Photoresolution of an Axially Chiral Bicyclo[3.3.0]octan-3-one: Phototriggers for a Liquid-Crystal-Based Optical Switch

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Abstract: A series of axially chiral bicyclo[3.3.0]octan-3-ones substituted with exocyclic alkenes was prepared and investigated for suitability as a chiroptical trigger for a liquid-crystal-based optical switch. Irradiation of the optically active ketone leads to its efficient photoracemization. Irradiation with circularly polarized light leads to partial photoresolution. The optical and photochemical properties of these ketones were studied and their twisting power for a nematic liquid crystal was measured.

Introduction

Erasable direct read after write (EDRAW)[1] memory devices form the foundation of our digital age. Magnetic materials currently dominate the technology for this application. However, it is widely recognized[2] that memory materials which can be reversibly written and read by light have powerful advantages over conventional magnetic materials. Development of a light-driven EDRAW device requires discovery of compounds that exist in two distinct chemical or physical forms that are interconverted by light and are sensed by light without their destruction. The most advanced materials for these applications are based upon reversible magneto-optical phase transitions of inorganic compounds.[3] However, difficult syntheses and structural limitations have led to an expanded search for organic compounds that satisfy these requirements.

Photochromic compounds are obvious candidates for light-driven EDRAW devices. However, they often suffer from poor thermal or photochemical stability and a destructive readout. Recently, photochromic systems designed to overcome these flaws have been described. Liu and co-workers reported a three-step process based upon the photoisomerization and electrochemical reduction of azobenzenes.[4] In an important breakthrough, Ringsdorf and co-workers[5] developed a fulgide-based photochromic system incorporated in a liquid-crystalline polymer. The photoisomers of the fulgide are stabilized by the polymeric matrix, and the orientation of the polymer is modified sufficiently by the form of the fulgide to cause development of distinctive optical properties. This system parallels the approach pursued in our work where the photochemical isomerization of a trigger initiates a phase transition in a liquid-crystalline medium.[6]

The trigger systems we investigate are based upon the induction and destruction of optical activity. It is well-known that the enantiomers of chiral molecules interact uniquely with polarized light.[7] In one approach, diastereomers having different optical spectra can be individually addressed,[6f,8] and their chiroptical properties can be monitored. In a second approach, the irradiation of a racemate with circularly polarized light (cpl)

can induce an enantiomeric excess (photoresolution) which can be reversed by irradiation with unpolarized light (photoracemization).

Despite the long-standing theoretical prediction of reversible photoresolution with cpl, only two unambiguous examples of this phenomenon are described heretofore in the literature. Stevenson[9] and Nordén[10] report the partial resolution of bidentate octahedral Cr(III) and Ru(II) complexes, and Michl and co-workers[11] describe the resolution of an unstable bridgehead imine at low temperature.

The successful resolution of a compound with circularly polarized light requires the simultaneous satisfaction of three key criteria. First, if we designate the two enantiomers of a chiral compound as **R** and **S**, irradiation should cause only their interconversion. If a photoproduct is formed, resolution can still be achieved but it will not be reversible.[12] The second requirement is based on the circular dichroism (CD) spectra of **R** and **S**. The extinction coefficients of enantiomers (ϵ_R, ϵ_S) absorbing cpl are different. Irradiation of the racemic mixture of **R** and **S** will lead to a photostationary state (pss) with an enantiomeric excess ($[\gamma]_{PSS}$) that depends on $\Delta\epsilon$ and ϵ according to eq 1, where g_λ is the Kuhn anisotropy factor.[7] Third, the quantum efficiency for photoracemization (Φ_{rac}, **R** → **R** + **S**) must be large, since the rate of photoresolution depends exponentially on this quantity.[13]

$$[\gamma]_{PSS} = \Delta\epsilon/2\epsilon = g_\lambda/2 \qquad (1)$$

We plan to amplify the photoresolution and photoracemization of the trigger molecules by inducing a reversible nematic to

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(7) (a) Kuhn, W.; Braun, E. *Naturwissenschaften* **1929**, *17*, 227. (b) Rau, H. *Chem. Rev.* **1983**, *83*, 535.
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(10) (a) Nordén, B. *Acta Chem. Scand.* **1970**, *24*, 349. (b) Nordén, B. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 355.
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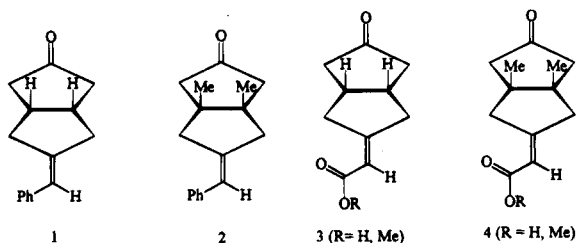(12) We are exploring the concept of a "reversible photodestruction" resolution based on chiral and achiral photochromic isomers. To date, no examples have been found.
(13) Stevenson, K. L.; Verdieck, J. F. *Mol. Photochem.* **1969**, *1*, 271.
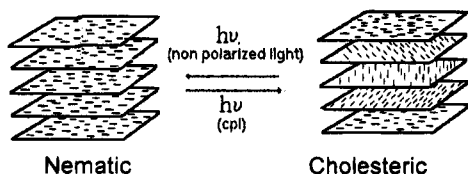
Figure 1. Reversible nematic to cholesteric liquid-crystal transition induced by light.

Chart 1. Axially Chiral Ketones

cholesteric liquid-crystal transition as shown schematically in Figure 1. Cholesteric liquid crystals have a macroscopic helical pitch (p) which affects light that passes through it.[14] The minimum pitch readily detected by optical microscopy is ca. 100 μm.[6b] The magnitude of p generated by the photoresolution of a trigger is determined by the concentration of the trigger (C), its optical purity at the photostationary state, and a material parameter (the helical twisting power, β_M) that is specific to the trigger and the liquid-crystal material. At low C, p is inversely related to $[\gamma]_{PSS}$ according to eq 2.[15] Assumption of a typical large β_M (50 μm^{-1}) and setting C to 10% reveals that the minimum $[\gamma]_{PSS}$ required for detection of the cholesteric phase is ca. 0.2%. We have been searching for trigger compounds that satisfy these criteria.

$$p = 1/(C\beta_M[\gamma]_{PSS}) \qquad (2)$$

In one approach,[6a] we sought to maximize g_λ by using the inherently dissymmetrical 1,1'-binaphthyl chromophore as the photoisomerizing unit. However, this proved to be unsatisfactory since g_λ and Φ_{rac} respond in opposite directions to the inter-ring dihedral angle. In a second approach,[6b] we applied exciton coupling theory to axially chiral benzylidene cycloalkanes. Here, large Φ_{rac} are obtained, but g_λ is too small.

We report herein the examination of the axially chiral bicyclic ketones shown in Chart 1 as potential triggers for a liquid-crystal-based optical switch. In contrast to the binaphthyl and benzylidene cycloalkanes investigated previously, the light-absorbing and photoisomerizing units in these compounds are separated and may be individually optimized. The ketone chromophore was selected as the absorbing unit because its nπ^* band has a high g_λ.[16] Further, ketone excited singlet states generally are short lived and undergo efficient intersystem crossing to the triplet state.[17] The relatively long-lived ketone triplet state will undergo efficient intramolecular energy transfer to an isomerizing unit if its triplet state has lower energy than

the ketone.[18] We selected the substituted styryl and acrylic acid (ester) groups to meet this requirement because their absorption spectra do not overlap with that of the ketone group. Finally, in an attempt to avoid averaging of CD spectra of opposite sign, and hence give rise to small g_λ values,[19] the relatively rigid bicyclo[3.3.0]octane skeleton was selected to link these groups. We find that irradiation of optically active samples of these bicyclic ketones with unpolarized light leads to their efficient photoracemization by isomerization about the carbon—carbon double bond. Irradiation of racemic mixtures with cpl leads to partial photoresolution with $[\gamma]_{PSS} \approx 0.4\%$ in the best case.

Results

(1) Synthesis of Racemic and Scalemic Ketones 1—4. The syntheses of ketones **1—4** follow a convergent route from bicyclo[3.3.0]octane-3,7-diones. Optically active samples of **1** and **2** were obtained by reaction of the "benzyl" Hannesian reagent[20] with the diones, eq 3. Methyl esters **3** and **4** were prepared from the diones by reaction with trimethyl phosphonoacetate and resolved, after hydrolysis, by formation of their quinine salts, eq 4.
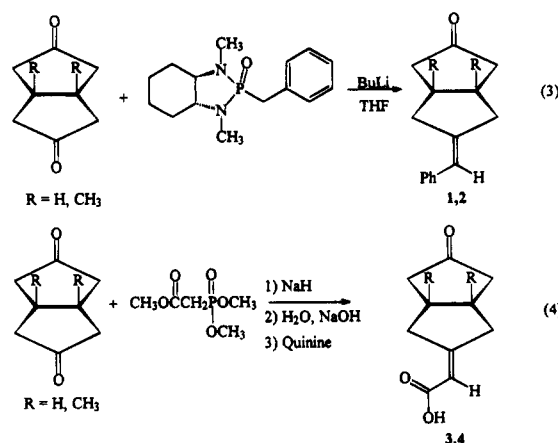
The optical purities of ketones **1** and **2** obtained in this synthesis are 44 ± 3% and 8 ± 3%, respectively. These values were determined by HPLC on a WHELK-01 column.[21] Similarly, the optical purities of **3** and **4** are 34 ± 2% and 27 ± 2%, respectively. These values were determined by chromatography after conversion to 3,5-dimethylanilides. Details of these syntheses and analyses are reported in the Experimental Section.

(2) Absorption and CD Spectra of Ketones 1—4. The absorption spectra of ketones **1—4** have nπ^* bands characteristic of aliphatic carbonyl compounds. Figure 2 shows the spectra of **1** and **3** in methylene chloride solution: the spectra of **2** and **4** are similar. The g_λ value of a chiral chromophore depends inversely on the extinction coefficient of the absorber. One reason ketones have comparatively large g_λ values is their small extinction coefficients. The extinction coefficients of ketones **1—4** at 305 nm (ϵ_{305}) are gathered in Table 1.

Inspection of Figure 2 shows a clear vibronic progression in the absorption of these ketones in methylene chloride solution. When the spectra are recorded in methanol solution, as expected, they broaden considerably. This phenomenon is usually at-

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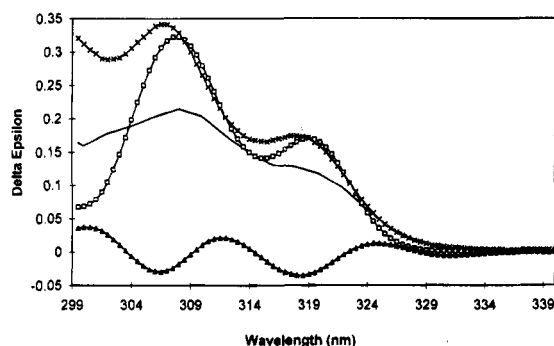
(21) This column is available commercially from Regis Chemical Company, Chicago, IL.
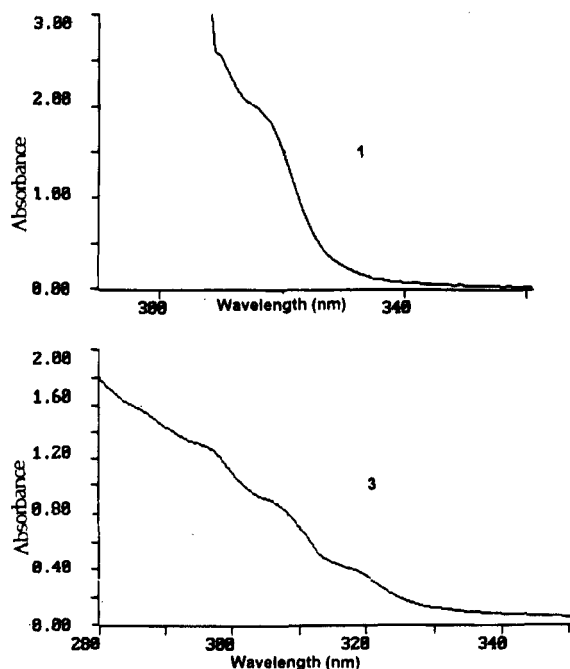
Figure 2. Absorption spectra of ketones **1** (0.12 M) and **3** (0.02 M) in methylene chloride solution.

Table 1. Absorption and Circular Dichroism Data for Ketones **1**−**4** in Methylene Chloride Solution

| compd	ϵ_{305} (M^{-1} cm^{-1})	$\Delta\epsilon_{305}$ (M^{-1} cm^{-1})	g_{305} ($\times 10^3$)
1	24	0.175	7.3
2	34	0.170	5.0
3	29	0.305	10.5
4	22	0.0	0.0

Figure 3. Circular dichroism spectra of ketones **1**−**4** recorded in methylene chloride solution: **1** (squares, 0.12 M); **2** (×, 0.30 M); **3** (solid line, 0.03 M); **4** (triangles, 0.29 M).

tributed to association of the carbonyl group with the alcohol solvent by hydrogen bonding.

The CD spectra of ketones **1**−**4** are complex and solvent dependent. Figure 3 shows their CD spectra recorded in methylene chloride solution. Particularly striking is the difference between the spectra of ketones **3** and **4**. Ketone **3**, having no bridgehead substitution, shows a normal nπ^* absorption. For this compound $\Delta\epsilon$ is positive throughout the spectrum, and it has maxima at ca. 308 and 320 nm. On the other hand, ketone **4**, which has methyl groups at the bridgehead positions, has an anomalous sinusoidal CD spectrum where $\Delta\epsilon$ oscillates between positive and negative values. The $\Delta\epsilon_{305}$ for ketones **1**−**4** are collected in Table 1.

Figure 4 shows the CD spectrum of ketone **4** in methanol and in methylene chloride solutions. The spectrum in methanol is normal but weak when compared with ketones **1**−**3**. We
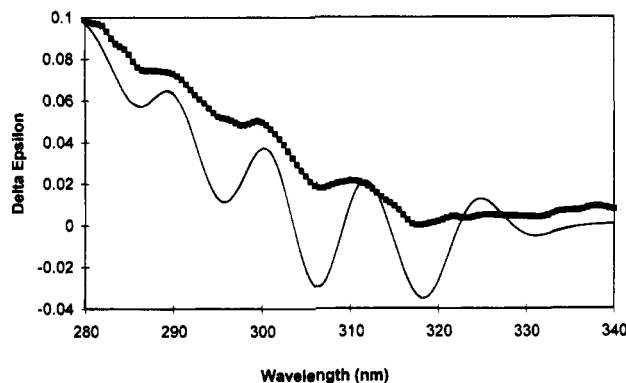

Figure 4. Circular dichroism spectra of ketone **4**: methanol solution (squares, 0.27 M), methylene chloride solution (solid line, 0.29 M).

considered the possibility that the anomalous CD spectrum of **4** in methylene chloride solution might be a consequence of its association into carboxylic acid dimers. This was ruled out by examination of the spectrum of its methyl ester, which is nearly identical with that of the acid. The anomalous behavior of **4** will be discussed below, but it is clear from the data in Table 1 that the g_λ values for these ketones are high enough for them to function as triggers in a liquid-crystal-based optical switch.

(3) Photostability, Photoracemization, and Photoresolution. In order to be considered as triggers for an optical switch, ketones **1**−**4** must not undergo any irreversible photodecomposition, they must photoracemize with high efficiency, and irradiation with cpl must lead to their partial resolution. We examined the photochemistry of **1**−**4** to assess their compliance with these requirements.

As a test of photostability under conditions simulating that of a solution in a liquid-crystalline environment, a 0.14 M hexane solution of **4** (as its methyl ester) was irradiated at 305 nm with a 1000 W Hg(Xe) lamp. After 12.5 h of irradiation, analysis by gas chromatography and by UV spectroscopy showed no significant consumption of the ketone. Ketones **1**−**3** behave similarly.

Photoracemization of ketones **1**−**4** requires rotation around the exocyclic carbon−carbon double bond, eq 5. The Φ_{rac} for

Photoracemization

(5)
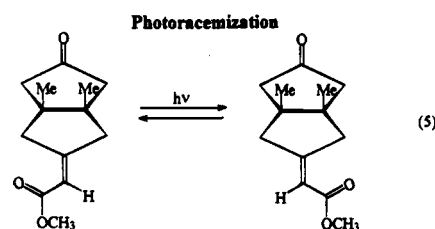
ketone **4** was determined to be 0.45 ± 0.05 by irradiation of a 0.11 M hexane solution of its methyl ester ([α]$_D$ = −5.4°) at wavelengths higher than 305 nm. The photoracemization was monitored by following the decrease in optical rotation of the ketone, and the photon flux was determined with 2-hexanone as an actinometer. Since the maximum value for Φ_{rac} is 0.5 (there is a 50% chance of forming either enantiomer from the excited state), it is clear that light absorbed by the ketone chromophore results in efficient isomerization of the carbon−carbon double bond. The mechanism for this reaction will be discussed below.

Photoresolution is more difficult to accomplish than photoracemization since the rate of the reaction slows as the system approaches the photostationary state. In order to achieve a measurable [γ]$_{PSS}$, both Φ_{rac} and g_λ must be large. We assessed the photoresolution of ketones **1**−**4** by irradiating a hexane
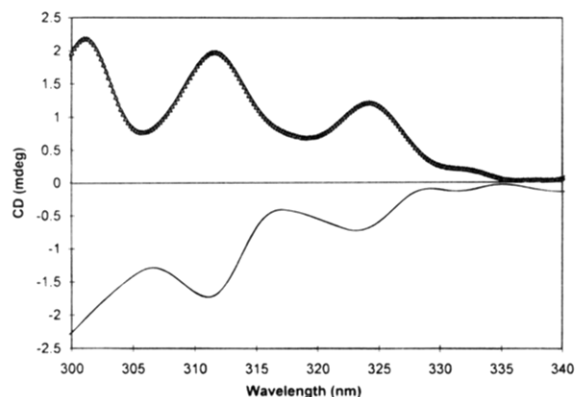
Figure 5. Circular dichroism spectra of ketone **3** (as its methyl ester) after irradiation of racemic samples with right-hand and left-hand circularly polarized light.

solution of **3** with cpl. Circularly polarized light with wavelengths higher than 305 nm was generated by passing the output of a 1000 W Hg(Xe) lamp through a cutoff filter, a Glan-Taylor linear polarizer, and then a Fresnel rhomb. The photon flux to the sample was determined to be ca. 5.8×10^{15} s^{-1} with a 2-hexanone actinometer. This light was focused on a 3-mL sample of a 0.27 M hexane solution of racemic **3** as its methyl ester. The photoresolution of **3** was monitored by following the circular dichroism of this solution. A CD spectrum became apparent after a few minutes of irradiation, and the photostationary state was reached after 400 min of irradiation. This result was confirmed by switching the sense of circular polarization by rotation of the Glan-Taylor polarizer through 90°. As shown in Figure 5, the sign of the CD spectrum changes with the sense of circular polarization, but the magnitude remains the same. The $[\gamma]_{PSS}$ observed in this experiment is 0.4%, which is a value consistent with calculation from g_λ.

(4) The Helical Twisting Power β_M. In order to sense the conversion of a nematic to a cholesteric liquid crystal by irradiation of a trigger with cpl, the product of $[\gamma]_{PSS}$, β_M, and C must be sufficiently large to give a detectable pitch, eq 2. We determined β_M for **4**, as its hexyl ester, in *trans*-1-*n*-heptyl-4-(*p*-cyano)phenylcyclohexane (Merck—S 1115 PCH). This liquid-crystalline material is transparent at 305 nm, and it is nematic between 30 and 59 °C.

The helical twisting power of **4** was determined by application of the Grandjean-Cano lens method[22] at 30 °C. A 2.7 wt % solution of scalemic **4** (18 ± 3% ee) in S 1115 PCH was observed microscopically to give disclination circles, Figure 6. The distance between consecutive circles is related to the pitch of the induced cholesteric phase and to the radius of curvature of the lens. For **4** as its *n*-hexyl ester, β_M in S 1115 PCH is a relatively modest 5.5 μm^{-1}.

The separation between the disclination circles increases when the twisted nematic is irradiated. This result is due to an increase of the pitch of the cholesteric liquid crystal caused by the photoracemization of the trigger ketone. After a few minutes of irradiation, the cholesteric liquid crystal turns nematic and the disclination circles disappear completely.

Discussion

A major challenge in the discovery of suitable optical triggers for switching liquid crystals with cpl is that most chromophores can only give a very small value of $[\gamma]_{PSS}$. To solve this
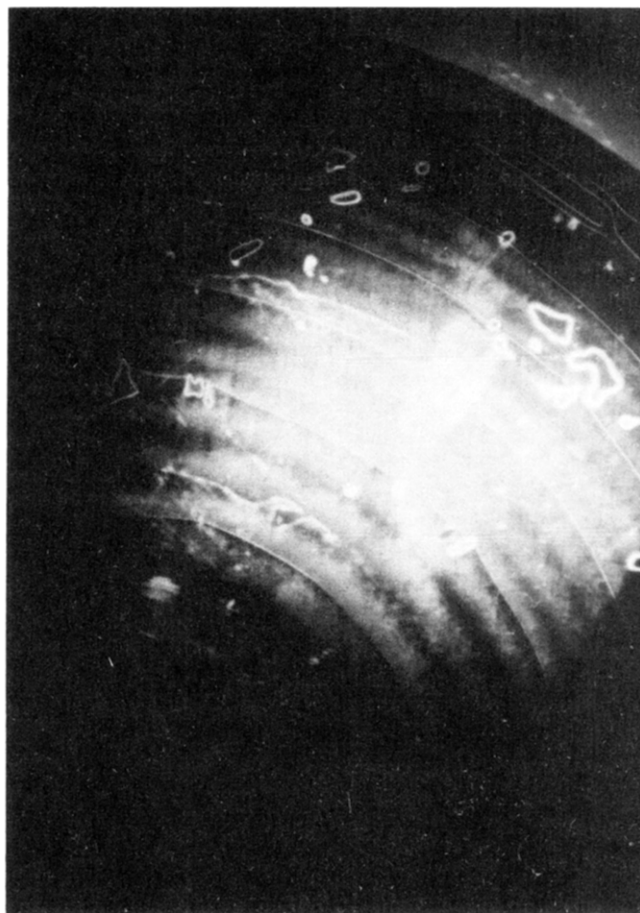
Figure 6. A 2.7 wt % solution of scalemic **4** (18 ± 3% ee) in S 1115 PCH viewed microscopically through crossed polarizers (original amplification 40×). The sample is placed on a plano convex lens with a radius of 52 mm. The pitch calculated from the distance between disclination lines is 36 μm.

problem, compounds with large g_λ that also photoracemize efficiently are required. Once such compounds are discovered, their structures may be modified to control β_M. In this work, we have successfully accomplished the first two steps of this sequence. Ketone **4** photoracemizes efficiently and gives $[\gamma]_{PSS}$ sufficiently large to be useful as an optical trigger. The key to this success is coupling the large g_λ value of the carbonyl chromophore by energy transfer to the remote, efficiently isomerizing carbon—carbon double bond.

(1) Circular Dichroism of Ketones 1−4. All chromophores in a chiral molecule must exhibit CD spectra in the region of their absorption. However, the $\Delta\epsilon$ values they exhibit vary considerably. It is useful to divide chromophores into two broad categories: the first are optically active due to their inherent geometry, i.e. hexahelicene and 1,1-biphenyls; the second are inherently achiral absorbers that are perturbed chirally. This latter class includes the extensively studied steroidal ketones.[23]

In the UV, the extinction coefficient of a chromophore (ϵ) is proportional to the square of the electric transition dipole moment.[24] In the CD, the rotational strength (R), defined as the area under the circular dichroism band, is proportional to the imaginary part of the scalar product of the electric and magnetic dipole transition moments.[25] This difference in the selection rules between UV and CD absorption predicts that

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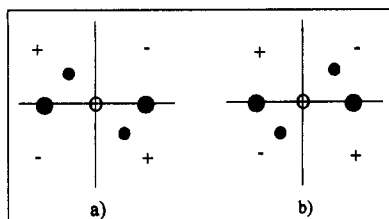
Figure 7. Two conformations of cyclopentanones showing the effect of occupancy of rear quadrants on the predicted sign of the circular dichroism spectrum.

transitions with small electric moments and large magnetic moments will have a high ratio of $\Delta\epsilon/\epsilon$. The $n\pi^*$ transition of ketones satisfies these criteria. The ketones examined in this work are consistent with these general principles, but the CD spectra they exhibit are complex.

The CD spectra of ketones **1–3** in either methanol or methylene chloride solution are normal, but the CD spectrum of **4** is anomalous. Even though the signs of CD bands of ketones have been successfully correlated with absolute configurations using empirical sector rules,[19] their interpretation is sometimes complicated since they contain information about the helicity of the ground state, the dynamics of the molecule, and its interactions with the solvent. The entanglement of these factors can create "anomalies", such as bands that change sign with solvent[26] or bisignated bands (the Cotton effect changes sign in between the band). In some cases, spectra are easily understood as arising from two forms in conformational equilibrium.[27] Cyclopentanone ring systems have chiral conformations, and their particular chiroptical properties are dependent mainly on the twisted form that is preferred.[28] Figure 7 shows the quadrant projections of the two lowest energy twisted conformations of cyclopentanone: (a) is predicted to give a positive Cotton effect, and (b) should give a negative Cotton band.[28]

Not all bisignated signals can be explained as due to a conformational equilibration. Some of the most intriguing spectra are those in the camphor family. These are rigid structures which can show bisignated bands that vary depending on the solvent. In these rigid structures, conformational equilibration cannot be an issue. An equilibrium between solvated and nonsolvated species has been suggested to rationalize these data.[29] This interpretation is challenged by rigid ketones that show bisignated bands in non-associative solvents (i.e. cyclohexane) and other compounds which show bisignated spectra in the gas phase.[16] It appears that the origin of a bisignated band (at least in some cases) can be a result of a static structural property of the compound and not a result of equilibration between different structures.[30]

Nevertheless, the CD spectra of **4** can be rationalized if we assume that it is a result of two superimposed bands of opposite sign. One band is the "natural" band of the chromophore for which the CD spectrum of **3** may be taken as a model. The second, "anomalous" band is obtained by subtracting the observed CD spectrum from the natural band. This process is shown graphically in Figure 8 for a methanol solution of **4** where it is clear that the anomalous band has the same shape as the natural band but with slightly different vibronic rotatory strengths and an opposite sign.

The bisignated CD problem has been studied for over twenty years and there is no general agreement on its origin. Conse-
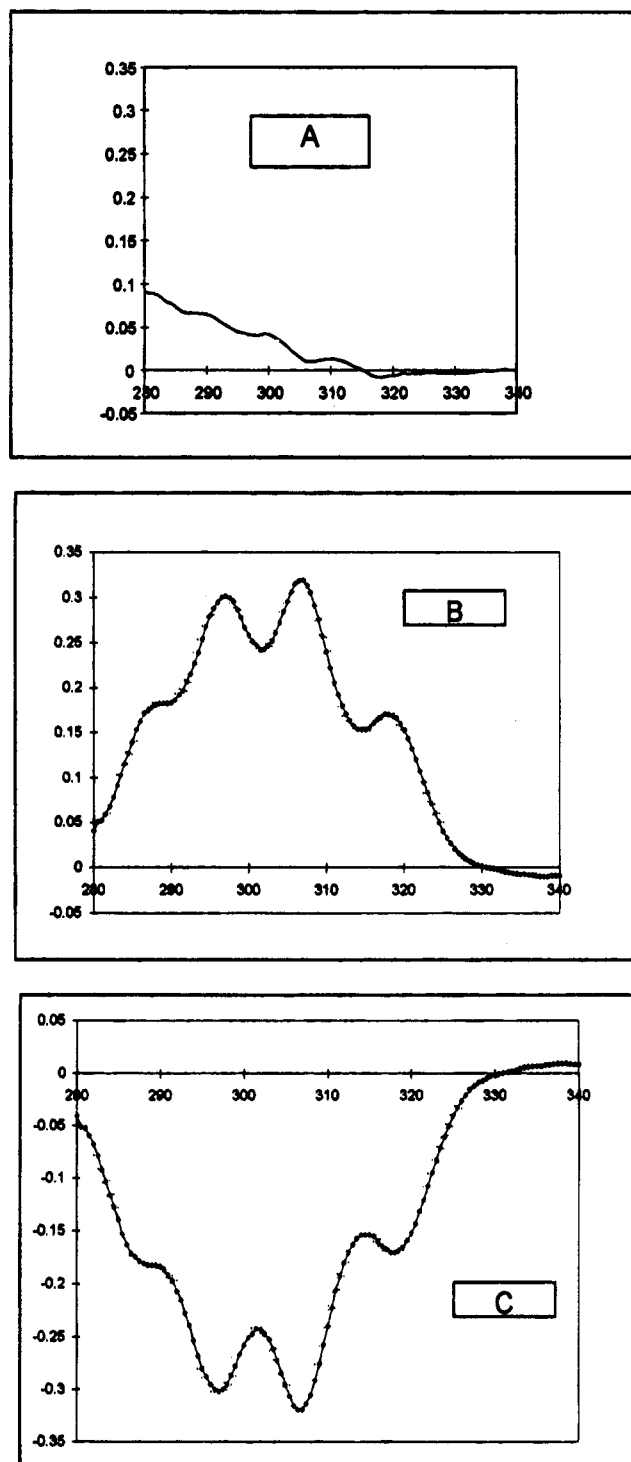
Figure 8. Decomposition of the observed CD spectrum of ketone **4** (A) into a normal band (B) and, by subtraction, an anomalous band (C).

quently, it is not possible to assign the origin of the anomalous CD band of **4** with confidence. Conformational equilibration involving pseudorotation of the cyclopentanone ring (as in Figure 7), asymmetric solvation, and the appearance of a "forbidden" band due to vibronic coupling or better Franck–Condon factors are possible. However, these explanations do not clearly account for the unique appearance of the anomalous band in **4**.

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Liquid-Crystal-Based Optical Switch Phototriggers

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(2) Photochemistry of Cyclopentanones and Energy Transfer. Cycloalkanones have a rich photochemistry[31] that must be circumvented in their application as reversible triggers so that they do not undergo an irreversible reaction. In our design, fast intramolecular energy transfer to a rotor moiety of the molecule protects the cyclopentanone and provides a path for efficient photoracemization.

Aliphatic ketones absorb light into their $n\pi^*$ transition, typically at wavelengths between 240 and 330 nm (ca. 85 kcal/mol). The excited singlet states ordinarily have lifetimes of 1 or 2 ns, and intersystem cross to a lower-energy (ca. 78 kcal/mol), longer-lived triplet (10−15 μs) with high efficiency ($\Phi_{ISC} \approx 1.0$).[32] Typically, the photochemistry of cyclopentanones is dominated by Norrish Type I cleavage that originates from the triplet state.[33] Stern−Volmer analysis indicates rate constants for carbon−carbon bond cleavage of ca. 3×10^7 s^{-1}.[34] Therefore, to inhibit this reaction, the energy transfer rate constant to the rotating group of the trigger molecule must be at least 1.0×10^9 s^{-1}. Consequently, energy transfer must be exothermic and proceed by a strongly coupled mechanism for the system to photoresolve without simultaneous photodestruction.

The first criterion is clearly met in ketones **1−4**. The triplet energy of styrene is 59.3 kcal/mol[17] and the ability of substituted styrenes to efficiently photoisomerize in the triplet state is well documented.[35] The thermodynamic data for the triplet states of α,β-unsaturated esters is not well developed. However, it has been shown that they isomerize with low-energy triplet sensitizers,[36] and the triplet energy of methyl 2-methyl-2-butenoate is reported to be 66 kcal/mol.[37]

The high Φ_{rac} for ketones **1−4** indicates that energy absorbed by the carbonyl group is effectively transferred to the rotating group, which is four bonds away. Since intramolecular singlet−singlet energy transfer is impossible on thermodynamic grounds, energy transfer must originate from the triplet state of the ketone. Triplet−triplet energy transfer does not occur efficiently by a Coulombic mechanism, and exchange energy transfer is inefficient over distances greater than 5 Å. Nevertheless, intramolecular triplet−triplet energy transfer over distances up to 15 Å can occur with high efficiency by a through bond coupled-exchange mechanism. Keller,[38] Zimmerman and co-workers,[39] and Closs and co-workers[40] have all attributed intramolecular triplet−triplet energy transfer to this mechanism; a similar process must operate for ketones **1−4**.

(3) Trigger for an Optical Switch. The partial photoresolution of ketone **3** by irradiation with circularly polarized light, its highly efficient photoracemization, and its photostability satisfy many of the requirements of a trigger for a liquid-crystal-based optical switch. However, the β_M value of **3** is relatively small, and its solubility in nematic liquid-crystal materials is limited. The minimum pitch that can be obtained by photoresolution of a 10% solution of **3** in S 1115 PCH is calculated

to be ca. 450 μm. This value is too large to be detected by optical microscopy. However, it has been previously noted that the transfer of chirality from an additive to the bulk liquid crystal occurs by a molecular recognition mechanism. According to this proposal, the magnitude of β_M depends on how well the additive fits into the liquid-crystal host.[41] Thus simple modification to the structure of ketone **3** by formation of esters that closely resemble liquid-crystal hosts has a strong likelihood of increasing β_M by an order of magnitude or more. These compounds would then be useful triggers for chiroptical liquid-crystal-based switches.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 200, U400 or a General Electric QE-300 as noted. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. UV−vis spectra were recorded on a Cary 1E UV−visible spectrophotometer. CD spectra were recorded on a Jasco J-720 spectropolarimeter. Optical rotations were measured on a JASCO DIP-360 digital polarimeter. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 instrument fitted with a flame ionization detector, using a Hewlett-Packard wide-bore 0.53-mm × 10-m HP-1 capillary column. 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. Microscopic analyses were performed with a Fisher Micromaster polarizing microscope equipped with a Mettler FP82 hot stage. Melting points were measured on a Büchi apparatus or Nalge hot stage and are uncorrected.

All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. Benzene, diethyl ether, and tetrahydrofuran (THF) were distilled under N$_2$ from Na/benzophenone and cyclohexane, and acetonitrile and dimethylformamide were distilled from CaH$_2$. The following compounds were prepared by literature procedures and shown to have the expected physical and spectral properties: cis-bicyclo[3.3.0]octane-3,7-dione, cis-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione,[42] [3aR-(2α,3aα,7aβ)]-2-benzyl octahydro-1,3-dimethyl-1H-1,3,2-benzodiazaphosphole 2-oxide, and (1R,2R)-cyclohexane-N,N'-dimethyl-1,2-diamine.[20] Elemental analyses were performed by the Microanalysis Laboratory of the University of Illinois.

(−)-7-(Phenylmethylene)-cis-bicyclo[3.3.0]octan-3-one (1). Under a N$_2$ atmosphere, 3 mL of dry THF was added to 0.22 g of [3aR-(2α,3aα,7aβ)]-2-benzyloctahydro-1,3-dimethyl-1H-1,3,2-benzodiazaphosphole 2-oxide (0.77 mmol), and the solution was cooled to −78 °C. A 0.4-mL portion of a 1.6 M solution of n-BuLi in hexanes was added by syringe and stirred for 30 min, after which a solution of 0.32 g (2.35 mmol) of cis-bicyclo[3.3.0]octane-3,7-dione in 1 mL of dry THF was added dropwise. When the addition was complete, the reaction mixture was stirred for 1 h and then quenched at −78 °C with 0.3 mL of glacial acetic acid. The mixture was warmed to room temperature, stirred for 1 h, poured into 15 mL of ether, and washed with water (5 mL), 5% aqueous NaOH (5 mL), and again with water (5 mL). The organic phase was dried (MgSO$_4$) and concentrated to give a yellow oil. Purification by flash chromatography on silica (8% ethyl acetate/hexane) yielded 0.057 g (35% yield) of a clear liquid, $[\alpha]_D = -37.5°$ (c 2.31, CH$_2$Cl$_2$), 44 ± 3% ee (determined by HPLC on a WHELK-01 column with 8% isopropyl alcohol/hexane, at 1 mL/min). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.00−2.20 (m, 2 H), 2.30−2.55 (m, 4 H), 2.70−3.05 (m, 4 H), 6.3−6.5 (m, 1 H), 7.17−7.40 (m, 5 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 36.71, 38.77, 40.78, 41.12, 43.37, 44.21, 123.22, 126.09, 128.05, 128.22, 138.02, 144.50, 220.26. HR-EI calcd for C$_{15}$H$_{16}$O 212.120115, found 212.120700.

(+)-7-(Phenylmethylene)-cis-1,5-dimethylbicyclo[3.3.0]octan-3-one (2). Under a N$_2$ atmosphere, 3 mL of dry THF was added to 0.17 g of [3aR-(2α,3aα,7aβ)]-2-benzyloctahydro-1,3-dimethyl-1H-1,3,2-

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benzodiazaphosphole 2-oxide (0.61 mmol) and the solution was cooled to −100 °C. A 0.4-mL portion of a 1.6 M solution of *n*-BuLi in hexanes was added by syringe and stirred for 30 min, after which a solution of 0.26 g of *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione in 1 mL of dry THF was added dropwise. When the addition was complete, the reaction mixture was stirred for 6 h and quenched at −78 °C with 0.3 mL of glacial acetic acid. The reaction mixture was warmed to room temperature and stirred for 10 h, poured into 15 mL of ether, and washed with water (5 mL), 5% aqueous NaOH (5 mL), and again with water (5 mL). The organic phase was dried (MgSO₄) and concentrated to give a yellow oil. Purification by flash chromatography on silica (8% ethyl acetate/hexane) yielded 0.044 g (49%) of a clear liquid, $[\alpha]_D = +8.4°$ (*c* 1.05, CHCl₃), 8 ± 3% ee (determined by HPLC on a WHELK-01 column with 8% isopropyl alcohol/hexane, at 1 mL/min). ¹H NMR (400 MHz, CD₂Cl₂) δ 1.114 (s, 3 H), 1.124 (s, 3 H), 2.14−2.42 (m, 4 H), 2.62−2.72 (m, 4 H), 6.22−6.51 (m, 1 H), 7.15−7.22 (m, 1 H), 7.24−7.36 (m, 4 H). ¹³C NMR (50 MHz, CDCl₃) δ 21.32, 21.99, 44.25, 46.78, 47.96, 48.82, 50.64, 51.36, 123.72, 126.14, 128.05, 128.30, 138.06, 142.19, 218.64. Anal. Calcd for C₁₇H₂₀O: C, 84.96; H, 8.39. Found: C, 84.89; H, 8.43.

7-((Methoxycarbonyl)methylene)-*cis*-bicyclo[3.3.0]octan-3-one (R = Me). A 2.91-g portion of NaH (60% by weight dispersion in mineral oil, 72.9 mmol), 13.7 g (75.0 mmol) of trimethyl phosphonoacetate, and 100 mL of dry benzene were added to a flask equipped with a reflux condenser, an addition funnel, and a mechanical stirrer. This mixture was stirred for 1 h after which a solution of *cis*-bicyclo[3.3.0]-octane-3,7-dione (11.1 g, 80.4 mmol) in 50 mL of dry benzene was added dropwise keeping the temperature below 30 °C. When the addition was complete, the reaction mixture was stirred for 30 min, then heated to 60 °C for 15 min, and cooled to room temperature and then the liquid was decanted from the brownish-gummy precipitate. This precipitate was washed 4 times with 50 mL of warm benzene. The combined benzene extracts were evaporated and the residue was purified by chromatography on silica gel (5% ethyl acetate/hexane) yielding 9.23 g (47.5 mmol, 66%) of a clear liquid. ¹H NMR (400 MHz, CDCl₃) δ 1.90−2.20 (m, 2 H), 2.30−2.55 (m, 3 H), 2.64−2.96 (m, 4 H), 3.10−3.22 (m, 1 H), 3.67−3.70 (s, 3 H), 5.82−5.86 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 37.84, 38.92, 40.01, 40.64, 42.97, 43.87, 50.92, 113.34, 166.61, 166.79, 219.44. HRMS(EI) calcd for C₁₁H₁₄O₃ 194.094294, found 194.094219.

7-(Carboxymethylene)-*cis*-bicyclo[3.3.0]octan-3-one (3, R = H). A 7.63-g (39.3 mmol) portion of methyl 7-((methoxycarbonyl)-methylene)-*cis*-bicyclo[3.3.0]octan-3-one was suspended in 1 L of water containing NaOH (pH = 12.5) and stirred for 7 d, keeping the pH constant. The homogenous reaction mixture was washed with diethyl ether and then neutralized with 5% HCl. The aqueous phase was extracted with CH₂Cl₂ (4 × 250 mL). The organic layer was evaporated yielding a white solid that was recrystallized from hexane to give 5.49 g (30.4 mmol; 77%) of a white solid: mp = 110−111 °C. ¹H NMR (400 MHz, CDCl₃) δ 1.96−2.06 (m, 1 H), 2.07−2.18 (m, 1 H), 2.40−2.54 (m, 3 H), 2.64−2.96 (m, 4 H), 3.12−3.24 (m, 1 H), 5.85−5.89 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 38.21, 38.94, 40.12, 41.00, 42.98, 43.90, 113.43, 169.69, 171.77, 219.43. Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H 6.71. Found: C, 66.41; H, 6.72.

7-((Methoxycarbonyl)methylene)-*cis*-1,5-dimethylbicyclo[3.3.0]-octan-3-one (4, R = Me). The procedure described above for the preparation of 7-((methoxycarbonyl)methylene)-*cis*-bicyclo[3.3.0]octan-3-one was followed with 4.1 g (102 mmol) of 60% by weight NaH, 16.9 g (102 mmol) of *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione, and 17 mL of trimethyl phosphonoacetate (19.1 g, 105 mmol) affording 16.5 g (73% yield) of a clear liquid. ¹H NMR (400 MHz, CDCl₃) δ 1.09 (s, 3 H), 1.12 (s, 3 H), 1.14−2.38 (m, 4 H), 2.56−2.62 (m, 2 H), 2.84−3.02 (m, 2H), 3.60−3.80 (s, 3 H), 5.80−5.84 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 21.1, 21.7, 45.2, 47.0, 47.3, 48.0, 50.3, 50.9, 51.0, 113.7, 164.4, 166.8, 217.7. HRMS(EI) calcd for C₁₃H₁₈O₃: 222.125594, found 222.126000.

7-(Carboxymethylene)-*cis*-dimethylbicyclo[3.3.0]octan-3-one (4, R = H). The procedure described for the preparation of 3 was followed with 5.06 g (22 mmol) of 7-((methoxycarbonyl)methylene)-*cis*-1,5-dimethylbicyclo[3.3.0]octan-3-one, and after recrystallization from hexane 4.0 g (19 mmol, 86%) of a white solid was obtained: mp = 120−121 °C. ¹H NMR (400 MHz, CDCl₃) δ 1.08 (s, 3 H), 1.12 (s, 3

H), 2.14−2.38 (m, 4 H), 2.60−2.66 (m, 2 H), 2.86−3.10 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 21.41, 22.04, 45.82, 47.35, 47.89, 48.43, 50.63, 51.28, 114.13, 167.84, 172.16, 218.19. Anal. Calcd for C₁₂H₁₆O₃: C, 69.21; H, 7.74. Found: C, 69.17; H, 7.75.

Resolution of 7-(Carboxymethylene)-*cis*-bicyclo[3.3.0]octan-3-one and 7-(Carboxymethylene)-*cis*-dimethylbicyclo[3.3.0]octan-3-one. A 2.27-g (12.6 mmol) portion of acid 3 was mixed with 2.42 g (7.5 mmol) of quinine. The mixture was dissolved in methanol and left for 30 min. The methanol was evaporated and the resulting viscous solid recrystallized three times from acetone. The resulting salt was hydrolyzed with 5% HCl and extracted with ethyl acetate. The organic layer was washed with brine, dried with Na₂SO₄, and evaporated to dryness. The off-white solid obtained was recrystallized from hexane−acetone to give 0.81 g of a white solid: mp = 121−122 °C. $[\alpha]_D = −20.6$ (*c* = 1.31, CHCl₃), 34 ± 2% ee (HPLC on a WHELK-01 column of the 3,5-dimethylanilide derivative, with 40% isopropyl alcohol/hexane at 1 mL/min).

The residue from recrystallization of the salt was hydrolyzed with 5% HCl and extracted with ethyl acetate. The organic layer was washed with brine, dried with Na₂SO₄, and evaporated to dryness. The off-white solid obtained was recrystallized from hexane−acetone to give 0.82 g of a white solid: mp = 119−120 °C. $[\alpha]_D = +15.1$ (*c* = 1.06, CHCl₃), 25 ± 2% ee.

Likewise, a 3.35-g (16 mmol) sample of 4 was resolved with 3.80 g (11.7 mmol) of quinine. The main fraction yielded 0.87 g of a white solid: mp = 116−118 °C $[\alpha]_D = +12.9$ (*c* = 1.5, CHCl₃) and 27 ± 3% ee (HPLC on a WHELK-01 column of the 3,5-dimethylanilide derivative with 30% isopropyl alcohol/hexane at 2 mL/min). From the hydrolysis of the residue from the recrystallizations, 0.90 g of acid with an opposite rotation was obtained: mp = 119−120 °C. $[\alpha]_D = −9.1$ (*c* = 1.10, CHCl₃), 19 ± 2% ee.

(+)-7-((Hexyloxycarbonyl)methylene)-*cis*-bicyclo[3.3.0]octan-3-one. A 0.83-g (4.6 mmol) portion of scalemic carboxylic acid 3 ($[\alpha]_D = +15.1$ (*c* = 1.06, CHCl₃), 25 ± 2% ee) was dissolved in 10 mL of anhydrous CH₂Cl₂ and 0.029 g (0.23 mmol) of 4-(dimethylamino)-pyridine (DMAP) and 2.7 mL (21.5 mmol) of hexanol were added with stirring. The reaction was cooled to 0 °C, and 1.26 g (5.2 mmol) of 1,3-dicyclohexylcarbodiimide (DCC) was added. The mixture was stirred for 5 min at 0 °C and then warmed to room temperature and stirred for 3 h. The precipitated urea was removed by filtration, and the filtrate was diluted with 50 mL of CH₂Cl₂, washed with 0.5 N HCl and NaHCO₃(sat), and dried over MgSO₄. The solution was concentrated, the resulting oil was kept under vacuum (0.1 mmHg) for 24 h to remove unreacted hexanol, and the residue was purified by chromatography on silica (8% ethyl acetate/hexane), affording 0.78 g (2.94 mmol, 64% yield) of a clear liquid: $[\alpha]_D = 7.8°$ (*c* 2.45, CHCl₃), 18 ± 3% ee. ¹H NMR (400 MHz, CDCl₃) δ 0.84−0.90 (t, 3 H), 1.2−1.4 (m, 6 H), 1.2−1.4 (m, 13 H), 1.56−1.66 (m, 4 H), 1.94−1.99 (m, 1 H), 2.0−2.4 (m, 1 H), 2.5−2.9 (m, 1 H), 2.10−2.12 (m, 1 H), 2.34−2.52 (m, 3 H), 2.62−2.94 (m, 4 H), 3.08−3.2 (m, 1 H), 4.04−4.09 (t, 2 H), 5.81−5.85 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 13.98, 22.50, 25.61, 28.62, 31.39, 37.88, 38.97, 40.15, 40.70, 43.04, 43.94, 63.94, 113.90, 166.11, 166.54, 219.45. Anal. Calcd for C₁₆H₂₄O₃: C, 72.69; H, 9.15. Found: C, 72.58; H, 9.20.

Helical Twisting Powers. A glass plate and a plano convex lens with a 52-mm radius were coated with a thin layer of polyvinyl alcohol and rubbed with a tissue. The cholesteric liquid crystal was prepared by mixing the liquid crystal and the scalemic dopant in a 1-mL reaction vessel (the mixture was melted and stirred to assure homogeneity). A drop of this cholesteric liquid crystal was placed between the lens and the glass plate, keeping the rubbing of these two elements in a parallel orientation. This preparation was observed through a polarizing microscope and the distance between the concentric circles in the liquid crystal was measured.