photochromism and Photoracemization. The lifetime of the excited singlet state of **1** is ca. 0.3 ns, it does not intersystem cross to the triplet with measurable efficiency, and $\Phi_{\mathrm{fl}} = 0.03$ at room temperature. The temperature dependence of Φ_{fl} indicates that there is only one major nonradiative reaction and we assign it to ring opening of the pyran to form **3** with a rate constant of 3×10^9 s^{-1}. Unlike 1,1′-binaphthyl, which has a more planar structure in its excited singlet state than the ground state,[42] **1** shows no Stokes shift and its fluorescence spectrum is essentially the same at room temperature and at 77 K. This indicates that there is little or no structural difference between the ground and excited state of **1**. Racemization from this geometry is unlikely to compete with rapid ring opening. The activation energy for the electrocyclic ring opening of singlet excited **1** measured by monitoring the temperature dependence of Φ_{fl} is 4.8 kcal/mol. Thus, it appears that **3** is formed by excitation of **1** rapidly, in high yield, and without racemization.

Under the conditions of the photoracemization experiment, the quantum yield for conversion of **1** to **2** is only 0.007, indicating that nearly all of the **3** generated reforms **1**. The time-resolved absorption experiment reveals a lifetime for **3** of 5 μs. These results give $k_2 = 2 \times 10^5$ s^{-1} and for $k_4[\mathrm{H_2O}] = 1.4 \times 10^3$ s^{-1}. These values are consistent with those observed for reactions of related compounds[43,44] and they explain why the observed lifetime of **3** is largely independent of the concentration of water or other nucleophilic trapping reagents in solution. Simply put, the path leading to formation of **2** from **3** amounts to only a small fraction of the reaction of **3**. From the value of Φ_{rac} for **1** in cyclohexane solution and the assumption that racemization of **3** is solvent independent, a magnitude for $k_3 = 5 \times 10^2$ s^{-1} is calculated. This process, too, competes primarily with the electrocyclization of **3** to **1** and, consequently, its efficiency is low and little racemization is seen from irradiation of **2**.

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$$\mathbf{1}^{\mathrm{P}}_{(t)} = a_1(e^{\beta t} + e^{-\beta t})e^{-\alpha t}$$

$$\mathbf{1}^{\mathrm{M}}_{(t)} = a_1(e^{\beta t} - e^{-\beta t})e^{-\alpha t}$$

$$\mathbf{2}^{\mathrm{P}}_{(t)} = \frac{a_1(\chi - \delta)}{\beta - \alpha}e^{(\beta-\alpha)t} + \frac{a_1(\chi + \delta)}{\beta + \alpha}e^{-(\beta+\alpha)t} + a_1\left(\frac{2\alpha\delta - 2\beta\chi - \beta\delta}{\beta^2 - \alpha^2}\right)$$

$$\mathbf{2}^{\mathrm{M}}_{(t)} = \frac{a_1(\chi - \delta)}{\beta - \alpha}e^{(\beta-\alpha)t} - \frac{a_1(\chi + \delta)}{\beta - \alpha}e^{-(\beta+\alpha)t} + a_1\left(\frac{2\beta\delta - \alpha\delta - \alpha\delta}{\beta^2 - \alpha^2}\right)$$

$$\alpha = k_1 + \frac{k_1k_2(k_2 + k_3 + k_4)}{k_3 - (k_2 + k_3 + k_4)^2} \qquad \chi = -\frac{k_1k_3k_4}{k_3^{\ 2} - (k_2 + k_3 + k_4)^2}$$

$$\beta = -\frac{k_1k_2k_3}{k_3 - (k_2 + k_3 + k_4)^2} \qquad \delta = \frac{k_1k_4(k_2 + k_3 + k_4)}{k_3^{\ 2} - (k_2 + k_3 + k_4)^2} \qquad (5)$$

The mechanism outlined in Scheme 1 can be readily analyzed by making the usual steady-state assumption for the concentration of intermediate **3** (eq 5) and by controlling the irradiation so that only **1** absorbs light ($\lambda > 390$ nm). The solution of the resulting differential equations leads to predictions of the time-dependent concentrations of the P and M enantiomers of **1** and **2** that are shown below (a_1 is one-half the starting concentrations of **1P**). The observable parameters in our experiment are the time dependence of the enantiomeric excess of **1** and **2**. Figure 6 shows a comparison of the experimental results with a simulation according to the mechanism in Scheme 1 and rate constants deduced from the chemical and spectroscopic experiments identified above. The fit is remarkably good, the time-dependence of the enantiomeric excess is reproduced, and this supports the conclusion that photoracemization of **1** occurs thermally through an intermediate quinone methide identified as **3** in Scheme 1.

Conclusion

In principle, the photochromism of **1** and **2** can be developed as an optical trigger to switch a liquid crystal between nematic and cholesteric forms based on the reversible photodestruction approach. In fact, this investigation of the spectroscopy and chemistry of this system shows that it is not well-suited for this application. The enantiomeric excess achievable at any reasonable conversion of **1** or **2** is inadequate. Analysis of the photochemistry of this system reveals the formation of an intermediate 1,1′-biaryl quinone methide (**3**) from irradiation of either **1** or **2**. The photochromic and photoracemization reactions proceed through the ground state of **3**. This is the first example of the photoracemization of a binaphthyl compound by direct irradiation that does not proceed through its triplet state. The chemical properties of **3** control the efficiency of the photochromism and photoracemization. Its predominant reaction under all conditions we examined is electrocyclization to form **1**. The thermal racemization of **3** and its reaction with H_2O are much slower than cyclization to form **1**, this, too, limits application of this system as an optical trigger.

Experimental Section

General. All solvents were dried before use by distillation from sodium. Reagents obtained from commercial sources were used without further purification, unless otherwise noted. Microscopic analyses were performed with a Fisher Micromaster polarizing microscope. The helical twisting power (β_{M}) was measured in K15 (BDH) with the "droplet" method.[45,46] Absorption spectra were recorded on a Varian Cary 1E UV−vis spectrophotometer. Steady-state fluorescence measurements were made on a Spex Fluorolog spectrometer. Circular dichroism spectra were acquired with a Jasco Model J-720 spectropolarimeter. HPLC separations and analyses were performed on a Hitachi system equipped with a diode array detector with a Regis analytical chiral (S, S) Whelk-O column (25 cm × 4.6 mm I. D.). GC/mass analysis was performed with a Hewlett-Packard G1800A GCD equipped with a electron ionization detector and an HP-5 column. Fluorescence lifetimes were measured on a PTI LS-1 spectrofluorimeter equipped with single photon electronics with a nitrogen flash lamp as the excitation source.

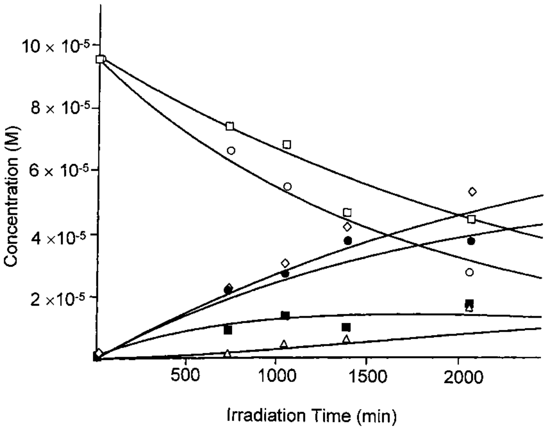

Figure 6. Plot of the observed concentrations of the reaction components (**1**M, ■; **1**P, ○; [**1**P + **1**M], □; **2**P, ●; **2**M, △; [**2**P + **2**M], ◇) and their predicted concentrations (lines) according to the reaction mechanism shown in Scheme 1.

Materials. The preparation of racemic **1** and **2** followed the literature procedure.[16−19] Their resolution into enantiomers was accomplished by HPLC. Samples of racemic **1** were injected in a hexane solution and eluted with hexane with a flow of 0.8 mL/min. Under these conditions, the retention times are (first eluted) **1** = 1200 s and (second eluted) **1** = 1520 s. Samples of racemic **2** were injected in a 3:1 hexane/CH_2Cl_2 solution and eluted with 98:2 hexane/2-propanol with a flow rate of 1 mL/min. Under these conditions, the retention times are (−)**2** = 1315 s and (+)**2** = 1420 s. Each enantiomer was collected and then re-injected under the same conditions to measure its optical purity.

Irradiation Conditions. Irradiations were performed at 11 °C with a high-pressure 1000 W Hg−Xe arc lamp. Sample solutions were prepared in 3.0 mL quartz cuvettes and normally purged with a stream of N_2 prior to irradiation. The solutions were stirred magnetically during the irradiation. The course of the reaction was monitored by GC/MS or by HPLC, as appropriate. For quantum yield measurements, a 365 nm interference filter was used to ensure that the actinometer (*trans*-azobenzene in MeOH)[47]and the samples absorbed measurable light doses. Quantum yields were determined at 5−10% conversion.

Fluorescence Measurements. Each sample was prepared in a 3.0 mL quartz fluorescence cuvette and purged with N_2 for 10 min prior to each measurement. The concentration of both sample solution and fluorescence standard (anthracene $\Phi_{\mathrm{fl}} = 0.3$ in cyclohexane) were adjusted to the same optical densities at 352 nm. The integrated areas under the emission curves were calculated.

Laser Flash Photolysis. Nanosecond laser flash photolysis was carried out by using a Q-switched Nd:YAG laser with 10 ns pulse width (355 nm third harmonic), at right angles to a pulsed 50 W Oriel QTH analyzing lamp. The rise time of the detection system (photomultiplier

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tube and digitizer) is 2.2 ns. The output of the laser is 50 mJ and the energy of the beam is in the range from 1 to 2 mJ. The detector output waveforms were processed by a Lecroy 93508 digitizer. The experimental solution (OD = 0.5 at 355 nm) was placed in rectangular quartz cells with a 1 cm path length and purged with N_2 prior to measurement. Fresh samples were prepared for each measurement.

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