# Liquid Crystalline Solvents as Mechanistic Probes. 3. The Influence of Ordered Media on the Efficiency of the Photodimerization of Acenaphthylene[1]

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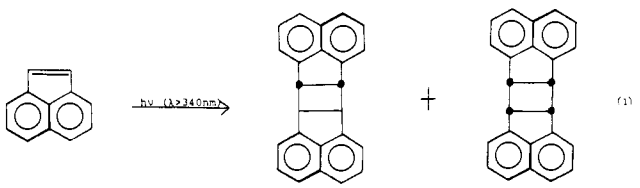
**Abstract:** An experimental approach, employing cholesteric liquid crystalline solvents, has allowed the preferred orientations of collisions leading to photodimerization of acenaphthylene to be determined. The distribution of the syn and anti dimers of acenaphthylene and dimerization quantum yields have been determined in toluene, *n*-butyl stearate, and a 1/1 mixture of 5α-cholestan-3β-yl acetate and 5α-cholestan-3β-yl nonanoate as a function of temperature, solvent phase, and acenaphthylene concentration. Quantum yields have been measured in compensated nematic and cholesteric mixtures of cholesteryl chloride and cholesteryl nonanoate, and in the cholestanyl ester mixture in the presence of tetralin. Large enhancements of the photodimerization rate were found only for irradiations conducted in cholesteric phases. For instance, the quantum yield for photodimerization of 0.02 M acenaphthylene at 35 °C is 0.76 in a 1/1 mixture of 5α-cholestan-3β-yl acetate–5α-cholestan-3β-yl nonanoate and is 0.012 in toluene. An explanation of the results which includes the effects of solvent order on the orientations of solute–solute collisions is advanced. The isomeric distribution of photodimers is much less dependent on solvent order than on acenaphthylene concentration and solvent viscosity. Factors which perturb the solvent order and, therefore, alter the reaction efficiency are discussed.

## Introduction

Liquid crystalline solvents are known to influence the rates[2] and stereochemical courses[3] of some unimolecular and bimolecular reactions. Previously, we reported[1a] that the photodimerization of acenaphthylene (eq 1) is accelerated in a




(1)

cholesteric liquid crystal, and ascribed the rate enhancement to a solvent-induced ordering effect on collisions between excited- and ground-state acenaphthylene molecules. Here, we demonstrate, further, the utility of anisotropic media in elucidating the mechanism of the photodimerization of acenaphthylene and in governing its efficiency. Results from irradiations in smectic, nematic, cholesteric, and isotropic solvent phases are reported. The effects of varying solvent order on the dimerization quantum yield and product distributions are explored.

Since the first report in 1912 by Dziewonski and Rapalski[4] of the photodimerization of acenaphthylene, numerous experimental[5,6] and theoretical[7] investigations of the mechanism have been reported. It is known that the dimerization quantum yield and the distribution of stereoisomeric cyclobutane dimers vary as a function of temperature,[5,8] acenaphthylene concentration,[5,8,9a] solvent,[5,9a-e,10] and the multiplicity of the excited state of acenaphthylene yielding products.[5,6,9a]

From these extensive investigations, several mechanistic schemes for the photodimerization have been proposed.[5,6,8,9a] However, the preferred orientations of collisions leading to dimerization have not been investigated. It is this aspect of the mechanism that we address here.

## Experimental Section

NMR spectra were obtained with a 90-MHz Fourier transform Bruker Model HFX-10 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Analytical gas chromatography was conducted on a Hewlett-Packard Model 700 gas chromatograph (6 ft × 1/8 in. 5% SE-30 on Chromosorb W (80–100 mesh) column at 128 °C). Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using matched 1.0-cm quartz curvettes or 1-in. diameter quartz disks whose optical paths were varied with Teflon spacers. Optical densities at individual wavelengths were obtained from a Beckman Model DU spectrometer. Melting points and transition temperatures (corrected) were measured on a Kofler micro-hot stage microscope with polarizing lenses or a Gallenkamp melting point apparatus. Boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Acenaphthylene (Aldrich, 99%) was recrystallized from 95% ethanol and sublimed, mp 91–92 °C (lit.[5,6] mp 92–93 °C). Toluene was distilled from sodium and stored in the dark. Hexane, purified by the method of Murray and Keller,[11] displayed no discernible absorption above 2100 Å. Cholesteryl nonanoate (Aldrich), recrystallized from 95% ethanol, exhibited an enantiotropic cholesteric phase from 78.5 to 91.5 °C (lit. smectic to cholesteric 77.5,[12a] 76.3 °C;[12b] cholesteric to isotropic 92,[12a] 92.1 °C[12b]). Cholesteryl chloride (Aldrich, 98%), recrystallized several times from acetone, exhibited a monotropic cholesteric phase with mp 95–96 °C (lit. mp 95.7,[13a] 96.5 °C[13b]). Tetralin (Fisher) was distilled, bp 30–31 °C (0.025 mm) (lit.[14] bp 90.8–91.2 ° C (17 mm)).

**5α-Cholestan-3β-yl Nonanoate.** Nonanoic acid[15] (16.4 g, 0.10 mol) was added to a stirred solution of 14 mL (0.21 mol) of thionyl chloride in 6 mL of anhydrous ether at a rate sufficient to maintain a reflux. Excess thionyl chloride was distilled (bp ≤76 °C) after gas evolution ceased. The undistilled liquid, in 50 mL of anhydrous ether, was added slowly to a stirred solution of 19.5 g (0.05 mol) of 3β-cholestanol (recrystallized from 95% ethanol, mp 139.5–140 °C (lit.[16] mp 141 °C)) in 400 mL of dry pyridine at 0 °C. The reaction mixture was stirred for several hours at 0 °C and brought slowly to room temperature. Petroleum ether (500 mL) was added and the solution extracted twice with 300 mL of water, twice with 300 mL of 5% hydrochloric acid, twice with 300 mL of 10% sodium bicarbonate, and twice with 300 mL of water. The dried ($MgSO_4$) organic layer was distilled under reduced pressure at room temperature to yield 20.1 g of a crude, yellow, oily residue. After seven recrystallizations from 9/1 (v/v) 95% ethanol–2-butanone,[17] 13.3 g (50%) of 5α-cholestan-3β-yl nonanoate, mp 80.5–81.0 °C (lit.[17] mp 81.2 °C), was obtained. Anal. Calcd for $C_{36}H_{64}O_2$: C, 81.75; H, 12.20. Found: C, 82.06; H, 11.94.

**5α-Cholestan-3β-yl Acetate.** A solution containing 25 g (0.064 mol) of purified 3β-cholestanol and 450 mL of dry pyridine was prepared in a dry atmosphere and cooled to −5 °C in an ice–salt bath. Acetyl chloride (6.0 g, 0.077 mol) in 50 mL of anhydrous ether was added *slowly* to the stirred solution, which was warmed to room temperature overnight. Diethyl ether (500 mL) and 500 mL of water were added, and the ether layer was extracted twice with 300-mL aliquots of water and three 300-mL portions of a saturated salt solution. The organic

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layer was dried ($MgSO_4$) and evaporated to a volume of 50 mL, and 200 mL of 95% ethanol was added. The yellow solid which precipitated was recrystallized from 9/1 (v/v) 95% ethanol–2-butanone[17] to yield 24.8 g (77%) of 5α-cholestan-3β-yl acetate, mp 108–109 °C (lit.[18] mp 109 °C). Anal. Calcd for $C_{29}H_{50}O_2$: C, 80.87; H, 11.70. Found: C, 81.00; H, 11.70.

***n*-Butyl Stearate.**[19] Boron trifluoride etherate and anhydrous ether were distilled and the fraction of bp 33–35 °C (4 mm) (lit.[20] bp 46 °C (10 mm)) was collected. A 100-mL portion of the distillate was added to a solution of 56 g (0.20 mol) of stearic acid in 400 mL of 1-butanol. The mixture was refluxed for 4 h and 500 mL of anhydrous ether was added. Extractions were performed twice with 200 mL of water and 200 mL of 20% aqueous sodium carbonate. The organic layer was evaporated to remove solvent and the residue distilled, bp 165–180 °C (0.1 mm), to yield 85 mL of a viscous, yellow oil. The oil was passed through a 20-cm column of alumina, irradiated neat (λ > 3000 Å) for 16 h with a 450-W medium-pressure Hg lamp, rechromatographed on alumina, and distilled under vacuum to yield 43.1 g (75%) of a clear liquid, $n^{28.5}_D$ 1.4418, bp 158–161 °C (0.025 mm) (lit.[21] bp 223 °C (25 mm)). The infrared spectra of this material and of a commercial sample of *n*-butyl stearate were indistinguishable. Anal. Calcd for $C_{22}H_{44}O_2$: C, 77.58; H, 13.02. Found: C, 77.33; H, 12.93.

**Syn Dimer of Acenaphthylene.**[22] Oxygen was bubbled through a solution of 1.0 g of acenaphthylene in 25 mL of *n*-hexane. Bubbling was continued while the solution was irradiated for 72 h through a Corning no. CS-054 filter (λ > 340 nm) with a 450-W medium-pressure mercury arc. The white solid which formed was removed periodically by vacuum filtration. The combined solids were recrystallized thrice from 6/1 (v/v) *n*-hexane–benzene to yield 0.1 g of white prisms: mp 224–225 °C dec (lit.[6] mp 231.5–233.5 °C); NMR (3/1 (v/v) $CCl_4$–$CD_3CN$) δ 7.21–6.95 (m, 12 H), 4.82 (s, 4 H). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 95.02; H, 5.04.

**Anti Dimer of Acenaphthylene.**[22] A nitrogen-saturated solution containing 1.0 g of acenaphthylene in 25 mL of carbon tetrachloride was irradiated for 24 h as described above. The solid was collected and recrystallized thrice from benzene to yield 0.12 g of white needles: mp 308–309 °C dec (lit.[6] mp 306–307 °C); NMR (5/1 (v/v) $CCl_4$–$CD_3CN$) δ 7.74–7.43 (m, 12 H), 4.05 (s, 4 H). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.89; H, 5.06.

**Irradiation Procedures.** Samples of 0.08 M acenaphthylene in various solvents were prepared in 2.0-mm (o.d.) Pyrex capillary tubes. The samples were sealed under nitrogen and rotated in a miniature "merry-go-round" apparatus in a thermostated bath. Light from a 450-W medium-pressure mercury arc was passed through a Corning no. CS-054 filter and delivered to the samples via a quartz light pipe. Experiments were performed at least in duplicate. Irradiation times were varied so that all samples were taken to 10–15% conversion of acenaphthylene. Experiments in which the concentration of acenaphthylene was varied from 0.02 to 0.40 M, as well as those in which the concentration of acenaphthylene was held constant at either 0.02 or 0.08 M while tetralin was added, were performed in an identical manner.

Irradiated samples were analyzed by diluting the contents of the capillary tubes with hexane in volumetric flasks. The ultraviolet spectra of these solutions indicated that no reaction, other than photodimerization, had occurred.

**Determinations of Percent Conversions and Product Distributions.** The concentration of acenaphthylene was monitored at 343 nm, where neither dimer absorbs. Subtraction of the absorbance of acenaphthylene from the spectra of the three components allowed the dimer concentration and product distributions to be determined. The most suitable pairs of wavelengths for these calculations, found by matrix analysis of the molar extinction coefficients, are 285 and 315, 295 and 315, and 285 and 305 nm. Average values determined from the optical densities at these wavelengths are reported. In experiments carried to low (10–15%) conversion of acenaphthylene, the concentrations of the dimers could not be measured independently by this method: small changes in the optical densities at each wavelength result in large variations in the calculated syn/anti ratios.

**Quantum Yields for Dimerization as a Function of Temperature.** Duplicate, nitrogen-saturated toluene solutions of 0.08 M acenaphthylene were irradiated in 10-mm (i.d.) Pyrex tubes in a merry-go-round apparatus[23] immersed in a thermostated water bath, with a 450-W medium-pressure mercury arc through Corning no. CS-054 and CS-737 filters (366 nm). In experiments conducted at 10 and 69 °C, nitrogen-saturated 0.08 M acenaphthylene solutions in toluene were irradiated in thermostated 10-mm (i.d.) quartz cuvettes. Corrections for solute concentration changes with temperature were made. Ultraviolet spectra of 0.08-mL aliquots of irradiated samples, diluted to 25 mL with hexane, were recorded. The changes in the optical density between irradiated and unirradiated samples were used to determine the number of moles of acenaphthylene which had reacted. In all cases, irradiations were carried to 10–15% conversion of acenaphthylene. Ferrioxalate actinometry,[24] at 25 °C, was performed at 24-h intervals when irradiations were continued for more than 1 day. Quantum yields are estimated to be accurate to within ±5%. Quantum yields in liquid crystalline solvents were measured with the light pipe–miniature merry-go-round setup and are relative to the efficiency of dimerization in toluene.

**Helical Pitch Measurements.**[25] Samples prepared from the cholestanyl esters and varying concentrations of acenaphthylene were placed between quartz plates (coated and cured with *N*-methyl-3-aminopropylmethoxysilane[26,27]) which were separated by 0.025-mm Teflon spacers. Visible and infrared spectra were recorded at 25 °C. The technique was calibrated with mixtures of cholesteryl chloride and cholesteryl nonanoate for which pitch data have been reported previously.[28]

## Results and Discussion

Bimolecular reactions performed in isotropic media provide little information concerning the preferred orientations of solute collisions leading to products. Individual molecules in an isotropic liquid phase exhibit no long-range order and solute–solute collisions occur without specificity. This is not true of liquid crystalline phases which display considerable long- and short-range order.[29] As evidenced by alterations in their spectroscopic properties[30,31] and reactivities,[1b,2,3] solute molecules are influenced by the ordered structure of liquid crystalline solvents. Therefore, information regarding the preferred orientations of collisions which lead to products in intermolecular reactions should be available from experiments conducted in liquid crystals.

A representation of the molecular order in smectic, nematic, and cholesteric liquid crystalline phases is given in Figure 1. In a smectic mesophase, solvent molecules are arranged in layers with their long molecular axes parallel to one another and perpendicular to the plane of the layers. A nematic phase, although not layered, is also characterized by a parallel arrangement of molecules. The individual molecules of a cholesteric mesophase are arranged in layers which, individually, have nematic-like order. The long axes of molecules within a layer are parallel and the layers are tilted with respect to one another, forming a twisted helical macrostructure. Of the three types of liquid crystals, the smectic phase is considered to be the most ordered.[32] Solutes in liquid crystals align themselves in the best packing arrangement based upon steric considerations[33] (e.g., planar solutes, like acenaphthylene, are expected to lie in the plane of the cholesteric layers, with their long molecular axes parallel to the long axis of the solvent molecules[34]).

**Quantum Yields.** In 1947, Bowen and Marsh[8] reported that the quantum yield for dimerization of acenaphthylene decreases with increasing temperature and is unaffected by the presence of oxygen. Later, however, it was demonstrated[5] that increasing temperature decreases the quantum efficiency in air-saturated solutions and increases the quantum yield in deoxygenated solutions. We find that the quantum yields for dimerization of 0.08 M acenaphthylene in nitrogen-saturated toluene solutions increase linearly with temperature over the range studied (Table I) and agree qualitatively and quantitatively with the results of Livingston and Wei.[5]

Quantum yields for the dimerization of 0.08 M acenaphthylene in toluene ($\Phi_t$), *n*-butyl stearate ($\Phi_s$), and a 1/1 (w/w) mixture of 5α-cholestan-3β-yl acetate and 5α-cholestan-3β-yl nonanoate ($\Phi_c$) are shown in Figure 2.[35] $\Phi_s$ varies slightly as a function of temperature and remains near $\Phi_t$. This similarity is unexpected if solvent viscosity (i.e., solute–solute collision

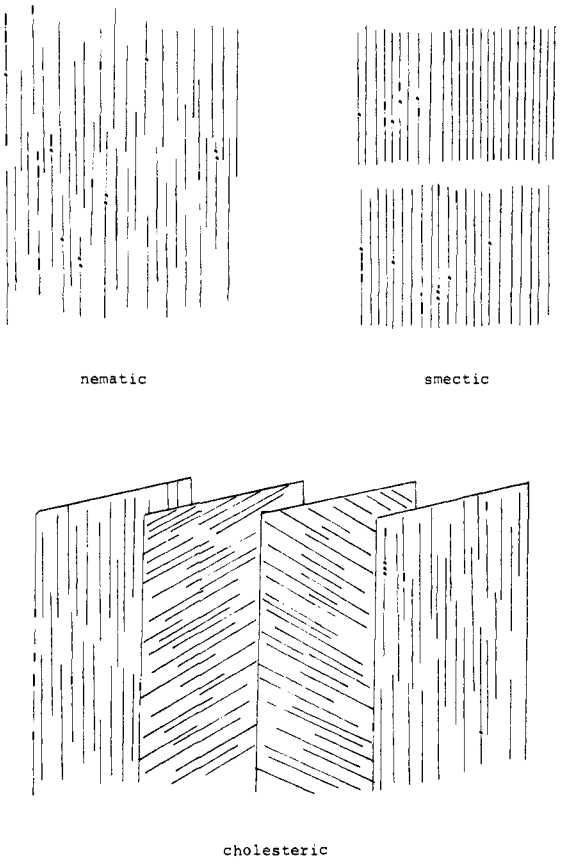


Figure 1. Representation of the molecular order in mesophases.

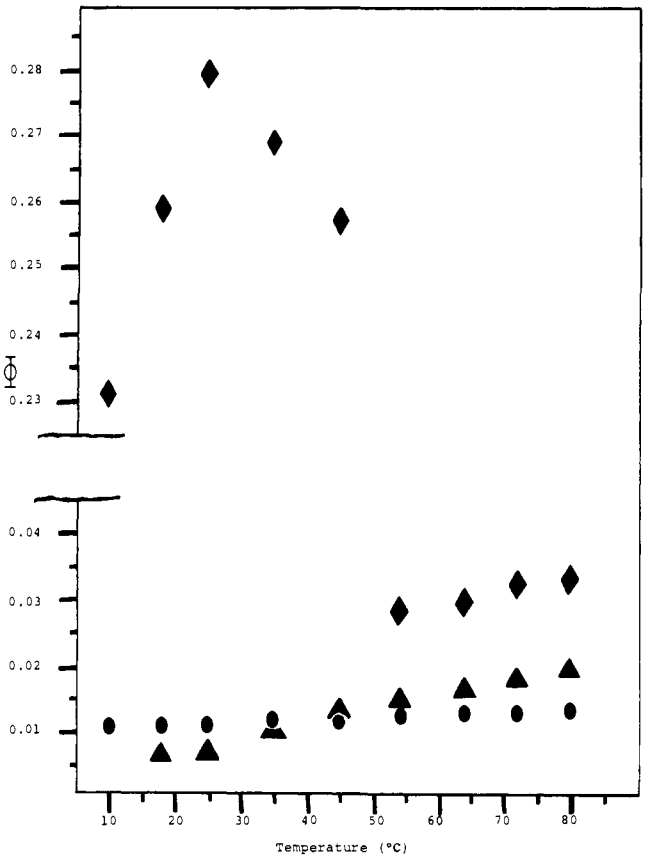


Figure 2. Φ for the dimerization of 0.08 M acenaphthylene in toluene (●), *n*-butyl stearate (▲), and a 1/1 mixture of 5α-cholestan-3β-yl nonanoate and 5α-cholestan-3β-yl acetate (♦) as a function of temperature.

**Table I.** Absolute Quantum Yields for the Dimerization of 0.08 M Acenaphthylene in Toluene

| temp, °C | Φ |
|---|---|
| 10 ± 0.5 | 0.0105 ± 0.0005 |
| 25 ± 0.5 | 0.0112 ± 0.0005 |
| 35 ± 0.5 | 0.0117 ± 0.0005 |
| 55 ± 0.5 | 0.0121 ± 0.0005 |
| 69 ± 0.5 | 0.0127 ± 0.0005 |

frequency) alone determines the dimerization quantum efficiencies at a given temperature. In the smectic phase of *n*-butyl stearate, below 25 °C,[36] $\Phi_s$ is ca. $0.6\Phi_t$, significantly higher than the quantum yield obtained by Livingston and Wei[37] for the dimerization of crystalline acenaphthylene at 20 °C.

In the isotropic phase of the cholestanyl ester mixture, from 55 to 80 °C, $\Phi_c$ remains approximately $2.5\Phi_t$. However, in the cholesteric phase from 10 to 45 °C, $\Phi_c$ increases dramatically to $21\text{-}25\Phi_t$, indicating an extremely strong influence of this phase on the efficiency of photodimerization.[38]

Although no experimental evidence for their existence has been found, ground-state complexes, which conceivably could be responsible for the rate enhancements observed in the cholesteric solvent, have been suggested to participate in the dimerization.[5,6] The formation of aggregates, if important in the cholesteric liquid crystal, is expected to exert two major in the cholesteric liquid crystal, is expected to exert two major effects on the dimerization efficiency: (1) the reaction should proceed more rapidly than in toluene; and (2) the quantum yield should increase more rapidly with increasing concentration of acenaphthylene than is predicted from diffusion-based arguments. The data in Figures 2 and 3 indicate that only the first effect is realized. Although the quantum yield increases linearly with the concentration of acenaphthylene in the isotropic phase (55 °C) as expected,[8,9a] *in the cholesteric phase (35 °C), $\Phi_c$ is greatest ($75\Phi_t$) at the lowest concentration (0.02 M) of acenaphthylene employed.* Furthermore, $\Phi_c$ *decreases* as the concentration is increased from 0.02 to 0.08 M and *increases* as the concentration is increased from 0.08 to 0.40 M. Clearly, these results are not compatible with a model in which ground-state aggregation plays a significant role. In the high-concentration portion of Figure 3 at 35 °C, $\Phi_c$ does not increase as rapidly with increasing concentration in the cholesteric phase as in the isotropic phase. However, the absolute magnitude of $\Phi_c$ is greater in the cholesteric phase than in the isotropic phase at all concentrations of acenaphthylene employed.

These results are explicable if the rate enhancements are due primarily to the cholesteric phase controlling the orientations of acenaphthylene collisions. From basic principles, the quantum yield for dimerization of acenapthhthylene depends upon the number of collisions experienced by an excited-state acenaphthylene during its lifetime as well as the orientations of those collisions. The absolute magnitude of $\Phi_c$ in the cholesteric phase, therefore, reflects the relative contributions from (1) a kinetic effect (the rate of a bimolecular reaction increases as the reactant concentrations increase) and (2) an ordering effect (the orientations of solute collisions will be influenced most by the layered structure of the cholesteric phase).

In order to separate the kinetic and ordering effects, quantum yields in the presence of varying concentrations of tetralin,[39] a solute which disturbs solvent order but does not interfere electronically with the acenaphthylene photodimerization, were determined (Figure 4). An increase in tetralin concentration decreases $\Phi_c$ (0.08 M acenaphthylene at 35 °C), indicating that an adequate explanation of the previous results

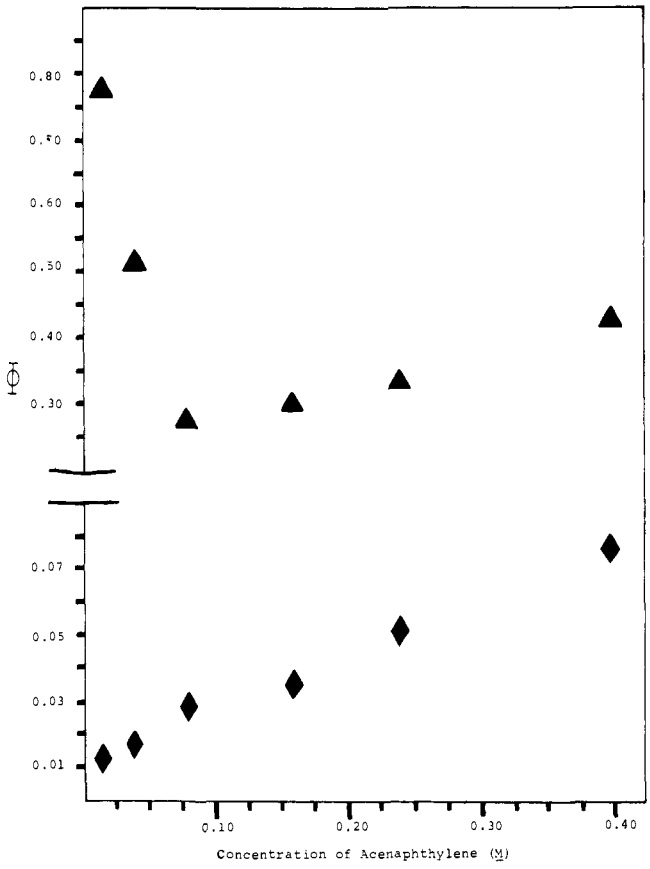


Figure 3. Φ for the dimerization of acenaphthylene in the cholestanyl ester mixture at 35 (▲) and 55 ° (♦) as a function of acenaphthylene concentration.

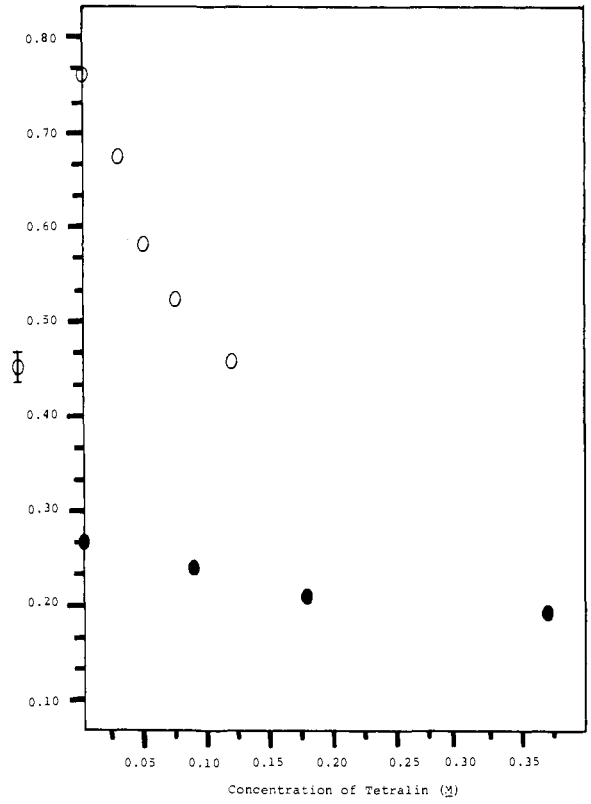


Figure 4. Φ for the dimerization of 0.02 (○) and 0.08 M (●) acenaphthylene in the cholestanyl ester mixture at 35 °C vs. concentration of tetralin.

must include the disordering influences of a solute on solvent order. It follows that variations in solvent order alter the fraction of collisions leading to dimerization since the number of excited acenaphthylene-ground-state acenaphthylene collisions per excited state lifetime is nearly constant when tetralin, in low concentrations, is the only variable.

For an initial acenaphthylene concentration of 0.02 M, $\Phi_c$ decreases as the tetralin concentration is increased from 0 to 0.12 M. The variations in $\Phi_c$ with total solute concentration are *less* than those measured at equal solute concentrations of acenaphthylene in the absence of tetralin (Figure 3 at 35 °C), indicating that variations in solvent order are a function not only of the concentration of added solute but, also, their structure. In this case, solvent order is disturbed to a much larger extent by acenaphthylene than tetralin. The relative magnitudes of the effects of these solutes on solvent order are further demonstrated by the fact that the phase transition temperatures of samples containing acenaphthylene and tetralin are lowered to a smaller extent than by samples containing the same molar quantity of acenaphthylene alone (Table II).

We interpret the low-concentration portion of Figure 3 at 35 °C to be dominated by the ordering effect since a kinetic effect requires that the quantum yields increase as the acenaphthylene concentration increases. In the high-concentration portion of Figure 3 at 35 °C, the kinetic effect is the more important ($\Phi_c$ increases as the acenaphthylene concentration increases), although the influence of variations in solvent order on solute reactivity is evident: as acenaphthylene concentrations become larger the rate of increase in $\Phi_c$ is slower in the cholesteric phase than in the less viscous isotropic phase.

**Effect of Acenaphthylene on the Cholesteric Phases.** The pitch of a cholesteric liquid crystalline phase measures the distance between layers of solvent molecules whose long axes are parallel (Figure 1). When the helical axis of the solvent is aligned parallel to a beam of incident irradiation, the pitch is available experimentally from the relationship $\lambda = 2np$,[25a,41,42] where $n$ (≈1.5) is the index of refraction of the medium, $p$ is the pitch, and $\lambda$ is the maximum of the reflectance band. We find that $p$ decreases as the acenaphthylene concentration is increased (Table II). At no solute concentration employed was the formation of a compensated nematic phase (vide infra) observed for a 1/1 5α-cholestan-3β-yl acetate-5α-cholestan-3β-yl nonanoate mixture.[43]

Table II. Reflectance Maxima and Transition Temperatures for a 1/1 Mixture of 5α-Cholestan-3β-yl Nonanoate and 5α-Cholestan-3β-yl Acetate Doped with Acenaphthylene

| acenaphthylene, M | $\lambda_{max}$, nm[a] | transition temp, °C | |
|---|---|---|---|
| | | S → I[b] | I → C[c] |
| 0.0 | 700 ± 5 | 72-73 | 60-59 |
| 0.02 | 705 ± 5 | 75.5-76.5 | 54-53 |
| 0.04 | 695 ± 5 | 74.5-75.5 | 52-51 |
| 0.08 | 685 ± 5 | 73.5-74.5 | 48.5-47.5 |
| 0.16 | 675 ± 5 | 72-73 | 46.5-45.5 |
| 0.24 | 670 ± 5 | 71-72 | 42.5-41.5 |
| 0.40 | 660 ± 5 | 70-71 | 38-37 |

[a] Reflectance maxima. [b] Solid to isotropic phase. [c] Isotropic to cholesteric phase.

**Effects of Solvent Phase Variations on Acenaphthylene Photodimerization.** The attribution of the rate enhancements for dimerization of acenaphthylene to solvent ordering (i.e., solvent control of solute-solute collisional orientations) is further supported by experiments conducted in cholesteryl nonanoate-cholesteryl chloride mixtures. It is known from pitch measurements that a 40/60 (w/w) ratio of these com-

ponents forms a compensated nematic phase ($p \rightarrow \infty$)[25b,28] in which solvent molecules are coparallel but do not reside in twisted layers (Figure 1). A 70/30 (w/w) ratio has a "normal" cholesteric phase ($p \simeq 2000$ Å).[28] The quantum yield for dimerization of 0.08 M acenaphthylene in the 70/30 mixture at 25 °C is $21\Phi_t$. *However, the quantum yield for dimerization in the 40/60 compensated nematic mixture at 25 °C is only* $2.5\Phi_t$, the same value obtained from reaction in the isotropic phase of the cholestanyl ester mixture.

These results demonstrate unambiguously that the increased efficiency of acenaphthylene photodimerization is linked to the specific ordering ability of the cholesteric liquid crystalline phase. Neither smectic nor nematic mesophases have a similar effect, even though the smectic phase is more ordered than the cholesteric.[32]

It is known that ordered media can enhance the excited-state lifetimes of some solutes.[2b,44,45] Although there is no reason to believe that ordered media do not have a similar effect on acenaphthylene's excited states, the magnitude of the increase should be nearly constant in 40/60 and 70/30 mixtures of cholesteryl nonanoate–cholesteryl chloride since a solute's local environment is not altered appreciably as a function of solvent pitch. Furthermore, the effect of longer excited-state lifetimes, to increase the quantum yields for dimerization, will be offset partially by the slower rates of diffusion in the ordered media. This and $\Phi_s$ being *lower* in the smectic phase than in the isotropic phase lead us to conclude that the photodimerization rate enhancements observed here are not controlled by solvent-induced changes in acenaphthylene's excited lifetimes.

**Distributions of Acenaphthylene Dimers.** The distribution of the syn and anti cyclobutane dimers of acenaphthylene from photolyses of 0.02 and 0.08 M acenaphthylene at 35 °C in toluene, *n*-butyl stearate, and the cholestanyl ester mixture are summarized in Table III. Only the syn dimer was detected at low percent conversion of 0.08 M acenaphthylene irradiated in toluene solutions. The proportion of the anti isomer in the total product increased with percent conversion. The anti dimer represented a significant portion of the total product in *n*-butyl stearate and the cholestanyl ester mixture, even at low percent conversions of acenaphthylene. In both solvents, the product distribution varied slightly as a function of percent conversion of starting material, and virtually identical results were obtained when the initial acenaphthylene concentrations were 0.02 M.

From these results, we conclude that product distributions are more dependent on solvent viscosities and collisional frequencies than on solvent order. Singlet dimerization of acenaphthylene is known to yield almost exclusively the syn product while the triplet reaction results in a mixture of the syn and anti dimers.[5,6,9a] In toluene, therefore, the singlet reaction predominates at low percent conversions of acenaphthylene: dimerization occurs before singlet acenaphthylene can intersystem cross to its triplet state. As the reaction proceeds, the concentration of acenaphthylene monomers decreases and the probability that an excited singlet acenaphthylene will encounter a ground-state acenaphthylene prior to intersystem crossing or internal conversion is diminished.[45]

The slight variations in the product ratios with percent conversion in the ordered and viscous media suggest that, in these solvents, the dimerization proceeds almost exclusively from the triplet state of acenaphthylene. This is reasonable since collisions between excited singlet acenaphthylene and ground-state acenaphthylene are less probable in the highly viscous cholesteric and *n*-butyl stearate solvents at 35 °C. The similarity between the dimer distributions obtained in the cholestanyl ester mixture and in *n*-butyl stearate solutions indicates that the multiplicity of the acenaphthylene excited state yielding products controls the stereochemical course of the reaction and, moreover, that solvent order *does not influence significantly the stereochemistries of the eventual products.* This observation supports our conclusions (vide ante) that solute aggregate formation is unimportant and that the number of solute–solute collisions per unit time is dependent primarily on solvent viscosity in the highly ordered media. Only the fraction of collisions whose orientations are appropriate for yielding products is strongly influenced by solvent order.

Table III. Stereoisomeric Product Distributions for the Dimerization of Acenaphthylene at 35 °C

| solvent | acenaphthylene, M | % conversion | syn/i[a] |
|---|---|---|---|
| toluene | 0.02 | 30 | 80/20 |
| | 0.02 | 70 | 60/40 |
| | 0.08 | 35 | 95/5 |
| | 0.08 | 65 | 60/40 |
| *n*-butyl stearate | 0.02 | 30 | 60/40 |
| | 0.02 | 50 | 50/50 |
| | 0.02 | 70 | 50/50 |
| | 0.08 | 25 | 60/40 |
| | 0.08 | 55 | 60/40 |
| | 0.02 | 20 | 50/5 |
| cholestanyl ester mixture | 0.02 | 20 | 50/50 |
| | 0.02 | 40 | 50/50 |
| | 0.02 | 60 | 40/60 |
| | 0.08 | 25 | 60/40 |
| | 0.08 | 50 | 50/50 |
| | 0.08 | 75 | 40/60 |

[a] The content of each dimer in the total product is estimated to be accurate to ±5 parts.

The lack of solvent-induced stereospecificity in photodimerization is surprising since liquid crystalline solvents do influence the stereochemical courses of other reactions,[3] and theoretical and experimental[46] studies of nuclear magnetic resonance spectra in liquid crystals have shown that solute molecules are highly oriented in these solvents. In a nematic liquid crystalline solution, benzene, although oriented with respect to the solvent, is free to rotate about its short molecular axis.[47] We expect that, in cholesteric phases, excited acenaphthylene–ground-state acenaphthylene collision complexes have similar rotational freedom which allows the selection of the stereoisomer of product to be determined by electronic factors. The efficiency of collisions leading to products is strongly influenced by solvent, but, at least in this photoreaction, the stereochemistry of the products is not.

**Solvent Phase Effects on Collisional Efficiencies.** Although acenaphthylene is expected to be oriented similarly by smectic, nematic, and cholesteric phases (i.e., with its long axis parallel to the long axis of the solvent molecules), the photochemical consequences of this alignment are very different.

A solute molecule in a smectic phase should diffuse equally well in any direction parallel to the solvent layers and at a different rate perpendicular to the layers. Diffusion of a solute in a nematic phase should occur at the same rate in any direction perpendicular to the long axis of the solvent but at a different rate parallel to the long axis. In fact, two diffusion constants, differing by only a factor of 2, have been measured for a solute in the nematic liquid crystal of the phenyl 4-benzoyloxybenzoate series (PBOB).[48] It follows, therefore, that a planar solute in a nematic or smectic phase is equally free to diffuse in any direction perpendicular to the long axis of the solvent molecules. As a result the fraction of acenaphthylene–acenaphthylene collisions in which the solutes are nonparallel is expected to be large in these solvents.

By analogy to the results obtained in nematic phases,[48] diffusion of an acenaphthylene molecule within a cholesteric layer should be more facile than diffusion between layers. The dramatic rate enhancements for dimerization in cholesteric

phases indicate that the layered structure of the solvent restricts diffusion along some directions more than others.[49] The cholesteric solvent's macrostructure forces acenaphthylene molecules, while diffusing, to remain parallel to the solvent layers. As a result, the fraction of acenaphthylene-acenaphthylene collisions which occurs either in the same plane or in parallel planes is much larger than in the other liquid crystalline or isotropic phases examined. Almost certainly, these orientations lead preferentially to products.

## Conclusions

The consequences of various types of anisotropic solvent order on the efficiency and specificity of acenaphthylene photodimerization have been investigated. It is found that the quantum yield for reaction is extremely sensitive to changes in the order (and pitch) of cholesteric liquid crystalline solvents. The very large rate enhancements in this mesophase are ascribed to increases in the *fraction* of acenaphthylene-acenaphthylene collisions which have coplanar or parallel-plane orientations, and not to increases in the total number of collisions per unit time. Nematic and smectic solvents appear to enhance to a much lesser extent the fraction of preferred preproduct collisions. The distribution of dimer stereoisomers is *not* controlled by solvent order, but is a function of solvent viscosity.

While the potential synthetic utility of cholesteric phases as reaction media has not been emphasized, we find no reason why similar rate enhancements should not be found for other thermal and photochemical reactions. In fact, it seems reasonable to assume that some reactions, whose transition states (or preproduct collision complexes) are less planar than their reactants will be retarded by cholesteric phases. We will report examples of each of these in future publications.

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(39) Tetralin was chosen owing to its thermal and photochemical stability under the reaction conditions and its lack of interference during spectroscopic determinations of acenaphthylene dimerization efficiencies: tetralin exhibits no appreciable absorption above 270 nm.
(40) The viscosities of tetralin-doped cholesteric liquid crystal mixtures should be no greater (and, probably, are less) than those of either the pure solvent or solvent in the presence of acenaphthylene. Thus, the number of ground-state acenaphthylene collisions experienced by an excited-state acenaphthylene during its lifetime will not be decreased by the addition of tetralin to the solutions.
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(50) A referee has suggested that the cylindrical capillary tubes in which the secondary actinometric measurements for quantum yield determinations were performed may introduce a systematic error: Vesley[51] has shown that when the indices of refraction between a curved glass surface and a liquid differ, a significant amount of incident irradiation can be reflected at the glass–liquid interface. If more light were being reflected at the Pyrex–toluene interface than at the Pyrex–liquid crystal interfaces, erroneously high (but reproducible) quantum yields for dimerization in the liquid crystalline solvents would be measured. The indices of refraction of Pyrex, toluene, a 31/69 (w/w) mixture of cholesteryl nonanoate–cholesteryl chloride, and *n*-butyl stearate at room temperature are 1.52,[51] 1.50, 1.49,[52] and 1.44, respectively. While the indices of refraction for the other cholesteric mixtures employed here have not been measured, it is reasonable to assume that they are near 1.5 also.[41,42] Thus, except for the birefringence of the liquid crystalline samples,[38] all of the solvents should reflect light about equally. We do not dismiss the possibility that an important factor has been overlooked. However, neither several knowledgeable colleagues nor we have been able to suggest what this might be.
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