A Search for Photoresolvable Mesogens: Synthesis and Properties of a Series of Liquid Crystalline, Axially Chiral 1-Benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]cyclohexanes

Yifan Zhang and Gary B. Schuster*

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

Received November 24, 1993®

A series of axially chiral 1-benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]cyclohexanes was prepared in racemic form and as optically active mixtures by application of the Hanessian olefination reaction. These compounds have two spectrally overlapping groups which leads to enhanced circular dichroism. And, with appropriate substituents, they form liquid crystal phases when heated above room temperature. The photochemical and material properties of these compounds were studied to assess their suitability for formation of a chiroptical liquid crystal switch. It was found that the Kuhn anisotropy factor (g_λ) is too small for this application.

Introduction

The liquid crystalline state of matter is unique because its intrinsic one- or two-dimensional order can be disturbed by application of very weak forces. For example, it is well known that the addition of a small amount of an optically active compound to a nematic liquid crystal will convert it to a cholesteric form.[1] Since nematic and cholesteric liquid crystals have easily distinguished optical properties, this conversion can be used as a basis of a "light valve" or, more generally, an optical switch.[2] In such a device, the liquid crystal would be switched between nematic and cholesteric forms with light, and this change would be sensed with light. A key to the development of a switch of this sort is the discovery of compounds that can be resolved by irradiation with circularly polarized light. A liquid crystal containing such a compound as a racemate will be nematic, and this photoresolution will convert the liquid crystal to the cholesteric form. Of course, irradiation of this cholesteric liquid crystal with unpolarized light will regenerate the racemic mixture and re-form the nematic phase. Conceptually, this reversible transition between nematic and cholesteric forms of the liquid crystal is a physical amplifier of a photochemical trigger. We have been searching for compounds that might be effective triggers.[3,4]

Compounds suitable for use as triggers in the liquid crystal-based optical switch described above must meet certain key requirements. The pitch of a cholesteric liquid crystal (p, the distance for a 360° rotation of the director) composed of an achiral mesogen and an optically active additive at low concentration is equal to $1/(\beta_M C\gamma)$.[5] In this equation, β_M (the helical twisting power) relates the concentration of the additive (C = mol of additive/mol of solution) and its optical purity (γ) to p. We have determined empirically that the maximum pitch that can be easily sensed by optical microscopy is ca. 100 μm.[3]

Photoresolution of a racemate with circularly polarized light may proceed by an equilibration or destruction mechanism.[6] The former is of relevance for the work reported herein. In this case, the optical purity of the additive at the photostationary state equals $\Delta\epsilon/2\epsilon$, and hence, γ for a particular additive can be calculated from knowledge of the circular dichroism ($\Delta\epsilon$) and absorption (ϵ) spectra. To be suitable for use as a trigger, the compound must possess β_M and γ values sufficiently large to generate a pitch of ca. 100 μm at an achievable concentration. Moreover, the compound must be stable photochemically. In this regard, stability means that irradiation must lead to efficient interconversion of its enantiomers (i.e., a large value for the quantum yield of photoracemization Φ_{rac}) without formation of any other product.

Previous work revealed that some axially chiral (arylmethylene)cycloalkanes possess many of the characteristics of a suitable trigger for the liquid crystal-based optical switch.[3] It seemed that the product of β_M and γ for these compounds would yield a detectable pitch if C were unity. In this case, the mesogen that forms the liquid crystal is itself photoresolvable. We report herein the synthesis of several 1-benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]cyclohexanes. Some of these compounds are mesogens, but, unfortunately, the γ obtainable for these compounds seems to be too small for application in a chiroptical switch.

Results and Discussion

(1) Selection of Chiral (Arylmethylene)cyclohexanes. We are guided in our search for possible photoresolvable mesogens in part by the theory of chiral exciton coupling.[7] When two chromophores of a molecule are located in chiral positions, the CD spectrum shows a split

* Abstract published in *Advance ACS Abstracts*, March 15, 1994.

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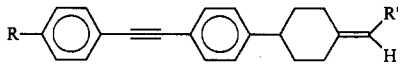
Chart 1. Potential Photoresolvable Mesogen



8: R = H; R' = Ph
9: R = H; R' = *p*-PhCN
10: R = H; R' = *p*-Ph-Ph
11: R = H; R' = 2-Naphthyl
12: R = C_5H_{11}; R' = Ph
13: R = C_5H_{11}; R' = *p*-PhCN
14: R = C_5H_{11}; R' = *p*-Ph-Ph
15: R = C_6H_{13}; R' = *p*-PhCN
16: R = H; R' = *p*-MeCOPh
17: R = H; R' = *p*-PhCOPh

Cotton effect and the magnitude of $\Delta\epsilon$ increases proportionately to the product of their extinction coefficients while ϵ increases with their sum. The magnitude of $\Delta\epsilon$ depends on the interchromophoric distance vector, the strength of the electric dipole transition moments of the two chromophores, and the magnitude of their interaction energy. These considerations indicate that for maximum $\Delta\epsilon$, the absorption spectra of the two chromophores should overlap in some region, that their individual extinction coefficients should be large, and that the two chromophores should be close together in space.

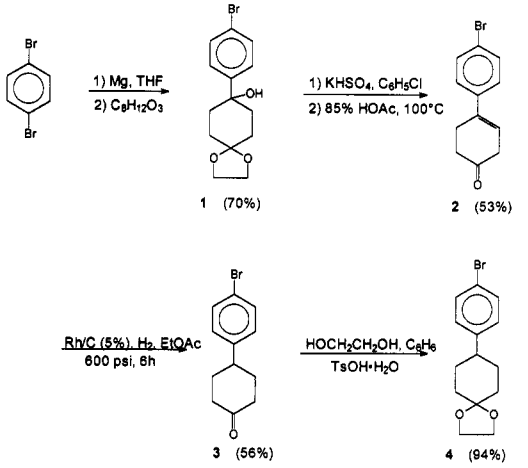
Since we seek photoresolvable compounds that will form liquid crystalline phases, we are guided also by the observation that many such compounds have semirigid, rodlike shapes. In particular, Miyazaki reported that cyclohexyl-substituted diphenylacetylenes form nematic liquid crystals with a wide mesogenic range.[8] The diphenylacetylene group thus seemed to be a good choice for one of the chromophoric units in a photoresolvable mesogen since its absorption spectrum shows a strong band at ca. 280 nm ($\epsilon = 2.84 \times 10^4$ M^{-1} cm^{-1}). We selected the β,β-dialkylstyrene group as the second chromophore since 4-substituted 1-benzylidenecyclohexanes are chiral and this photoresolvable functional group shows an absorption at 245 nm with $\epsilon \approx 10^4$ M^{-1} cm^{-1}. Thus, the spectral properties of these two chromophores appear to satisfy the requirements of chiral exciton coupling theory. Moreover, it seemed likely that suitable liquid crystalline chiral 1-benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]cyclohexanes could be found. We prepared the series of such compounds shown in Chart 1, measured their spectral properties, examined their photochemistry, and tested their liquid crystalline behavior.

(2) Synthesis of Chiral 1-Benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]cyclohexanes. The synthetic strategy selected for the preparation of the 1-benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]-cyclohexanes is outlined in Scheme 1. The approach is designed to be triply convergent. The key compound in this strategy is ketal **4**. The synthesis of **4** is outlined in sequence 1. Acid-catalyzed hydrolysis following palladium-catalyzed coupling of phenylacetylenes (see sequence 2 of Scheme 1) with **4** gives the series of ketones shown in sequence 3 in good yield. These ketones were converted to racemic benzylidene compounds by the Wittig reaction as shown in sequence 4 (except for **9** and **13** where the Horner–Emmons modification was used). The optically active benzylidene compounds **8**, **9**, **10**, **12**, and **13** were prepared from the substituted ketones by application of the chiral Hanessian reagent as shown in sequence 5. The required optically active reagents were prepared by modification of reactions described in the literature.[9] Ketones **16** and **17** were prepared by alkylation or arylation of nitrile **9**. Detailed descriptions of these reactions are presented in the Experimental Section.

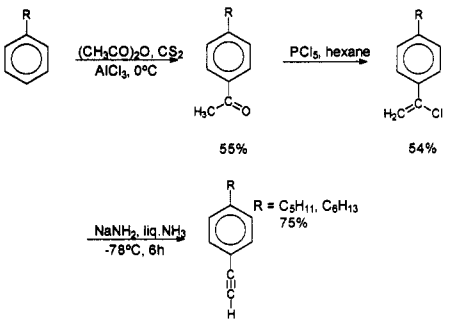
(8) Miyazaki, R. Jpn. Kokai, Tokkyo Koho JP 01,247,481, 1988; *Chem. Abstr.* **1990**, *112*, 208083t.

Scheme 1. Synthesis of 1-Benzylidene-4-[4′-[(*p*-alkylphenyl)ethynyl]phenyl]cyclohexanes

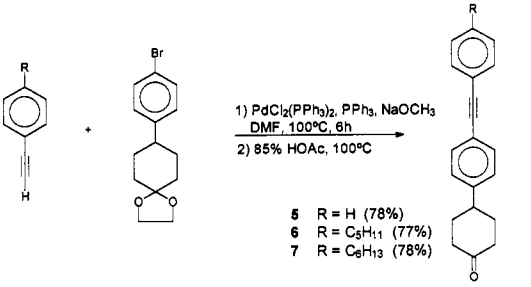
Sequence 1. Synthesis of Ketal **4**



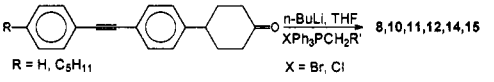
Sequence 2. Synthesis of Substituted Phenylacetylenes



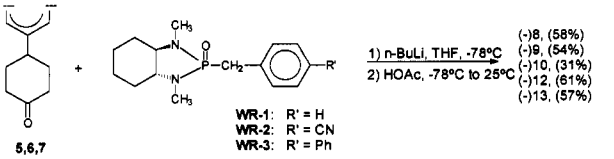
Sequence 3. Synthesis of Acetylene-Substituted Cyclohexanones



Sequence 4. Synthesis of Benzylidene Cyclohexanes



Sequence 5. Preparation of Optically Active Benzylidene Cyclohexanes



(3) Determination of Enantiomeric Purity. The optically active benzylidene compounds prepared by the Hanessian olefination[9] reaction could not be directly resolved by HPLC on a WHELK-01 column.[10] These olefins were converted to epoxides by reaction with *m*-chloroperoxybenzoic acid. Analysis of the mixture from epoxidation of racemic **9** on the WHELK-01 column, for example, shows four peaks corresponding to the stereo-

Table 1. Chiroptical Properties of the Optically Active Compounds

compd	$\Delta\epsilon$ (λ_{ext}), M^{-1} cm^{-1} (nm) (100% ee)	g_λ ($\times 10^4$)	enantiomeric excess (synthesis) (%)
(−)-8	−12.3 (270)	4.1	80
	−4.33 (303)	1.4	
(−)-9	−36.5 (286)	7.2	83
	−20.6 (303)	5.8	
(−)-10	−37.4 (287)	5.9	85
	−30.4 (304)	6.7	
	−4.82 (310)	8.4	
(−)-12	−12.8 (273)	4.2	88
	−1.54 (311)	3.4	
(−)-13	−29.1 (290)	6.3	88
	−13.1 (304)	4.7	
	−6.96 (310)	7.8	
(−)-16	−26.3 (287)	5.1	83
	−10.8 (308)	9.3	
	0.14 (355)	14	
(−)-17	−33.6 (304)	8.3	83
	−13.7 (310)	12	
	−0.29 (346)	2.3	

isomers of the epoxide. Column chromatography of this mixture and recrystallization of appropriate fractions separates it into two diastereomers, each containing equal amounts of two enantiomers as revealed by HPLC. On the basis of these experiments, the relative configurations of the four stereoisomers of the epoxides could be assigned. The epoxides formed from the nonracemic mixtures of the olefins were analyzed similarly. For compounds **8**, **9**, **10**, **12**, and **13** the enantiomeric purities (ee) were determined by integration and combination of the HPLC peaks assigned an origin with each olefin enantiomer. According to this analysis, the ee for the olefins prepared by the Hanessian procedure ranges from 80 to 88% (see Table 1). The enantiomeric purities of compounds **16** and **17** were presumed to be the same as for **9** since they were prepared from **9** by a procedure that should not lead to a change in ee.

(4) Optical and Chiroptical Properties. As expected, the electronic absorption spectra of compounds **8**–**15** appear as the sum of two components. Figure 1 shows the absorption spectrum of **8** and spectra of diphenylacetylene and 1-benzylidene-4-phenylcyclohexane (**18**) for comparison. The relatively sharp band at 303 nm in the spectrum of **8** clearly is related to an absorption localized mainly on the diphenylacetylene chromophore. It is also apparent that the absorption of the benzylidene cyclohexane unit underlies the absorptions of the acetylene group. Chiral exciton coupling theory predicts that the interaction of these chromophores should be observable in the CD spectrum. Figure 2 shows the CD spectrum of (−)-**8** and (−)-**18** recorded in cyclohexane solution. Both spectra have a split Cotton bands characteristic of bichromophoric systems. The extreme (a minimum for the (−)-enantiomer) in the CD spectrum of (−)-**18** occurs at 230 nm, a value close to the 245 nm maximum in its absorption spectrum. The CD spectrum of (−)-**8** shows a minimum at 270 nm with several bands extending to 310 nm. This spectrum clearly reveals that the interaction of the diphenylacetylene chromophore with the styrene unit induces circular dichroism in the spectrum of the former. For (−)-**8**, this interaction leads to a $\Delta\epsilon_{270}$ of -12.3 M^{-1} cm^{-1} (the maximum

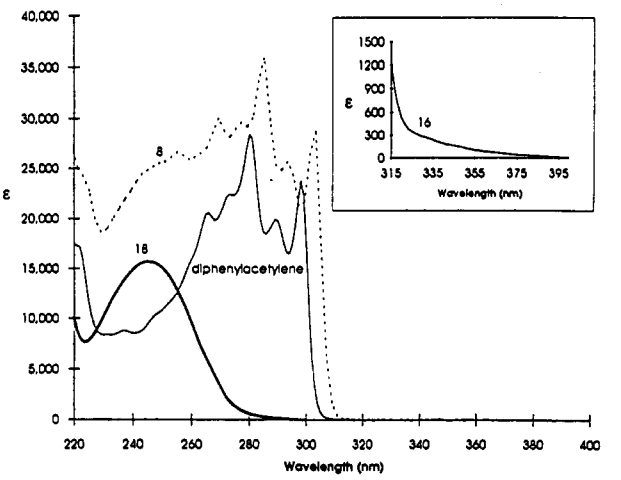


Figure 1. UV–vis absorption spectra of relevant compounds recorded in cyclohexane solution: diphenylacetylene, 4.6×10^{-5} M; **8**, 4.76×10^{-5} M; **16**, 1.13×10^{-3} M (inset shows the long-wavelength absorption); **18**, 3.86×10^{-5} M.

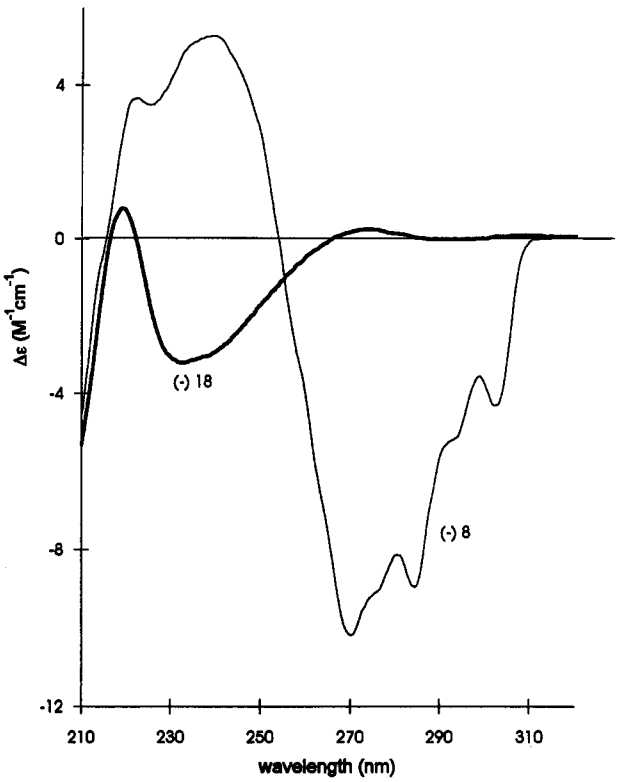


Figure 2. Circular dichroism spectra of (−)-**8** (3.27×10^{-4} M, $\Delta\epsilon_{max} = -10$ M^{-1} cm^{-1}) and (−)-**18** (3.0×10^{-4} M, $\Delta\epsilon_{max} = -2.5$ M^{-1} cm^{-1}), both recorded in cyclohexane solution in a 0.1-cm path length cell.

value) and $\Delta\epsilon_{303} = -4.3$ M^{-1} cm^{-1}. The absorption and the CD spectra of (−)-**8** permit calculation of the Kuhn anisotropy factor $g_\lambda = \Delta\epsilon/\epsilon$. In this case, g_{270} and g_{303} are -4.1×10^{-4} and -1.4×10^{-4}, respectively. Consequently, irradiation of **8** with circularly polarized light will lead to a maximum ee at the photostationary state of 0.02%. This optical enrichment is too small for **8** to function as a trigger in the liquid crystal based optical switch.

The magnitude of g_λ should increase proportionally to the spectral overlap of the styrene and acetylene chromophores. We sought to increase the overlap by varying the substituents on the phenyl ring of the benzylidene group of **8**. The results are summarized in Table 1. The

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(10) This column is available from Regis Chemical Co., Inc.

maximum value of g_λ we obtained is -14×10^{-4} for (−)-16 at 355 nm. This is an absorption in the $n\pi^*$ region of the carbonyl chromophore of 16 (see Figure 1), and g_λ is greater mainly because the extinction coefficient for this transition is small (these spectra are measured at relatively high concentration). Photoresolution of 16 would yield an ee sufficient for an optical trigger if its β_M value is large enough.

(5) Photochemical Properties. A key parameter to the successful application of these benzylidene cyclohexanes as chiroptical triggers is Φ_{rac}. This quantity determines both the efficiency of the photoracemization and the photoresolution. Indeed, these compounds were selected for investigation based in part on the expectation that Φ_{rac} would be large since it requires only the rotation about the carbon–carbon double bond in the excited state of the styrene unit. The photochemistry of aryl olefins is well studied, and this rotation is expected to be efficient.[11] In fact, this is the case; irradiation of a N_2-saturated cyclohexane solution of each of the optically active benzylidene cyclohexanes (ca. 10^{-3} M) at 300 nm for 1 or 2 min results in their complete racemization as indicated by the loss of optical activity. The Φ_{rac} for 17 was determined to be 0.51 ± 0.07 by irradiation at 313 nm of a N_2-purged 1.4×10^{-3} M cyclohexane solution. An azobenzene actinometer[12] was used for comparison. It should be noted that 0.5 is the theoretical maximum value for Φ_{rac} since there is a 50% chance of forming either enantiomer from the excited state. We expect that the quantum yields for racemization of the other benzylidene compounds will also be close to this theoretical limit.

Efficient photoracemization in solution does not ensure the same in a neat liquid phase since the reaction might depend on the viscosity of the medium or the concentration of the chromophore. This issue was addressed by investigation of the photochemistry of (−)-13, since this compound forms liquid crystal phases (see below). The racemic and optically active forms of 13 can be distinguished microscopically and by the temperature dependence of their phase transitions. Irradiation of a partially masked sample of neat (−)-13 through a 305-nm cutoff filter for 2 min at 125 °C (above the clearing temperature) leads to efficient racemization in the irradiated region. When this sample is cooled, the irradiated region forms textures characteristic of racemic samples, and the phase-transition temperatures in this region are the same as for the authentic racemic sample. Moreover, there is a clearly visible transformation at the irradiation boundary between racemic and optically active liquid crystal phases. On the basis of these experiments, it appears that the photoracemization reaction of (−)-13 readily occurs in the neat liquid as well as in solution.

To be useful as a photochemical trigger, the benzylidenecyclohexanes also must be stable photochemically. This issue was examined by their irradiation in a Rayonet photoreactor at 300 nm in N_2-purged cyclohexane solution (ca. 1.0×10^{-3} M). Under these conditions, in all but one case, no consumption of the benzylidenecyclohexanes was detected by UV spectroscopy even when the irradiation was carried out for 30 times longer than would be required for complete photoracemization. In the case of 11, irradiation for 30 min leads to a ca. 17% decrease in its absorption.

(6) Liquid Crystalline Properties. The liquid crystalline properties of 12–15 were examined to assess their suitability to function as photoresolvable mesogens. Shown in Figure 3 are photomicrographs of racemic 13 and (−)-13 recorded at 74 and 91.1 °C, respectively. Under these conditions racemic 13 melts directly to this fan-shaped texture which is characteristic of a smectic phase. Further heating of this material leads to clearing at 137 °C without visible formation of a nematic phase. In contrast, (−)-13 forms the texture shown in Figure 3 when it is cooled slowly from the isotropic phase.

It is difficult to assign the liquid crystalline order of 13 and (−)-13 with certainty from their textures since the patterns they form do not fall into a unique, recognized group.[13] However, based on comparison with standards, it is clear that both of these mesogens form smectic phases. The texture of racemic 13 shown in Figure 3 appears to be a variant of the focal conic domains typical of an S_A. The texture of (−)-13 resembles that of an S_E phase with strongly double refracting lancets.

The twisting powers (β_M) of the optically active mesogens were determined in ZLI-1167 by application of the droplet method in a glycerol suspension.[14] Microscopic inspection of droplets containing ca. 3.5% of the dopants reveals β_M values of 23, 14, and 24 μm^{-1} for (−)-9, (−)-12, and (−)-13, respectively.

(7) Suitability of Photoresolvable Mesogens in a Chiroptical Switch. A primary objective of this investigation was the discovery of a chiral mesogenic compound that could function as an optical switch when it is irradiated alternatively with circularly polarized and unpolarized light. The compounds described in this report were designed to that end by application of chiral exciton theory and consideration of molecular architectures typical of liquid crystalline materials. The results are modestly encouraging, but ultimately, these compounds fall short of our goal.

A complete optimization of this system would require preparation of a compound which incorporates simultaneously the structure that gives the largest g_λ and the greatest β_M value and, in its racemic form, has a nematic phase. We did not do this. The maximum value for g_λ was obtained for 16; the maximum β_M was observed for 13. If we assume that combination of these features in one compound would give a photoresolvable mesogen with the β_M of 13 and the g_λ of 16, then the minimum pitch that could be obtained for such a cholesteric liquid crystal is ca. 60 μm. This value is within the detectable range according to empirical determination of the long-pitch limit by optical microscopy and, therefore, could function as a chiroptical switch. However, this conclusion is based on a linear extrapolation of β_M from a 3.5% solution to a neat phase, which is uncertain. Since a decrease in β_M of only a factor of 2 would make the cholesteric phase undetectable, we chose not to proceed with the optimization.

(11) Lewis, F. D.; Bassani, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 7523.
(12) Zimmerman, G.; Chow, L.-Y.; Paik, U.-J. *J. Am. Chem. Soc.* **1958**, *80*, 3528.
(13) (a) Demus, D.; Ritchter, L. *Texture of Liquid Crystals*; Verlag Chemie: Weinheim, 1978. (b) Gary, G. W.; Goodby, J. W. G. *Smectic Liquid Crystal-Textures and Structures*; Heyden & Son: Leonard Hill, 1984.
(14) (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.

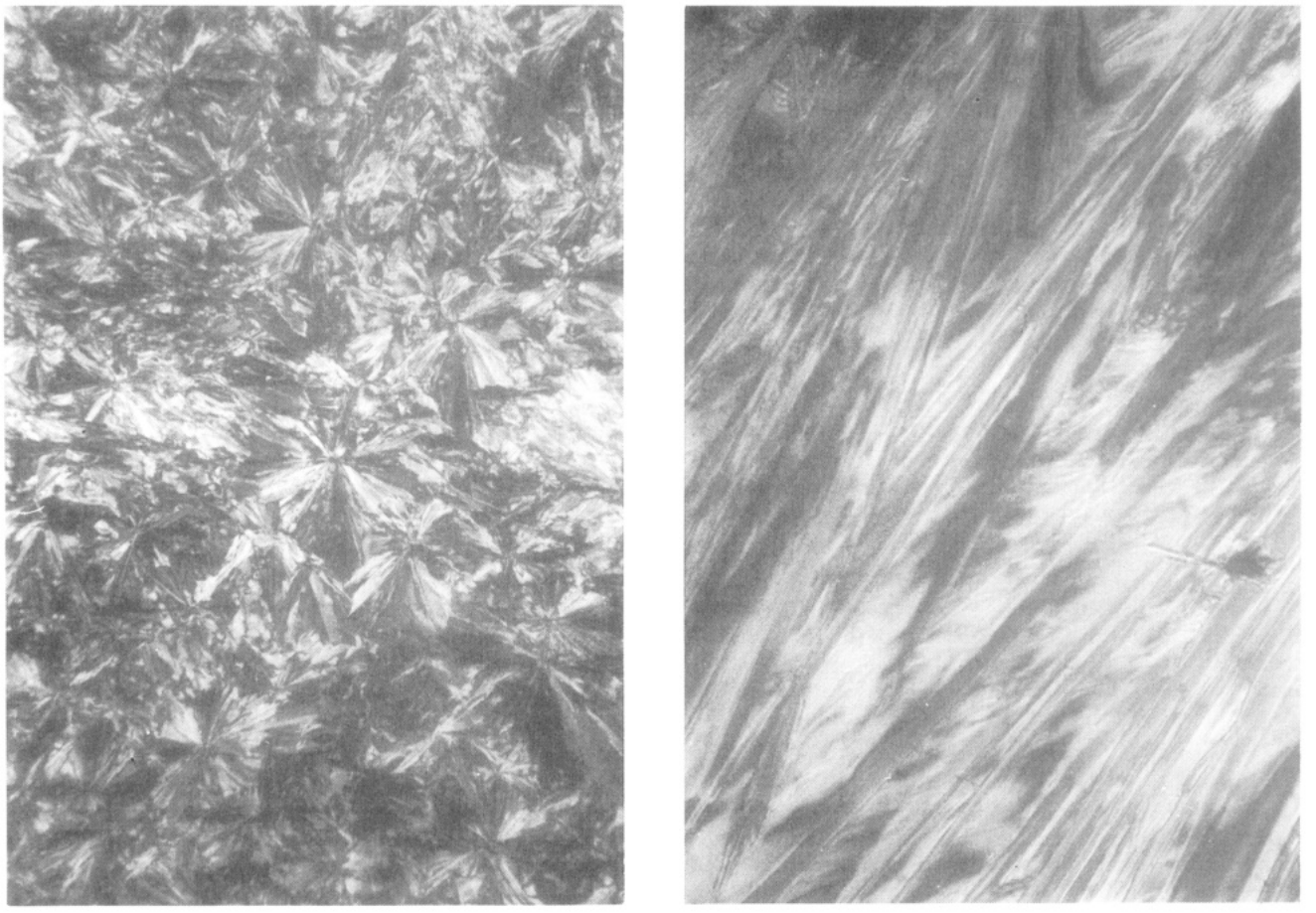

Figure 3. Photomicrographs of liquid crystal phases viewed through cross polarizers at 100× magnification. Left: (±)-**13** heating from solid phase to 74 °C. Right: (−)-**13** cooling of isotropic melt to 91.1 °C.

Conclusions

We prepared a series of photoresolvable mesogens based upon the benzylidenecyclohexanes as the chiral unit. In this work, we showed that the optical properties of these compounds can be estimated by application of chiral exciton coupling theory and that, with suitable substituents, these compounds form detectable liquid crystalline phases. However, these findings also reveal that this chiral unit will probably be unsatisfactory for the development of a chiroptical switch based upon their photoresolution with circularly polarized light. The values of g_λ obtainable for these compounds, even when the spectral overlap is optimized, are too small. We attribute this to too great a distance between the two chromophoric units since the value of g_λ is much greater in the case of benzylidene cyclobutanes.[3] Further experiments are underway that incorporate chiral units with intrinsic g_λ values much greater than that of the benzylidene cyclohexanes.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian XL 200 or a GE QE-300 spectrometer in $CDCl_3$. Chemical shifts, δ (ppm), are reported relative to internal TMS. Low-resolution EI mass spectra were recorded on a Varian-MAT CH5 mass spectrometer with an ionization voltage of 70 eV; peaks are expressed as m/z (percent intensity relative to base peak). High-performance liquid chromatography (HPLC) was performed on an IBM Instruments Inc. LC/9560 Ternary Gradient liquid chromatograph with a Perkin-Elmer LC-75 detector. A WHELK-01 column (25-cm × 4.6-mm i.d., Regis Chemical Co.) was used. UV spectra were recorded on a Perkin-Elmer 552 or a Cary 1E UV–vis spectrophotometer in cyclohexane or methylene chloride solution. CD spectra were recorded on a SPEX CD VI (Jobin-Yvon, France) spectrometer in cyclohexane or methylene chloride solution (0.1-cm pathlength). Optical rotations were performed on a JASCO DIP-360 digital polarimeter at room temperature at the sodium D line. Photolyses were carried out in a Rayonet photoreactor equipped with 300-nm lamps. Elemental analyses were performed by the University of Illinois Microanalysis Service Laboratory. Microscopic analyses were performed with a Fisher Micromaster polarizing microscope equipped with a Mettler FP 82 hot stage. The helical twisting powers (β_M) were measured in ZLI-1167 (E. Merck) liquid crystal using the droplet method.[14] Quantum yield experiments were carried out by irradiation with a 1000-W Oriel lamp through appropriate band-pass filters. Melting points were measured on a Büchi apparatus and are uncorrected.

Materials. All solvents and reagents were obtained from commerical sources and used without further purification, unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether were distilled from Na/benzophenone; dimethylformamide (DMF) was distilled from CaH_2; acetic anhydride and carbon disulfide (CS_2) were distilled from P_2O_5 before use. Diphenylacetylene was recrystallized from ethanol before use. Cyclohexane was of spectrophotometric grade (Burdick & Jackson) and used without further purification. The chiral Wittig reagents were prepared by the Hanessian method.[9]

4-Hydroxy-4-(*p*-bromophenyl)cyclohexanone Ethylene Ketal (1). To magnesium turnings (1.19 g, 49.6 mmol) was added a solution of 1,4-dibromobenzene (11.1 g, 47 mmol) dissolved in THF (80 mL). The suspension was stirred and heated at reflux until the formation of the Grignard began, and then the heat was removed and the reaction continued until all of the Mg had reacted. The flask was cooled to room temperature, and a solution of 1,4-cyclohexanedione monoethylene ketal (6.99 g, 44.8 mmol) in THF (80 mL) was added dropwise, and the reaction mixture

was heated at reflux for 24 h. The reaction was quenched by the addition of saturated NH_4Cl (100 mL), and the resultant mixture was extracted with Et_2O (300 mL). The combined organic layers were washed again with aqueous NaOH (40 mL) and H_2O (100 mL). The organic layer was then dried ($MgSO_4$) and concentrated to give a crude solid. Recrystallization from benzene afforded 9.85 g (70%) of a white solid: mp 148–149 °C: ^1H NMR ($CDCl_3$) δ 1.8–2.2 (m, 9H), 4.0 (s, 4H), 7.3–7.6 (m, 4H); MS m/z (relative intensity) 296 ($M^+ - H_2O$, 1), 294 ($M^+ - H_2O$, 1), 239 (3), 237 (3), 185 (8), 183 (8), 99 (100), 86 (47). Anal. Calcd for $C_{14}H_{17}BrO_2$: C, 53.69; H, 5.47; Br, 25.51. Found: C, 53.51; H, 5.47; Br, 25.53.

4-(*p*-Bromophenyl)cyclohexen-3-one (2). The alcohol 1 (8.6 g, 27.5 mmol), together with potassium bisulfate (4 g, 29.4 mmol), was heated at reflux in chlorobenzene (50 mL) for 12 h. After the mixture was washed with water until neutral, the organic layer was dried and concentrated to afford the major product, 4-(*p*-bromophenyl)-3-cyclohexenone ethylene ketal. The product was characterized by ^1H NMR spectroscopy and GC/MS. Without further purification, this compound was heated at 100 °C in 85% acetic acid (30 mL) for 3 h. The resulting solution was washed with 10% aqueous NaOH (50 mL) and extracted with Et_2O. The ether layer was washed with H_2O (50 mL), dried ($MgSO_4$), and concentrated to afford a crude yellow oil. The oil was subjected to column chromatography (silica gel, 2:1, hexane/ethyl acetate) to give 3.7 g (53%) of solid 2: ^1H NMR ($CDCl_3$) δ 2.5–3.2 (m, 6H), 6.1 (m, 1H), 7.3 (d, J = 7.2 Hz, 2H), 7.5 (d, J = 7.3 Hz, 2H); MS m/z (relative intensity) 252 (M^+, 50), 250 (M^+, 50), 210 (19), 208 (19), 143 (8), 141 (8), 129 (100), 115 (18), 89 (4), 63 (2). This product was used in the next step without further purification or characterization.

4-(*p*-Bromophenyl)cyclohexanone (3). The 4-(*p*-bromophenyl)cyclohexen-3-one (2) (1 g, 3.98 mmol) was hydrogenated at ca. 600 psi for 6 h over rhodium on carbon (5%, 250 mg) in EtOAc (40 mL) at room temperature. After the catalyst was filtered off, the filtrate was concentrated in vacuum, and the residue was subjected to column chromatography (silica gel, 2:1 hexane/ethyl acetate) to afford a white solid. Recrystallization from hexane gave 570 mg (56%) of a white solid: mp 58–60 °C; ^1H NMR ($CDCl_3$) δ 1.8–2.7 (m, 8H), 3.0 (m, 1H), 7.2 (d, J = 7.3 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H); MS m/z (relative intensity) 254 (M^+, 100), 252 (M^+, 100), 199 (40), 197 (40), 184 (46), 182 (46), 171 (18), 169 (18), 116 (37), 103 (13), 77 (16), 57 (46). Anal. Calcd for $C_{12}H_{13}BrO$: C, 56.92; H, 5.14; Br, 31.62. Found: C, 57.02; H, 5.16; Br, 31.38.

4-(*p*-Bromophenyl)cyclohexanone Ethylene Ketal (4). To a solution of 4-(*p*-bromophenyl)cyclohexanone (3, 373 mg, 1.47 mmol) in dry benzene (5 mL) was added ethylene glycol (116 mg, 1.87 mmol) and a catalytic amount of *p*-toluenesulfonic acid monohydrate. The solution was heated at reflux for 10 h and quenched with 10% aqueous NaOH (5 mL). After extraction with Et_2O (20 mL), the organic layer was washed with H_2O (20 mL), dried ($MgSO_4$), and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, 2:1 hexane/ethyl acetate) to give 410 mg (94%) of a white solid: mp 69–71 °C; ^1H NMR ($CDCl_3$) δ 1.6–2.0 (m, 8H), 2.5 (br s, 1H), 4.0 (s, 4H), 7.1 (d, J = 7.3 Hz, 2H), 7.4 (d, J = 7.7 Hz, 2H); GC/MS, 298 (296) (M^+). Anal. Calcd for $C_{14}H_{17}BrO_2$: C, 56.56; H, 5.72; Br, 26.93. Found: C, 56.74; H, 5.75; Br, 26.76.

4-[4′-(Phenylethynyl)phenyl]cyclohexanone (5). Under a N_2 atmosphere, a suspension of bis(triphenylphosphine)-palladium(II) chloride (109 mg, 0.16 mmol), triphenylphosphine (63 mg, 0.24 mmol), and sodium methoxide (147 mg, 2.72 mmol) in dry DMF (10 mL) was stirred for 10 min. Then, a solution of phenylacetylene (248 mg, 2.4 mmol) and 4-(*p*-bromophenyl)-cyclohexanone ethylene ketal (4) (594 mg, 2 mmol) in dry DMF (5 mL) was added dropwise. The solution was warmed to 100 °C and kept at that temperature for 3 h, quenched with H_2O (10 mL), and extracted with Et_2O (30 mL). After filtering to remove the catalyst, the organic layer was washed with 10% aqueous HCl (20 mL), brine (30 mL), and H_2O (20 mL), dried ($MgSO_4$), and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, 2:1 hexane/ethyl acetate) to afford 4-[4′-(*p*-phenylethynyl)phenyl]cyclohexanone ethylene ketal which was characterized by ^1H NMR, GC/MS, and elemental analysis. The ethylene ketal was then directly reacted with 85% acetic acid (12 mL) at 100 °C for 2 h. The solution was quenched with H_2O (10 mL) and extracted with Et_2O (25 mL). The organic layer was washed with 10% aqueous NaOH (30 mL) and H_2O (15 mL), dried ($MgSO_4$), and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, 2:1 hexane/ethyl acetate) to give 430 mg (78%) of white crystals: mp 150–152 °C; ^1H NMR ($CDCl_3$) δ 1.8–2.7 (m, 8H), 3.3 (m, 1H), 4.0 (s, 4H), 7.2–7.8 (m, 9H); MS (EI, 70 eV) m/z (relative intensity) 274 (M^+, 100), 217 (40), 204 (82), 191 (11), 178 (6), 165 (4), 115 (7), 101 (8), 89 (7), 77 (4), 57 (28). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.52; H, 6.62.

4-[4′-[(*p*-Amylphenyl)ethynyl]phenyl]cyclohexanone (6). The procedure described for the preparation of 5 was used for bis(triphenylphosphine)palladium(II) chloride (95 mg, 0.135 mmol), triphenylphosphine (73 mg, 0.279 mmol), sodium methoxide (146 mg, 2.7 mmol), 4 (470 mg, 1.58 mmol), and 4-amylphenylacetylene (320 mg, 1.58 mmol) to afford 420 mg (77%) of a white solid: ^1H NMR ($CDCl_3$) δ 0.8–4.2 (m, 20H), 7.1–7.6 (m, 8H); MS (EI, 70 eV) m/z (relative intensity) 344 (M^+, 100), 217 (26), 202 (6), 189 (4), 115 (4), 91 (2), 55 (8). Anal. Calcd for $C_{25}H_{28}O$: C, 87.16; H, 8.19. Found: C, 87.16; H, 8.21.

4-[4′-[(*p*-Hexylphenyl)ethynyl]phenyl]cyclohexanone (7). The procedure described for the preparation of 5 was used with bis(triphenylphosphine)palladium(II) chloride (213 mg, 0.3 mmol), triphenylphosphine (174 mg, 0.66 mmol), sodium methoxide (400 mg, 7.4 mmol), 4 (871 mg, 2.93 mmol), and 4-hexylphenylacetylene (700 mg, 3.76 mmol) to afford 820 mg (78%) of a white solid: ^1H NMR ($CDCl_3$) δ 0.8–4.2 (m, 22H), 7.1–7.6 (m, 8H); MS (EI, 70 eV) m/z (relative intensity) 358 (M^+, 100), 287 (84), 231 (12), 217 (41), 202 (8), 189 (6), 115 (8), 91 (2), 55 (10), 43 (23). Anal. Calcd for $C_{26}H_{30}O$: C, 87.10; H, 8.43. Found: C, 87.06; H, 8.46.

(±)-1-(Phenylmethylene)-4-[4′-(phenylethynyl)phenyl]-cyclohexane (8). Under a N_2 atmosphere, n-BuLi (0.2 mL, 1.59 M in hexane, 0.32 mmol) was added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide (155 mg, 0.35 mmol) in dry THF (10 mL) at 0 °C. After the mixture was stirred at 25 °C for 30 min, a solution of 5 (89 mg, 0.32 mmol) in dry THF (5 mL) was added. The mixture was heated at reflux for 20 h, quenched with H_2O (5 mL), and extracted with Et_2O (20 mL). The organic layer was washed with 10% HCl (5 mL), brine (5 mL), and H_2O (5 mL), dried ($MgSO_4$), and concentrated to afford a yellow solid. Purification by column chromatography (silica gel, 10:1 hexane/ethyl acetate) afforded 60 mg (54%) of a white solid: mp 103–105 °C; ^1H NMR ($CDCl_3$) δ 1.4–3.2 (m, 9H), 6.3 (s, 1H), 7.1–7.8 (m, 14H); MS (EI, 70 eV) m/z (relative intensity) 348 (M^+, 100), 257 (28), 243 (11), 230 (17), 215 (18), 204 (90), 191 (35), 170 (20), 129 (41), 115 (37), 91 (46), 79 (17), 65 (8); UV (C_6H_{12}) λ_{max} 269 (log ϵ 4.48), 285 (4.56), 290 (4.39), 298 (4.31), 303 (4.48). Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 93.09; H, 6.95.

(−)-1-(Phenylmethylene)-4-[4′-(phenylethynyl)phenyl]-cyclohexane (8). Under a N_2 atmosphere, the chiral Wittig reagent 1 (WR-1) (116 mg, 0.416 mmol) was added to dry THF (6 mL) at room temperature and stirred for 20 min. Then the mixture was cooled to −78 °C and stirred for an additional 20 min. Next, n-BuLi (0.25 mL, 1.59 M in hexane, 0.4 mmol) was added dropwise, and the solution was stirred for 30 min. A solution of 5 (110 mg, 0.4 mmol) in dry THF (3 mL) was then added slowly, and the mixture was stirred for 2 h. Then glacial acetic acid (0.3 mL) was added to the mixture, and it was allowed to warm to room temperature for another 1.5 h. The mixture was diluted with Et_2O (15 mL), washed with H_2O (5 mL), 10% $NaHCO_3$ (10 mL), and H_2O (5 mL), dried ($MgSO_4$), and concentrated to afford a solid. Purification by column chromatography (silica gel, hexane) gave 80 mg (58%) of a white solid: mp 121–122 °C; $[\alpha]_D$ = −169.4 (*c* 0.15, C_6H_{12}); ^1H NMR, MS, and UV spectra were the same as (±)-8; CD (C_6H_{12}) λ_{ext} 241 ($\Delta\epsilon$ 5.42), 270 (−9.84), 281 (−7.19), 285 (−8.14), 290 (−4.79), 300 (−2.74), 303 (−3.47), 305 (−2.46). Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 92.94; H, 6.89.

(±)-1-[(*p*-Cyanophenyl)methylene]-4-[4′-(phenylethynyl)-phenyl]cyclohexane (9). Under a N_2 atmosphere, n-BuLi solution (0.9 mL, 1.6 M in hexane, 1.44 mmol) was added dropwise to a solution of diethyl *p*-cyanobenzylphosphonate (369 mg, 1.45 mmol) in dry THF (15 mL) at 0 °C and then stirred at 25 °C for 30 min. A solution of 5 (354 mg, 1.3 mmol) in dry THF (10 mL)

was then added dropwise, and the mixture was heated at reflux for 4 h. The reaction was quenched with H_2O (15 mL) and extracted with Et_2O (50 mL). The organic layer was washed with 10% aqueous HCl (10 mL) and H_2O (20 mL) and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, 10:1 hexane/ethyl acetate) to afford 404 mg (83%) of a white solid: mp 152–154 °C; ^{1}H NMR ($CDCl_3$) δ 1.4–3.1 (m, 9H), 6.35 (s, 1H), 7.1–7.8 (m, 13H); MS (EI, 70 eV) m/z (relative intensity) 373 (M^+, 100), 344 (6), 257 (15), 243 (4), 230 (15), 215 (14), 204 (44), 191 (32), 178 (35), 140 (7), 127 (6), 116 (8), 91 (6), 79 (15); UV (C_6H_{12}) λ_{max} 277 (log ϵ 4.68), 285 (4.72), 290 (4.57), 298 (4.43), 303 (4.54). Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.06; H, 6.19; N, 3.75.

(−)-1-[(*p*-Cyanophenyl)methylene]-4-[4′-(phenylethynyl)-phenyl]cyclohexane (9). The procedure described for the preparation of (−)-8 was used with chiral Wittig reagent **2** (WR-2) (126 mg, 0.416 mmol), **5** (108 mg, 0.4 mmol), and n-BuLi (0.25 mL, 1.59 M in hexane, 0.4 mmol). The product was purified by column chromatography (silica gel, 2:1 hexane/ethyl acetate), and recrystallization from hexane afforded 81 mg (54%) of a white solid: mp 145–147 °C; $[\alpha]_D$ = −215.7 (*c* 0.2, $CHCl_3$); ^{1}H NMR, MS, and UV spectra were the same as for (±)-8; CD (C_6H_{12}) λ_{ext} 254 ($\Delta\epsilon$ 8.10), 275 (−11.30), 280 (−18.51), 286 (−30.30), 290 (−23.99), 292 (−22.29), 295 (−21.05), 300 (−15.80), 303 (−17.07), 306 (−9.74), 309 (−1.80). Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.06; H, 6.21; N, 3.76.

(±)-1-(Biphenylmethylene)-4-[4′-(phenylethynyl)phenyl]-cyclohexane (10). The procedure described for the preparation of (±)-8 was used with biphenyltriphenylphosphonium chloride (187 mg, 0.4 mmol) and **5** (96 mg, 0.35 mmol) to afford 50 mg (34%) of a white solid: mp 133–135 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–4.3 (m, 9H), 6.35 (s, 1H), 7.1–7.8 (m, 18H); MS (EI, 70 eV) m/z (relative intensity) 424 (M^+, 100), 395 (4), 332 (23), 257 (25), 204 (87), 191 (43), 178 (18), 167 (62), 141 (5), 128 (8), 115 (12), 91 (18), 77 (9), 58 (2); UV (C_6H_{12}) λ_{max} 280 (log ϵ 4.78), 285 (4.84), 290 (4.72), 293 (4.71), 300 (4.61), 303 (4.68), 310 (3.76), 315 (3.36). Anal. Calcd for $C_{33}H_{28}$: C, 93.35; H, 6.65. Found: C, 93.27; H, 6.64.

(−)-1-(Biphenylmethylene)-4-[4′-(phenylethynyl)phenyl]-cyclohexane (10). The procedure described for the preparation of (−)-8 was used with chiral Wittig reagent **3** (WR-3) (148 mg, 0.416 mmol), **5** (111 mg, 0.405 mmol), and n-BuLi (0.25 mL, 1.59 M in hexane, 0.4 mmol) to afford 53 mg (31%) of a white solid: mp 144–146 °C; $[\alpha]_D$ = −255.8 (*c* 0.27, C_6H_{12}); ^{1}H NMR, MS, and UV spectra were the same as (±)-**10**; CD (C_6H_{12}) λ_{ext} 261 ($\Delta\epsilon$ 10.92), 270 (2.15), 280 (−12.50), 284 (−19.38), 287 (−31.77), 290 (−27.0), 295 (−26.22), 300 (−20.53), 304 (−25.85), 310 (−4.10), 315 (−0.91). Anal. Calcd for $C_{33}H_{28}$: C, 93.35; H, 6.65. Found: C, 93.24; H, 6.65.

(±)-1-(2-Naphthalenylmethylene)-4-[4′-(phenylethynyl)-phenyl]cyclohexane (11). The procedure described for the preparation of (±)-8 was used wth (2-naphthalenylmethyl)-triphenylphosphonium bromide (244 mg, 0.5 mmol) and **5** (139 mg, 0.5 mmol) to afford 70 mg (35%) as a white solid: mp 131–133 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–4.2 (m, 9H), 6.45 (s, 1H), 7.1–8.0 (m, 16H); MS (EI, 70 eV) m/z (relative intensity) 398 (M^+, 73), 256 (100), 243 (5), 215 (12), 204 (66), 191 (27), 179 (48), 165 (40), 141 (28), 128 (8), 115 (12), 91 (6), 79 (4); UV (C_6H_{12}) λ_{max} 248 (log ϵ 4.74), 284 (4.69), 302 (4.61). Anal. Calcd for $C_{31}H_{26}$: C, 93.42; H, 6.58. Found: C, 93.37; H, 6.63.

(±)-1-(Phenylmethylene)-4-[4′-[(*p*-amylphenyl)ethynyl]-phenyl]cyclohexane (12). The procedure described for the preparation of (±)-8 was used with benzyltriphenylphosphonium bromide (150 mg, 0.35 mmol) and **6** (150 mg, 0.35 mmol) to afford 71 mg (55%) of a white solid: ^{1}H NMR ($CDCl_3$) δ 0.8–3.2 (m, 20H), 6.3 (s, 1H), 7.0–7.6 (m, 13H); MS (EI, 70 eV) m/z (relative intensity) 418 (M^+, 100), 389 (7), 361 (12), 327 (12), 300 (10), 274 (21), 261 (14), 217 (49), 204 (13), 170 (21), 141 (7), 129 (26), 115 (19), 91 (26), 79 (10), 43 (30); UV (C_6H_{12}) λ_{max} 280 (log ϵ 4.50), 288 (4.59), 297 (4.45), 307 (4.51), 310 (4.05), 315 (2.79). Anal. Calcd for $C_{32}H_{34}$: C, 91.81; H, 8.19. Found: C, 91.82; H, 8.17.

(−)-1-(Phenylmethylene)-4-[4′-[(*p*-amylphenyl)ethynyl]-phenyl]cyclohexane (12). The procedure described for the preparation of (−)-8 was used with chiral Wittig reagent **1** (WR-1) (87 mg, 0.312 mmol), **6** (104 mg, 0.3 mmol), and n-BuLi (0.19 mL, 1.6 M in hexane, 0.304 mmol) to afford 77 mg (61%) of a white solid: mp 81–83 °C; $[\alpha]_D$ = −127.1 (*c* 0.27, C_6H_{12}); ^{1}H NMR, MS, and UV spectra were the same as (±)-**12**; CD (C_6H_{12}) λ_{ext} 244 ($\Delta\epsilon$ 5.15), 2.67 (−9.01), 272 (−11.28), 279 (−10.71), 284 (−8.28), 290 (−8.97), 295 (−5.83), 300 (−4.67), 305 (−4.37), 308 (−4.31), 310 (−2.36), 312 (−0.63). Anal. Calcd for $C_{32}H_{34}$: C, 91.81; H, 8.19. Found: C, 91.68; H, 8.21.

(±)-1-[(*p*-Cyanophenyl)methylene]-4-[4′-[(*p*-amylphenyl)ethynyl]phenyl]cyclohexane (13). The procedure described for the preparation of (±)-9 was used with diethyl (*p*-cyanobenzyl)phosphonate (172 mg, 0.5 mmol) and **6** (139 mg, 0.55 mmol) to afford 87 mg (40%) of a white solid: ^{1}H NMR ($CDCl_3$) δ 0.8–3.1 (m, 20H), 6.3 (s, 1H), 7.0–7.7 (m, 12H); MS (EI, 70 eV) m/z (relative intensity) 443 (M^+, 100), 386 (32), 300 (5), 274 (11), 261 (9), 248 (22), 217 (38), 204 (14), 191 (17), 154 (9), 140 (5), 116 (9), 91 (5), 79 (7), 55 (3); UV (C_6H_{12}) λ_{max} 280 (log ϵ 4.65), 288 (4.70), 297 (4.52), 307 (4.53), 310 (3.95), 315 (2.70). Anal. Calcd for $C_{33}H_{33}N$: C, 89.34; H, 7.50; N, 3.16. Found: C, 89.21; H, 7.51; N, 3.05.

(−)-1-[(*p*-Cyanophenyl)methylene]-4-[4′-[(*p*-amylphenyl)-ethynyl]phenyl]cyclohexane (13). The procedure described for the preparation of (−)-8 was used with chiral Wittig reagent **2** (WR-2) (97 mg, 0.32 mmol), **6** (102 mg, 0.3 mmol), and n-BuLi (0.19 mL, 1.6 M in hexane, 0.304 mmol) to afford 76 mg (57%) of a white solid: $[\alpha]_D$ = −204.3 (*c* 0.51, $CHCl_3$); ^{1}H NMR, MS, and UV spectra were the same as (±)-**13**; CD (C_6H_{12}) λ_{ext} 257 ($\Delta\epsilon$ 7.91), 275 (−7.41), 280 (−14.49), 284 (−17.99), 288 (−23.82), 290 (−25.63), 296 (−17.50), 300 (−14.19), 304 (−11.50), 310 (−6.13), 312 (−1.88), 315 (−0.25). Anal. Calcd for $C_{33}H_{33}N$: C, 89.34; H, 7.50; N, 3.16. Found: C, 89.25; H, 7.48; N, 3.10.

(±)-1-(Biphenylmethylene)-4-[4′-[(*p*-amylphenyl)ethynyl]-phenyl]cyclohexane (14). The procedure described for the preparation of (±)-8 was used with biphenyltriphenylphosphonium chloride (143 mg, 0.3 mmol) and **6** (104 mg, 0.3 mmol) to afford 45 mg (30%) of a white solid: mp 115–116 °C; ^{1}H NMR ($CDCl_3$) δ 0.8–3.2 (m, 20H), 6.35 (s, 1H), 7.0–7.7 (m, 17H); MS (EI, 70 eV) m/z (relative intensity) 494 (M^+, 100), 465 (4), 437 (6), 327 (16), 300 (8), 274 (27), 261 (12), 246 (15), 217 (51), 205 (19), 191 (16), 167 (40), 115 (8), 91 (11), 79 (6), 42 (8); UV (C_6H_{12}) λ_{max} 280 (log ϵ 4.72), 288 (4.76), 297 (4.65), 307 (4.59), 310 (4.09), 315 (3.29). Anal. Calcd for $C_{38}H_{38}$: C, 92.26; H, 7.74. Found: C, 91.97; H, 7.66.

(±)-1-[(*p*-Cyanophenyl)methylene]-4-[4′-[(*p*-hexylphenyl)-ethynyl]phenyl]cyclohexane (15). The procedure described for the preparation of (±)-8 was used with (*p*-cyanobenzyl)-triphenylphosphonium bromide (165 mg, 0.36 mmol) and **7** (111 mg, 0.31 mmol) to afford 27 mg (20%) of a white solid: mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 0.8–3.2 (m, 22H), 6.31 (s, 1H), 7.0–7.7 (m, 12H); MS (EI, 70 eV) m/z (relative intensity) 457 (M^+, 100), 386 (35), 358 (3), 314 (5), 288 (11), 275 (10), 262 (21), 217 (49), 204 (18), 191 (20), 154 (10), 140 (5), 116 (11), 91 (3), 79 (8), 44 (70); UV (C_6H_{12}) λ_{max} 287 (log ϵ 4.71), 306 (4.55). Anal. Calcd for $C_{34}H_{35}N$: C, 89.23; H, 7.71; N, 3.06. Found: C, 89.02; H, 7.67; N, 3.09.

(±)-1-[(*p*-Acetylphenyl)methylene]-4-[4′-(phenylethynyl)-phenyl]cyclohexane (16). Under a N_2 atmosphere, a solution of (±)-**9** (111 mg, 0.3 mmol) in dry benzene (4 mL) was added dropwise to a solution of methyllithium (0.24 mL, 1.4 M in Et_2O, 0.34 mmol) in dry benzene (3 mL). The reaction mixture was kept below 20 °C and stirred for 3 h at that temperature and another 2 h at room temperature. Next, a solution of 6 N sulfuric acid (3 mL) in 1,4-dioxane (3 mL) was added, and the mixture was heated at reflux for 2 h and quenched by 10% KOH (15 mL). After extraction with benzene (20 mL), the organic layer was washed with H_2O (20 mL) and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, 6:1 hexane/ethyl acetate) and then recrystallized from a hexane and ethyl acetate mixture to afford 35 mg (30%) of a white solid: mp 123–125 °C: ^{1}H NMR ($CDCl_3$) δ 1.4–3.2 (m, 12H), 6.38 (s, 1H), 7.1–7.7 (m, 11H), 7.95 (d, J = 9 Hz, 2H); MS (EI, 70 eV) m/z (relative intensity) 390 (M^+, 100), 361 (6), 257 (24), 243 (7), 230 (15), 218 (7), 204 (54), 191 (31), 178 (10), 169 (8), 143 (8), 128 (15), 105 (5), 91 (10), 79 (8), 43 (63); UV (C_6H_{12}) λ_{max} 285 (log ϵ 4.75), 290 (4.65), 295 (4.63), 300 (4.57), 303 (4.65), 310 (3.75), 315 (3.16); (CH_2Cl_2) λ_{max} 327 (log ϵ 3.21), 335 (2.71), 340 (2.47), 345 (2.27), 350 (2.13), 360 (1.89). Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.91; H, 6.69.

(−)-1-[(*p*-Acetylphenyl)methylene]-4-[4′-(phenylethynyl)-phenyl]cyclohexane (16). The procedure described for the preparation of (±)-16 was used with (−)-9 (86 mg, 0.23 mmol) and methyllithium (0.19 mL, 1.4 M in Et_2O, 0.266 mmol) to afford 36 mg (40%) of a white solid: mp 139–141 °C; $[\alpha]_D$ = −227.8 (*c* 0.21, $CHCl_3$); ^1H NMR, MS, and UV spectra were the same as (±)-16; CD (C_6H_{12}) λ_{ext} 262.3 ($\Delta\epsilon$ 8.13), 280 (−5.41), 285 (−14.83), 287 (−21.80), 290 (−19.65), 295 (−20.13), 300 (−16.57), 304 (−21.07), 310 (−4.82), 313 (−2.02), 317 (−0.80); (CH_2Cl_2) λ_{ext} 327 ($\Delta\epsilon$ −0.40), 330 (−0.10), 335 (0.132), 340 (0.198), 342 (0.203), 345 (0.192), 350 (0.151), 355 (0.115), 360 (0.089). Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.91; H, 6.60.

(±)-1-[(*p*-Benzoylphenyl)methylene]-4-[4′-(phenylethynyl)phenyl]cyclohexane (17). Under a N_2 atmosphere, phenylmagnesium bromide (0.15 mL, 3.0 M in Et_2O, 0.45 mmol) was added to a solution of (±)-9 (110 mg, 0.3 mmol) in dry THF (15 mL) with a catalytic amount of copper(II) bromide (5 mg) at room temperature. The reaction mixture was heated at reflux for 4 h. After cooling, H_2O (2 mL) and 3 N H_2SO_4 (4 mL) were added, and the mixture was heated at reflux for another 5 h and then extracted with Et_2O (25 mL). The organic layer was washed with 10% KOH (15 mL) and H_2O (20 mL) and concentrated in vacuum. The residue was subjected to column chromatography (silica gel, CH_2Cl_2) and then recrystallized from a hexane and ethyl acetate mixture to afford 80 mg (59%) of a white solid: mp 114–117 °C; ^1H NMR ($CDCl_3$) δ 1.4–3.2 (m, 9H), 6.4 (s, 1H), 7.1–7.7 (m, 14H), 7.7–8.0 (m, 4H); MS (EI, 70 eV) *m/z* (relative intensity) 452 (M^+, 100), 423 (5), 274 (15), 257 (27), 243 (8), 230 (13), 215 (13), 204 (63), 196 (14), 191 (29), 178 (8), 169 (5), 143 (6), 128 (10), 115 (11), 105 (83), 91 (8), 77 (34); UV (C_6H_{12}) λ_{max} 285 (log ε 4.67), 290 (4.59), 300 (4.56), 303 (4.63), 310 (4.05), 315 (3.78); (CH_2Cl_2) λ_{max} 342 (log ε 3.23), 350 (2.94), 355 (2.79), 360 (2.65), 365 (2.49), 370 (2.33), 376 (2.09), 380 (1.88). Anal. Calcd for $C_{34}H_{28}O$: C, 90.23; H, 6.24. Found: C, 89.99; H, 6.10.

(−)-1-[(*p*-Benzoylphenyl)methylene]-4-[4′-(phenylethynyl)-phenyl]cyclohexane (17). The procedure described for the preparation of (±)-17 was used with (−)-9 (161 mg, 0.311 mmol), phenylmagnesium bromide (0.47 mL, 1.0 M in THF, 0.47 mmol), and a catalytic amount of copper(II) bromide (5 mg) to afford 97 mg (67%) of a white solid: mp 105–106 °C; $[\alpha]_D$ = −240.6 (*c* 0.285, $CHCl_3$); ^1H NMR, MS, and UV spectra were the same as (±)-16; CD (C_6H_{12}) λ_{ext} 285 ($\Delta\epsilon$ −8.07), 288 (−18.20), 296 (−21.43), 300 (−19.33), 304 (−27.89), 310 (−11.33), 315 (−5.79), 320 (−2.26), 324 (−0.82); (CH_2Cl_2) λ_{ext} 342 ($\Delta\epsilon$ −0.456), 346 (−0.240), 350 (−0.117), 355 (−0.031), 360 (0.011), 365 (0.022), 370 (0.027), 376 (0.028), 380 (0.023). Anal. Calcd for $C_{34}H_{28}O$: C, 90.23; H, 6.24. Found: C, 90.25; H, 6.25.

(±)-1-Benzylidene-4-phenylcyclohexane (18). To a homogeneous solution of sodium (700 mg, 26.5 mmol) in absolute ethanol (30 mL) under a N_2 atmosphere was added a solution of benzyltriphenylphosphonium chloride (5.64 g, 14.5 mmol) in absolute ethanol (20 mL). After the mixture was stirred for 40 min, a solution of 4-phenylcyclohexanone (1.97 g, 11.5 mmol) in absolute ethanol (25 mL) was added, and the mixture was heated at reflux for 5 h. After workup, the crude product was purified by column chromatography (silica gel, hexane) to afford 930 mg (33%) of a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.4–3.2 (m, 9H), 6.3 (s, 1H), 7.1–7.5 (m, 10H); MS (EI, 70 ev) *m/z* (relative intensity) 248 (M^+, 100), 157 (51), 129 (77), 91 (63), 77 (14); UV (C_6H_{12}) λ_{max} 235 (log ε 4.11), 245 (4.19), 260 (3.98). Anal. Calcd for $C_{19}H_{20}$: C, 91.94; H, 8.06. Found: C, 91.94; H, 8.07.

(−)-1-Benzylidene-4-phenylcyclohexane (18). The procedure described for the preparation of (−)-8 was used with chiral Wittig reagent (WR-1) (277 mg, 0.996 mmol), 4-phenylcyclohexanone (166 mg, 0.957 mmol), and n-BuLi (0.61 mL, 1.57 M in hexane, 0.957 mmol) to afford 155 mg (63%) of a white solid: mp 53–55 °C; [α] = −99.8 (*c* 0.37, C_6H_{12}); ^1H NMR, MS and UV spectra were the same as (±)-18; CD (C_6H_{12}) λ_{ext} 230 ($\Delta\epsilon$ −2.93). Anal. Calcd for $C_{19}H_{20}$: C, 91.94; H, 8.06. Found: C, 91.91; H, 8.08.

Acknowledgment. This work was supported by grants from the National Science Foundation and the Army Research Office, for which we are grateful. Drs. R. P. Lemieux and B. S. Udayakumar prepared some of the chiral Wittig reagents. Circular dichroism spectra were recorded at the laboratory for fluorescence dynamics, University of Illinois.