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Chirochromism–Photochromism by Epimerization: Search for a Liquid Crystal Phototrigger

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Abstract: A new class of photochromic reactions was investigated as a possible trigger for phase transitions in liquid crystals. Chirochromic compounds have two chiral units. One unit is fixed, and the other can be switched with light. A series of diastereomeric compounds based on ketals and acetals of 1,1′-bi-2-naphthol was prepared. In some cases, the absorption spectra of the diastereomers are measurably different. The ketals do not undergo efficient photoepimerization, apparently because the activation barrier for atropisomerism in their triplet state has increased. However, certain of the acetal derivatives do photoepimerize and are chirochromic. These compounds may be developed into triggers.

Introduction

Light provides unique opportunities for the control of chemical reactions. Unlike most thermal processes, photochemical reactions may be initiated in specific micrometer-sized domains in a three-dimensional object. Since information can be encoded in light by intensity, wavelength, or polarization modulation, photochemical reactions provide a means for the storage and retrieval of data. In this function, the light-driven process often triggers a sequence of events that amplifies the effect of the photochemical reaction. The best known process of this kind is photography, where the development of an activated silver halide grain results in the 10 000-fold (or more) amplification of the photochemical trigger. Currently there is a great deal of interest in developing light-triggered bistable molecules for applications in data storage and computing.[1] In this regard, we have been searching for reversible photochemical reactions that can induce a physical change in a liquid crystalline host medium.[2]

Nematic liquid crystals can be converted to a cholesteric form by the introduction of a small amount of an optically active compound.[3] The cholesteric form has a helical pitch which can be sensed by its effect on plane-polarized light. The pitch length (p) is inversely proportional to the enantiomeric excess of the additive, its concentration (C), and its twisting power (β_M). It is well known that irradiation of certain racemic mixtures with circularly polarized light leads to their partial resolution.[4] The enantiomeric excess at the photostationary state ($[\gamma]_{PSS}$) that can be achieved in this process is determined by $\Delta\epsilon/\epsilon$, the difference in extinction coefficients of enantiomers with circularly polarized light divided by their average. For most organic compounds, $[\gamma]_{PSS}$ is too small to induce a measurable pitch (ca. 100 μm) in a nematic liquid crystal.[2]

Photochromism is defined as a photoinduced transformation of a molecular structure, photochemically or thermally reversible, that produces a spectral change.[5] Numerous photochromic systems have been discovered in which a ring-opening reaction, for example, extends π-electron conjugation so that the photoproduct absorbs at a longer wavelength than the starting compound.[6] Since, as a matter of principle, diastereomers must have different absorption spectra, photochromic reactions can be transformations between diastereomers.

Consider a pair of diastereomers (D_1 and D_2) that are formed from two chiral units: one unit that has fixed stereochemistry and a second whose stereochemistry can be switched photochemically. Further, in selection of these chiral groups, a switchable unit is chosen with a large β_M, and the fixed group is picked, in part, because it has a small β_M. In this circumstance, the pitch of a cholesteric liquid crystal host will be controlled primarily by the absolute configuration of the switchable unit. If D_1 absorbs with a greater extinction coefficient than D_2 at λ_1, then irradiation of the mixture of diastereomers at λ_1 will result in enrichment of D_2 and a change in the pitch of the liquid crystal. Similarly, if there is a wavelength (λ_2) at which the extinction coefficient of D_1 is equal to or less than that of D_2, irradiation at λ_2 will either restore the original mixture of diastereomers or result in the enrichment of D_1. The diastereomeric excess at the photostationary state $\{[de]_{pss}\}$ that results from irradiation of a mixture of diastereomers thus depends on λ, the extinction coefficients (ε), and the quantum yields for interconversion of the diastereomers (Φ_{12} and Φ_{21}) according to eq 1.

$$[de]_{pss} = [([D_1] - [D_2])/([D_1] + [D_2])] = [(\epsilon_2\Phi_{21} - \epsilon_1\Phi_{12})/(\epsilon_2\Phi_{21} + \epsilon_1\Phi_{12})]_\lambda \quad (1)$$

The control of $[de]_{pss}$ by irradiation at λ_1 and λ_2 generates a class of photochromic reactions that arise from switching the handedness of one chiral unit of a pair that we refer to as *chirochromism*. We report herein the preparation and analysis of a chirochromic system based on the light-triggered atropisomerism of a 1,1′-binaphthyl group.

Results and Discussion

Selection of Switchable and Fixed Chiral Units. The 1,1′-binaphthyl group was selected as the photoswitchable chiral unit

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

[1] (a) Feringa, B. L.; Jager, W. F.; De Lange, B.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5468. (b) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445. (c) Engler, E. M. *Adv. Mater.* **1990**, *2*, 166. (d) Feringa, B. L.; Jager, W. F.; De Lange, B. *Tetrahedron* **1993**, *49*, 8267.

[2] Zhang, M.; Schuster, G. B. *J. Phys. Chem.* **1992**, *96*, 3063. Lemieux, R. P.; Schuster, G. B. *J. Org. Chem.* **1993**, *58*, 100.

[3] Solladie, G.; Zimmerman, R. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348. Kreysig, D.; Stumpe, J. In *Selected Topics in Liquid Crystal Research*; Koswig, H. D., Ed.; Verlag: Berlin, 1990; p 69.

[4] Inoue, Y. *Chem. Rev.* **1992**, *92*, 741. Rau, H. *Chem. Rev.* **1983**, *83*, 535.

[5] *Handbook of Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 425.

[6] *Photochromism, Molecules and Systems*; Durr, H., Bouas-Laurent, B., Eds.; Elsevier: New York, 1990.

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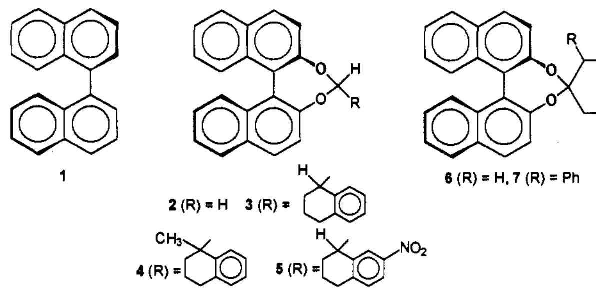
Chart 1



because of its unique properties. The photochemistry of the 1,1′-binaphthyl chromophore has been studied by us and others.[2,7] Irradiation of optically active 1,1′-binaphthyl itself (**1**, Chart 1) leads to racemization in its triplet excited state. For **2**, the quantum efficiency for racemization is very high ($\Phi_{rac} \approx 0.5$, its maximum theoretical value). Time-resolved spectroscopic analysis shows that the racemization of **2** results from rotation about the inter-ring bond in its triplet state. However, increasing the number of methylene groups in the acetal link of **2** causes a dramatic decrease in Φ_{rac}. This is attributed to an increase in the activation barrier for racemization. Apparently, additional methylene groups enlarge the inter-ring dihedral angle and lead to stabilization of the ground state. For this reason, we explored potential chirochromic systems derived from the single-methylene-bridged compound **2**.

The fixed chiral unit in the diastereomeric compounds was selected on the basis of its ability to perturb the absorption spectrum of the 1,1′-binaphthyl group. Since absorption spectra are sensitive to long-range π-electron interactions,[8] we sought to place a π-electron-containing group in the fixed chromophore at a different distance or orientation from the binaphthyl group in the two diastereomers. To enhance this effect, the conformations available to the second group should be restricted to avoid averaging of the spectra in solution. Consequently, the potential chirochromic systems selected for examination contain the second π-electron group either in a tetralin ring (**3**, **4**, and **5**) or as part of a spirocyclic system (**6** and **7**). Two series of compounds, ketals and acetals of 1,1′-bi-2-naphthol, were prepared in the attempt to discover chirochromic triggers for liquid crystals.

Chirochromic Compounds Based on Cyclic Ketals of 1,1′-Bi-2-naphthol. Ketal **6** was prepared in racemic form from 1,1′-bi-2-naphthol and cyclohexanone. Since this compound has only one chiral unit, it exists as enantiomers, and rotation about the inter-ring bond will cause racemization. The absorption (Figure 1) and, in particular, the fluorescence (Figure 2) spectra of **6** indicate some differences between it and **2**. The Φ_{Fl} of **6** is 0.34, which is significantly greater than that of **2** ($\Phi_{Fl} = 0.2$).[7] Further, while the absorption spectra of **2** and **6** are very similar, the fluorescence emission for **6** occurs at higher energy than for **2**. This observation is attributed to an increase in the rigidity of **6**. The absorption spectra indicate that **2** and **6** have similar inter-ring dihedral angles in the ground state, but inhibition of the rotation of **6** in the excited singlet state[9] increases Φ_{Fl} and shifts the fluorescence spectrum to higher energy. Molecular mechanics calculations[10] give inter-ring dihedral angles for **2** and **6** of 54°, which is consistent with the analysis of their absorption spectra.

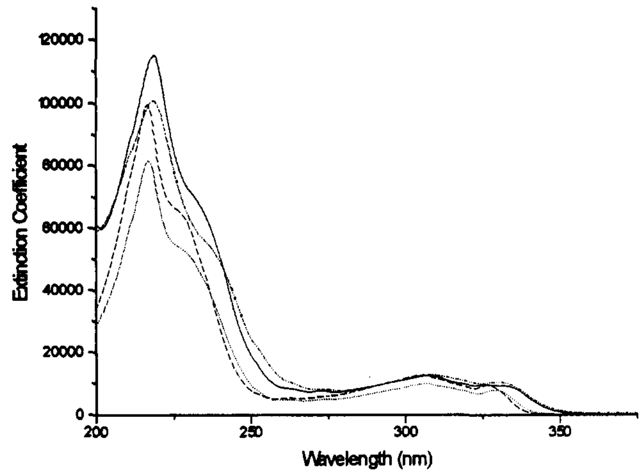


Figure 1. UV spectra of the binaphthyl derivatives in CH_3CN: **4** (—); **2** (– – –); **6** (···); and **7** (-···-).

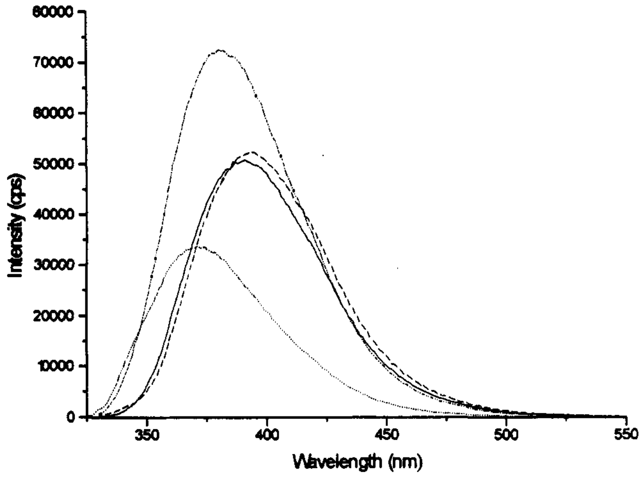


Figure 2. Fluorescence spectra of the binaphthyl derivatives in CH_3CN: **4** (—); **2** (– – –); **6** (···); and **7** (-···-).

Since photoracemization requires formation of the triplet state, the triplet yield and triplet lifetime of **6** were measured by time-resolved spectroscopy. Pulsed irradiation of a N_2-saturated CH_3CN solution of **6** (308 nm, 20 ns) gave a transient spectrum characteristic of the 1,1′-binaphthyl chromophore[11] with a maximum at 650 nm and a half-life of ca. 3.4 μs. The triplet yield of **6** is estimated to be 65% based upon comparison with the triplet–triplet absorption spectrum of **2** and the assumption that **2** and **6** have the same extinction coefficients. These experiments seemed to indicate that photoracemization of **6** would be nearly as efficient as it is for **2**. However, investigation of **7** caused us to question this conclusion, and optically active **6** was prepared from (*R*)-1,1′-bi-2-naphthol to address this matter directly. Irradiation of (–)-**6** in a N_2-purged THF solution (300 nm, Rayonet Photoreactor) did not lead to racemization. The Φ_{rac} for (–)-**6** was estimated to be at least 100 times smaller than that for **2**.

The reaction of (±)-1,1′-bi-2-naphthol and 2-phenylcyclohexanone was expected to give **7** as a mixture of diastereomers [(*RR*,*SS*) and (*RS*,*SR*)]. However, analysis of the product of this reaction by ^1H and ^{13}C NMR spectroscopy reveals formation of only one diastereomer. The absorption spectrum of **7** (Figure 1) shows evidence of the desired π-electron interaction between the phenyl ring of the fixed chiral group and the binaphthyl chromophore. In particular, the absorption edge of **7** is shifted to lower energy by ca. 15 nm (1000 cm^{-1}) compared with **2**. Similarly, comparison of the fluorescence spectra of **6** and **7** also

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(7) Irie, M.; Yoshida, K.; Hayashi, K. *J. Phys. Chem.* **1977**, *81*, 969. Yorzozu, T.; Yoshida, K.; Hayashi, K.; Irie, M. *J. Phys. Chem.* **1981**, *85*, 459. Schippers, P. H.; Dekkers, H. P. J. M. *Tetrahedron* **1982**, *38*, 2089. Tetreau, C.; Lavalette, D.; Cabaret, D.; Geraghty, N.; Welvart, Z. *Nouv. J. Chim.* **1982**, *6*, 461.

(8) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.

(9) Post, M. F. M.; Langelaar, J.; Van Voorst, J. D. W. *Chem. Phys. Lett.* **1975**, *32*, 59.

(10) The molecular mechanics calculations were performed with the PCMODEL program supplied by Serena Software, Bloomington, IN. The structures were optimized with a full SCF π-electron calculation using the MMX force field.

(11) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

reveals that interaction with the phenyl group in **7** induces a shift of the singlet state to lower energy. This is precisely the desired effect. If irradiation of **7** (a racemate) caused atropisomerization by rotation about the inter-ring bond in the excited state, then one diastereomer would become two. Unfortunately, just as in the case of (−)-**6**, it did not.

The effect of structure on the efficiency of these reactions may be understood by examination of their transition states. The racemization of **6** and the epimerization of **7** require that the two naphthyl rings become approximately coplanar at the transition-state geometry. In order to accommodate the 8 and 8′ hydrogen atoms at this geometry, the inter-ring bond angle (ring junction, C_1, C_1') must increase. This motion causes a concomitant decrease in the O_1CO_2 angle of the ketal or acetal. Evidently, the bending force constant of the OCO bond is greater for the ketal function of **6** and **7** than it is for the acetal function of **2**. This may be understood in part as a consequence of an increase in the steric strain of the other substituents on the ketal carbon atom and a concomitant reduction in the O_1CO_2 bond angle that stabilizes the ground state and in part as a manifestation of the anomeric effect,[12] where the synclinal orientation of the lone pair electrons of the oxygen atoms with the carbon–carbon (hydrogen) bond of the ketal (acetal) in the ground state takes on a more nearly planar orientation in the transition state. Since the atropisomerization of the binaphthyl group must occur within the short lifetime of the triplet state, an increase in the activation energy of only 2 kcal/mol will decrease the efficiency of this reaction ca. 30-fold. On the basis of these findings, we abandoned the search for a chirochromic compound based upon the cyclic ketals of 1,1′-bi-2-naphthol.

Chirochromic Compounds Based on Acetals of 1,1′-Bi-2-Naphthol. The mixture of diastereomeric acetals (**4**) formed from reaction of 1,1′-bi-2-naphthol with tetralin-1-carboxaldehye was separated by HPLC on a C_{18} column with a methanol–water mixture as eluent. The absorption spectra of the diastereomeric mixture is shown in Figure 1 and the fluorescence spectra in Figure 2. Just as for **7**, the low-energy absorption of **4** is shifted to longer wavelength than the comparable absorption of **2**. However, comparison of the absorption spectra of the diastereomers of **4** {(*RR,SS*) with (*RS,SR*)} shows them to be nearly identical. Evidently, the interaction between the binaphthyl chromophore and the phenyl group of **4** is similar in the two diastereomers.

Insight into the conformations of the two diastereomers of **4** comes from analysis of their ^{1}H NMR spectra. The chemical shift of the hydrogen atom on the acetal carbon of these two compounds is nearly the same ($\Delta\delta = 0.011$ ppm). In contrast, the chemical shifts of the methyl groups of the two diastereomers are significantly different ($\Delta\delta = 0.14$ ppm). For comparison, we prepared the acetal of 1,1′-bi-2-naphthol (**3**), which is related to **4** but lacking the methyl group. The hydrogen atoms on the acetal diastereomers of this compound have a much greater chemical shift difference ($\Delta\delta = 0.17$ ppm) than do the hydrogen atoms of **4**. Molecular mechanics calculations help to explain the results of the ^{1}H NMR experiments and the similarity of the absorption spectra of the two diastereomers of **4**.

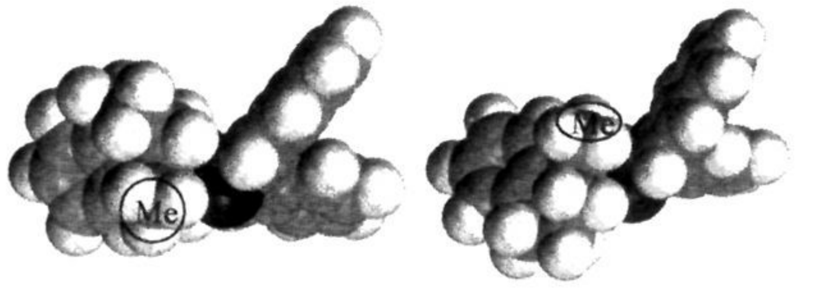

Figure 3. Lowest energy conformations for the diastereomers of **4** predicted from molecular mechanics calculations.[10] Left, diastereomers **A**; right, diastereomer **B**.

Figure 3 shows the lowest energy conformations predicted for the diastereomers of **4**. These structures are consistent with the ^{1}H NMR spectra of these two compounds. Inspection of the calculated structures reveals that for diastereomer A, the methyl group points away from the binaphthyl groups and, therefore, should be relatively unaffected by their π-electron ring currents. In contrast, the methyl group of diastereomer **B** is predicted to be close to the π-face of a naphthyl group, and, consequently, its NMR resonance should be shifted upfield. The acetal hydrogen atoms of both diastereomers of **4** have very similar orientations with respect to the π-electron systems, and thus they should have similar chemical shifts. The good agreement between the molecular mechanics calculations and the NMR spectra for the diastereomers of **4** supports the validity of the computational results.

The molecular mechanics calculations also provide some insight into the spatial relationships between the binaphthyl groups and the phenyl group of **4**. In both diastereomers, the phenyl group adopts a similar orientation with respect to the naphthyl groups. Consequently, any difference between the absorption spectra of the two diastereomers is expected to be small, and we observe none.

In contrast to the results for **4**, molecular mechanics calculations indicate that the spatial relationships between the binaphthyl group and the phenyl group are quite different for the diastereomers of compound **3**, which lacks the methyl group of **4**. Evidently, for **4**, the lowest energy rotamer is determined by a balance of interactions between the methyl and the ring methylene groups with the hydrogen atom bound to the acetal carbon atom. For this reason, we selected acetals for further investigation that have a hydrogen atom on the aldehyde-derived chiral unit. Further, to enhance the π-electron interaction between the two chiral groups, it was decided to make the aldehyde-derived center electron deficient since the binaphthyl center is electron rich.

The synthesis of the nitrophenyl-containing acetal **5** from 1,1′-bi-2-naphthol and the nitroaldehyde proceeds in painfully low yield to give a mixture of diastereomers that can be separated by HPLC on a C_{18} column. The absorption spectra of the two diastereomers and their difference spectrum in the region from 315 to 400 nm are shown in Figure 4. Clearly, the absorption spectra of the diastereomers of **5** are different from that of the simple acetal **2** and are significantly different from each other. The quantity $(\Delta\epsilon/\epsilon)_\lambda$ serves as a measure of the difference in absorption spectra. If $\Phi_{12} = \Phi_{21}$, then $(\Delta\epsilon/2\epsilon)$ gives $[\mathrm{de}]_{\mathrm{pss}}$ (see eq 1), and this quantity is the upper limit to the diastereomeric excess that can be achieved by selective irradiation of the mixture. At this limit, irradiation of **5** at 335 nm would give a $[\mathrm{de}]_{\mathrm{pss}} \approx 0.14$, and irradiation at 325 nm would give a $[\mathrm{de}]_{\mathrm{pss}} \approx 0.0$. Since β_M is large for the binaphthyl group,[13] a change in composition of this magnitude would produce an easily detected change in pitch of a liquid crystalline host.

The differences in absorption spectra of the diastereomers of **5** are attributed to their existence in different conformations that modulate the electronic interaction between the binaphthyl and nitrophenyl chromophoric groups. Molecular mechanics calculations predict that one diastereomer of **5** will adopt a "V"-shape and the other a "T"-shape. These structures are shown in Figure 5. Experimental support for this result comes from analysis of their ^{1}H NMR spectra. The coupling constant of the proton on the acetal carbon atom with its vicinal proton (J_{HH}) is sensitive to the dihedral angle along the carbon–carbon bond (Θ_D) according

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(12) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: New York, 1983.

(13) Buckingham, A. D.; Ceasar, G. P.; Dunn, M. B. *Chem. Phys. Lett.* **1969**, *3*, 540. Solladie, G.; Ruxer, J. M. *Mol. Cryst. Liq. Cryst.* **1978**, *41*, 109. Gottarelli, G.; Samori, B.; Stremmenos, C.; Torre, G. *Tetrahedron* **1981**, *37*, 395. Solladie, G.; Zimmermann, R. G. *Angew. Chem., Int. Ed. Engl* **1984**, *23*, 348. Gottarelli, G.; Hibert, M.; Samori, B.; Solladie, G.; Spada, G. P.; Zimmerman, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318. Gottarelli, G.; Spada, G. P. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 377.

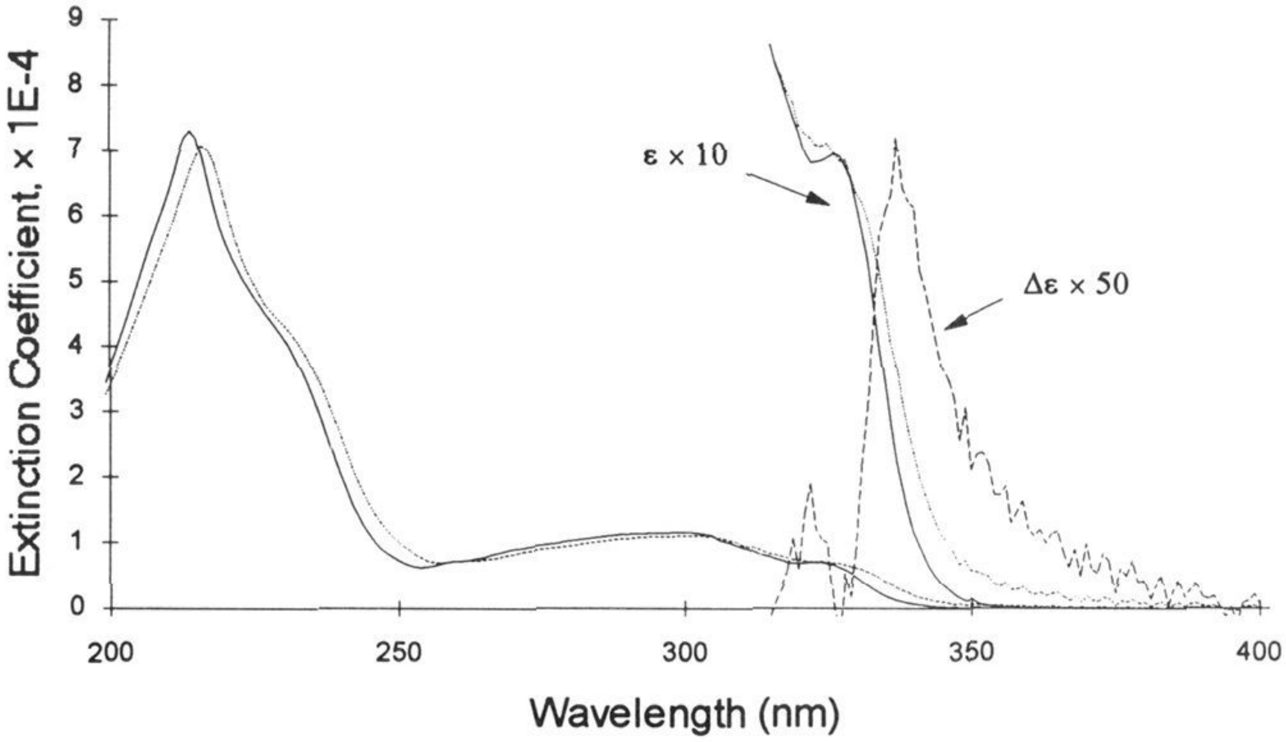

Figure 4. Absorption spectra of the diastereomers of **5** recorded in CH_3CN solution. The solid line is for the T-shaped diastereomer, and the dotted line is for the V-shaped diastereomer. The difference spectrum ($\Delta\epsilon$, dashed line) for the two diastereomers is also shown.

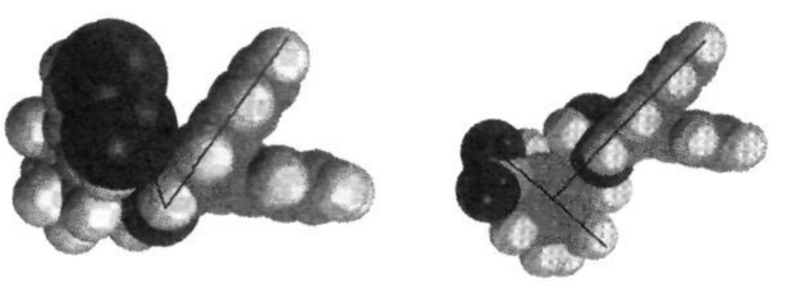

Figure 5. The minimum energy structures for the two diastereomers of **5** predicted from molecular mechanics calculations.[10] Left, V-shaped diastereomer; right, T-shaped diastereomer.

to the Karplus relationship.[14] Experimentally, the two diastereomers of **5** have J_{HH} equal to 4.06 and 8.43 Hz in CD_3CN solution. For the V-shaped diastereomer, the molecular mechanics calculation predicts that $\Theta_D = 70°$, and for the T-shaped diastereomer, Θ_D is predicted to be 43°. These values are consistent with the observed coupling constants and permit us to assign the V-shape to the diastereomer of **5** with the enhanced low-energy absorption spectrum.

The diastereomers of **5** are interconverted when they are irradiated in a N_2-saturated acetonitrile solution. The V-shaped and T-shaped diastereomers were irradiated separately at 313 nm, and the ratio of the diastereomers was determined by HPLC and by ^1H NMR spectroscopy. Both diastereomers produce the same mixture at the photostationary state with $[de]_{pss} = 0.2$ (enriched in the T-shaped diastereomer). Critically, $[de]_{pss}$ is controlled by the wavelength of the irradiating light. When the mixture of diastereomers is irradiated in a Rayonet Photoreactor equipped with 300-nm lamps, $[de]_{pss} = 0.20$, and when 350-nm lamps are used, $[de]_{pss} = 0.26$.[15] The mixture of diastereomers can be switched between these values by irradiating alternatively with the different lamps with no measurable consumption of either diastereomer. It is clear that the diastereomers of **5** are chirochromic when irradiated with UV light.

Analysis of eq 1 shows that $[de]_{pss}$ is determined by both the difference in absorption spectra for the two diastereomers and the quantum yields for their interconversion. We estimated the quantum yields for interconversion of the diastereomers (Φ_{TV} and Φ_{VT}) by analyzing the rate of approach to the photostationary state according to the usual kinetic model, eq 2 (starting with the T-shaped diastereomer and with the requirement that ϵ_T and ϵ_V are approximately equal at the selected irradiating wavelength).

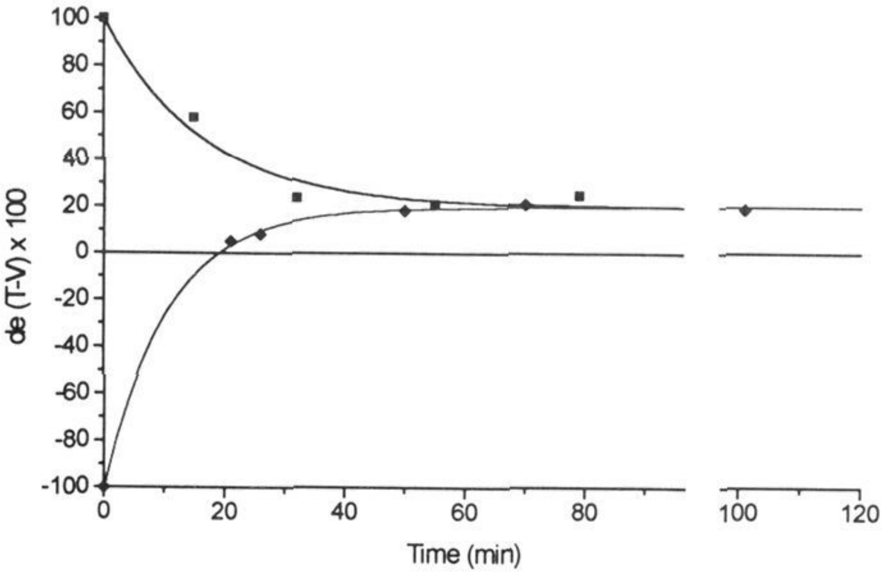

Figure 6. Plot of the diastereomeric excess (T-shaped minus V-shaped) for **5** irradiated at 313 nm in a N_2-saturated CH_3CN solution. The lower curve is for an experiment starting with pure V-shaped diastereomer, and the upper curve is for pure T-shaped diastereomer.

$$[V]/[T] = \frac{\Phi_{TV}\{1 - \exp[-(\Phi_{TV} + \Phi_{VT})t\epsilon_T]\}}{\Phi_{VT} + \Phi_{TV}\exp[-(\Phi_{TV} + \Phi_{VT})t\epsilon_V]} \qquad (2)$$

The data are shown in Figure 6, and least-squares analysis gives the quantum yields of photoepimerization: $\Phi_{TV} = 0.011 \pm 0.005$ and $\Phi_{VT} = 0.017 \pm 0.005$. Unhappily, both quantum yields are nearly 50 times lower than that for the photoracemization of **2**.

The low quantum efficiencies for photoepimerization of the diastereomers of **5** might be due either to inefficient formation of their triplet states or to inefficient atropisomerization from this state. We carried out a series of experiments to investigate these possibilities. Not surprisingly, the Φ_{Fl} of **5** is more than 300 times lower than it is for **2**. Most nitro-substituted aromatic hydrocarbons show weak fluorescence because of an enhanced intersystem crossing rate constant.[16] However, time-resolved absorption spectra indicate that the triplet yield of **5** is much reduced from that of **2**. Laser flash photolysis of an acetonitrile solution of **5** (308 nm, 20 ns) gives a triplet–triplet absorption spectrum with a maximum at 650 nm characteristic of the binaphthyl chromophore. Comparison of the spectrum of **5** with that of **2** under the same conditions, and with the assumption that the triplets have the same extinction coefficients, reveals that the

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[14] Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1987.

[15] The lamps in the Rayonet are spectrally broad, the nominal wavelength is the maximum, and the output is ca. 50 nm wide.

[16] Ermolaev, V. L. *Sov. Phys. Usp.* **1963**, *80*, 333.

yield of triplet 5 is 0.17 for the V-shaped diastereomer and 0.10 for the T-shaped compound. Consequently, the low quantum efficiencies for photoepimerization of 5 are due in part to their reduced intersystem crossing efficiency and in part to a decrease in efficiency for atropisomerization in the triplet state.

The efficiency of intersystem crossing in substituted aromatic hydrocarbons is determined by competition between the rates of processes that originate from the excited singlet state. In most cases, the singlet state is deactivated by chemical reaction, fluorescence, internal conversion, and intersystem crossing. For 1,1′-binaphthyl itself, the primary deactivation route for the singlet state is fluorescence ($\Phi_{Fl} = 0.77$),[17] and intersystem crossing is ca. 20% efficient. For **2**, the intersystem crossing efficiency increases to ca. 80%. For **5**, however, both Φ_{Fl} and the yield of triplet are low. This result appears to be a consequence of a change in the electronic nature of the lowest excited singlet from a $\pi\pi^*$ state localized mainly on the binaphthyl chromophore to a charge-transfer state involving the nitrophenyl group. Ironically, this compound was prepared because we anticipated that the charge-transfer states of its diastereomers would have different absorption spectra. This hope was realized, but the internal conversion rate of this singlet state was accelerated relative to the intersystem crossing rate and, consequently, the yield of the triplets plummet.

Conclusions

In this work we sought to discover chirochromic triggers for liquid crystal phase transitions. In the current approach, a binaphthyl group is selected as the photoresponsive chromophore, and the fixed chromophore is incorporated as either a ketal or an acetal. The results reveal that the efficiency for atropisomerization of 1,1′-binaphthyl derivatives is a very sensitive function of their structure. Two factors appear to be critical for the determination of the efficiency of this process. The first is the yield of the triplet state. The attempt to assure a measurable difference between the absorption spectra of the two diastereomers led us to investigate compounds with low-energy charge-transfer states. This attempt was partially successful: the diastereomers of **5** have significantly different absorption spectra. Unfortunately, internal conversion of the charge-transfer state is accelerated, and there is a very large decrease in the triplet yield of **5**. The second factor that controls the efficiency of atropisomerization of the binaphthyl group is, of course, the activation energy for this process. However, since this reaction must occur from a relatively short-lived excited state, it is very sensitive to this quantity, and small changes have a dramatic effect on the efficiency of atropisomerism. Surprisingly, simply changing the structure from an acetal to a ketal greatly reduces the efficiency of this reaction.

None of the compounds we have described is a fully suitable chirochromic trigger for liquid crystal phase transitions because of difficulty in synthesis and the low quantum yields for photoepimerization. Currently we are investigating photoswitchable groups that may be less sensitive to details of structure.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a GE QE-300 spectrometer in $CDCl_3$ solution unless otherwise indicated. The chemical shifts are referenced to TMS, and coupling constants are reported in hertz. UV-vis spectra were recorded on a Cary 1E UV-visible spectrophotometer in acetonitrile solution unless otherwise noted. Fluorescence spectra were recorded on a Spex 1681 0.22 m spectrometer. The transient absorption spectra and the triplet lifetimes were obtained in a N_2-purged acetonitrile solution with excitation at 308 nm; the apparatus has been described elsewhere.[18] High-performance liquid chromatography (HPLC) was carried out on an IBM LC/9560 ternary gradient liquid chromatograph coupled with a Perkin-Elmer LC-75 spectrophotometric detector and a Hewlett-Packard 3390A integrator with a reverse-phase C_{18} analytical column (250-mm × 4.6-mm i.d.). GC–MS analyses were performed at 70 eV with a 0.25-mm × 12-m HP capillary column on a Hewlett-Packard 5890 GC and HP-5970 mass selective detector. Low-resolution EI mass spectra were obtained on a Varian-MAT CH-5 mass spectrometer; peaks are listed as m/z (percent intensity relative to the base peak). Elemental analyses were performed at the University of Illinois Microanalytical Service Laboratory. Melting points were measured on either a Büchi or a Nalge apparatus and are uncorrected.

Materials. All solvents and reagents were obtained from commerical sources and used as received, unless otherwise specified. Benzene, diethyl ether, and THF were distilled from Na/benzophenone under N_2 before use. The following compounds were prepared according to literature procedures: (±)-and (*R*)-(−)-binaphthyl acetal **2**,[19] diethyl isocyanomethanephosphonate,[20] and 1,2,3,4-tetrahydro-1-naphthalenecarboxaldehyde.[21] 1,2,3,4-Tetrahydro-1-methyl-1-naphthalenecarboxaldehyde was prepared by methylation of 1,2,3,4-tetrahydro-1-naphthalenecarboxaldehyde with iodomethane in THF.[22] 2-Phenylcyclohexanone was prepared by oxidation[23] of 2-phenyl-1-cyclohexanol, which was obtained from hydroboration–oxidation[24] of 1-phenylcyclohexene.

2,2′-Bis(trimethylsiloxy)-1,1′-binaphthyl (8).[25] To a 100-mL 3-necked round-bottomed flask containing dry THF (40 mL) were added (±)-1,1′-bi-2-naphthol (2.9 g, 10 mmol), $Me_3SiNHSiMe_3$ (4.6 mL, 22 mmol), and TMSOTf (20 μL, 1 mol %) under N_2 at 0 °C. The reaction mixture was stirred for 1 h, after which ^{1}H NMR spectroscopy showed complete reaction. The solvent was removed, and the residue was purified by column chromatography on silica gel with benzene as the eluent to afford 3.7 g of pure **8** as an oil (86%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.124 (s, 18H), 7.16–7.34 (m, 8H), 7.84 (dd, J_1 = 8.00 Hz, J_2 = 2.43 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.30, 121.35, 122.39, 123.38, 125.89, 127.74, 128.73, 129.31, 134.35, 151.22; GCMS m/z (relative intensity), 430 (M^+, 100), 431 (M + 1, 40), 73 (75).

1,2,3,4-Tetrahydro-1-naphthalenecarboxaldehyde 1,1′-Bi-2-naphthyl Acetal (3).[26] To dry CH_2Cl_2 (4 mL) was added a catalytic amount of TMSOTf (8 μL, 1 mol %) under N_2. Siloxy derivative **8** (1.5 g, 3.5 mmol) was added to the flask via syringe, followed by injection of 1,2,3,4-tetrahydro-1-naphthalenecarboxaldehyde (480 mg, 3 mmol). The mixture was stirred at room temperature for 48 h. ^{1}H NMR spectral analysis showed formation of the diastereomers **3**. The reaction was quenched by addition of a few drops of dry pyridine, and then it was poured into 20 mL of saturated aqueous sodium bicarbonate solution. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layer was dried over $MgSO_4$ and concentrated to yield crude product. The product was purified by chromatography on silica gel eluted with benzene: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.80–2.00 (m), 2.61 (m), 2.86 (m), 3.28 (m), 3.44 (m), 5.79 (d, J = 8.54 Hz), 5.95 (d, J = 5.81 Hz), 7.33 (m), 7.94 (m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.40, 20.59, 24.62, 24.78, 29.47, 29.65, 41.37, 42.23, 115.01, 116.52, 120.72, 120.97, 122.83, 124.81, 124.90, 124.94, 124.99, 125.58, 125.79, 125.83, 125.93, 125.96, 126.22, 126.23, 126.39, 126.52, 126.94, 126.99, 127.04, 128.20, 128.28, 128.36, 128.91, 129.23, 129.25, 129.28, 129.36, 126.62, 130.11, 130.29, 131.15, 131.35, 131.78, 131.80, 132.09, 132.18, 132.22, 132.29, 134.72, 135.84, 137.69, 138.29, 144.49, 149.90, 152.44, 152.47; MS (70 eV, EI) m/z (relative intensity), 428 (M^+, 64.9), 429 (M + 1, 23.7), 297 (100), 286 (90.1); HRMS calcd. for $C_{31}H_{24}O_2$ 428.1776, found 428.1775. A completely acceptable elemental analysis was not obtained. Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65. Found: C, 85.84; H, 5.53.

1,2,3,4-Tetrahydro-1-methyl-1-naphthalenecarboxaldehyde 1,1′-Bi-2-naphthyl Acetal (4). A mixture of (±)-1,1′-bi-2-naphthol (319 mg, 1.1 mmol), 1,2,3,4-tetrahydro-1-methyl-1-naphthalenecarboxaldehyde (174

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[17] Berlman, I. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: London, 1965.

[18] Zhu, Y.; Koefod, R. S.; Devadoss, C.; Shapley, J.; Schuster, G. B. *Inorg. Chem.* **1992**, *31*, 3505.

[19] Simpson, J. E.; Daub, G. H.; Hayes, F. N. *J. Org. Chem.* **1973**, *38*, 1771.

[20] Schöllkopf, U.; Schröder, R.; Stafforst, D. *Liebigs Ann. Chem.* **1974**, 44. Rachon, J.; Schöllkopf, U.; Wintel, T. *Liebigs Ann. Chem.* **1981**, 709.

[21] Moskal, J.; Leusen, M. v. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 137.

[22] Behnken, P. E.; Belmont, J. A.; Busby, D. C.; Delaney, M. S.; King, R. E., III; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3011.

[23] Brown, H. C.; Garg, C. P.; Liu, K.-T. *J. Org. Chem.* **1971**, *36*, 387.

[24] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses Via Boranes*; Wiley-Interscience: New York, 1975.

[25] Harada, T.; Wada, T.; Oku, A. *J. Org. Chem.* **1989**, *54*, 2599.

[26] Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357.

mg, 1 mmol), and a catalytic amount of *p*-toluenesulfonic acid and *p*-toluenesulfonyl chloride in dry benzene (5 mL) was heated at reflux for 20 h under N_2 with a Dean–Stark trap to remove the water formed by the reaction. After being cooled to room temperature, the reaction mixture was poured into dilute aqueous KOH solution (5 mL), the organic layer was separated, and the aqueous layer was extracted with benzene (3 × 5 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. Removal of the solvent yielded crude product, which was purified by chromatography on silica gel with benzene as the eluent and further purified by preparative TLC on silica gel with a benzene–cyclohexane (1:2, v/v) mixture as the eluent to yield 45 mg of the diastereomeric mixture of **4** (white solid) (10%): mp 104–114 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (s), 1.56 (s), 1.74 (m), 1.89 (m), 2.20 (m), 2.75 (m), 2.85 (m), 5.90 (s), 5.91 (s), 7.00–7.40 (m), 7.58 (m), 7.90 (m); MS (70 eV, EI) *m/z* (relative intensity) 442 (M$^+$, 32.8), 443 (M + 1, 11.4), 297 (100), 286 (38.6), 268 (11.0), 239 (16.5), 145 (28.4), 129 (15.7). Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92. Found: C, 86.72; H, 6.24.

3,4-Dihydro-7-nitro-1(2*H*)-naphthalenone (9). A mixture of α-tetralone (3.4 g, 23 mmol) and concentrated H_2SO_4 (7.2 mL) was cooled to −15 °C in an ice–salt bath with vigorous mechanical stirring. To this solution was added carefully over a period of 30 min a precooled mixture of concentrated HNO_3 (1.8 mL) and H_2SO_4 (2.8 mL). Efficient stirring and cooling are essential to avoid side reactions. After addition was complete, the mixture was stirred for 15 min below 0 °C and then poured onto a mixture of ice (40 g) and water (40 mL). The brownish precipitate that formed was collected by filtration. It contained both **9** and its isomer, 3,4-dihydro-5-nitro-1(2*H*)-naphthalenone, in a ratio of 2:1. Recrystallization from a 1:1 mixture of ethanol and water yielded 2.4 g of pure **9** (55%): mp 104–106 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (m, 2H), 2.73 (t, J = 6.53 Hz, 2H), 3.08 (t, J = 6.07 Hz, 2H), 7.46 (d, J = 8.47 Hz, 1H), 8.29 (dd, J_1 = 8.44 Hz, J_2 = 2.45 Hz, 1H), 8.84 (d, J = 2.37 Hz, 1H); GC–MS *m/z* (relative intensity), 191 (M$^+$, 64), 176 (16), 163 (100), 135 (27), 115 (34). Anal. Calcd for $C_{10}H_9NO_2$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.86; H, 4.72; N, 7.29.

The mother liquor was concentrated and purified by chromatography on silica gel with benzene as the eluent to afford pure 3,4-dihydro-5-nitro-1(2*H*)-naphthalenone (yellow solid): mp 98–100 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.17 (m, 2H), 2.72 (t, J = 6.62 Hz, 2H), 3.21 (t, J = 6.12 Hz, 2H), 7.48 (t, J = 7.92 Hz, 1H), 8.09 (dd, J_1 = 8.05 Hz, J_2 = 0.93 Hz, 1H), 8.34 (dd, J_1 = 8.00 Hz, J_2 = 0.83 Hz, 1H); GC–MS *m/z* (relative intensity) 191 (M$^+$, 44), 174 (60), 115 (100), 105 (35). Anal. Calcd for $C_{10}H_9NO_2$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.85; H, 4.72; N, 7.30.

1,2,3,4-Tetrahydro-7-nitro-1-naphthalenecarboxaldehyde (10).[21] A mechanically stirred solution of diethyl isocyanomethanephosphonate (3.5 g, 20 mmol) in dry diethyl ether (56 mL) was treated carefully with *n*-butyllithium (1.6 M in hexane from Aldrich) (13.6 mL, 21.6 mmol) under N_2 at −60 °C. Ketone **9** (3.2 g, 17 mmol) dissolved in dry diethyl ether (44 mL) was added dropwise to the resulting mixture. When the addition was complete, the reaction mixture was warmed to −10 °C and stirred at that temperature for 2 h, and then concentrated hydrochloric acid (32 mL, 36.5% by weight) was carefully added. The resulting mixture was stirred vigorously at room temperature for 10 h and extracted with diethyl ether (3 × 50 mL), and the combined ether layer was washed with water, dried over $MgSO_4$, and concentrated to yield crude product. The crude product was purified by chromatography on silica gel with benzene as the eluent to give 0.9 g of **10** (26%): mp 78–80 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.75 (m, 1H), 1.95 (m, 2H), 2.38 (m, 1H); 2.85 (m, 2H), 3.75 (m, 1H), 7.30 (m, 1H), 8.05 (m, 2H), 9.75 (s, 1H); GC–MS *m/z* (relative intensity), 205 (M$^+$, 7), 176 (100), 130 (71), 115 (35). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.32; H, 5.35; N, 6.86.

1,2,3,4-Tetrahydro-7-nitro-1-naphthalenecarboxaldehyde 1,1′-Bi-2-naphthyl Acetal (5). A mixture of (±)-1,1′-bi-2-naphthol (286 mg, 1 mmol), the aldehyde **10** (205 mg, 1 mmol), and a catalytic amount of *p*-toluenesulfonic acid and *p*-toluenesulfonyl chloride in dry benzene (5 mL) was heated at reflux for 24 h under N_2 with a Dean–Stark trap to remove the water. After being cooled to room temperature, the reaction mixture was poured into dilute aqueous KOH solution (5 mL), the organic layer was separated, and the aqueous layer was extracted with benzene (3 × 5 mL). The combined organic layer was washed with brine and dried over $MgSO_4$, and the solvent was removed. Purification by chromatography on silica gel with benzene gave a yellow oil containing two compounds separated by TLC (silica gel with benzene/hexane, 1:2 v/v) to yield 39 mg of the desired acetal as a mixture of diastereomers (8%): MS (70 eV, EI) *m/z* (relative intensity) 473 (M$^+$, 56.4), 297 (100). Anal. Calcd for $C_{31}H_{23}NO_4$: C, 78.63; H, 4.90; N, 2.96. Found: C, 78.64; H, 4.86; N, 2.93. The two diastereomers are predicted to have V-shape and T-shape, respectively, by PCMODEL calculations (see text). ^{1}H NMR data for the V-shaped diastereomer: (acetonitrile-d_3, 300 MHz) 2.07 (m, 3H), 2.85–3.03 (m, 3H), 3.55 (m, 1H), 6.01 (d, J = 4.06 Hz, 1H), 7.06 (d, J = 8.82 Hz, 1H), 7.27–7.51 (m, 8H), 7.70 (d, J = 8.83 Hz, 1H), 7.86 (m, 2H), 8.02 (d, J = 8.38 Hz, 1H), 8.09 (d, J = 8.75 Hz, 1H), 8.38 (d, J = 2.18 Hz, 1H). T-shaped diastereomer: (acetonitrile-d_3, 300 MHz) δ 2.00 (m, 2H), 2.53 (m, 1H), 2.96 (m, 3H), 3.36 (m, 1H), 5.85 (d, J = 8.43 Hz, 1H), 7.21 (d, J = 8.73 Hz, 1H) 7.30–7.59 (m, 8H), 7.80–8.11 (m, 6H).

Cyclohexanone 1,1′-Bi-2-naphthyl Ketal (6). The procedure described for **4** was applied with (±)-1,1′-bi-2-naphthol (286.3 mg, 1 mmol) and cyclohexanone (207.3 mL, 2 mmol) to give 86 mg of ketal **6**: mp 209–211 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60–1.87 (m, 10H), 7.30–7.51 (m, 8H), 7.92 (d, J = 8.52 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.25, 25.51, 34.50, 117.57, 123.15, 124.76, 125.79, 125.96, 127.12, 128.36, 129.23, 131.47, 132.37, 150.29; MS (70 eV, EI) *m/z* (relative intensity) 366 (M$^+$, 97.4), 367 (M + 1, 27.8), 286 (100), 268 (31.6), 239 (33.9). Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.50; H, 6.33.

2-Phenylcyclohexanone 1,1′-Bi-2-naphthyl Ketal (7). The same procedure as described for acetal **4** was used with (±)-1,1′-bi–2–naphthol (600 mg, 2.1 mmol) and 2-phenylcyclohexanone (400 mg, 2.3 mmol) to afford 100 mg of pure ketal **7** as a single diastereomer: mp 212–214 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (m, 4H), 2.09 (m, 4H), 3.18 (dd, J_1 = 11.15 Hz, J_2 = 3.35 Hz, 1H), 6.79 (m, 3H), 7.19–7.65 (m, 12H), 7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.56, 25.43, 34.15, 35.11, 54.51, 119.02, 122.82, 123.74, 124.06, 124.79, 125.07, 125.68, 125.78, 126.22, 126.67, 127.25, 127.33, 127.79, 128.12, 128.19, 129.06, 129.73, 130.48, 131.42, 131.68, 132.49, 141.85, 149.76, 151.64; MS (70 eV, EI) *m/z* (relative intensity) 442 (M$^+$, 100), 443 (M + 1, 33.4), 286 (40.1), 91 (47.9). Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92; Found: C, 87.17; H, 6.15.

Separation of the Diastereomers of 5. The V-shaped and T-shaped diastereomers of **5** were separated on a C_{18} analytical column with an acetonitrile–water mixture (82/18, v/v) as the mobile phase. The V-shaped diastereomer eluted first. The purity of each diastereomer was determined by reinjecting enriched samples in the HPLC.

Photoepimerization of the Diastereomers of 5. The photoepimerization of **5** was studied by ^{1}H NMR spectroscopy and by HPLC. Each diastereomer in a N_2-purged CD_3CN solution was irradiated at 300 nm in a Rayonet photoreactor. The reaction was monitored by ^{1}H NMR spectroscopy. The only photoproduct detected was the opposite diastereomer. A stirred, N_2-saturated acetonitrile solution (2 mL) of the V-shaped diastereomer was irradiated in a square quartz cell at 313 nm (isolated with a band-pass filter) with a 1-kW Hg (Xe) lamp. Analysis by HPLC (C_{18} column) at 239 nm (V- and T-shaped diastereomers absorbed equally) gave the diastereomeric excess directly. A similar experiment was performed for the T-shaped diastereomer. For these experiments, the light intensity was monitored with (*R*)-(−)-**2** as an actinometer.

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