Photochemistry of Axially Chiral (Arylmethylene)cycloalkanes: A Search for Suitable Photoswitchable Liquid Crystalline Materials

Robert P. Lemieux[1] and Gary B. Schuster*

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

Received September 30, 1992

A series of chiral (arylmethylene)cycloalkanes was synthesized in racemic and optically active form to examine their suitability for incorporation in a liquid crystal-based optical switch. Irradiation of these compounds with UV light leads to their rapid photoracemization and, in some cases, their simultaneous destruction. The absorption spectra and circular dichroism spectra of these optically active compounds were determined. Chiral exciton coupling theory proves to be a good guide for predicting the magnitude of $\Delta\epsilon$ and g_λ (the Kuhn anisotropy factor). Addition of the optically active (arylmethylene)cycloalkanes to nematic liquid crystal materials induces cholesteric behavior. The helical twisting power (β_M) was determined for each compound, and a limit of 90 μm was established for the detection of a long-pitch cholesteric liquid crystal. Irradiation of the cholesteric liquid crystals formed by addition of the optically active (arylmethylene)cycloalkanes induces the transition to a compensated nematic phase that is readily sensed by optical microscopy.

Introduction

Conversion or modification of a liquid crystal phase with light provides access to valuable means for the display, storage, or transmission of information.[2] In one approach, destruction of an optically active compound with light causes the conversion of a cholesteric (twisted nematic) liquid crystal to a nematic phase.[3] In another, irradiation of certain materials with linearly polarized light causes reorientation of a nematic liquid crystal and alteration of easily monitored bulk properties.[4] This latter approach is especially attractive since it provides a basis for the development of an optical switch. A device of this sort can be transformed reversibly with light between two or more states each of which may be specifically sensed with light.[5] For example, cholesteric liquid crystals are optically active since they rotate the plane of polarized light. In contrast, aligned nematic liquid crystal phases are optically inactive—they do not rotate light. Thus it may be possible to develop an optical switch based on the light-induced interconversion between nematic and cholesteric liquid crystals sensed by the accompanying change in optical activity.[6] A goal of the work reported herein is to investigate key aspects of this approach to the modification of liquid crystal phases with light.

The pitch (p) of a cholesteric liquid crystal phase is readily controlled by chemical and physical means. For example, it is generally observed that addition of small quantities of optically active compounds to nematic liquid crystals induces cholesteric properties.[7] The pitch generated in such a phase depends on β_M, the helical twisting power of the additive, its concentration (C, mol of additive/mol of solution) in the host liquid crystal, and its optical purity (γ) according to eq 1.[8] When $\gamma = 0$, the additive is racemic and the liquid crystal phase is analogous to a compensated nematic since its pitch is infinite. A compensated nematic phase does not rotate plane polarized light.

$$p = [\beta_M C\gamma]^{-1} \quad (1)$$

$$[ee]_{PSS} = g_\lambda/2 \quad (2)$$

Photoresolution of racemic compounds can be accomplished by their irradiation with circularly polarized light. This result is predicted by theory[9] and has been demonstrated experimentally for several examples.[10] Two general mechanistic categories of reactions leading to photoresolution have been found to operate. In the first, irradiation leads to more rapid destruction of one enantiomer ($R \rightarrow$ X) than the other ($S \rightarrow$ X). In the second, irradiation results only in interconversion of one enantiomer to the other ($R \rightleftarrows S$). Here, the enantiomeric excess at the photostationary state {[ee]$_{PSS}$} obtained by irradiation with circularly polarized light at wavelength λ may be calculated from the absorption and circular dichroism spectra of the compound according to eq 2, where g_λ is the Kuhn anisotropy factor ($\Delta\epsilon_\lambda/\epsilon_\lambda$). The second case is relevant to the work reported herein. We hope to show that irradiation of a compensated nematic liquid crystal containing a suitable chiral compound with circularly polarized light will induce cholesteric behavior and that irradiation of this cholesteric liquid crystal with unpolarized light will regenerate the compensated nematic phase. This interconversion of liquid crystal phases could serve as the basis for an optical switch.

Compounds suitable for use in the optical swtich described above must simultaneously satisfy several key

(1) Present address: Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

(2) Kreysig, D. Stumpe, J. In *Selected Topics in Liquid Crystal Research*; Koswig, H. D., Ed.; Verlag: Berlin, 1990; p 69.

(3) Haas, W.; Adams, J.; Wysocki, J. *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 371. Sackmann, E. *J. Am. Chem. Soc.* **1971**, *93*, 7088. Kurihara, S.; Ikeda, T.; Sasaki, T.; Kim, H.-B.; Tazuke, S. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 251.

(4) Eich, M.; Wendorff, J. H. In *International Symposium on Polymers and Advanced Technology*; Wendorff, J. H., Leuin, J., Eds.; VCH Publishers: New York, 1988; p 501.

(5) Gibbons, W. M.; Shannon, P. J.; Sun, S. T.; Swetlin, B. J. *Nature* **1991**, *351*, 49.

(6) Shiyanovskii, S. V.; Reznikov, Yu. A. *Sov. Phys.-Dokl. (Engl. Transl.)* **1985**, *30*, 1053.

(7) Solladie, G.; Zimmermann, R. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348.

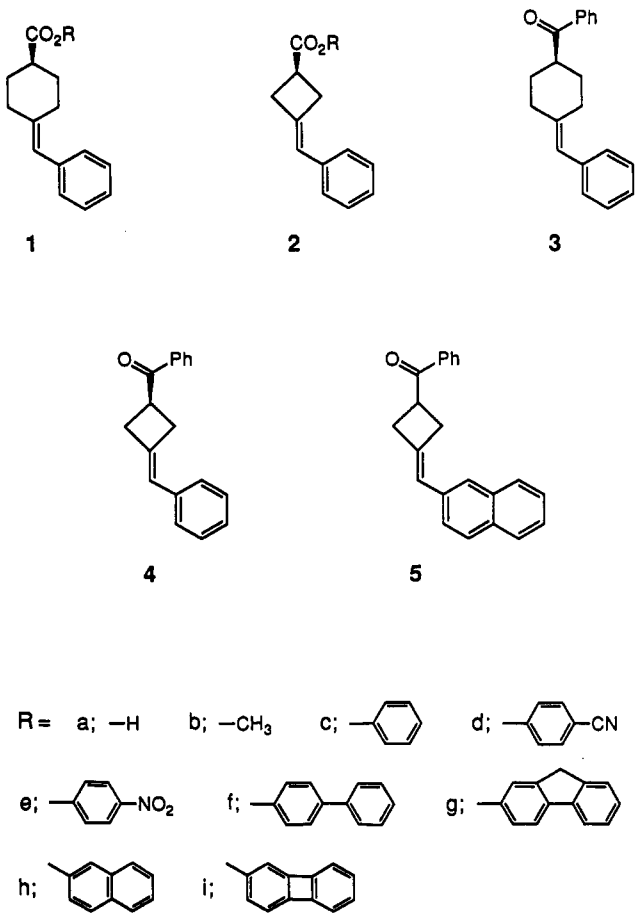
(8) (a) Korte, E. H.; Schrader, B.; Baulek, S. *J. Chem. Res. Synop.* **1978**, 236. (b) Ruxer, J. M.; Solladie, G.; Candau, S. *Mol. Cryst. Liq. Cryst.* **1978**, *41*, 109.

(9) Kuhn, W.; Braun, E. *Naturwissenschaften* **1929**, *17*, 227.

(10) Rau, H. *Chem. Rev.* **1983**, *83*, 535.

0022-3263/93/1958-0100$04.00/0

Chart I

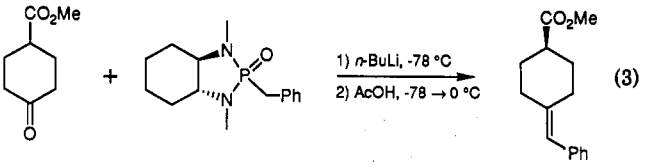


requirements. These compounds must contain a chiral chromophore having g_λ sufficiently large to yield an acceptable $[ee]_{PSS}$. The minimum acceptable $[ee]_{PSS}$ is determined in part by β_M and the maximum pitch that can be sensed in a cholesteric liquid crystalline phase. Also, these compounds must be stable photochemically. In this regard, stability means that irradiation of the homochiral compound leads to no reaction other than its racemization. Finally, photoracemization should occur with a high quantum efficiency (Φ_{Rac}) since the rate of approach to $[ee]_{PSS}$ is exponentially dependent on both g_λ and Φ_{Rac}.

In this paper we report the synthesis and examination of the axially chiral (arylmethylene)cycloalkanes shown in Chart I. In analogy to the well-studied photochemistry of styrenes,[11] we find that their irradiation leads to efficient isomerization of the carbon–carbon double bond and concomitant racemization. Further, although chiral (arylmethylene)cycloalkanes with only one chromophoric group are expected to have very small g_λ values, we find that application of the chiral exciton coupling model[12] for bichromophoric compounds leads to acceptable g_λ values. Finally, although β_M values for a wide range of chiral compounds have been obtained, only a few values for (arylmethylene)cycloalkanes have been reported.[13] We measure the helical twisting power for a series of (arylmethylene)cycloalkanes as well as the detection limit for the long-pitch cholesteric liquid crystal they induce. Although none of the compounds represented in Chart I are suitable for development into an optical switch, their study provides important insight about the necessary criteria for such an application.

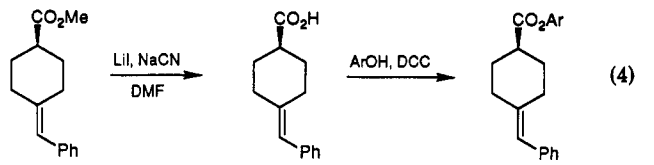
Results

(1) Synthesis of (Arylmethylene)cycloalkanes. Preparation of methyl ester (*R*)-**1b** follows from the adaptation of the Horner–Emmons reaction introduced by Hanessian for preparation of optically active olefins.[14] The reaction sequence, illustrated in eq 3, gives ester **1b** in 70% yield. The optical purity (ee) of **1b** was determined to be 76% by means of ^1H NMR spectroscopy in $CDCl_3$ solution with $Eu(hfc)_3$ as a chiral shift reagent. The *R* absolute configuration of **1b**, assigned by rotation-sign analogy with the ethyl ester prepared by Bestmann,[15] is obtained when the (*R*,*R*)-enantiomer of phosphonate **7** is used with keto ester **6**.



6 7 (*R*)-**1b**

Aryl esters (*R*)-**1c–i** were prepared by hydrolysis of (*R*)-**1b** under neutral, nonaqueous conditions[16] to carboxylic acid (*R*)-**1a** followed by esterification of the acid by dehydration with dicyclohexylcarbodiimide (DCC) and the appropriately substituted phenol derivative as shown in eq 4. That no racemization occurs during this process was deduced from the regeneration of (*R*)-**1b** from (*R*)-**1a** with no loss of optical activity.

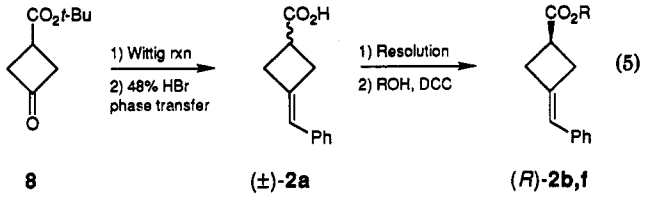


(*R*)-**1b** (*R*)-**1a** (*R*)-**1c-i**

The attempted synthesis of optically active benzylidenecyclobutane esters from methyl 3-ketocyclobutanecarboxylate by the Hanessian adaptation of the Horner–Emmons reaction does not give an acceptable yield. Racemic carboxylic acid **2a** was prepared by the Wittig olefination of *tert*-butyl 3-ketocyclobutanecarboxylate followed by hydrolysis of the *tert*-butyl ester under phase-transfer catalysis conditions.[17] This racemic acid was resolved classically with quinine in ethyl acetate solution to give (*R*)-**2a** having an optical purity of 45% after one crystallization. The carboxylic acid was converted to esters (*R*)-**2b,f** by reaction catalyzed with DCC. These reactions are illustrated in eq 5. A similar procedure was followed for the preparation of the naphthylidenecyclobutanecarboxylic acid precursor of (+)-**5**. The absolute configuration of compounds **2a,b,f** was assigned by analogy of the split Cotton effect in the circular dichroism spectrum

(11) *Essentials of Molecular Photochemistry*; Gilbert, A., Baggott, J., Eds.; CRC Press: Boca Raton, FL, 1991; p 229.
(12) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Photochemistry*; University Science Books: Mill Valley, CA, 1983.
(13) Bonaccorsi, P. M. A.; Dunmur, D. A.; Stoddart, J. F. *Nuv. J. Chem.* **1988**, *12*, 83.
(14) (a) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754. (b) Hanessian, S. Private communication.
(15) Bestmann, H. J.; Heid, E.; Ryschka, W.; Lienert, J. *Liebigs Ann. Chem.* **1974**, 1684.
(16) McMurry, J. E.; Wong, G. B. *Synth. Commun.* **1972**, 389.
(17) Landini, D.; Rolla, F. *J. Org. Chem.* **1982**, *47*, 154.

of **2f** with that of (*R*)-**1f**. These experiments will be described later.



8 (±)-**2a** (*R*)-**2b,f**

The preparation of ketones (*R*)-**3**, (*R*)-**4**, and (+)-**5** was accomplished by reaction of the respective carboxylic acids with phenyllithium. The optical purity of these compounds was determined by means of ^{1}H NMR spectroscopy with Eu(hfc)$_3$ as a chiral shift reagent. There was no detectable racemization during the synthesis of **3** or **4**, but the optical purity of **5** is reduced to 10%, indicating that considerable racemization had occurred.

(2) Photoracemization of (Arylmethylene)cycloalkanes in Isotropic Solution. Irradiation of cyclohexane solutions (2.2×10^{-2} M) of (*R*)-**1b** at 254 nm in a Rayonet photoreactor leads to its complete racemization in less than 15 min without detectable formation of any decomposition products. Indeed, this compound is remarkably stable under these conditions: irradiation of a 3×10^{-3} M solution for 1 h results in the consumption of less than 10% of the ester. Interestingly, the rate of the photoracemization reaction is unaffected by the presence of O_2—a quencher of triplet states. The simultaneous irradiation of N_2-purged and air-saturated solutions of (*R*)-**1b** gives equally efficient racemization of both samples.

In contrast to the behavior observed for **1b**, aryl esters **1c–i** are unstable photochemically. Ultraviolet irradiation of ester (*R*)-**1f**, for example, in O_2-free cyclohexane solution leads to its efficient photoracemization but with its concomitant consumption as monitored by gas chromatography. Although the photochemistry of **1c–i** was not studied in detail, we suspect that the photo-Fries reaction[18] accounts for the instability. The behavior of the methyl cyclobutyl ester (*R*)-**2b** is similar. Photoracemization occurs rapidly, but the compound is unstable photochemically. In this case, the instability is attributed to rupture of a carbon–carbon bond in the cyclobutane ring due, in part, to its high strain.[19] Significantly, the decomposition of ester **2b**, but not its photoracemization, is stopped when its excited state is formed by triplet sensitization with xanthone. This observation encouraged us to prepare ketones **4** and **5**, where intersystem crossing of the singlet state formed by light absorption to the racemizing triplet state will be accelerated by the presence of the carbonyl group. Ketone **3** was prepared to provide a standard for analysis of the circular dichroism spectra of **4** and **5**, its irradiation will lead to rapid decomposition by γ-hydrogen abstraction.

Irradiation of an O_2-free cyclohexane solution of (*R*)-**4** (1.1×10^{-2} M) with a 1000-W Hg–Xe lamp through a 305-nm cut-off filter leads to its complete photoracemization in less than 1 min with no detectable consumption of **4**. However, when the irradiation of (now) racemic **4** is continued for 3 h under these conditions, ca. 50% photodestruction occurs. Similar results are obtained from the irradiation of naphthylidene **5**. Evidently, cleavage of a strained carbon–carbon bond in **4** and **5** is sufficiently rapid to compete even with the accelerated intersystem crossing rate.

(18) *Essentials of Molecular Photochemistry*; Gilbert, A., Baggott, J., Eds.; CRC Press: Boca Raton, FL, 1991; p 407.
(19) DeMare, G. R. *Photochem. Photobiol.* **1978**, *28*, 603.

Table I. Circular Dichroism and Helical Twisting Power Data for Esters 1 and 2

compd	R	$\Delta\epsilon$ (λ_{ext})[a,b]	g_λ (×10^{-4})	β_M (μm^{-1})[b,c] K15[d]	β_M (μm^{-1})[b,c] ZLI-1167[e]
(*R*)-**1b**	CH_3	+0.89 (251)	0.75	9.9	9.0
(*R*)-**1c**	C_6H_5	−3.26 (239)	2.2	18.2	14.3
(*R*)-**1d**	*p*-CNC_6H_4	+5.46 (227)	2.4	27.7	20.0
		−10.4 (245)	4.9		
(*R*)-**1e**	*p*-$NO_2C_6H_4$	+3.36 (241)	1.9	22.9	16.4
		−5.54 (266)	3.9		
(*R*)-**1f**	[1,1′-biphenyl]-4-yl	+5.03 (235)	2.4	29.1	18.0
		−9.96 (258)	3.4		
(*R*)-**1g**	9*H*-fluoren-2-yl	+4.58 (243)	1.8	26.7	19.4
		−10.6 (266)	3.6		
		−1.32 (292)	1.7		
		−1.26 (303)	1.4		
(*R*)-**1h**	2-naphthalenyl	+20.8 (222)	2.6	23.8	16.4
		−15.3 (237)	5.9		
(*R*)-**1i**	2-biphenylenyl	+21.2 (238)	4.2	24.0	19.3
		−46.2 (254)	9.9		
		−0.68 (343)	1.1		
		−0.67 (362)	0.8		
(*R*)-**2f**	[1,1′-biphenyl]-4-yl	+11.1 (238)	4.0	<1.1	1.6
		−33.3 (260)	8.3		

[a] In cyclohexane. [b] Corrected for optical purity of 100% ee. [c] Measured at 25 °C. [d] Dopant concentrations of 0.8–1.8% (w/w). [e] Dopant concentrations of 2.4–6.1% (w/w).

Table II. Circular Dichroism and Helical Twisting Power Data for Ketones 3–5

compd	$\Delta\epsilon$ (λ_{ext})[a,b]	g_λ (×10^{-4})	β_M (μm^{-1})[b,d] K15[e]	β_M (μm^{-1})[b,d] ZLI-1167[f]
(*R*)-**3**	−4.04 (232)	2.0	4.8	5.4
	+8.44 (250)	4.4		
	−0.11 (289)	1.3		
	−0.14 (322)	17.5		
	−0.14 (333)	18.7		
	−0.09 (346)	18.5		
	−0.03 (362)	18.9		
(*R*)-**4**	−10.5 (238)	4.2	6.5	9.3
	+0.80 (253)	0.3		
	−1.16 (262)	0.6		
	−0.42 (293)	8.6		
	−0.47 (320)	50.0		
	−0.49 (332)	59.8		
	−0.36 (345)	69.2		
	−0.16 (361)	100.0		
(+)-**5**	+38.6 (239)	9.0	<5.4	8.6
	+11.9 (256)	1.9		
	+12.2 (280)	8.8		
	+12.9 (288)	7.5		
	+13.2 (302)	8.4		
	+8.81 (312)	25.7		
	+1.54 (328)[c]	21.4		
	+1.10 (342)[c]	21.9		
	+0.36 (358)[c]	73.0		

[a] In cyclohexane. [b] Corrected for optical purity of 100% ee. [c] In benzene. [d] Measured at 25 °C. [e] Dopant concentrations of 0.8–1.5% (w/w). [f] Dopant concentrations of 4.1–6.6% (w/w).

(3) Absorption and Circular Dichroism Spectra of (Arylmethylene)cycloalkanes. In order to assess the utility of the (arylmethylene)cycloalkanes as components of the liquid crystal-based optical switch described in the introduction, the maximum $[ee]_{PSS}$ that can be achieved by photoresolution must be determined. We systematically examined the absorption and circular dichroism spectra of esters **1** and **2** and ketones **3–5** to probe the effect of exciton coupling on $[ee]_{PSS}$ in these compounds. The data are summarized in Tables I and II.

The absorption and circular dichroism spectra of esters **1b**, **1f**, and **2f** in cyclohexane solution are shown in Figures 1 and 2, respectively. These spectra for **1b** are simply

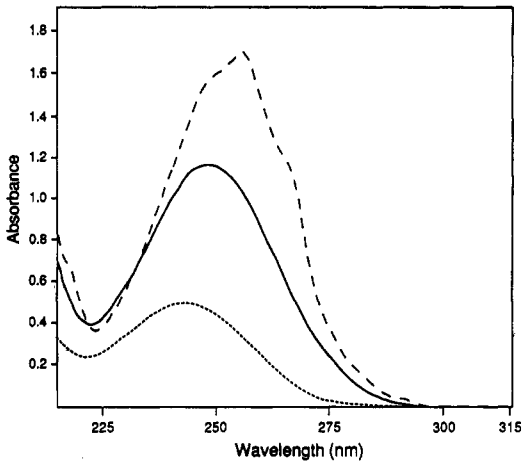


Figure 1. Absorption spectra of esters **1b** (dotted line), **1f** (solid line), and **2f** (dashed line) in cyclohexane solution. The concentration of each ester is 3.6×10^{-3} M.

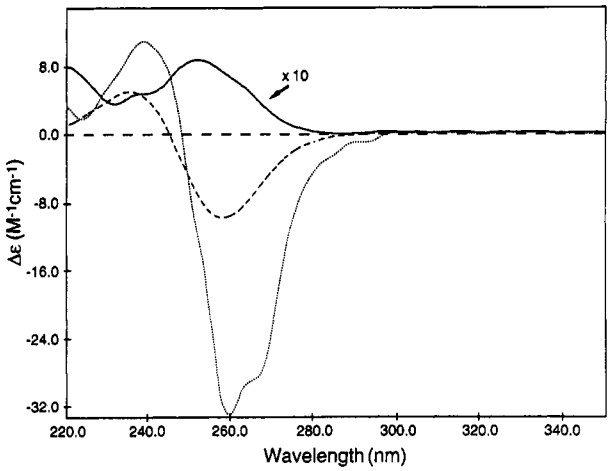


Figure 2. Circular dichroism spectra of esters (*R*)-**1b** (solid line), (*R*)-**1f** (dashed line), and (*R*)-**2f** (dotted line) in cyclohexane solution with concentrations: [**1b**] = 1.2×10^{-3} M; [**1f**] = 3.7×10^{-4} M; [**2f**] = 2.1×10^{-4} M.

interpreted by reference to the electronic properties of styrene. The lowest energy electronic transition (0→0 band, $^1A_{1g} \rightarrow {}^1B_{2u}$) of **1b** occurs at ca. 290 nm.[20] The extinction coefficient (ϵ) of this band at the maximum (243 nm) is 12 500 M^{-1} cm^{-1}. Similarly, the circular dichroism spectrum of (*R*)-**1b** in this region shows a single positive peak with a maximum $\Delta\epsilon$ at 251 nm of 0.89 M^{-1} cm^{-1} (for comparison purposes, $\Delta\epsilon$ values in the text and tables herein are reported for 100% ee based on known optical purities and the observed circular dichroism spectra). These experiments permit calculation of g_λ for **1b**. The maximum anisotropy for this compound, $g_{251} = 7.5 \times 10^{-5}$. According to eq 2, this g_λ value corresponds to a possible $[ee]_{PSS}$ for irradiation of **1b** with circularly polarized light of 3.8×10^{-3}%. This enrichment is too small to detect by optical rotation or other chiroptical techniques, or by liquid crystal-based methods to be described later.

It is well-known that chiral bichromophoric compounds exhibit enhanced g_λ values due to chiral exciton coupling.[12] Consequently, chromophores having large ϵ are most desirable for increasing g_λ. Similarly, chiral exciton coupling theory predicts that the magnitude of $\Delta\epsilon$ will depend on the spectral overlap, separation distance, and orientation of the transition dipoles of the two chromophores. Operation of chiral exciton coupling is usually not detected in absorption spectra, but its occurrence causes the unmistakable split Cotton effect in circular dichroism spectra. We prepared esters (*R*)-**1c–i** and (*R*)-**2b,f** to examine chiral exciton coupling in the (arylmethylene)cycloalkanes.

The absorption spectrum of ester **1f**, shown in Figure 1, is essentially the sum of the spectra of the appropriate model compounds: benzylidenecyclohexane and 4-acetoxy-1,1′-biphenyl. In contrast, the circular dichroism spectrum of (*R*)-**1f**, shown in Figure 2, clearly shows the split Cotton effect. Its characteristic sigmoid shape reveals unsymmetrical Davydov splitting of the two coupled electronic transitions. Significantly, the values of $\Delta\epsilon$ for (*R*)-**1f** are much greater than for (*R*)-**1b**. At the positive maximum (235 nm) $\Delta\epsilon = 5$ M^{-1} cm^{-1} and at the negative extreme (258 nm) $\Delta\epsilon = -10$ M^{-1} cm^{-1}. This latter value is more than 10 times larger than it is for (*R*)-**1b**. The corresponding data for esters (*R*)-**1c–i** are reported in Table I. On the basis of these findings, the maximum $[ee]_{PSS}$ achievable for these compounds is for **1i** and corresponds to 50×10^{-3}%—a value sufficiently large to induce detectable cholesteric behavior in nematic liquid crystal constituted with mesogens containing this group (see below).

The cyclobutyl esters (*R*)-**2b,f** were prepared to examine the effect of distance on $\Delta\epsilon$. The chiral exciton coupling model predicts that this value should increase inversely with the distance between the chromophores. The absorption spectrum of **2f** is shown in Figure 1. Clearly it is different from that of **1f**; however, this difference is not due to an exciton interaction since the absorption spectrum of **2f** is essentially the sum of its chromophoric parts. Instead, the difference between the absorption spectra of **1f** and **2f** is a consequence of perturbation of the simple styrene chromophore by its incorporation in the four-membered ring. There are also meaningful differences between the circular dichroism spectra of esters (*R*)-**1f** and (*R*)-**2f**. Both show the split Cotton effect, but $\Delta\epsilon$ for (*R*)-**2f** is much greater than it is for (*R*)-**1f** (see Table I). It is likely that this increase is due to both a decrease in the interchromophoric distance and an increase in the spectral overlap for the two chromophores.

Figure 3 is the absorption spectra of ketones **3** and **4**, and Figure 4 shows the long-wavelength portion of their circular dichroism spectra. In addition to the features already described in the absorption spectra of esters **1** and **2**, ketones **3** and **4** show distinct $n\pi^*$ absorption bands at relatively low energy. Significantly, their circular dichroism spectra in the $n\pi^*$ absorption region show specially large g_λ values since the unsymmetrical Davydov splitting shifts the strong split Cotton band onto the weakly absorbing $n\pi^*$ transition. Consequently, the $[ee]_{PSS}$ calculated for irradiation of **4** at 361 nm is 500×10^{-3}%. This value is more than 100 times greater than **1b** and is well above the minimum required to induce cholesteric behavior in a suitably constituted nematic liquid crystal. The data are summarized in Table II.

(4) Chiral (Arylmethylene)cycloalkanes in Liquid Crystals. Previous work by Solladie and Zimmermann has shown that axially chiral methylenecyclohexane compounds, when appropriately substituted, form liquid

(20) *Theory and Applications of Ultraviolet Spectroscopy*; Jaffe, H. H., Orchin, M., Eds.; John Wiley and Sons: New York, 1962; p 242.

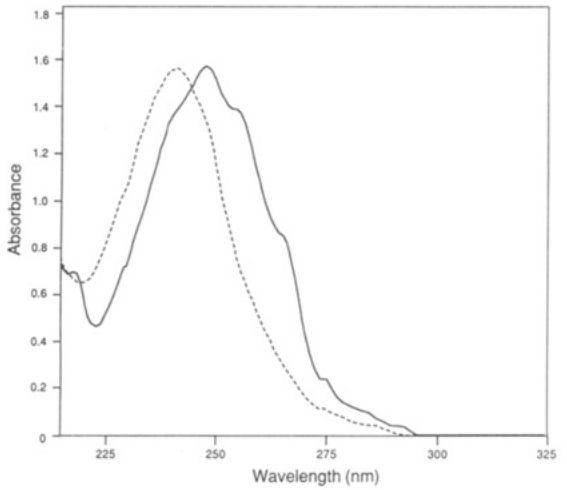


Figure 3. Absorption spectra of ketones **3** (solid line) and **4** (dashed line) in cyclohexane solution with concentrations [**3**] = 6.0×10^{-5}; [**4**] = 5×10^{-5} M.

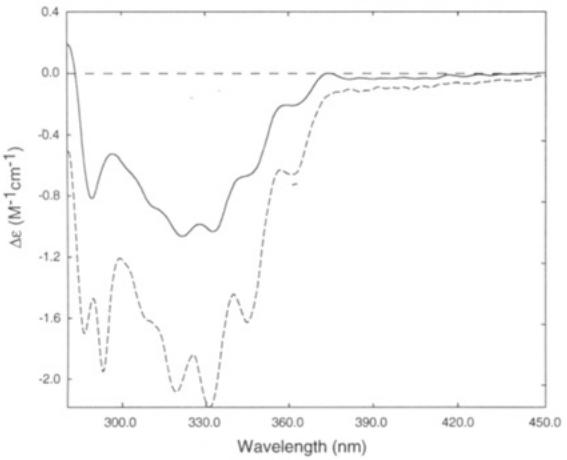


Figure 4. Circular dichroism spectra of ketones (*R*)-**3** (solid line) and (*R*)-**4** (dashed line) in cyclohexane solution with concentrations: [**3**] = 1.1×10^{-2} M; [**4**] = 1.1×10^{-2} M.

crystal phases.[21] Similarly, Bonaccorsi and co-workers have shown that addition of optically active (arylmethylene)cyclohexane derivatives to a nematic liquid crystal induces a cholesteric phase.[13] On the basis of these results, we hoped that optically active esters (*R*)-**1** and (*R*)-**2** and ketones (*R*)-**3**, (*R*)-**4**, and (+)-**5** would similarly induce cholesteric behavior in nematic liquid crystals and, when appropriately substituted, themselves form liquid crystal phases. In addition, we sought to verify the hypothesis that irradiation of cholesteric liquid crystals containing a photoracemizable, optically active (arylmethylene)cycloalkane with unpolarized light will convert it to a compensated nematic phase and that irradiation of this compensated nematic phase with circularly polarized light will regenerate the cholesteric liquid crystal.

All of the optically active (arylmethylene)cycloalkanes examined induce cholesteric behavior when they are added to a nematic liquid crystal host. Experiments were conducted with K15 (4-*n*-pentyl-4′-cyano-1,1′-biphenyl) and with ZLI-1167 (a mixture of 4-*n*-alkyl-4′-cyano-1,1′-bicyclohexyls) and were analyzed by optical microscopy.[22]

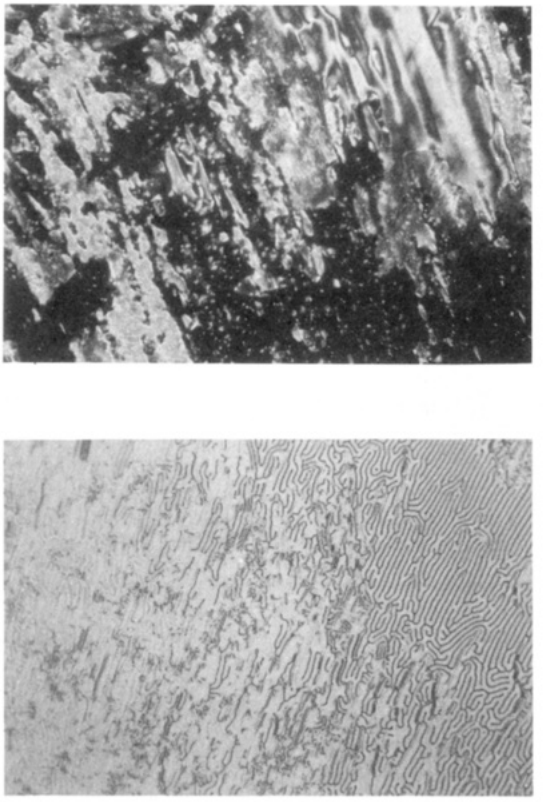


Figure 5. (a) Marbled texture of unoriented K15 at room temperature viewed microscopically through crossed polarizers at 100× magnification. (b) Cholesteric fingerprint texture formed by the addition of 1% (*R*)-**1f** to K15 viewed under the same conditions as in a.

Figure 5a shows the "marbled" texture characteristic of unoriented K15 at 25 °C. Addition of 1% (by weight) (*R*)-**1f** (76% ee) to the K15 sample results in the formation of a cholesteric liquid crystal as evidenced by the "fingerprint" texture of the sample shown in Figure 5b. Similar results were obtained for the other compounds examined.

The β_M values for the (arylmethylene)cycloalkanes were determined by the "droplet" method[23] and the results obtained compared with the fingerprint texture formed when **1f** is dissolved in homeotropically aligned K15 at 25 °C. Surprisingly, these analyses give somewhat different results. Figure 6a shows droplets of K15 containing 1% of (*R*)-**1f** suspended in glycerol. Calculation of β_M by measurement of the distance between the rings of the spirals (distance = $1/2p$) gives a value of 29 μm^{-1} (18 μm^{-1} in ZLI-1167). Figure 6b shows the same sample of K15 homeotropically aligned by treatment of the lower glass surface with octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride according to the procedure reported by Labes.[24] Examination of the characteristic fingerprint texture of this preparation shows a line-spacing of 30 μm which corresponds to an apparent $\beta_M \approx 6\ \mu m^{-1}$. Evidently, the helical twisting power of an additive in these liquid crystals is dependent on the nature of the alignment. The results obtained from related experiments with the other (arylmethylene)cycloalkanes examined are reported in Tables I and II.

The limit of detectability for induction of cholesteric behavior by the (arylmethylene)cycloalkanes must be

(21) Solladie, G.; Zimmermann, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 64.

(22) (a) Hartshore, N. H. *The Microscopy of Liquid Crystals*; Microscope Publications Ltd.: London, 1974. (b) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.

(23) (a) Seuron, P.; Solladie, G. *Mol. Cryst. Liq. Cryst.* **1979**, *56*, 1. (b) Candau, S.; LeRoy, P.; Debeauvais, F. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 283.

(24) Labes, M. M.; Shang, W. *J. Am. Chem. Soc.* **1991**, *113*, 2773.

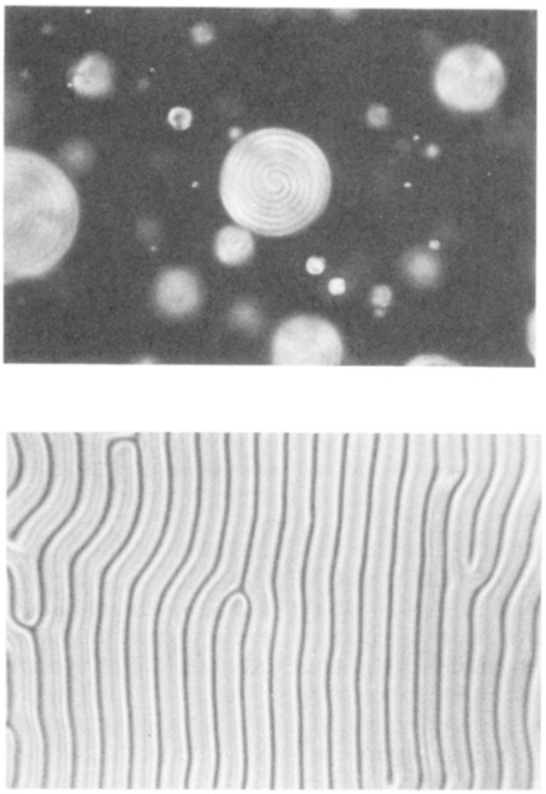


Figure 6. (a) A droplet of K15 containing 1% by weight of (*R*)-**1f** viewed microscopically in glycerol between crossed polarizers at 400× magnification. The pitch, twice the spacing between lines in the spiral, is 6 μm. (b) A homeotropically aligned solution of K15 identical to that in part a viewed under the same conditions. The spacing between the lines in the fingerprint texture is 30 μm.

determined in order to assess the feasibility of detecting their photoresolution with circularly polarized light. Figure 7a shows the edge of a drop of pure K15 observed by optical microscopy at 25 °C. Addition of 0.38% (by weight) of (*R*)-**1c** converts these droplets to the one shown in Figure 7b. The drop in Figure 7b exhibits a fingerprint texture characteristic of cholesteric liquid crystal behavior. The pitch in this sample, estimated from eq 1 and the results reported in Table I, is 22 μm. Figure 7c,d shows similar preparations containing 0.15% and 0.093% (*R*)-**1c** in K15, respectively. The pitch determined for these samples is 56 and 91 μm, respectively. On the basis of these experiments, and for the purposes of this work, we set a pitch of 90 μm as the limit for detection of inducible cholesteric behavior by the arylmethylene cycloalkanes.

The photochemistry of (*R*)-**1b** and (*R*)-**4** was examined in liquid crystalline media. Figure 8a shows a sample of ZLI-1167 containing 2.3% of (*R*)-**1b** at 35 °C. The "oily streak" texture characteristic of a short-pitch cholesteric liquid crystal is readily apparent. A thin, air-saturated preparation of this solution was irradiated through a quartz slide for 5 s with the 1000-W lamp through a 230-nm cutoff filter. Microscopic examination of the resulting liquid crystal phase, Figure 8b, shows that complete conversion to a marbled texture characteristic of a nematic phase has occurred. We attribute this change in the liquid crystal phase to the photoracemization of (*R*)-**1b** based on analogy with the observed photochemistry in isotropic solution.

Discussion

A primary goal of this work was to investigate the feasibility of using axially chiral (arylmethylene)cycloalkanes as light-sensitive components in a liquid crystal-based optical switch. As one step toward this objective, we prepared a series of optically active esters and ketones and investigated their photochemistry and chiroptical properties in isotropic solution and in liquid crystalline phases. This investigation shows that these compounds satisfy most of the critical criteria established thus far for application as a liquid crystal-based optical switch.

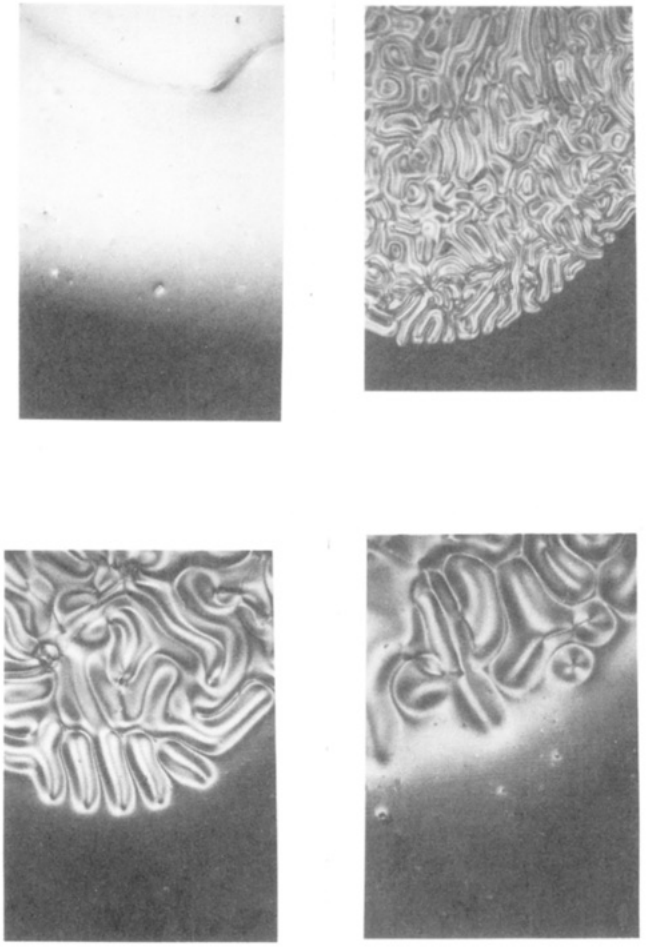


Figure 7. (a) A free drop of K15 at room temperature viewed microscopically through crossed polarizers at 100× magnification. (b) A free drop of K15 containing 0.38% (*R*)-**1c**. The fingerprint texture, p = 22 μm. (c) Same as b but with 0.15% (*R*)-**1c**. The pitch = 56 μm. (d) Same as b but with 0.093% (*R*)-**1c**. The pitch = 91 μm. This is the experimentally determined limit of detectability for a long-pitch cholesteric phase.

(1) Photochemistry of (Arylmethylene)cycloalkanes. The photochemistry of esters **1** and **2** and ketones **3**, **4**, and **5** is simultaneously simple and complex. As expected by analogy with the previous examination of styrene derivatives,[11] excitation of these compounds leads to rotation about the carbon–carbon double bond. In related systems, this reaction occurs from both singlet and triplet excited states. For the optically active compounds studied in this work, rotation about the carbon–carbon double bond causes racemization. In the case of ester **1b**, racemization is essentially the only photochemical process observed, but for the other compounds studied photodecomposition processes compete with photoracemization.

Photoracemization of these esters and ketones occurs with high efficiency on the triplet excited state surface. The sensitization experiment shows clearly that isomerization can originate from the triplet state. The observation that isomerization is unaffected by the presence of O_2 implicates either an important role for the singlet

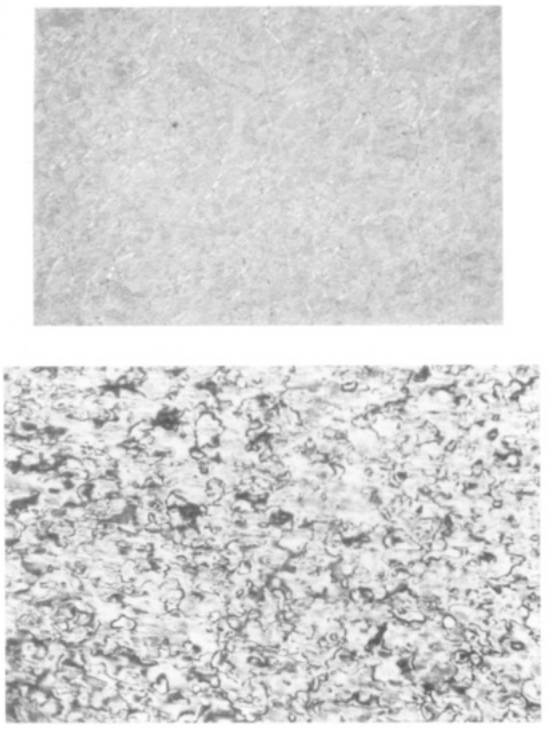


Figure 8. (a) A sample (*R*)-**1d** (2.3%) in ZLI-1167 at 35 °C viewed microscopically between crossed polarizers at 100× magnification. An oily streak texture characteristic of a cholesteric phase is apparent. (b) Same preparation viewed under identical conditions as in a but after 5 s irradiation. A marbled texture indicating a nematic liquid crystal phase is observed.

excited state or, more likely, very rapid rotation in the triplet to a "perpendicular" state which either cannot be quenched by O_2 or, if quenched, gives equal amounts of the two enantiomers.

Apart from ester **1b**, irradiation of the compounds studied in this work leads to their eventual irreversible consumption. These photochemical reactions were not studied in detail. However, it is likely that the well-known photo-Fries carbon–oxygen bond cleavage of aryl esters is responsible for consumption of **1c–i**. The reactions of cyclobutane-containing compounds **2**, **4**, and **5** are more complex. A detailed study of their photochemistry is presently underway.

(2) Circular Dichroism and Chiral Exciton Coupling. Achievement of the objectives of this research requires the discovery of compounds able to undergo photoresolution by irradiation with circularly polarized light. The $[ee]_{PSS}$ that can be obtained in such a process is determined by g_λ as shown in eq 1. Although all homochiral compounds have finite g_λ values, normally they are very small and thus yield an $[ee]_{PSS}$ too small for our purposes. An excellent example of this case is ester **1b** where the maximum anisotropy, g_{251}, is 7.5×10^{-5}. The magnitude of g_λ is much larger in inherently chiral chromophores[25] such as the helicenes than it is in homochiral compounds with isolated chromophores. This fact has been exploited in the photochemical synthesis of hexahelicene with circularly polarized light.[26,27] Similarly, directly linked chromophores such as 1,1′-binaphthyl derivatives can have large g_λ values. The suitability of these compounds for photoresolution in liquid crystals is presently being explored.[28]

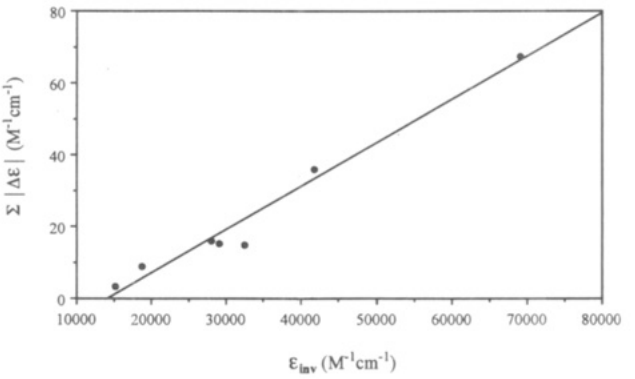


Figure 9. The approximate magnitude of the split Cotton effect for esters **1c–i** versus the extinction coefficient in the UV spectrum at the wavelength of the zero crossing (ϵ_{inv}) for the split Cotton band.

A second way to increase the magnitude of g_λ is by taking advantage of the chiral exciton coupling of two separate chromophores in the same molecule.[12] In this approach, the two chromophores are located in chiral positions with respect to each other. Exciton interaction between the chromophores splits the excited states of the molecule into two levels that are separated in energy by the Davydov splitting. The circular dichroism spectra of such molecules show opposite Cotton effects for absorption to these two levels. This interaction gives rise to a characteristic sigmoid circular dichroism feature known as the split Cotton effect. The magnitude ($\Delta\epsilon$) and the sign of the split Cotton effect depends on the interchromophoric distance vector, the electric transition dipole moments of excitation, and the interaction energy between the two chromophoric groups. In general, therefore, the magnitude of $\Delta\epsilon$ will increase directly with the spectral overlap of the two chromophores and with the product of their extinction coefficients and inversely with the distance between them. An excellent example is provided by Harada and Nakanishi:[12] A mono-*p*-(dimethylamino)benzoate-substituted steroid has $\Delta\epsilon_{Max} = 2.9$, the 3,4-bis-*p*-(dimethylamino)benzoate derivative of this steroid has $\Delta\epsilon_{Max} = 39.7$.

Our objective is to maximize g_λ for photoresolvable compounds. The magnitude of g_λ will increase directly with $\Delta\epsilon$ and decrease inversely with ϵ. Thus to achieve this objective, the magnitude of $\Delta\epsilon$ in a bichromophoric molecule must increase more than the magnitude of ϵ. This is precisely the prediction from application of chiral exciton coupling theory to bichromophoric compounds: $\Delta\epsilon$ should increase approximately as the product of ϵ, whereas the extinction coefficient of the bichromophoric compound should increase only as the sum of the ϵ values for the individual chromophores. We prepared the series of esters **1b–i** to test and exploit this prediction.

The data in Table I and Figures 1 and 2 reveal the success of chiral exciton coupling theory in predicting the behavior of the chiral (arylmethylene)cycloalkanes. Changing the aryl group in the esters **1** leads to more than a 50-fold increase in $\Delta\epsilon$ and a 1 order of magnitude increase in g_λ (compare **1b** and **1i**). Indeed, Figure 9 shows that the magnitude of the Cotton effect on the (arylmethylene)cycloalkanes is approximately linearly related to the extinction coefficient of the aryl ester chromophore. Similarly, comparison of the cyclohexane derivative **1f** with

(25) O,Loane, J. K. *Chem. Rev.* **1980**, *80*, 41.
(26) Mosdpour, A.; Nicoud, J. F.; Balavoine, G.; Kagan, H.; Tsoucaris, G. *J. Am. Chem. Soc.* **1971**, *93*, 2353.
(27) Bernstein, W. J.; Calvin, M.; Buchardt, O. *J. Am. Chem. Soc.* **1972**, *94*, 494.
(28) Zhang, M.; Schuster, G. B. *J. Phys. Chem.* **1992**, *96*, 3063.

the cyclobutane derivative **2f** shows a 3-fold increase in both $\Delta\epsilon$ and g_λ. In this case we attribute the increased values to both better spectral overlap of the styrene-like and ester chromophores and to the decrease in distance between these groups in the cyclobutane derivative. The absorption of the benzylidenecyclobutane group is shifted to low energy, and its extinction coefficient is increased when compared with the benzylidenecyclohexane group. These shifts may be an effect of the increased angle strain and improved planarity of the π-system in the four-membered ring case.

We prepared ketones **3–5** primarily in an attempt to enhance the intersystem crossing rate of their excited singlets and thereby stabilize the (arylmethylene)cyclobutanes against photodegradation. This change in structure also has an important effect on the circular dichroism spectra of these compounds. The data in Table II show that g_λ reaches the maximum value obtained in this investigation in the case of (*R*)-**4**. The circular dichroism spectrum of this compound shows the expected split Cotton band for the stronger $\pi\pi^*$ transitions, but the spectrum in the $n\pi^*$ region shows only a simple negative Cotton effect band. However, there must be some borrowing of intensity from the more allowed transitions since $\Delta\epsilon$ is larger than expected for a simple carbonyl-containing chromophore. This interaction, and the small ϵ characteristic of $n\pi^*$ absorptions, leads to very large g_λ values. Also, comparison of ketones **3** and **4** reveals that change from the six-membered to four-membered ring cycloalkanes in this instance, too, gives enhanced $\Delta\epsilon$. These findings direct our search for compounds with large g_λ values to those that have intense split Cotton bands at slightly higher energy than a symmetry-forbidden electronic transition.

(3) Chiral (Arylmethylene)cycloalkanes as Additives to Liquid Crystals. Achievement of the objectives of this research requires compounds that undergo photoresolution and are simultaneously able to induce cholesteric behavior in liquid crystals with high efficiency. The helical twisting power (β_M) is a measure of a compounds ability to induce cholesteric behavior. It is generally observed that the more a chiral additive is chemically or structurally "like" the molecules of the liquid crystal material, the greater is the value for β_M.[29] The results reported in Tables I and II are generally consistent with this tendency. Extrapolation of this trend to its extreme suggests that the maximum values for β_M will be obtained for addition of one enantiomer of a chiral compound to a liquid crystal material made from the racemic mixture of that compound. On this basis we consider the β_M values in Tables I and II to be lower limits to the values that would be obtained if the structures of these ketones and esters were modified so that they themselves formed liquid crystals.

The experimental limit of detection for the pitch induced in a nematic liquid crystal by the chiral arylmethylene cycloalkanes studied is ca. 90 μm. Substitution of this limit into eq 2 when the concentration of molecules in a neat liquid crystal phase (C) is defined to be 1.0 gives as a minimum necessary value of $[\beta_M\gamma]$ of 1×10^{-2}. Inspection of the data in Tables I and II shows that three of the compounds examined (**1f**, **4**, and **5**) fulfill this requirement. Thus, in principle, they might be suitable components of a liquid crystal-based optical switch of the kind described in the introduction section.

Conclusion

Photoresolvable Mesogens. A mesogen is a molecule that forms a liquid crystal phase at some temperature and pressure. In this work we have shown the feasibility of the construction of a photoresolvable mesogen based on the chiral arylmethylene cycloalkane structure. A suitably substituted version of such a compound will have $[\beta_M\gamma] > 10^{-2}$ and, when racemic, form a compensated nematic phase at or near room temperature. In principle, on the basis of these findings we predict that irradiation of a homeotropically oriented nematic preparation of such a liquid crystal with circularly polarized light will convert it to a detectable cholesteric form. Irradiation of the cholesteric form with unpolarized light will reform the nematic phase. We have demonstrated the key requirements needed to accomplish this sort of light-induced phase modification. In future work we will incorporate these principles in compounds selected for their photochemical stability and substituted so as to be mesogens themselves.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on General Electric QE-300 and GN-500 spectrometers, respectively; the chemical shifts in $CDCl_3$ and DMSO-d_6 are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low-resolution EI mass spectra were recorded on a Varian-MAT CH-5 mass spectrometer with an ionization voltage of 70 eV; peaks are reported as m/e (% intensity relative to base peak). UV spectra were recorded on a Perkin-Elmer 552 spectrometer in cyclohexane. CD spectra were recorded on a SPEX CD VI (Jobin-Yvon, France) spectrometer in cyclohexane. Optical rotations were measured on a JASCO DIP-360 digital polarimeter at room temperature. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Gas chromatography 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. Microscopic analyses were performed with a Fisher Micromaster polarizing microscope equipped with a Mettler FP82 hot stage. Helical twisting power (β_M) values were measured in K15 (BDH) and ZLI-1167 (E. Merck) liquid crystals using the "droplet" method.[23] Homeotropically aligned preparations of cholesteric liquid crystals were obtained using the method of Labes.[24] Flash chromatography was performed with 32–63-μm silica gel (Woelm) or Activity 1 neutral alumina (Brinkmann) according to the method of Still.[30] Melting points were measured on a Buchi apparatus and are uncorrected.

Materials. All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. Benzene, diethyl ether (ether), and tetrahydrofuran (THF) were distilled from Na/benzophenone, acetonitrile (CH_3CN), and dimethylformamide (DMF) from CaH_2, and methylene chloride (CH_2Cl_2) from P_2O_5. Cyclohexane was of spectrophotometric grade (Burdick & Jackson) and used without further purification. Solutions of *n*-BuLi (Aldrich) were titrated using the method of Tischer and Tishler.[31] The optical purities of compounds (*R*)-**1b**, (*R*)-**2b**, (*R*)-**3**, (*R*)-**4**, and (+)-**5** were determined by ^{1}H NMR spectroscopy at 500 MHz using Eu(hfc)$_3$ (3 equiv, Aldrich) as chiral shift reagent. In all cases, baseline resolution was achieved for the vinyl proton signal. The following compounds were prepared by literature procedures and shown to have the expected physical and spectral properties: methyl 4-oxocyclohexanecarboxylate (**6**),[32] [3a*R*-(2α,3aα,7aβ)]-2-benzyloctahydro-1,3-dimethyl-1*H*-1,3,2-benzodiazaphos-

(29) Gottarelli, G.; Samori, B.; Fuganti, C.; Graselli, C. *J. Am. Chem. Soc.* **1981**, *103*, 471.

(30) Still, W. C.; Hahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(31) Tischer, A. M.; Tishler, M. H. *Aldrichimica Acta* **1978**, *11*, 20.
(32) Black, R. M. *Synthesis* **1981**, 829.

phole 2-oxide (7),[14] 2-biphenylenol,[33] 3-oxocyclobutanecarboxylic acid,[34] (2-naphthalenylmethyl)triphenylphosphonium bromide,[35] [1,1'-biphenyl]-4-yl acetate,[36] (cyclohexylidenemethyl)benzene,[37] and (cyclobutylidenemethyl)benzene.[38]

Methyl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1b). Under a N_2 atmosphere, a 1.57 M solution of *n*-BuLi in hexanes (1.34 mL) was added by syringe to a stirred solution of 7 (584 mg, 2.1 mmol) in dry THF (10 mL) cooled to −78 °C. The mixture was stirred at −78 °C for 0.5 h, and a solution of 6 (312 mg, 2.0 mmol) in dry THF (3 mL) was added dropwise. The resulting mixture was stirred at −78 °C for 1.5 h and quenched with glacial AcOH (1 mL). The mixture was then allowed to warm to 25 °C over 1 h, poured into 50 mL of ether, and washed with water (15 mL), saturated aqueous $NaHCO_3$ (15 mL) and water (15 mL). The organic phase was dried ($MgSO_4$) and concentrated to give a yellow oil. Purification by flash chromatography on neutral alumina (10% EtOAc/hexane) afforded 325 mg of 1b (71% yield, 76% ee) as a clear oil: $[\alpha]_D$ = −41.8° (*c* 0.80, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51–1.75 (m, 2 H), 1.95–2.11 (m, 3 H), 2.20–2.29 (m, 1 H), 2.39–2.46 (m, 1 H), 2.50–2.60 (m, 1 H), 2.81–2.88 (m, 1 H), 3.68 (s, OCH_3), 6.28 (s, 1 H), 7.17–7.22 (m, 3 H), 7.29–7.34 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.7, 29.7, 30.4, 35.8, 42.8, 51.6, 123.2, 126.0, 128.1, 128.8, 137.9, 140.7, 175.8; MS (70 eV, EI) *m/e* 230 (M^+, 48), 199 (4), 170 (100), 155 (16), 141 (18), 129 (42), 115 (31), 91 (48), 87 (28), 78 (33); UV (C_6H_{12}) λ_{max} 243 (log ε 4.10); CD (C_6H_{12}) λ_{ext} 251 (Δε +0.68).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.25; H, 7.86.

(*R*)-4-(Phenylmethylene)cyclohexanecarboxylic Acid (1a). Under a N_2 atmosphere, 1b (264 mg, 1.15 mmol, 76% ee), LiI (790 mg, 5.9 mmol), and NaCN (56 mg, 1.15 mmol) were combined in dry DMF (2 mL). The mixture was refluxed with stirring for 45 min. After cooling, the mixture was poured into 20 mL of water and carefully acidified to pH 2 by dropwise addition of 2 M aqueous HCl. The mixture was extracted with ether (2 × 25 mL), and the combined extracts were washed with water (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated to give 241 mg (96%) of 1a as a thick oil: $[\alpha]_D$ = −29.3° (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53–1.78 (m, 2 H), 1.99–2.15 (m, 3 H), 2.22–2.31 (m, 1 H), 2.41–2.48 (m, 1 H), 2.53–2.63 (m, 1 H), 2.82–2.89 (m, 1 H), 6.30 (s, 1 H), 7.17–7.22 (m, 3 H), 7.29–7.34 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 29.4, 30.1, 35.6, 42.6, 123.4, 126.1, 128.1, 128.8, 137.8, 140.4, 181.9; MS (70 eV, EI) *m/e* 216 (M^+, 68), 198 (2), 180 (16), 170 (50), 155 (11), 143 (15), 141 (16), 129 (63), 125 (17), 115 (33), 104 (20), 91 (100), 79 (41).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.50.

Phenyl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1c). Under a N_2 atmosphere, 120 mg (0.58 mmol) of solid DCC was added to a stirred solution of 1a (114 mg, 0.53 mmol) and phenol (105 mg, 1.1 mmol) in dry CH_2Cl_2 (2 mL). The mixture was stirred at 25 °C for 24 h and then filtered through a coarse fritted-glass funnel. The filtrate was washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), and concentrated to give a crude solid. Purification by flash chromatography on neutral alumina (5% EtOAc/hexane) afforded 102 mg (66%) of 1c as a white solid: mp 58–60 °C; $[\alpha]_D$ = −51.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66–1.91 (m, 2 H), 2.06–2.28 (m, 3 H), 2.32–2.38 (m, 1 H), 2.47–2.54 (m, 1 H), 2.76–2.85 (m, 1 H), 2.89–2.96 (m, 1 H), 6.33 (s, 1 H), 7.05–7.08 (m, 2 H), 7.19–7.25 (m, 4 H), 7.30–7.41 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 29.6, 30.1, 35.6, 42.9, 121.5, 123.5, 125.7, 126.1, 128.1, 128.9, 129.4, 137.8, 140.4, 150.8, 173.8; MS (70 eV, EI) *m/e* 292 (M^+, 36), 198 (16), 171 (94), 155 (4), 143 (17), 129 (100), 117 (24), 115 (32), 105 (8), 94 (22), 91 (83); UV (C_6H_{12}) λ_{max} 242 (log ε 4.18); CD (C_6H_{12}) λ_{ext} 239 (Δε −2.48).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.12; H, 6.91.

4-Cyanophenyl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1d). The procedure described for the preparation of 1c was used with 108 mg (0.5 mmol) of 1a, 119 mg (1.0 mmol) of 4-cyanophenol, and 116 mg (0.56 mmol) of DCC to afford 27 mg (17%) of 1d as a white solid: mp 74–77 °C; $[\alpha]_D$ = −55.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65–1.90 (m, 2 H), 2.04–2.38 (m, 4 H), 2.47–2.54 (m, 1 H), 2.77–2.96 (m, 2 H), 6.34 (s, 1 H), 7.16–7.23 (m, 5 H), 7.30–7.35 (m, 2 H), 7.69 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5, 29.4, 30.1, 35.5, 42.9, 109.6, 118.2, 122.7, 123.8, 126.2, 128.1, 128.8, 133.6, 137.7, 139.9, 154.1, 172.9; MS (70 eV, EI) *m/e* 317 (M^+, 27), 199 (22), 171 (100), 143 (15), 129 (94), 117 (21), 115 (29), 105 (7), 91 (83); UV (C_6H_{12}) λ_{max} 236 (log ε 4.45); CD (C_6H_{12}) λ_{ext} 227 (Δε +4.15), 235 (0.0), 245 (−7.87).

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.20; H, 6.17; N, 4.66.

4-Nitrophenyl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1e). The procedure described for the preparation of 1c was used with 108 mg (0.5 mmol) of 1a, 139 mg (1.0 mmol) of 4-nitrophenol, and 116 mg (0.56 mmol) of DCC to afford 55 mg (33%) of 1e as a white solid: mp 83–86 °C; $[\alpha]_D$ = −62.3° (*c* 0.78, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66–1.91 (m, 2 H), 2.07–2.39 (m, 4 H), 2.48–2.55 (m, 1 H), 2.79–2.98 (m, 2 H), 6.34 (s, 1 H), 7.17–7.36 (m, 7 H), 8.25–8.30 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5, 29.5, 30.2, 35.5, 42.9, 122.4, 123.8, 125.2, 126.2, 128.1, 128.8, 137.7, 139.9, 145.2, 155.6, 172.8; MS (70 eV, EI) *m/e* 337 (M^+, 26), 199 (18), 171 (100), 143 (17), 129 (82), 117 (19), 115 (24), 109 (6), 105 (7), 99 (6), 91 (90); UV (C_6H_{12}) λ_{max} 249 (log ε 4.28); CD (C_6H_{12}) λ_{ext} 241 (Δε +2.55), 252 (0.0), 266 (−4.21).

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.33; H, 5.79; N, 4.05.

[1,1'-Biphenyl]-4-yl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1f). The procedure described for the preparation of 1c was used with 206 mg (0.95 mmol) of 1a, 360 mg (2.0 mmol) of [1,1'-biphenyl]-4-ol, and 220 mg (1.06 mmol) of DCC to afford 243 mg (70%) of 1f as a white solid: mp 90–92 °C; $[\alpha]_D$ = −64.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 1.68–1.93 (m, 2 H), 2.07–2.29 (m, 3 H), 2.34–2.39 (m, 1 H), 2.49–2.56 (m, 1 H), 2.78–2.88 (m, 1 H), 2.90–2.98 (m, 1 H), 6.34 (s, 1 H), 7.12–7.17 (m, 2 H), 7.19–7.23 (m, 3 H), 7.31–7.37 (m, 3 H), 7.41–7.46 (m, 2 H), 7.53–7.61 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 29.6, 30.3, 35.6, 42.9, 121.8, 123.5, 126.1, 127.1, 127.3, 128.11, 128.13, 128.8, 128.9, 137.8, 138.9, 140.3, 140.4, 150.1, 173.9; MS (70 eV, EI) *m/e* 368 (M^+, 7), 198 (11), 170 (100), 141 (8), 129 (32), 117 (8), 115 (14), 105 (3), 91 (32); UV (C_6H_{12}) λ_{max} 248 (log ε 4.52); CD (C_6H_{12}) λ_{ext} 235 (Δε +3.82), 245 (0.0), 258 (−7.57).

Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.56. Found: C, 84.76; H, 6.54.

9*H*-Fluoren-2-yl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1g). The procedure described for the preparation of 1c was used with 108 mg (0.5 mmol) of 1a, 91 mg (0.5 mmol) of 9*H*-fluoren-2-ol, and 116 mg (0.56 mmol) of DCC to afford 124 mg (66%) of 1g as a white solid: mp 162–165 °C; $[\alpha]_D$ = −69.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69–1.94 (m, 2 H), 2.08–2.30 (m, 3 H), 2.34–2.39 (m, 1 H), 2.49–2.56 (m, 1 H), 2.79–2.88 (m, 1 H), 2.91–2.98 (m, 1 H), 3.90 (s, 2 H), 6.34 (s, 1 H), 7.07 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.20–7.40 (m, 8 H), 7.53 (d, *J* = 7.4 Hz, 1 H), 7.75–7.80 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 29.6, 30.3, 35.6, 36.9, 42.9, 118.4, 119.8, 120.0, 120.3, 123.5, 125.0, 126.1, 126.6, 126.8, 128.1, 128.9, 137.8, 139.4, 140.4, 140.9, 143.2, 144.5, 149.8, 174.1; MS (70 eV, EI) *m/e* 380 (M^+, 5), 182 (100), 171 (4), 152 (5), 129 (15), 117 (4), 115 (6), 91 (18); UV (C_6H_{12}) λ_{max} 257 (log ε 4.49), 262 (4.49), 292 (3.89), 303 (3.96); CD (C_6H_{12}) λ_{ext} 243 (Δε +3.48), 252 (0.0), 266 (−8.03), 292 (−1.0), 303 (−0.96).

Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 85.21; H, 6.40.

2-Naphthalenyl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1h). The procedure described for the preparation of 1c was used with 109 mg (0.5 mmol) of 1a, 144 mg (1.0 mmol) of 2-naphthalenol, and 166 mg (0.56 mmol) of DCC to afford 127 mg (74%) of 1h as a white solid: mp 103–105 °C; $[\alpha]_D$ = −68.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71–1.96 (m, 2 H), 2.09–2.40 (m, 4 H), 2.51–2.57 (m, 1 H), 2.82–2.99 (m, 2 H), 6.35 (s, 1 H), 7.19–7.23 (m, 4 H), 7.31–7.36 (m, 2 H), 7.43–7.58 (m, 3 H), 7.78–7.87 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 29.6,

(33) Blatchly, J. M.; Gardner, D. V.; McOmie, J. F. W.; Watts, M. L. *J. Chem. Soc. C* **1968**, 1545.
(34) Pigou, P. E.; Schiesser, C. H. *J. Org. Chem.* **1988**, *53*, 3841.
(35) Geerts, J. P.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1960**, *69*, 563.
(36) Kaiser, L. *Liebigs Ann. Chem.* **1890**, *257*, 102.
(37) Wittig, G.; Haag, W. *Chem. Ber.* **1955**, *88*, 1654.
(38) Bestmann, H. J.; Hartl, R.; Haberlein, H. *Liebigs Ann. Chem.* **1969**, *718*, 33.

30.3, 35.6, 43.0, 118.4, 121.1, 123.5, 125.6, 126.1, 126.5, 127.6, 127.7, 128.1, 128.9, 129.3, 131.4, 133.7, 137.8, 140.4, 148.4, 173.9; MS (70 eV, EI) *m/e* 342 (M^+, 14), 198 (21), 171 (24), 144 (100), 129 (45), 117 (10), 115 (26), 105 (4), 91 (41); UV (C_6H_{12}) λ_{max} 222 (log ϵ 4.91), 248 (4.25), 275 (3.81), 286 (3.56); CD (C_6H_{12}) λ_{ext} 222 ($\Delta\epsilon$ +15.8), 228 (0.0), 237 (−11.6).

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.14; H, 6.52.

2-Biphenylenyl (*R*)-4-(Phenylmethylene)cyclohexanecarboxylate (1i). The procedure described for the preparation of **1c** was used with 181 mg (0.84 mmol) of **1a**, 235 mg (1.4 mmol) of 2-biphenylenol, and 174 mg (0.84 mmol) of DCC to afford 176 mg (57%) of **1i** as a white solid: mp 135–137 °C; $[\alpha]_D$ = −87.5° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.64–1.88 (m, 2 H), 2.05–2.23 (m, 3 H), 2.26–2.36 (m, 1 H), 2.45–2.52 (m, 1 H), 2.70–2.79 (m, 1 H), 2.86–2.92 (m, 1 H), 6.32 (s, 1 H), 6.36–6.40 (m, 2 H), 6.58–6.64 (m, 3 H), 6.72–6.79 (m, 2 H), 7.18–7.35 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5, 29.5, 30.2, 35.5, 42.8, 113.1, 117.1, 117.6, 117.7, 119.6, 123.4, 126.1, 128.0, 128.3, 128.7, 128.8, 137.8, 140.3, 148.2, 149.1, 150.2, 150.7, 152.5, 173.7; MS (70 eV, EI) *m/e* 366 (M^+, 4), 168 (100), 139 (9), 129 (15), 117 (4), 115 (5), 91 (18); UV (C_6H_{12}) λ_{max} 242 (log ϵ 4.84), 249 (5.00), 341 (3.82), 360 (3.97); CD (C_6H_{12}) λ_{ext} 238 ($\Delta\epsilon$ +16.1), 243 (0.0), 254 (−35.1), 343 (−0.52), 362 (−0.51).

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.33; H, 6.09.

***tert*-Butyl 3-Oxocyclobutanecarboxylate (8).** Under a N_2 atmosphere, a solution of DCC (4.54 g, 22 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to a stirred mixture of 3-oxocyclobutanecarboxylic acid (2.28 g, 20 mmol), *t*-BuOH (2.96 g, 40 mmol), and DMAP (1.95 g, 16 mmol) in dry CH_2Cl_2 (10 mL). The mixture was stirred at 25 °C for 24 h, then filtered through a coarse fritted-glass funnel. The filtrate was washed with 0.5 M aqueous HCl (10 mL) and saturated aqueous $NaHCO_3$ (10 mL), dried ($MgSO_4$), and concentrated to give a dark yellow oil. Distillation under high vacuum afforded 2.52 g (74%) of **8** as a clear oil: $bp_{0.4}$ 54 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 9 H), 3.07–3.41 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.4, 51.5, 81.4, 173.2, 204.3; MS (70 eV, EI) *m/e* 155 (M − CH_3, 2), 114 (1), 97 (29), 86 (4), 57 (100), 42 (43).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.41; H, 8.26.

***tert*-Butyl (±)-3-(Phenylmethylene)cyclobutanecarboxylate (9).** Under a N_2 atmosphere, a 1.59 M solution of *n*-BuLi in hexanes (6.3 mL) was added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide (4.33 g, 10 mmol) in dry benzene (30 mL). After stirring at 25 °C for 0.5 h, the ylide solution was cooled to 0 °C, and a solution of **8** (1.7 g, 10 mmol) in dry benzene (10 mL) was rapidly added by cannula. The resulting mixture was refluxed for 24 h and then poured onto ice (20 g). The phases were separated, and the organic phase was washed with saturated aqueous NH_4Cl (25 mL) and brine (25 mL), dried ($MgSO_4$), and concentrated to give a crude oil. Purification by flash chromatography on silica gel (5% EtOAc/hexane) afforded 810 mg (33%) of **9** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 9 H), 3.10–3.30 (m, 5 H), 6.14–6.15 (m, 1 H), 7.16–7.20 (m, 3 H), 7.27–7.32 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 35.7, 35.8, 36.0, 80.4, 122.3, 126.1, 127.1, 128.4, 137.5, 138.5, 174.2; MS (70 eV, EI) *m/e* 244 (M^+, 5), 188 (27), 179 (8), 171 (8), 165 (25), 143 (100), 128 (25), 115 (29), 57 (78).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.94; H, 8.46.

(±)-3-(Phenylmethylene)cyclobutanecarboxylic Acid [(±)-2a]. A mixture of **9** (810 mg, 3.3 mmol), hexadecyltrimethylammonium bromide (120 mg, 0.33 mmol), and 48% aqueous HBr (2 mL) was stirred at 25 °C for 2 h. The mixture was then poured into ether (20 mL), the phases were separated, and the organic phase was washed with water (10 mL) and extracted with 5% aqueous $NaHCO_3$ (3 × 15 mL). The combined aqueous extracts were acidified to pH 2 with 12 M aqueous HCl and extracted with ether (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated to give 547 mg (88%) of (±)-**2a** as a white solid: mp 87–90 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.10–3.43 (m, 5 H), 6.17–6.18 (m, 1 H), 7.15–7.20 (m, 3 H), 7.28–7.36 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.6, 35.8, 35.9, 122.8, 126.3, 127.2, 128.4, 137.2, 137.4, 181.3; MS (70 eV, EI) *m/e* 188 (M^+, 22), 143 (100), 128 (47), 115 (81), 105 (5), 91 (11), 89 (11).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.56; H, 6.47.

(*R*)-3-(Phenylmethylene)cyclobutanecarboxylic Acid [(*R*)-2a]. A mixture of (±)-**2a** (660 mg, 3.51 mmol) and quinine (1.15 g, 3.51 mmol) in EtOAc (7 mL) was heated to reflux on a steam bath until dissolution was complete. The hot solution was stored in a freezer for 24 h, and the precipitated salts were collected by filtration. After drying, the salts were decomposed in 6 M aqueous HCl (50 mL), the aqueous phase was extracted with ether (2 × 50 mL), and the combined extracts were washed with water (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated to afford 252 mg (1.34 mmol) of (*R*)-**2a** as a white solid: mp 90–94 °C; $[\alpha]_D$ = −80.8° (*c* 1.0, CH_2Cl_2).

Methyl (*R*)-3-(Phenylmethylene)cyclobutanecarboxylate (2b). The procedure described for the preparation of **1c** was used with 72 mg (0.38 mmol) of (*R*)-**2a**, 32 mg (1.0 mmol) of methanol, and 87 mg (0.42 mmol) of DCC to afford 47 mg of **2b** (61% yield, 45% ee) as a clear oil: $[\alpha]_D$ = −45.0° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.05–3.40 (m, 5 H), 3.73 (s, 3 H), 6.16–6.17 (m, 1 H), 7.15–7.23 (m, 3 H), 7.28–7.33 (m, 2 H); MS (70 eV, EI) *m/e* 202 (M^+, 21), 143 (100), 128 (40), 115 (61); UV (C_6H_{12}) λ_{max} 255 (log ϵ 4.34), 265 (4.14), 281 (3.05), 292 (2.77).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.30; H, 7.01.

[1,1′-Biphenyl]-4-yl (*R*)-3-(Phenylmethylene)cyclobutanecarboxylate (2f). The procedure described for the preparation of **1c** was used with 75 mg (0.4 mmol) of (*R*)-**2a**, 136 mg (0.8 mmol) of [1,1′-biphenyl]-4-ol, and 95 mg (0.46 mmol) of DCC to afford 54 mg (40%) of **2f** as a white solid: mp 150–152 °C; $[\alpha]_D$ = −81.8° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.19–3.29 (m, 1 H), 3.32–3.46 (m, 2 H), 3.51–3.63 (m, 2 H), 6.22–6.23 (m, 1 H), 7.16–7.26 (m, 5 H), 7.30–7.38 (m, 3 H), 7.42–7.46 (m, 2 H), 7.56–7.62 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.9, 36.0, 36.1, 121.7, 122.9, 126.3, 127.1, 127.2, 127.3, 128.2, 128.5, 128.8, 137.2, 137.3, 139.0, 140.3, 150.1, 173.4; MS (70 eV, EI) *m/e* 340 (M^+, 12), 170 (100), 143 (21), 141 (15), 128 (29), 115 (22), 105 (11), 91 (6); UV (C_6H_{12}) λ_{max} 255 (log ϵ 4.67), 266 (4.51), 291 (3.15); CD (C_6H_{12}) λ_{ext} 238 ($\Delta\epsilon$ +4.98), 248 (0.0), 260 (−15.0), 266 (−13.0), 293 (−0.39).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: 84.69; H, 5.93.

(*R*)-[4-(Phenylmethylene)cyclohexyl]phenylmethanone (3). Under a N_2 atmosphere, a 1.8 M solution of PhLi in Et_2O/hexane (0.6 mL) was added by syringe to a stirred solution of **1a** (128 mg, 0.59 mmol) in dry Et_2O (7 mL). The resulting white suspension was stirred at 25 °C for 0.5 h and then poured into saturated aqueous NH_4Cl (5 mL). The layers were separated, and the organic layer was washed with brine (5 mL), dried ($MgSO_4$), and concentrated to give a crude oil. Purification by flash chromatography on neutral alumina (5% EtOAc/hexane) afforded 104 mg of **3** (64% yield, 74% ee) as a white solid: mp 90–92 °C; $[\alpha]_D$ = −18.9° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.57–1.80 (m, 2 H), 1.96–2.14 (m, 3 H), 2.32–2.42 (m, 1 H), 2.49–2.53 (m, 1 H), 2.96–3.02 (m, 1 H), 3.46–3.55 (m, 1 H), 6.32 (s, 1 H), 7.17–7.22 (m, 3 H), 7.29–7.34 (m, 2 H), 7.45–7.50 (m, 2 H), 7.54–7.59 (m, 1 H), 7.95–7.98 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 30.0, 30.8, 36.1, 45.3, 123.3, 126.0, 128.1, 128.2, 128.6, 128.9, 132.9, 136.2, 137.9, 140.8, 202.9; MS (70 eV, EI) *m/e* 276 (M^+, 16), 185 (9), 171 (4), 144 (14), 133 (100), 129 (17), 115 (12), 105 (45), 91 (14), 77 (32), 55 (39); UV (C_6H_{12}) λ_{max} 241 (log ϵ 4.42), 287 (2.94), 323 (1.90); CD (C_6H_{12}) λ_{ext} 232 ($\Delta\epsilon$ −2.99), 239 (0.0), 250 (+6.25), 283 (0.0), 289 (−0.083), 312 (−0.088), 322 (−0.108), 333 (−0.104), 346 (−0.067), 362 (−0.021).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.91; H, 7.41.

(*R*)-[3-(Phenylmethylene)cyclobutyl]phenylmethanone (4). The procedure described for the preparation of **3** was used with 90 mg (0.48 mmol) of (*R*)-**2a** and 0.5 mL of a 1.8 M solution of PhLi in Et_2O/hexane to afford 67 mg of **4** (56% yield, 45% ee) as a white solid: mp 87–90 °C; $[\alpha]_D$ = −59.2° (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.11–3.21 (m, 1 H), 3.28–3.38 (m, 2 H), 3.47–3.56 (m, 1 H), 4.07–4.18 (m, 1 H), 6.19–6.21 (m, 1 H), 7.14–7.33 (m, 5 H), 7.45–7.50 (m, 2 H), 7.55–7.60 (m, 1 H), 7.93–7.96 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.5, 35.6, 38.6, 122.6, 126.2, 127.2, 128.4, 128.7, 133.1, 135.3, 137.4, 138.0, 199.7; MS (70 eV, EI) *m/e* 248 (M^+, 34), 233 (9), 205 (4), 171 (10), 157 (15), 143 (34), 128 (34), 115 (57), 105 (100), 91 (16), 89 (9), 77 (75); UV

(C_6H_{12}) λ_{max} 248 (log ϵ 4.50), 254 (4.44), 265 (4.24), 290 (2.97), 317 (1.98); CD (C_6H_{12}) λ_{ext} 238 ($\Delta\epsilon$ −4.74), 250 (0.0), 253 (+0.36), 257 (0.0), 262 (−0.52), 293 (−0.19), 308 (−0.16), 320 (−0.21), 332 (−0.22), 345 (−0.16), 361 (−0.07).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.84; H, 6.60.

***tert*-Butyl (±)-3-(2-Naphthalenylmethylene)cyclobutanecarboxylate (10).** The procedure described for the preparation of **9** was used with 1.7 g (10 mmol) of **8** and 4.83 g (10 mmol) of (2-naphthalenylmethyl)triphenylphosphonium bromide to afford 885 mg (30%) of **10** as a white solid: mp 72–74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 9 H), 3.04–3.46 (m, 5 H), 6.30–6.31 (m, 1 H), 7.36–7.47 (m, 3 H), 7.60 (s, 1 H), 7.74–7.79 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 35.7, 35.9, 36.1, 80.4, 122.4, 125.4, 125.8, 126.0, 127.5, 127.8, 127.9, 131.9, 133.6, 135.0, 139.1, 174.2; MS (70 eV, EI) *m/e* 294 (M^+, 17), 238 (29), 221 (7), 193 (100), 178 (24), 165 (32), 152 (6), 141 (3), 139 (4), 115 (5), 96 (6), 89 (7), 57 (52).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.68; H, 7.58.

(±)-3-(2-Naphthalenylmethylene)cyclobutanecarboxylic Acid [(±)-11]. A mixture of **10** (798 mg, 2.71 mmol), hexadecyltrimethylammonium bromide (100 mg, 0.27 mmol), and 48% aqueous HBr (2.5 mL) was stirred at 25 °C for 1.5 h. The mixture was then poured into ether (200 mL), the phases were separated, and the organic phase was washed with water (50 mL) and extracted with 5% aq $NaHCO_3$ (4 × 200 mL). The combined aqueous extracts were acidified to pH 2 with 12 M aqueous HCl and extracted with ether (2 × 150 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated to give 531 mg (82%) of (±)-**11** as a white solid: mp 189–190 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.25–3.39 (m, 5 H), 6.33–6.34 (m, 1 H), 7.40–7.51 (m, 3 H), 7.69 (s, 1 H), 7.84–7.88 (m, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 33.9, 35.4, 35.6, 121.8, 125.2, 125.3, 125.5, 126.1, 127.3, 127.6, 127.8, 131.4, 133.1, 134.6, 139.7, 175.8; MS (70 eV, EI) *m/e* 238 (M^+, 7), 193 (20), 178 (10), 165 (16), 150 (8), 122 (11), 105 (14), 91 (100), 77 (9), 65 (12).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.63; H, 5.94.

(−)- and (+)-3-(2-Naphthalenylmethylene)cyclobutanecarboxylic Acid [(−)-11 and (+)-11]. A mixture of (±)-**11** (509 mg, 2.14 mmol) and quinine (700 mg, 2.16 mmol) in EtOAc (5 mL) was heated to reflux on a steam bath until dissolution was complete. The hot solution was stored in a freezer for 24 h, and the precipitated salts were collected by filtration. After drying, the salts were decomposed in 6 M aqueous HCl (50 mL), the aqueous phase was extracted with ether (2 × 100 mL), and the combined extracts were washed with water (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated to afford 289 mg (1.21 mmol) of (−)-**11** as a white solid: mp 183–185 °C; $[\alpha]_D$ = −38.4° (*c* 0.5, THF). The mother liquor was concentrated to a yellow salt that was decomposed and worked up in a similar manner to afford 135 mg of (+)-**11** as a white solid: mp 173–174 °C; $[\alpha]_D$ = +88.4° (*c* 0.5, THF).

(+)-[3-(2-Naphthalenylmethylene)cyclobutyl]phenylmethanone (5). Under a N_2 atmosphere, a 1.8 M solution of PhLi in Et_2O/hexane (0.58 mL) was added by syringe to a stirred solution of (+)-**11** (125 mg, 0.52 mmol) in dry 3:1 ether/THF (15 mL). The resulting red suspension was stirred at 25 °C for 2.5 h, poured into saturated aqueous NH_4Cl (30 mL), and extracted with EtOAc (2 × 50 mL). The combined extracts were washed with brine (50 mL), dried ($MgSO_4$), and concentrated to give a yellow solid. Purification by flash chromatography on neutral alumina (5% EtOAc/hexane) afforded 58 mg of **5** (38 yield, 10% ee) as a white solid: mp 130–132 °C; $[\alpha]_D$ = +16.7° (*c* 0.55, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.18–3.27 (m, 1 H), 3.33–3.47 (m, 2 H), 3.57–3.67 (m, 1 H), 4.11–4.22 (m, 1 H), 6.35–6.36 (m, 1 H), 7.39–7.52 (m, 5 H), 7.56–7.60 (m, 1 H), 7.62 (s, 1 H), 7.75–7.79 (m, 3 H), 7.95–7.98 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.68, 35.70, 38.5, 122.7, 125.5, 125.9, 126.1, 127.6, 127.8, 127.9, 128.4, 128.7, 132.0, 133.2, 133.6, 135.0, 135.3, 138.6, 199.7; MS (70 eV, EI) *m/e* 298 (M^+, 33), 193 (100), 178 (51), 165 (52), 157 (8), 152 (9), 141 (20), 128 (11), 115 (16), 105 (99), 91 (31), 77 (55), 71 (26), 57 (41); UV (C_6H_{12}) λ_{max} 240 (log ϵ 4.64), 248 (4.81), 258 (4.83), 279 (4.23), 289 (4.23), 302 (4.20), 312 (3.54); (C_6H_6) λ_{max} 325 (log ϵ 2.96), 342 (2.70); CD (C_6H_{12}) λ_{ext} 239 ($\Delta\epsilon$ +3.86), 256 (+1.19), 280 (+1.22), 288 (+1.29), 302 (+1.32), 312 (+0.881); (C_6H_6) λ_{ext} 328 ($\Delta\epsilon$ +0.154), 342 (+0.110), 358 (+0.036).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.38; H, 6.17.

2-(Cyclobutylidenemethyl)naphthalene. Under a N_2 atmosphere, a 1.59 M solution of *n*-BuLi in hexanes (3.1 mL) was added dropwise to a stirred suspension of (2-naphthalenylmethyl)triphenylphosphonium bromide (2.42 g, 5.0 mmol) in dry benzene (15 mL). The ylide solution was stirred at 25 °C for 0.5 h, and a solution of cyclobutanone (350 mg, 5.0 mmol) in dry benzene (5 mL) was added dropwise. The mixture was refluxed for 12 h and then poured onto ice (10 g). The phases were separated, and the organic phase was washed with saturated aqueous NH_4Cl (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated to give a crude solid. Purification by flash chromatography on silica gel (1% EtOAc/hexane) afforded 567 mg (58%) of **20** as a white solid: mp 79–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09–2.20 (m, 2 H), 2.90–2.96 (m, 2 H), 3.12–3.18 (m, 2 H), 6.22–6.24 (m, 1 H), 7.36–7.45 (m, 3 H), 7.59 (s, 1 H), 7.62–7.78 (m, 3 H); MS (70 eV, EI) *m/e* 194 (M^+, 71), 179 (100), 165 (88), 154 (12), 139 (11), 128 (5), 115 (11), 96 (7), 89 (10); UV (C_6H_{12}) λ_{max} 240 (log ϵ 4.54), 248 (4.76), 258 (4.81), 279 (4.12), 289 (4.22), 302 (4.20), 310 (3.57), 325 (2.94), 341 (2.75).

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.50; H, 7.23.

Photolyses. All irradiations were carried out at room temperature with a Rayonet photoreactor equiped with 254- or 350-nm bulbs, or with a high-pressure 1000-W Hg–Xe arc lamp (Oriel). Unless otherwise noted, the photostability experiments were carried out in cyclohexane (1×10^{-3} M) using a square quartz cell (1-cm path length) fitted with a rubber septum; the solutions were purged with N_2 for 10 min prior to irradiation and were stirred magnetically during irradiation to maintain homogeneity. The occurrence of photodecomposition was detected by UV spectroscopy or by capillary GC using octadecane as internal standard.

Photoracemization in Isotropic Solution. Solutions of optically active (arylmethylene)cycloalkane in cyclohexane (ca. 10^{-2} M, 2 mL) were purged with N_2 for 10 min and irradiated with stirring in a Rayonet photoreactor (254 nm), or with a 1000-W lamp fitted with a 305-nm cut-off filter. The extent of photoracemization was determined by polarimetry (589 nm), and the photostability of each sample was monitored by capillary GC using octadecane as internal standard.

Triplet-Sensitized Photoracemization. A solution of (*R*)-**2b** (6.8×10^{-3} M) and xanthone (1.7×10^{-2} M) in benzene was purged with N_2 for 10 min and irradiated in a Rayonet photoreactor (350 nm). The extent of photoracemization was monitored by polarimetry (589 nm), and the photostability of **2b** was monitored by capillary GC.

Photoracemization in ZLI-1167. A 5-mg sample of a mixture of optically active (arylmethylene)cycloalkane in ZLI-1167 (2–4% by weight) was deposited on a clean microscope glass slide (quartz) and covered with a glass cover to produce a thin (ca. 5 μm), uniform layer. This preparation was irradiated using a high-pressure 1000-W Hg–Xe arc lamp fitted with a 230- or 305-nm cut-off filter. The beam was focused on a 5-mm aperture, in front of which the sample slide was placed with the quartz surface facing the lamp. The extent of photoracemization was determined by monitoring the change in the texture of the sample from that of a cholesteric liquid crystal (oily streaks) to that of a nematic liquid crystal (marbled) using a polarizing microscope (100×).

Acknowledgment. We specially thank Professor Hanessian of the University of Montreal for telling us about the adaptation of the Emmons–Wadsworth reaction to benzyl substituents before its publication. Mr. Mauricio Suarez of this department assisted in the preparation of the biphenylene derivatives. The circular dichroism spectra were measured at the Laboratory for Fluorescence Dynamics of the University of Illinois. This work was supported by a grant from the Army Research Office and the National Science Foundation for which we are grateful.