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THERMOTROPIC LIQUID CRYSTALS AS REACTION MEDIA FOR MECHANISTIC INVESTIGATIONS[1]

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CONTENTS

1. INTRODUCTION

This review presents a critical analysis of the use of liquid crystals as ordered solvents in which to conduct solute reactions. It is developed phenomenologically, according to the author's biases and includes in the Introduction his personal hypotheses on how reacting solutes and ordered solvents interact. Studies which demonstrate the potential of liquid crystals to follow solute shape changes along a reaction coordinate, to alter rates and product ratios, and to investigate the micromorphology of ordered solvents are covered. Also included are examples for which no manifestation of solvent order on solute reactivity has been detected: they are frequently as illustrative as the examples that do. Only applications in thermotropic liquid crystals (i.e. those which owe their mesomorphism to thermally induced processes) are included; lyotropic liquid crystals (i.e. those in which the mesomorphic state is solvent induced) are omitted. A cursory overview of reactions in liquid crystals has appeared as part of a general treatment of reactions in ordered media.[2] The properties of liquid crystals have been reviewed extensively.[3] As an aid to the reader, the structures of many of the liquid crystals discussed here and their acronyms are collected in Table 1.

The discovery of liquid crystals is generally credited to F. Reinitzer in 1888.[4] Since that time, an enormous number of organic crystals have been observed to become liquid-crystalline (or mesomorphic[5]) upon being melted or upon cooling of the isotropic liquid. The first example of a solute reaction in a liquid crystal was reported in 1916 by Theodore Svedberg who noted that the rate at which picric acid reacts with the solvent, *p*-azoxyphenetole, changes abruptly at the mesophase–isotropic phase transition temperature of the latter.[6]

1.1. *Classification of liquid crystals*[3]

A simple view of liquid crystals is that they are very disturbed solids or ordered liquids. Macroscopic characterization requires that the phases be both fluid and anisotropic. They differ

Table 1. Structures and acronyms of liquid crystals discussed in this Report

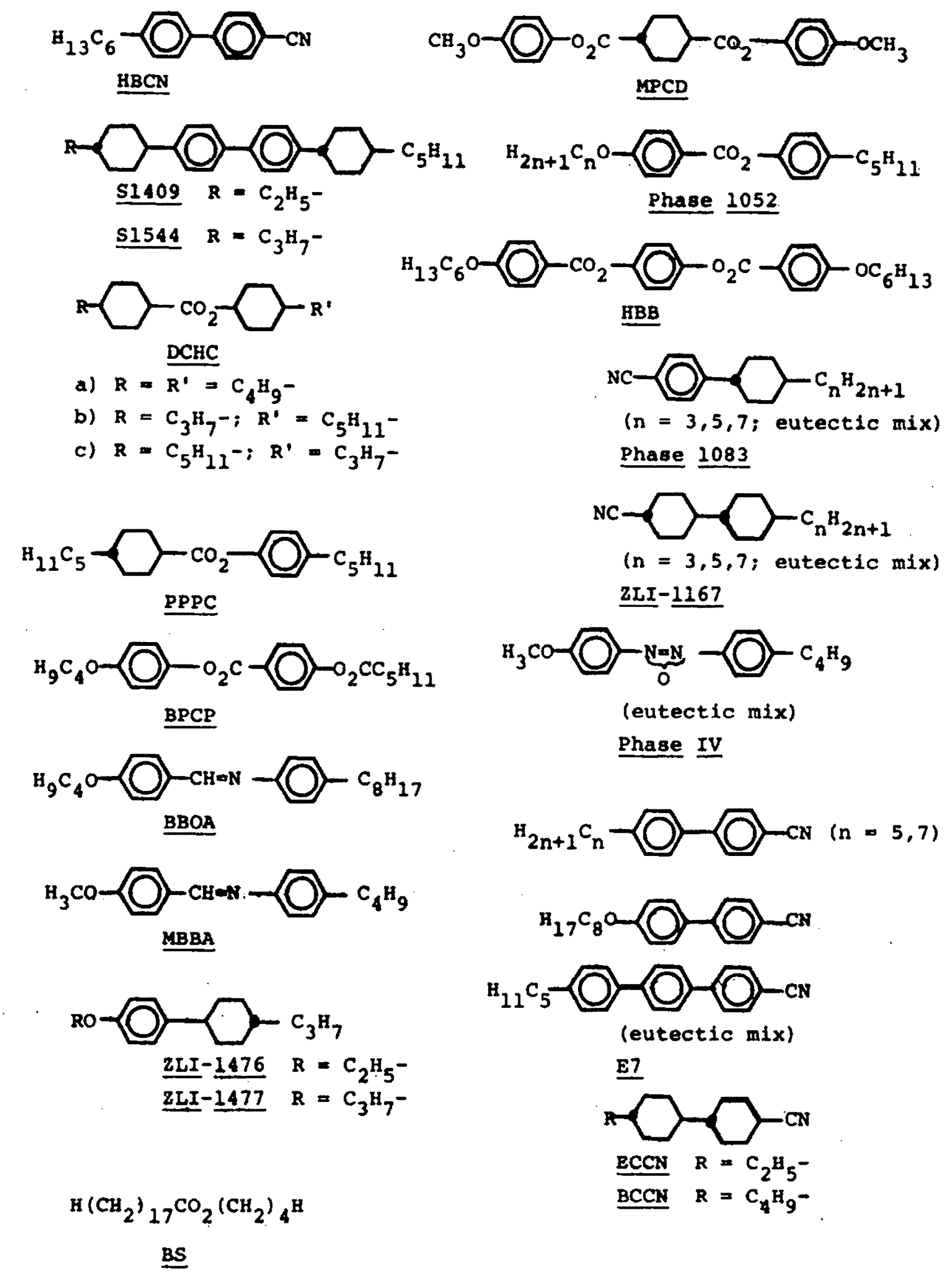
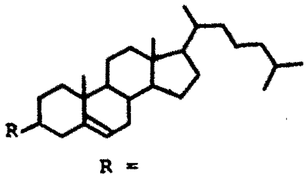
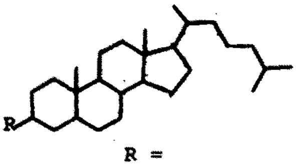


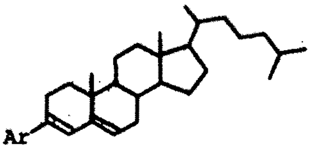
Table 1—*continued*



	R =
CA	$CH_3CO_2^-$
CB	$PhCO_2^-$
CBCl	$p\text{-}Cl(C_6H_4)CO_2^-$
CCl	Cl^-
CL	$C_{11}H_{23}CO_2^-$
CLI	$H_{11}C_5CH{=}CHCH_2CH{=}CHC_7H_{14}CO_2^-$
CMY	$C_{13}H_{27}CO_2^-$
CN	$C_8H_{17}CO_2^-$
CNB	$O_2N(C_6H_4)CO_2^-$
CNN	$C_6H_5CH{=}CHCO_2^-$
CO	$H_{17}C_8CH{=}CHC_7H_{14}CO_2^-$
COC	$H_{17}C_8CH{=}CHC_8H_{16}OCO_2^-$
CP	$H_{31}C_{15}CO_2^-$
CPP	$PhC_2H_4CO_2^-$
CT	$p\text{-}H_3C(C_6H_4)CO_2^-$



	R =
CHA	$CH_3CO_2^-$
CHN	$H_{17}C_8CO_2^-$
CHNN	$PhCH{=}CHCO_2^-$
CHT	$p\text{-}H_3C(C_6H_4)CO_2^-$



ACD

a) Ar = $o\text{-}H_3C(C_6H_4)\text{-}$

b) Ar = $m\text{-}H_3C(C_6H_4)\text{-}$

c) Ar = $p\text{-}CH_3O(C_6H_4)\text{-}$

d) Ar = Ph

e) Ar = $p\text{-}H_3C(C_6H_4)\text{-}$

f) Ar = $4\text{-}(C_6H_5)\text{-}(C_6H_4)\text{-}$

from plastic crystals which have little or no orientational order and three degrees of translational order. Liquid-crystalline phases may be thermodynamically stable (enantiotropic) or unstable (monotropic). The latter can be formed only by cooling from a higher temperature phase. Since the period during which a monotropic phase persists cannot be predicted accurately, it is advantageous to perform reactions in thermotropic liquid crystals whenever possible.

Four classes of liquid crystals—nematic, cholesteric, smectic and discotic—and several distinct sub-classes of the smectic and discotic types are known. Generally, nematic, cholesteric, and smectic molecules are rod-like, and discotic molecules are plate-like. A representation of the molecular order of each class of liquid crystals is shown in Fig. 1. In this figure, the director (or common axis about which their order may be defined) is the longest molecular axis.

1.1.1. *Nematic and cholesteric phases.* Nematic phases exhibit one degree of orientational order. The directors of the constituent molecules are parallel to one another on average.

Cholesteric phases are sometimes referred to as 'twisted' nematics because cholesteric molecules exhibit nematic-like order locally. As the name implies, cholesteric molecules are frequently steroids and always include an optically active center.[7] Due to their chirality, the molecules are packed in a slightly twisted array along a direction perpendicular to their directors. A model of the cholesteric phase includes 'layers' of nematic-oriented molecules, each layer being twisted slightly with respect to the ones above and below it. The angle of twist between layers is typically much less than one degree.

1.1.2. *Smectic phases.* Smectic phases exhibit one degree of translational and one degree of orientational order. Molecules are in layers which stack atop each other. The packing arrangement of molecules within a layer and the angle between the long molecular axes and the layer plane are

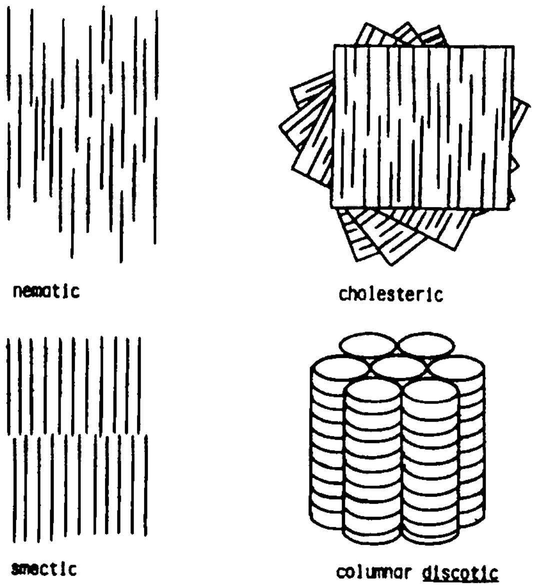


Fig. 1. Representation of the molecular shapes and orientations of the major liquid-crystalline phase types.

the characteristics which distinguish the various smectic phases. For instance, in a smectic B phase, the constituent molecules are normal to the layer plane and are packed hexagonally within it. The various packing arrangements which have been identified are shown in Fig. 2.[8]

1.1.3. *Discotic phases.*[9] The most recently discovered class of liquid crystals is discotic mesophases.[9b] A sub-class of discotic packing, a columnar arrangement, is shown in Fig. 1. Molecules within a column can be ordered or disordered; the columns, themselves, may be either as shown, twisted, or tilted.

1.2. *A model for solute reactivity in mesophases*

Conformationally-labile isotropic solvent molecules can adapt themselves to remain in close contact with a solute of any size or shape (Fig. 3). By remaining at van der Waals distances and

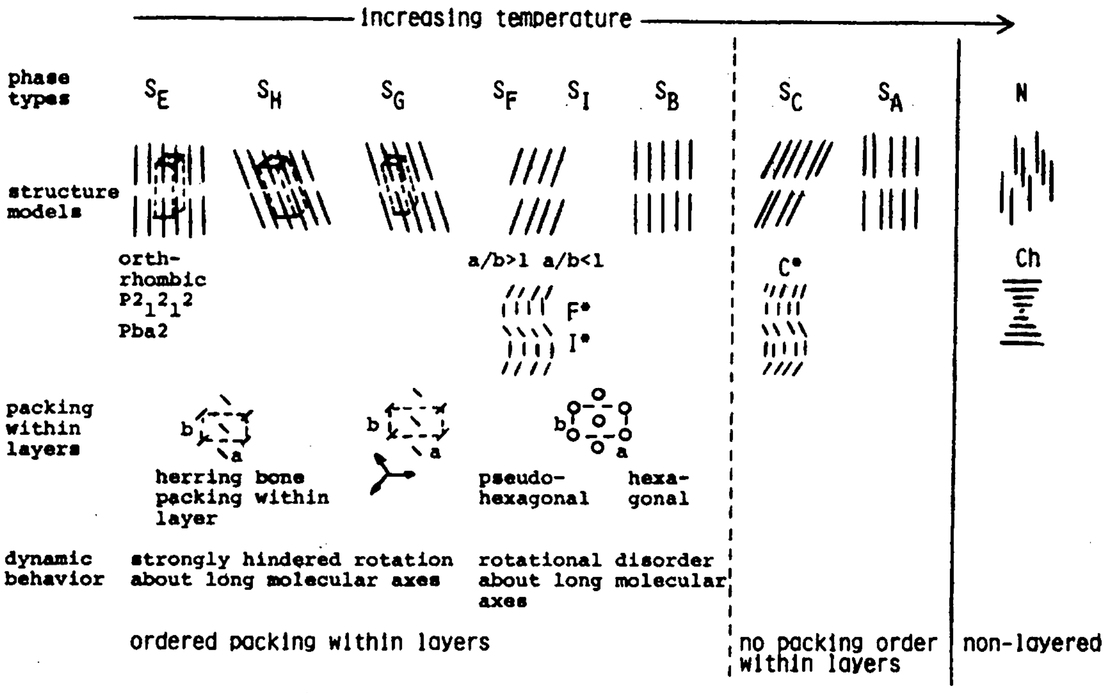


Fig. 2. Phase types (especially smectic) according to relative order.[8] [Modified from Fig. 22 of ref. 8. Printed with permission of Academic Press, Inc.]

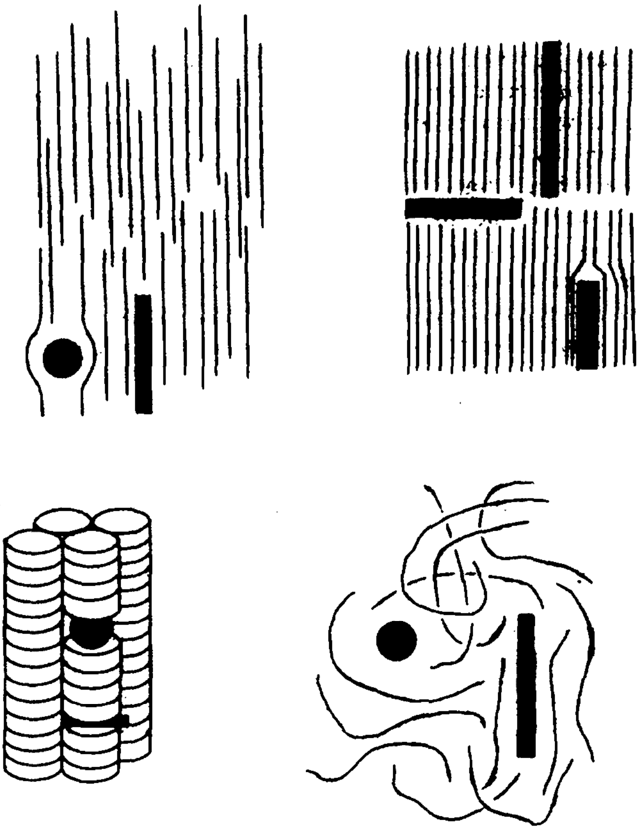


Fig. 3. Cartoon representation of possible solubilization sites of rod-like and ball-like solutes (filled shapes) in liquid-crystalline and isotropic phases.

maximizing dispersion interactions, the solvent and solute minimize the energy of mixing. If no specific solute–solvent interactions (such as hydrogen-bonding) occur, introduction of a solute will neither increase nor decrease appreciably the random arrangement of solvent molecules.

Packing constraints imposed on individual solvent molecules by mesophase ordering do not allow a solute to be solvated as efficiently as in the isotropic phase. Even when the mesophase constituents are flexible, they cannot interconvert differently shaped conformers without disturbing local order. Thus, introduction of a solute into a mesophase matrix results either in less efficient solvation or disordering of the phase. In either case, the energy of the system will increase.

Studies conducted to date[10] tend to confirm these hypotheses. The degree to which a non-polar solute differs in size and shape from the solvent determines the extent of energy increase. There is also evidence that components of a mesophase solvent mixture can segregate themselves partially in quasi-domains.[11] It follows that solutes may also be surrounded preferentially by mesophase solvent components which match their size best.[12,13]

When strong polar interactions are present, they can dominate size and shape considerations. Thus, some polar liquid-crystalline molecules align themselves according to dipole–dipole interactions.[14] Also, solutes that associate strongly with solvent molecules can raise mesophase transition temperatures.[15] Apparently the stabilizing energy from association is greater than the increase in energy from disturbance of solvent order in these systems. For these reasons, models which treat the influence of a solute on a mesophase must consider both structural *and* electronic factors (when the latter is energetically important). Unfortunately, electronic interactions between a solute and solvent cannot be generalized in liquid-crystalline solutions: the specificity and type of each association can have different ramifications on cybotactic order.

Frequently, the influence of low concentrations of a solute on the bulk properties of a phase (e.g. temperatures and heats of transition, spectroscopic properties, optical micrograph patterns, etc.) is not detectable. In spite of this, the order and mobility of solvent molecules about a solute may be very different from those in the neat mesophase. In the worst case a highly disturbed cybotactic region which is undetected by macroscopic measurements may mislead one into believing that the order of the mesophase has no influence on solute dynamics.

To understand how intermolecular (solute–solvent) steric factors can influence unimolecular reactions in mesophases, we consider several hypothetical solute shape changes. Figure 4a contains a cartoon representation of several differently-shaped solutes and their reversibly-formed products. Each reaction involves a large, but different, shape change along a reaction coordinate. For the purposes of argument, we assume that the shape changes between a reactant and its rate-limiting transition state are no greater than those between the reactant and product.[16] Thus, for each reaction, solvent order should favor the reactant or transition state which resembles more the mesophase molecules in size and shape. This is a 'structure–reactivity' relationship which is not easily quantified. It is completely analogous to the 'reaction cavity' concept developed by Cohen to explain selectivity in solid state reactions.[17]

Accordingly, cigar-shaped A will react more slowly than bulky B or globular C in a nematic or cholesteric matrix. If solutes are incorporated *within* the layers of a smectic phase, the A which reacts most slowly should be closest in length to a solvent molecule: shorter or longer A will induce undesirable bending in either the solute, the solvent, or both. The length of A should have little influence on its reactivity if the solutes occupy sites *between* smectic layers. In such a case, it is difficult to predict whether smectic order would encourage A over a cyclic molecule D or a plate-like species E.

The shape and size considerations of solute unimolecular reactions in mesophases apply as well to bimolecular (or multimolecular) processes, except that collisional orientations and diffusion anisotropy must be considered also. Figure 4b shows three types of solutes undergoing various collisions, representative of the spectrum of possibilities in an isotropic solvent. If only some of

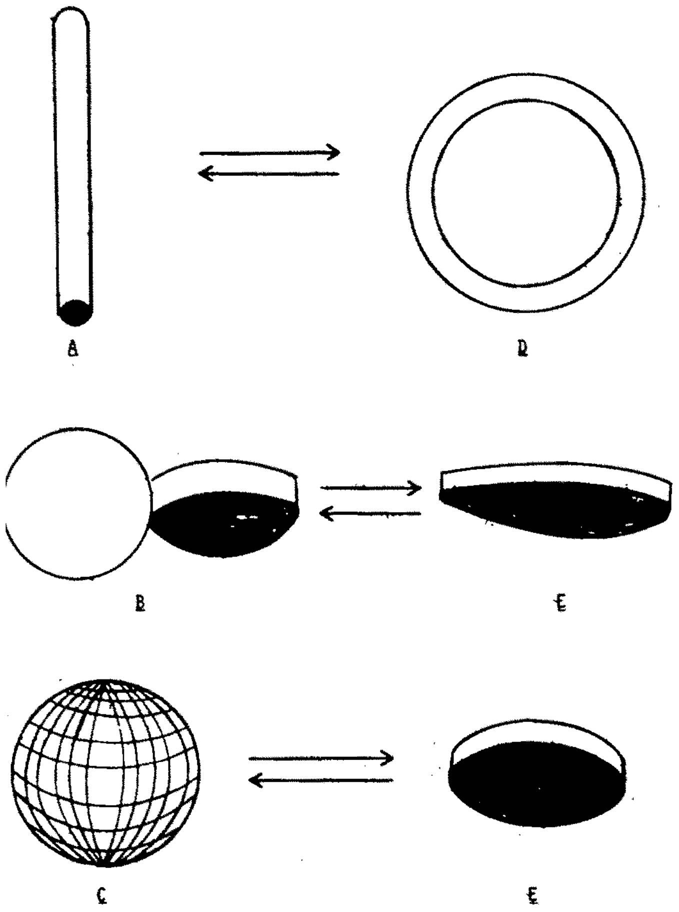


Fig. 4a. Cartoon representation of some possible shape changes in unimolecular reactions.

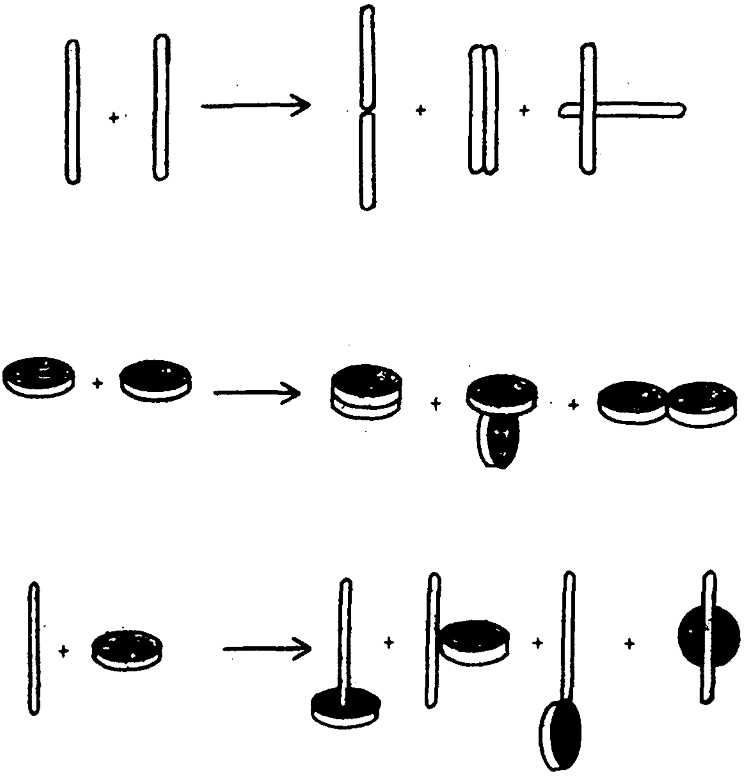


Fig. 4b. Cartoon representation of some possible collision geometries in bimolecular reactions.

these lead to products, an anisotropic solvent which favors them over non-productive collisional orientations will enhance the efficiency of reaction. For instance, a perpendicular collision between two rod-like molecules (Fig. 4b) should be more difficult than an end-on or edge-on collision in a nematic, cholesteric, or smectic phase. Similarly, edge-on or face-to-face collisions between plate-like solutes in mesophases *may* be preferred to edge-face collisions which produce a very globular complex. The same argumentation for collisions between a rod-like and a plate-like molecule leads to the conclusion that edge-to-edge or face-to-face orientations will be enhanced.

1.2.1. *Comparisons between mesophase and 'model' phase data.* At best, the influence of solvent order on a reaction can be measured relatively: data for one reaction in one solvent cannot be dissected to allow the effect of solvent order to be assessed. In a meaningful experiment, the properties of a reaction conducted in a mesophase and a 'model' solvent must be compared.

The choice of the model solvent depends upon which aspect of the reaction is to be compared and what information is sought. No single solvent can be disordered and identical in all other aspects to a liquid crystal. A commonly employed model solvent is the isotropic phase of the liquid crystal. It is disordered and less viscous than the mesophase, but possesses microscopic electronic properties which are nearly identical to it. If the reaction must be conducted in the mesophase and model solvent at the same temperature, the isotropic phase of the liquid crystal cannot be employed. However, the reaction can be conducted at nearly the same temperature in the two media (i.e. a few degrees above and below the mesophase–isotropic phase transition temperature). When this approach is undesirable, the model solvent should consist of molecules whose structure and polarity approximate those of the liquid crystal but which form a viscous, isotropic phase.

Several options are available if the influence of two different types of solvent order are to be compared. For instance, reaction can be compared in one solvent which possesses more than one mesophase. An example of such a solvent is *trans,trans'*-4'-*n*-butyl[1,1'-bicyclohexyl]-4-carbonitrile (BCCN). It exhibits a smectic B phase between 29 and 54°C and a nematic phase to 79°C.[18] When the morphology of the solid phase is known, it can be used as a less-mobile model solvent for the mesophase. In the best cases, results from one reaction can be compared in the crystalline, liquid-crystalline, and isotropic phases of one solvent.

Two different solvents which possess the same mesophase type (especially at a common temperature) are useful to compare the influence of solvent molecular structure on solute dynamics. However, as with reactions conducted in 'normal' isotropic solvents, detailed interactions between a solute and solvent molecules can alter drastically the course of a reaction.

All of these approaches have been attempted, but they have met with varying degrees of success. Specific examples will be discussed in the following sections.

1.3. *Macroscopic properties of liquid crystals—complications to the analyses of solute reactions*

Many of the microscopic properties of liquid crystals which make them attractive as solvents to follow solute shape changes or collision trajectories are responsible for macroscopic properties that complicate the application of normal analytical methods.

1.3.1. *Viscosities*[19] *and diffusion.* Although measurements are complicated by the non-Newtonian nature of mesophases,[20] bulk viscosities (η) in smectic and cholesteric phases are usually much larger than in nematic phases.[21] In spite of the enormous viscosities measured for mesomorphic cholesteryl esters at low shear rates (10^3–10^5 poise),[20] their flow activation energies (E_{FA}) are only *ca* 3–4 kcal/mol higher than in the isotropic Newtonian phases (Table 2).[22]

In isotropic solvents, the Debye expression [which relates the rate constant for self-diffusion, k_{diff}, to viscosity and temperature as in eqn (1)][23] is used routinely to determine the maximum rate at which a collisionally-induced bimolecular reaction can occur. In mesophases, the complex morphological changes induced by external forces (required to measure bulk viscosities),[19] the large influences of solutes on viscosity,[20,22] and the intrinsic solvent anisotropy make calculation of k_{diff} by the Debye expression almost meaningless (see Fig. 5): extrapolation of macroscopic to microscopic properties in mesophases is very tenuous.

$$k_{\mathrm{diff}} = \frac{8RT}{3000\eta}\ \text{l/mol-sec} \tag{1}$$

More complex experiments have been employed to calculate k_{diff}, diffusion coefficients, and activation energies for self-diffusion in liquid crystals.[24] Unfortunately, the values obtained depend upon the experimental method employed.[25] All of the experiments support the initial results of Miesowicz that diffusion rates are orientation dependent in mesophases.[26] Figure 6 presents the orientational dependence of chloroform diffusion in the mesophases of *p*-*n*-butoxybenzylidene-*n*-octylaniline (BBOA).[27] $D_\parallel$ and $D_\perp$ are the diffusion coefficients parallel and perpendicular to the solvent director. Even in the most ordered mesophases, $D_\parallel$ and $D_\perp$ appear to differ by less than an order of magnitude. The values of D in Fig. 6 indicate that the mesophases of this solvent are polymer-like. In other mesophases, D can be much larger, approaching values of non-viscous isotropic solvents. Essentially (and unfortunately), the rates and anisotropies of the solute motions in mesophases cannot be generalized.

While rates of anisotropic diffusion are important in calibrating the influence of liquid-crystalline solvent order on intermolecular reactions, intramolecular processes are more dependent upon the rates of solvent relaxation (or, expressed differently, upon solvent friction[28]):[29,30] the measured effect of solvent order on unimolecular processes depends upon the response of the solvent matrix to solvent shape changes or reorientations.[31] This is an *additional* parameter (to solute ordering) which determines the solvent's influence on solute reactivity. A reacting solute will be restrained to its initial space in a very slowly responding mesophase; in the extreme, this situation can be modeled by clathrate complexes or doped crystals. Solute shape changes will be accommodated easily by a rapidly responding mesophase.

Table 2. Flow activation energies for cholesteric esters[22]

	E_{FA}(kcal/mol)	
Ester	Mesophase*	Isotropic
Acetate (CA)	15.5(c)	11.9
Myristate (CMY)	11–16(s)	8.2
Palmitate (CP)	10(c)	8.1

* c = cholesteric; s = smectic.

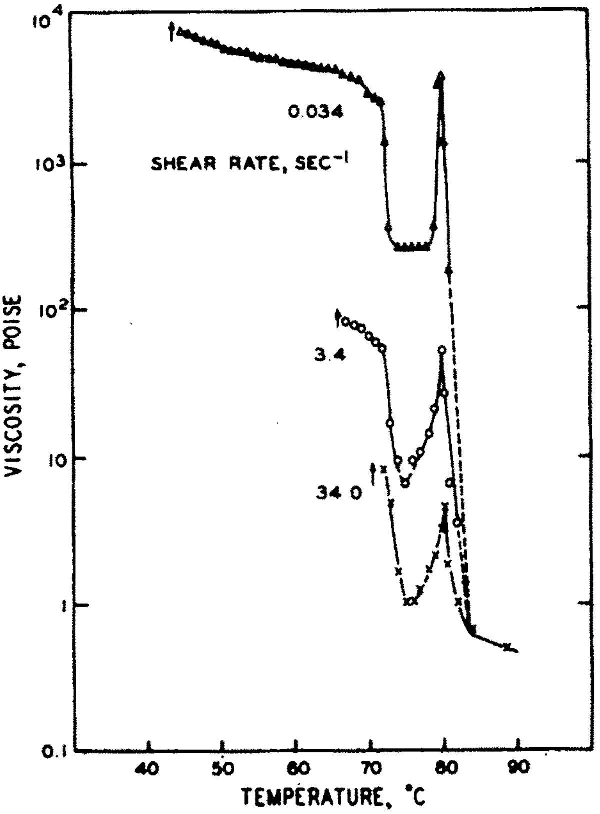


Fig. 5. Viscosity changes of 97/3 CMY/CA versus temperatures at several shear rates.[20b] The largest discontinuity occurs near the cholesteric–isotropic phase transition (83°C). [Reprinted with permission of Gordon and Breach Science Publishers, S.A.]

Several types of relaxation phenomena have been identified in liquid crystals.[31] Some are nearly as rapid as in isotropic phases and others are much slower. Thus, the nature of the solvent, the solute, and the shape changes experienced by the solute along its reaction coordinate determine whether the cybotactic region can adapt slowly or rapidly.

1.3.2. *Optical characteristics.* Like isotropic solvents, liquid crystals must be comprised of

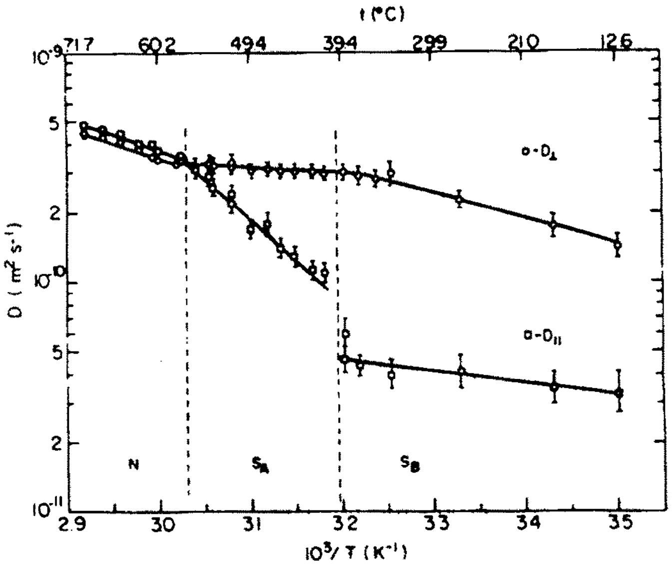


Fig. 6. Arrhenius plots of parallel and perpendicular diffusion coefficients (D) for chloroform in the nematic (N), smectic A (S_A), and smectic B (S_B) phases of BBOA.[27] [Reprinted with permission of Gordon and Breach Science Publishers, S.A.]

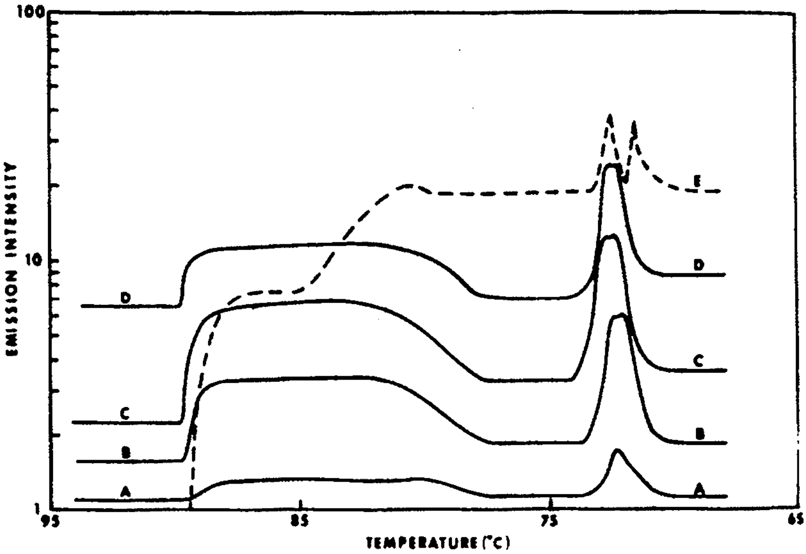


Fig. 7. Fluorescence emission intensities (475 nm) as a function of temperature for 0.2% pyrene in CN.[33] Excitation wavelengths: A, 225 nm; B, 250 nm; C, 275 nm; D, 295 nm. Curve E represents transparency vs temperature as obtained using a Cary 14 spectrophotometer. (The ordinate of curve E is optical density multiplied by 10^2). [Reprinted with permission of Gordon and Breach Science Publishers, S.A.]

molecules which, individually, do not absorb or emit in the same wavelength regions as their solutes. This requires that the liquid-crystalline molecules contain no near UV absorbing chromophores if light absorption or emission is the analytical method of choice. Unfortunately, other criteria must be met if anisotropic aggregates of these molecules are to remain transparent.

Most liquid crystals exhibit birefringence whose intensity is dependent upon the angle of incidence of the light and the director of the molecules.[32] Also, unoriented bulk samples scatter light in a fashion which is dependent upon the size of domains of molecular aggregates.[32] Thus, the amount of light absorbed or transmitted by an unoriented liquid crystalline sample cannot be reproduced quantitatively; large fluctuations even within one sample are usually observed.

The thermal motions of domains (or molecules within them) further complicate the optical properties of liquid crystals. The changes in emission intensity from pyrene singlets in cholesteryl nonanoate (CN) vs temperature are shown in Fig. 7.[33] The variations in intensity do not correlate with the optical density of the sample or with changes in the quantum efficiency for emission of pyrene. They can be attributed to variations in the light scattering of the sample. As a result, the optical properties of unoriented liquid crystals can lead to erroneous interpretations of data.[34]

An additional factor, selective reflection by one component of circularly polarized light, arises in cholesteric phases and is responsible for a pitch band which can be detected either as reduced transmittance (pseudo absorption) or enhanced reflection. The pitch band maximum (λ_p) can be expressed in terms of the index of refraction of the medium (n) and the distance (p) between 'layers' in which the directors of constituent molecules are parallel by eqn (2).[35] Frequently, the pitch can be changed by temperature or pressure so that it does not interfere with sample irradiations.

$$\lambda_p = np \qquad (2)$$

Quantitative measurements of light absorption or emission must take into account each of the above factors: the light path through a liquid-crystalline sample need not be equal to its thickness. One method to obviate these difficulties is to orient the bulk phase so that each of the molecules is aligned at a particular angle with respect to an external reference. Essentially, this makes the sample one large domain and allows light scattering in many cases to be neglected. Regardless, light absorption and transmittance are reproducible in aligned mesophases. A great deal of information concerning the electronic characteristics and degree of order of solutes can be obtained in aligned phases.[34b,36] Similarly, the pitch band of cholesteric phases[37] and twisted nematic phases can provide information concerning the structure, order, and concentration of solutes.[38] We will discuss these properties later as analytical tools to follow solute reactions in liquid crystals. However, the various methods to align liquid crystals[39] and the problems encountered in aligning smectic phases[40] will not be discussed. In part, dynamic aspects of phase alignment can be neglected because there are no *documented* examples in which phase alignment has been shown to affect the microscopic environment of a solute.[41] This is reasonable since the environment experienced by a reacting solute is much smaller than a single domain.

1.3.3. *Physical separations of solutes and solvents.* Wet analyses of reaction mixtures in mesophases avoid the complications encountered in spectroscopic techniques. However, physical separations are frequently made difficult by the very high boiling points and viscosities of the solvents: the separation of solutes from liquid crystals—quantitatively and without altering their absolute (or relative) concentrations—is not trivial.

Distillation of volatile products from reaction mixtures or crystallizations from them can lead to incomplete separation or, if conducted under forcing conditions, to inclusion of solvent related species. This specific problem led to some of the uncertainty concerning the degree of optical induction in solute reactions conducted in cholesteric phases.[42,43]

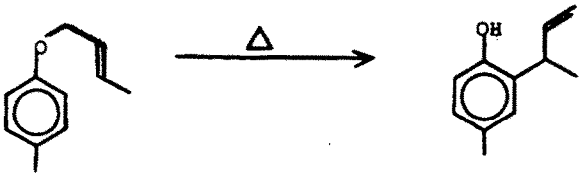
Chromatographic separations avoid many of the problems mentioned for distillation. Gas and high-performance liquid chromatographies, especially, have been shown to provide efficient, sensitive, and precise analyses of product mixtures. However, even these methods must be used with caution: experiences in the author's own laboratory have shown that the presence of liquid crystals on a column, even in small amounts, can alter its separation characteristics.

Thus, development of appropriate analytical procedures for physical separations of solute–mesophase mixtures is usually the *first* hurdle to be overcome. The difficulty of isolating reaction products and the high cost of liquid crystals precludes the use of thermotropic mesophases to synthesize large quantities of materials in all but extraordinary cases. Reactions in liquid crystals will probably remain of primary importance to answer mechanistic questions which cannot be addressed by more conventional chemical tools unless the price of the solvents is reduced significantly.

2. ASYMMETRIC INDUCTIONS AND RACEMIZATIONS

With very limited success, chiral products have been isolated from thermal reactions of prochiral substrates conducted in optically pure isotropic solvents.[44] Attempts to attain some enantiomeric excess in products of photochemical reactions conducted in chiral isotropic solvents have been equally discouraging.[45] Since the degree of asymmetric inductions should increase with greater solute–chiral solvent interactions,[46] a logical extension of the isotropic phase experiments would be to attempt them in cholesteric phases. From results obtained thus far, one must conclude that the local asymmetry experienced by a reactive solute in a cholesteric phase is insufficient to induce synthetically useful enantiomeric excesses in the products.

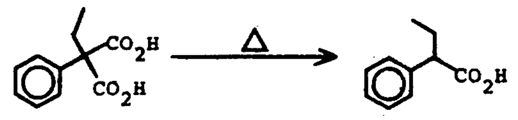
Initial interest in this topic was spurred by Saeva *et al.*[47] who demonstrated unequivocally that the Claisen rearrangement of methylallyl-*p*-tolyl ether **1** produces chiral 2-(α-methylallyl)-4-methylphenol **2** of unknown optical purity in the cholesteric phase of cholesteryl *p*-nitrobenzoate (CNB) [eqn (3)]. The reaction, when conducted in the isotropic phase of the same solvent, led to no detectable optical activity in **2**.



1 2

(3

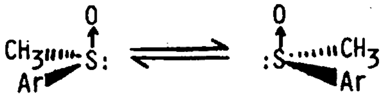
Shortly thereafter, Verbit *et al.*[48] published their work on the thermal decarboxylation of the prochiral ethylphenylmalonic acid **3** [eqn (4)] in the cholesteric phase of cholesteryl benzoate and in an isotropic chiral solvent, bornyl acetate. The reported 18% enantiomeric excess (ee) in **4** from the mesophase solvent (vs essentially racemic product from the isotropic solvent experiment)



3 4 (4

attracted a great deal of attention. Tanaka *et al.*[49] and Kagan *et al.*[42] carefully repeated the decarboxylation experiments of Verbit but were unable to obtain more than 0.2–0.3% enantiomeric excess from decarboxylation of 3 and two of its analogs in cholesteryl benzoate and three other cholesteric solvents. Thus, it must be concluded that the initial observation by Verbit probably resulted from the presence of an impurity of high optical rotation in his product.

Pirkle and Rinaldi[50] examined the enantiomeric interconversion of three aryl sulfoxides 5 and an oxaziridine 6, and the diastereomeric interconversion of cholesteryl methanesulfinate 7 in several cholesteric phases. The reactions cannot be classified strictly as equilibrations since they were accompanied by varying amounts of decomposition (which may have been enantiomer selective). No real correlation between the handedness of the cholesteric phase twist and either the configuration or structure of the favored solute isomer could be discerned. However, enantiomeric excesses as high as 9.2 and 20% for 5c and 6, respectively, were reported. Again, these results must be questioned since Kagan *et al.*[42] were unable to reproduce the optical induction in 5c (even at lower temperatures using photoinduced interconversion of enantiomers) and found a very low specific rotation for the oxaziridine 9, obtained upon photocyclization of the nitrone 8. However, since the absolute rotation of 9 was not reported and the photocyclization may not reflect the thermodynamic preference for enantiomer formation, direct comparison between results with 6 and 9 should not be made.



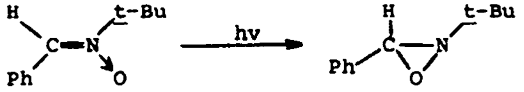
a) Ar = phenyl
b) Ar = 4-biphenyl
c) Ar = 1-naphthyl

5 (5a

6 (5b

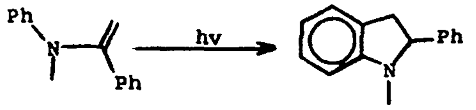
$$CH_3\overset{O}{S}O(\text{cholesteryl})$$

7



8 9 (6

Several other thermal and photochemical, unimolecular and bimolecular reactions of achiral solutes in which a chiral center is formed in the products have been shown to proceed in cholesteric phases, but without measurable induction of optical activity [eqns (7–12)].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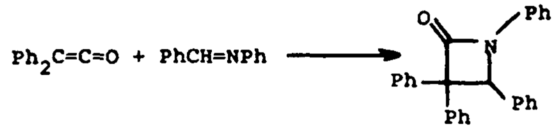
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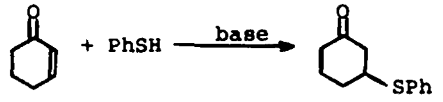
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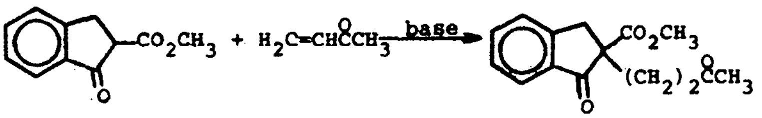
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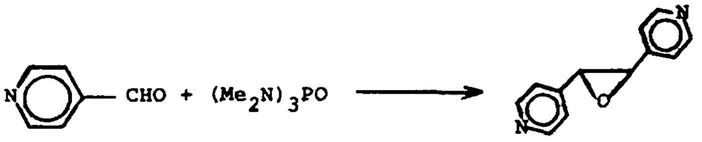
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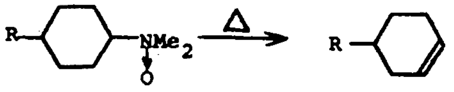
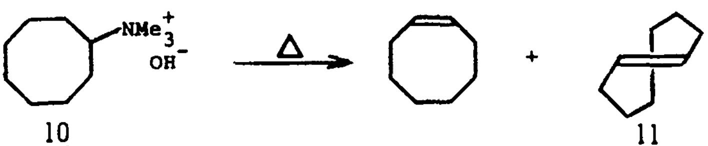

R = Me or t-Bu

(12[51]

Fortunately, some positive results which may point the way toward improved chiral recognition by mesophases do exist. Hofmann elimination of trimethylcyclooctyl ammonium hydroxide **10** to yield *trans*-cyclooctene **11** has been carried out in mesophases of 3-aryl-3,5-cholestadienes (ACD) by Seuron and Solladie.[51] Enantiomeric excesses of (*R*)-**11** varied between 1 and 7.2% depending upon the initial concentration of **10**, the aromatic substituent on ACD, and the temperature. No optically active **11** was obtained from pyrolysis conducted in isotropic ACD-*d* or in twisted nematic phases consisting of *p*-azoxyanisole and a small concentration of a cholesteric molecule. Heating racemic **11** in cholesteric phases led to an excess of one enantiomer whose magnitude depends upon the structure of the solvent molecules. As noted in Table 3, greater selectivity obtained in ACD-type solvents than in the more flexible cholesteric esters. In fact, Cope elimination of *trans*-*N*,*N*-dimethyl-4-alkylcyclohexylamine *N*-oxide, shown in eqn (13), produces minimal or no optical activity in the cyclohexane products when the solvent is the mesophase of CN or CNB.[51] It would be interesting to compare these results with those obtained for Cope elimination in the cholesteric phases of ACD.


10 11

(13

Another mechanistically interesting application of chiral recognition is the atropisomerization of racemic 1,1′-binaphthyl **12** in cholesteric phases.[52] Thermal equilibration of **12** for several half-

Table 3. Equilibration of racemic **11** in various solvents[51]

[11] %	Solvent	Phase	Temperature (°C)	Time (h)	ee, %*
2.8	ACD-*c*	cholesteric	182	8	1.9
5.8	ACD-*d*	cholesteric	153	24	1.06
5.7	ACD-*e*	cholesteric	185	8	1.17
4.8	CNB	cholesteric	185	8	0
2.0	ACD-*c* + decalin	isotropic	180	7	0.014†
4.4	bis(*p*-ethoxybenzylidene) hydrazone + 13% ACD-*e*	twisted nematic	180	8	0

* Excess *R* except as noted.

† Excess *S*.

lives in several cholesteric mixtures led to virtually no enantiomeric excess. Photoresolution attempts were slightly more successful: in a 1/1 mixture of 5α-cholestan-3β-yl acetate/5α-cholestan-3β-yl nonanoate (CHA/CHN) at 40°C, irradiation for 1 h produced a 1% excess of the *S* atropisomer. The somewhat larger ee obtained upon irradiation may arise from the greater polarizability of the excited states, their longer residence time near the thermal transition state geometry, or to selective excitation of one atropisomer by the partially circularly polarized light (produced by the cholesteric matrix). However, the latter factor cannot be solely responsible since the photostationary state of **12** obtained upon irradiation with circularly polarized light in dichloromethane favors one atropisomer by no more than 0.2%.[53]

The kinetics of thermal racemization of *S*(+)-**12** was investigated initially at room temperature in the cholesteric phase of a 60/26/14 (w/w/w) mixture of cholesteryl oleate (CO)/CN/CHA. From the observation that the rate constant for racemization, k_R, in CO/CN/CHA is 3–4 times k_R in benzene or in two telomers of polybutadiene,[52] it was hypothesized that the cholesteric matrix may press upon **12**, forcing the angle between the two naphthyl rings to be more acute (i.e. to be flatter) and, thus, closer in structure and energy to the transition state for racemization.

To test this hypothesis, a detailed investigation of the thermal racemization of **12** was undertaken in several mesophases whose structures approximate the shape of **12** more closely than the cholesteric molecules.[54] The activation data are summarized in Table 4. The polarity of isotropic solvents does not appear to influence atropisomerization.[55,56] Therefore, differences among the activation parameters in Table 4 were attributed primarily to microscopic changes in the solvent order of the nematic phases (but not differing viscosities[52]). As expected of a process in which a bulky solute becomes planar in its transition state, $\Delta S^{\ddagger}$ is very negative. The decrease in $\Delta H^{\ddagger}$ (as compared to the isotropic phase data) is consistent with the previous hypothesis[52] that solvent order forces **12** to lie closer to the transition state.

Of special interest is the data reported for the nematic and solid phases of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA). In the very restrictive matrix of the solid phase, $\Delta H^{\ddagger}$ is much lower and $\Delta S^{\ddagger}$ is much more negative than in the nematic phase. These results may be interpreted within the

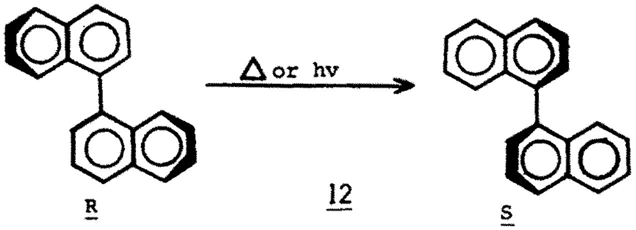
Table 4. Activation parameters for atropisomerization of **12**[54]

Solvent	Phase	$\Delta H^{\ddagger *}$ (kcal/mol)	$\Delta S^{\ddagger *}$ (cal/mol-deg)
E7	Nematic	15.5 ± 1.0	−26 ± 3.4
Phase 1083	Nematic	16.5 ± 0.4	−22 ± 1.4
Phase IV	Nematic	17.3 ± 0.7	−21 ± 2
ZLI-1167	Nematic	17.7 ± 1.6	−18 ± 5
Phase 1052	Nematic	19.7 ± 1.0	−13 ± 3.5
MBBA	Nematic (+ plastic)	23.5 ± 0.4	−8.9 ± 1.4
	Solid	8.0 ± 0.7	−63.2 ± 5.4
Benzene†	Isotropic	22.2	−5.8
Dimethylformamide†	Isotropic	21.5	−6.5
Cyclohexane†	Isotropic	21.9	−7.1

* Errors are one standard deviation.

† Refs 55 and 56.

same context as the data above: as **12** moves toward its transition state, neighboring solvent molecules may 'relax' to a more ordered position (leading to a decrease in total entropy); at the same time, the energy required to attain the transition state of **12** is smaller in the solid phase because it flattens initially the solutes to a greater extent.

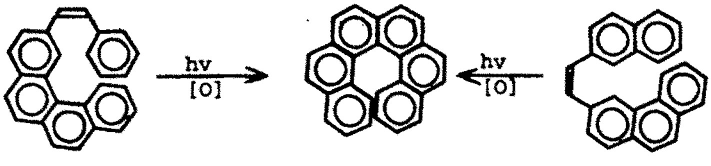


12

(14

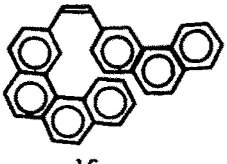
The photochemical synthesis of hexahelicene **15** from precursors **13** and **14** has been examined in chiral mesophases. The enantiomer determining step in each case is the ring closure to form dihydro-**15**; subsequent oxidation serves only to aromatize the new ring and those adjacent to it. Using circularly polarized light, Kagan *et al.*[57] found that **15** could be produced with a small (<0.2%), but real, excess of one enantiomer. Unpolarized light and chiral solvents produced **15** with up to 2.1% ee (ethyl *S*-mandelate as solvent).[58]

By contrast, irradiation of **13** or a precursor of octahelacene **16** in an oriented mechanically twisted nematic phase (which produces a cholesteric-like arrangement) of 1/1 *p*-cyanophenyl *p*-butylbenzoate/*p*-cyanophenyl *p*-heptylbenzoate results in a very small (<0.2%) ee.[59] Since the *local* environment experienced by the precursor is virtually achiral in a twisted nematic phase, the only source of asymmetry which can lead to optical induction is the medium-produced circularly polarized light. Thus, in the right-hand twisted nematic phase, the (+) enantiomers of **15** and octahelacene are in excess; in the left-hand twisted nematic phase, the (−) enantiomers are formed preferentially.[59]



13 15 14

(15



16

The photochemical **13** → **15** transformation has been investigated in cholesteric mesophases by two groups.[60,61] Nakazaki *et al.*[60] found that *ca* 1% ee of **15** obtained upon irradiation of **13** in either a 3/2 mixture of CN/CCl or CNB; only racemic **15** was isolated from irradiations in the isotropic phase of the former solvent. Hibert and Solladie[61] explored the influence of cholesteric twist and solvent structure on the selectivity of **14** formation. They observed that at 32°C, where the pitch of the CN/CCl mixture of Nakazaki *et al.*[60] approaches infinity (i.e. becomes a compensated nematic phase), the ee of **15** is similar to the amounts found *by them* in other cholesterics. Some discrepancies exist between the absolute ee of **15** measured by the two groups. However, the data of Hibert and Solladie[61] do not support solvent pitch as being the dominant factor in influencing the mode of **13** ring closure. They do suggest that solute–solvent interactions, when made specific by mesophase ordering, can be more important than the influence of circularly polarized light. Results which demonstrate this point are collected in Table 5.

In a different approach, Solladie *et al.* have used the twisting power of chiral molecules in nematic phases[62] to follow the rates of solute racemizations. They observed that the chiral ketone **17** undergoes photodecarboxylation to yield the corresponding dihydrophenanthrene **18** in the

Table 5. Dependence of enantiomeric excess in **15** (from **13**) on solvent pitch and phase of a 1.75/1 CCl/CMY mixture[61]

T(°C) (±1°)	Helix handedness (or phase)	Pitch (μ)	%ee*
31	Left	−3.5	0.05
41	(Nematic)	∞	0.19
51	Right	+4.9	0.29
61	Right	+1.6	0.43
70	(Isotropic)		0.03
80	(Isotropic)		0.02

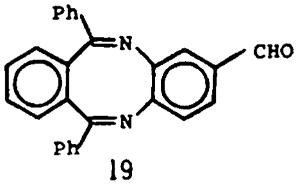
* In all cases, the (+) enantiomer was produced in excess.

nematic phase of *p*-cyano-*p'*-*n*-hexylbiphenyl (HBCN).[63] Photoracemization competes slowly with the decarboxylation process and **18** undergoes facile thermal racemization under the reaction conditions. Thus, the progress of decarboxylation was followed from changes in the pitch of the induced cholesteric phase as measured by the droplet method of Candau.[64] In fact, the use of the droplet method to follow the course of a reaction was probably a more important contribution than the photochemistry. It demonstrated the feasibility of a new mechanistic technique and led to several new applications.[54,62]

One of the earliest of these was measurement of the rate of racemization of diazocine (**19**) in the *isotropic* phase of a mixture of aromatic esters (Merck Licristal IX; nematic range from −20 to 60°C).[65] Aliquots of the reaction mixture were cooled periodically and their pitch was measured by the droplet method. From these data, an activation energy of 38 ± 2 kcal/mol was calculated.

17 18

(16



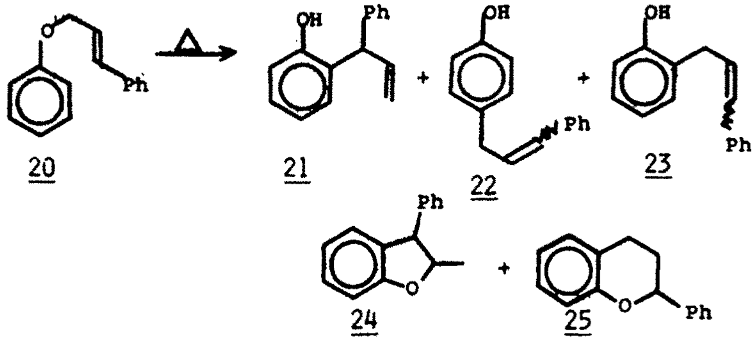
19

From all of these examples, we conclude that chiral recognition in cholesteric phases may be of mechanistic interest, but it holds little promise of providing a practical method for the synthesis of optically active molecules. It is apparent that the type and degree of solute–solvent interactions play a role in controlling enantiomer production. In spite of the extensive experimentation performed to date, the best systems for studying chiral recognition in mesophases may not have been investigated: for instance, very few attempts to match solute and solvent shapes have been made;[48] no experiments have employed other, more ordered chiral mesophases such as smectic C^{*}[42] or chiral discotic phases.[66] Clearly, more research is needed in this area.

3. UNIMOLECULAR THERMAL REACTIONS

Controversy has followed the Claisen rearrangement from the initial report by Bacon and Brown,[67] that the rate of rearrangement of **20a** proceeds more rapidly in nematic than in isotropic solvents, to their subsequent retraction,[68] and confirmation of the lack of effect by nematic solvents by Dewar and Nahlovsky[69] who investigated **20**.

Rearrangement of **20** may include a concerted and step-wise route to **21**. In either case, the molecule probably prefers a much more extended conformation in the mesophases than the one shown. Thus, in principle, the Claisen rearrangement should require large shape changes along its reaction coordinate, and be a good candidate to observe the influence of solvent order.



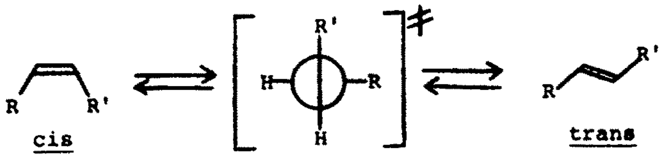
(17

In the nematic and isotropic phases of hydroquinone di-*p*-*n*-hexyloxybenzoate (HHB), $\Delta H^{\ddagger} = 29.5 \pm 0.85$ kcal/mol and $\Delta S^{\ddagger} = -15.1 \pm 0.35$ cal/mol-deg for rearrangement of **20**.[69] Furthermore, the product ratio (**21**+**24**)/**23** exhibited no discontinuity between the nematic and isotropic phases of HHB.

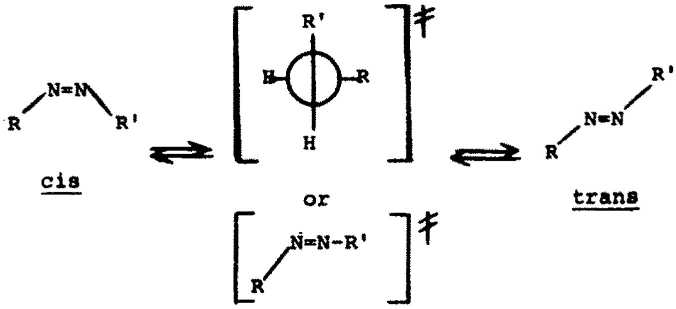
Since Saeva *et al.*[47] showed conclusively that the Claisen rearrangement of **1** in the cholesteric phase of CNB yields **2** of unknown, but non-zero optical purity, Anderson and Weiss[70] investigated the reaction of **20** in the cholesteric and isotropic phases of cholesteryl cinnamate (CNN). The activation parameters, $\Delta H^{\ddagger} = 28.7 \pm 1.4$ kcal/mol and $\Delta S^{\ddagger} = -17.0 \pm 3.0$ cal/mol-deg, were the same in both phases; the values calculated in an isotropic solvent, diphenyl ether ($\Delta H^{\ddagger} = 28.1 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -19.5 \pm 2.2$ cal/mol-deg) were within experimental error of the parameters reported by Dewar and Nahlovsky.[69] Thus, only the most sensitive measure indicates any influence of mesophase solvent order on the Claisen rearrangement.

Neither Bacon and Brown[67,68] nor Dewar and Nahlovsky[69] mentioned the effect of **20** on the mesophase–isotropic transition of their nematic solvents. Anderson and Weiss[70] found that 1.2% of **20** plus 1.5% of pyrene (internal standard) depressed the phase transition temperature of CNN by 8°. On this basis, it is reasonable to assume that **20** causes a large disturbance to its microscopic environment. If similar depressions obtain with **20** in the other mesophases, it may be necessary to reexamine the influence of liquid-crystalline order on the dynamics of the rearrangement of **20** in a solvent which is able to accommodate it well.

Geometric isomerization about a double bond requires more subtle shape changes along the reaction coordinate than does the Claisen rearrangement. The mode of isomerization involves rotation about carbon–carbon double bonds [eqn (18a)] and either rotation or inversion about



(18a

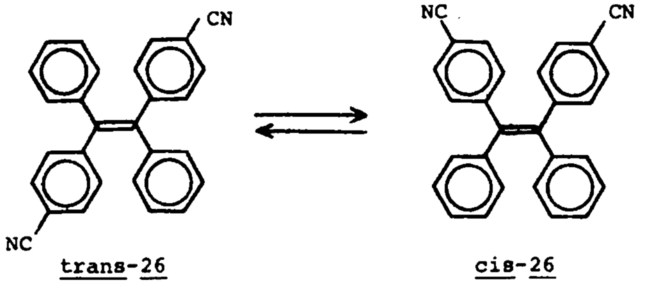


(18b

N=N double bonds [eqn (18b)]. The perpendicular transition state for alkene isomerization, being more globular than the *cis* and *trans* isomers from which it forms, is expected to cause the greatest disturbance to its anisotropic environment: the rate of isomerization will be retarded to the extent that mesophase order resists the out-of-phase motions necessary to attain the transition state.

Preliminary evidence of exactly the opposite effect was reported by Torgova *et al.*[71] who examined the thermal *cis* to *trans* isomerization of stilbene at 156°C in the nematic phase of a 1/8/1 mixture of *cis*-stilbene/1,4-bis(4-hexyloxybenzoyloxy)benzene/hexadecane and in the isotropic phase of a 1/2/1 mixture of the same components. The rate in the nematic mixture was consistently twice as large as in the isotropic solvent. The mechanistic importance of these experiments is compromised by the very high stilbene concentrations and the lack of consistency in absolute rates from experiment to experiment.

Leigh *et al.*[72] performed a very careful study of the thermal *trans–cis* isomerization of *trans*-1,2-di(4-cyanophenyl)-1,2-diphenylethene(*trans*-**26**) in several isotropic and cholesteric phases. As seen in Table 6, solvent order has no discernible effect on the isomerization. However, these results should not be interpreted to mean that cholesteric solvent order is insensitive to the shape changes of eqn (18a). Crystallographic studies show that the phenyl groups of **26** are propeller-like and the double bond is twisted by *ca* 8°.[73] Thus, the alkene and its transition state are both globular: neither is expected to be incorporated into a cholesteric matrix without severely disrupting it.



trans-26 cis-26

(19

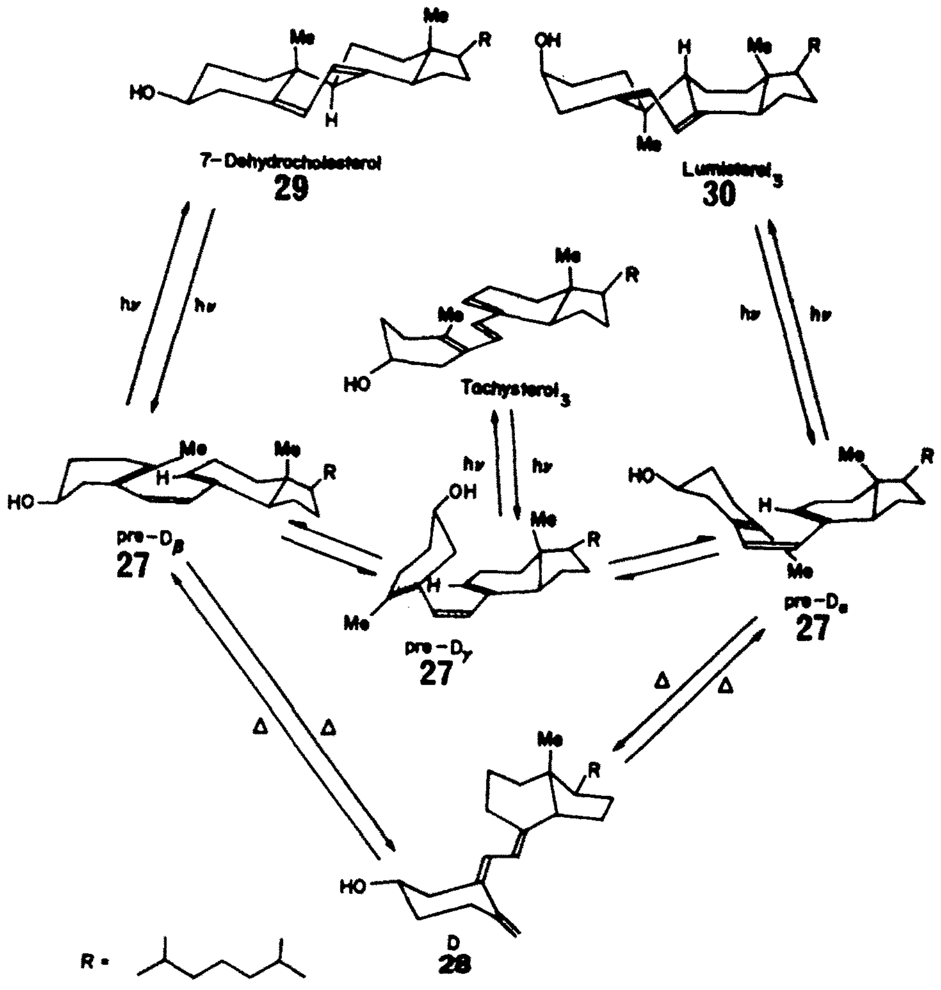
Another reaction which has been investigated in mesophases is the geometric isomerization of azobenzenes [eqn (18b)]. The feasibility of following the progress of the thermally or photochemically induced process by pitch band changes in the cholesteric phase of a 35/65 (w/w) mixture of CCl/CN was demonstrated by Sackmann.[74] Although no mechanistic conclusions were derived by Sackmann, he recognized that different shape-dependent interactions between each isomer of azobenzene and neighboring solvent molecules were responsible for the pitch band shifts. Later Nerbonne and Weiss[75a] followed the thermal isomerization of *cis*-azobenzene and two of its *para*-substituted derivatives to the corresponding *trans* isomers by direct UV-vis absorption measurements. They reported erroneously that the activation energies for isomerization were phase dependent for some substituted azobenzenes, but not for others. A detailed study was conducted by Otruba and Weiss[75b] on 15 mono-, di-, tri-, tetra-, and hexa-substituted low-'bipolarity' azobenzenes in benzene, in the isotropic and cholesteric phases of CCl/CN, in the isotropic phase of *n*-butyl stearate (BS), and in a variable composition of CCl and CN which remained a compensated nematic mixture at the

Table 6. Activation parameters for thermal isomerization of **26**[72]

Solvent	Phase	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (kcal/mol-deg)
CB	Isotropic	35.0 ± 0.6	-1.4 ± 0.6
CBCl	Cholesteric	36.4 ± 0.8	-0.2 ± 0.9
Cholesteryl 6-methoxy-2-naphthoate	Cholesteric	36.3 ± 0.6	-0.5 ± 0.6
n-decyl-4-anisoate	Isotropic	34.6 ± 0.5	-2.0 ± 0.5
CB/CT/CBCl	Isotropic	34.8 ± 0.2	-1.5 ± 0.5
	Cholesteric	36.0 ± 0.3	-0.5 ± 0.6

experimental temperatures. They observed no clear evidence that solvent order alters the activation parameters for *cis* → *trans* isomerization of the azobenzenes. On this basis, they concluded that low-'bipolarity' azobenzenes undergo thermal isomerization via in-plane (inversion) motions: an out-of-plane (rotational) motion should have led to different activation parameters in the cholesteric and isotropic phases of CCl/CN for at least some of the azobenzenes.

However, this expectation must be tempered with other negative observations of solvent order effects on solute isomerizations. Thus, Cassis and Weiss[76] measured the rates for conversion of pre-vitamin D_3 (**27**) to vitamin D_3 (**28**) and of **28** to **27** in the cholesteric phase of a 60/26/14 (w/w/w) mixture of CO/CN/CCl and in two saturated hydrocarbon solvents (*n*-hexane and 2,2,4-trimethylpentane) (Scheme 1). The rates of the **27** → **28** conversion in the cholesteric phase were found to be independent of whether **27** is generated from 7-dehydrocholesterol (**29**) or lumisterol$_3$ (**30**). The two precursors of **27** are diastereomeric and yield different conformations of **27** which, in principle, may interconvert with great difficulty in a cholesteric matrix. Thus, either conformational equilibration is more rapid than the **27** → **28** isomerization or the two initial conformations of **27** undergo [1,7]-sigmatropic *H*-transfer with equal efficiency. Evidence against both the former hypothesis and the importance of solvent order for the $\mathbf{27} \rightleftarrows \mathbf{28}$ conversions is found in the activation parameters obtained from the cholesteric phase of the CO/CN/CCl mixture and the hydrocarbons. The activation parameters are collected in Table 7. They demonstrate that in spite of (potentially) large shape changes which accompany **27** → **28** and (especially) **28** → **27**, the rearrangements are unaffected by the cholesteric matrix.



Scheme 1. Thermal and photochemical interconversions between vitamin-D_3 (**28**) and related compounds.[76]
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Table 7. Activation parameters for **27** ⇆ **28** isomerization[76]

Solvent	**27** → **28** $\Delta H^{\ddagger}$ (kcal/mol)	**27** → **28** $\Delta S^{\ddagger}$ (cal/mol-deg)	**28** → **27** $\Delta H^{\ddagger}$ (kcal/mol)	**28** → **27** $\Delta S^{\ddagger}$ (cal/mol-deg)
Hydrocarbon	20.5 ± 0.7	-16.6 ± 2.0	25.6 ± 0.7	-3.6 ± 2.1
CO/CN/CCl	20.1 ± 0.7	-15.4 ± 2.3	24.9 ± 0.6	-3.3 ± 2.0

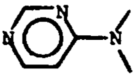
Table 8. Activation parameters for rotation of the dimethylamino-aromatic bond of **31**

Solvent	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol-deg)	Reference
ZLI 2142	53 ± 1	20 ± 6	77
CD_2Cl_2	35 ± 1	-39 ± 3	77
$CHCl_3$	45 ± 2	-21 ± 4	81a
CD_3OD	52 ± 1	-8 ± 4	81b
$(CH_3)_3CNH_2$	49 ± 2	46 ± 6	81a

An unresolved, key question concerns the preferred conformation of **28** in the cholesteric phase. If it is *cisoid* about the exocyclic diene link between the A and C rings, the shapes of **27** and **28** would be sufficiently similar to be almost indistinguishable to the cholesteric matrix. Re-examination of the isomerization mechanism in a cholesteric phase using **29** which is esterified with nonanoic acid, for instance, may increase the specificity of solute–solvent interactions and allow smaller shape changes to be detected.

Another subtle shape change in solutes occurs with rotation about σ-bonds. Fung *et al.*[77] examined by dynamic NMR measurements the influence of mesophase order on the rotation of the dimethylamino group about the aromatic moiety in 4-(dimethylamino)pyrimidine (**31**). They found that in the mesophase of Merck mixture ZLI 2142 (structure of components was not well-specified), the activation enthalpy is *ca* 50% higher than in CD_2Cl_2. The authors suggested that this difference is probably due to the liquid-crystalline phase favoring the planar conformation of **31**. However, the data do not warrant this conclusion since the absolute difference in $\Delta H^{\ddagger}$ between the two solvents and between other solvents can be attributed easily to their viscosity differences (Table 8). In fact, several other isomerizations[78] or conformational changes[79] which involve very small shape changes have been studied in liquid crystals by dynamic NMR[80] and do not appear to be affected by solvent order. It would appear, then, that relatively large shape changes which emanate from molecules which initially fit well into their ordered environments are required if the influence of mesophase order is to be detected.

Several other unimolecular rearrangements and fragmentations have been investigated in liquid crystals without evidence of control by solvent order. Thus, Melone *et al.*[82] found that limonene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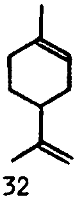
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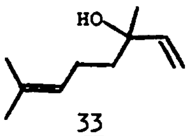

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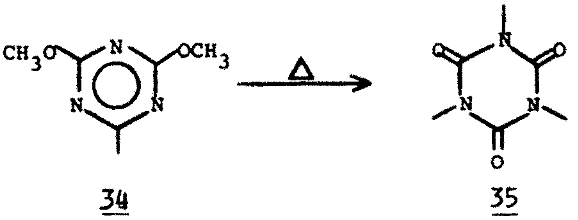
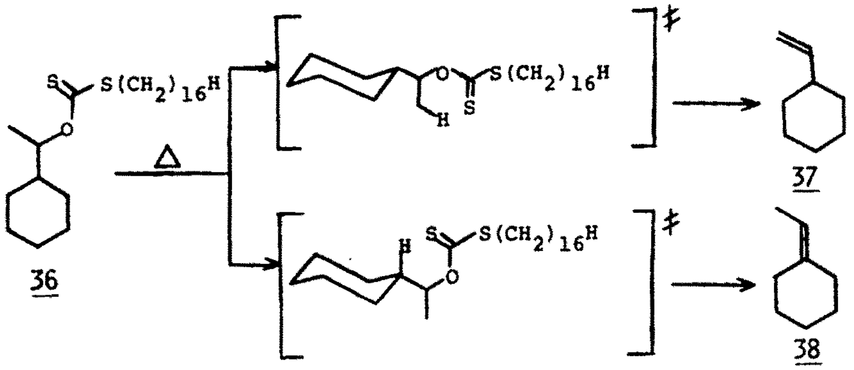
(**32**) and linalool (**33**) rearrange in smectic B phases of alkylcyclohexylcarboxylic acids and alkylbicyclohexylcarboxylic acids. While the product distributions did not correlate with solvent order, they did follow the influence of temperature and acidity.

The second-order rearrangement of 2,4,6-trimethoxy-*s*-triazine (**34**) to 1,3,5-trimethyl-2,4,6-trioxyhexahydro-*s*-triazine (**35**) was found to proceed with a slightly higher activation enthalpy and less negative activation entropy in the nematic phase of di-(*p*-methoxyphenyl) *trans*-cyclohexane-1,4-dicarboxylate (MPCD) than in its isotropic phase (induced by 21.37 mol% of CHT).[83] Again, the differences can be explained easily on the basis of slightly differing solvent polarities or viscosities.



(20

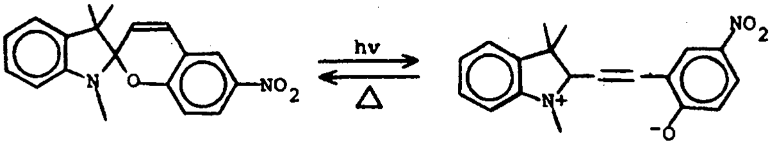
Barnett and Sohn[84] studied the rates of hexadecyl xanthate (**36**) eliminations in several nematic phases, including MPCD, and in isotropic solvents. Since the mechanism of elimination involves concerted 6-member ring transition states [eqn (21)], it should be sensitive to solvent ordering effects. However, in the solvents employed, there appears to be no clear evidence that the solutes interact sufficiently with the ordered solvents to allow one to be observed. The authors proposed to present in a future publication the results from a study of the product ratio **37**/**38**. Unfortunately, this report, which would offer a more sensitive measure of solute-ordered solvent interaction, has not appeared.



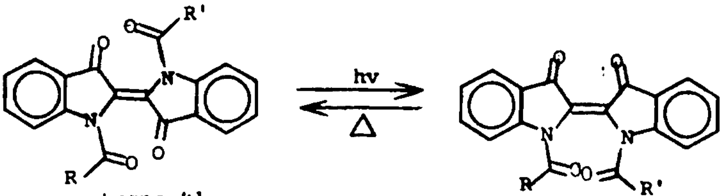
(21

To be contrasted with these negative observations are studies conducted in BS on the thermal isomerizations of a merocyanine dye (**40**) to its indolinospiropyran (**39**)[85] and of the *cis* to *trans* forms of *N*,*N'*-diacylindigos (**41**).[86] The shape changes associated with the transformations of eqns (22 and 23) are shown in cartoon form in Scheme 2. Each of the initial species can be considered to consist of two connected 'plates'. The preferred angle between the plates in **40** is 0° and in *cis*-**41** is $>0°$. At the transition state, the angles change to $>0°$ and *ca* 90°, respectively. Finally, the products **39** and *trans*-**41** exhibit angles of 90 and 180°, respectively, between their plates. Since only those electronic shape changes that occur between a reactant and its transition state are measurable kinetically, solvent order must exert its influence at the early stages of isomerizations or it will not be detected. The shape changes leading to the transition states of **40** and *cis*-**41** are somewhat different but involve rotations leading to more globular species.

The rate of isomerization of **40** to **39** is known to be very dependent upon solvent polarity. To explore its dependence upon solvent viscosity, the rate constant at 25°C was measured in three telomers of polybutadiene (Table 9). The span of rate constants from at least four independent runs are reported. Thus, at least within the range explored, there is no discernible dependence of the rate of isomerization on the viscosity.

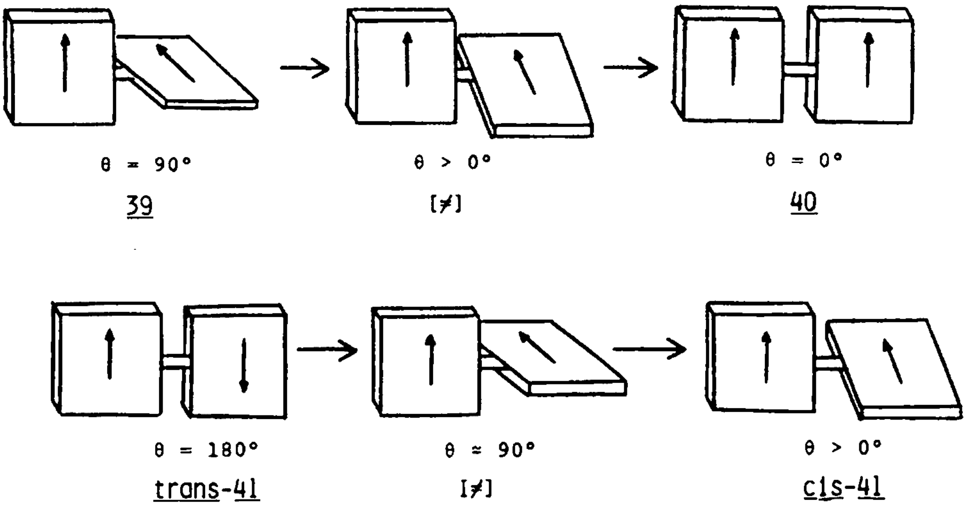


39 40 (22



trans-41 cis-41 (23

a) R = R' = CH_3
b) R = R' = Ph
c) R = CH_3; R' = $C_{17}H_{35}$
d) R = R' = $C_{17}H_{35}$



Scheme 2. Representation of the rotational motions suffered during ring closure of **40** and during *cis* → *trans* isomerization of **41**.[86]

Table 9. Rate constants for **40** → **39*** at 25°C in telomers of polybutadiene (PB) and their properties[85]

Solvent	M_n†	Viscosity, 25°C‡	Density, 25°C§	k(min⁻¹) × 10⁵
PB500	420	13.1	0.82	1.28–1.41
PB1000	960	87.5	0.91	2.69–3.60
PB2500	2350	506	0.92	1.00–1.10

* Initial concentrations of **39** + **40** were *ca* 10^{-5} M.
† Number average molecular weight.
‡ In cp.
§ In g/cc.

Table 10. Activation parameters for **40** → **39** in various solvents

Solvent	Phase	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol-deg)	Ref.
PB500	Isotropic	17 ± 1	-11 ± 2	85
Polystyrene		17.6	-14.6	87
BS	Smectic	38 ± 2	$+55 \pm 7$	85
	Isotropic	17 ± 1	-9 ± 2	85
Polymethylmethacrylate		24.4	$+3.9$	87
Polyisobutylmethacrylate copolymer	Below glass transition	15.1	-25.5	88
	Above glass transition	32.3	± 25.8	88
Ethyl acetate	Isotropic	27.4		

The activation parameters for isomerization *do* respond drastically to changes in solvent order. Thus, the activation energy and activation entropy of the isomerization in the smectic B phase of BS are 22 kcal/mol greater and 64 eu more positive than in the isotropic phase! The data are summarized in Table 10. As can be seen, the dynamics of isomerization in a series of solvents which contain ester functionality varies enormously according to phase order. Due to the extreme sensitivity of the reaction to solvent polarity, some of the results in Table 10, especially the larger E_a values from isotropic solvents, may arise from traces of very polar impurities.

The location of the solutes in smectic BS may be within a layer or between layers. Experiments to date cannot distinguish between these sites. Presumably, a long alkyl chain on nitrogen would push the merocyanine to a layer interface. Regardless, the trend is clear: smectic phase order retards the movements required to bring **40** to its transition state. The extremely large differences in the activation parameters from the smectic B and isotropic phases of BS are probably due to involvement of several solvent molecules (along with each solute) in the smectic phase reaction.

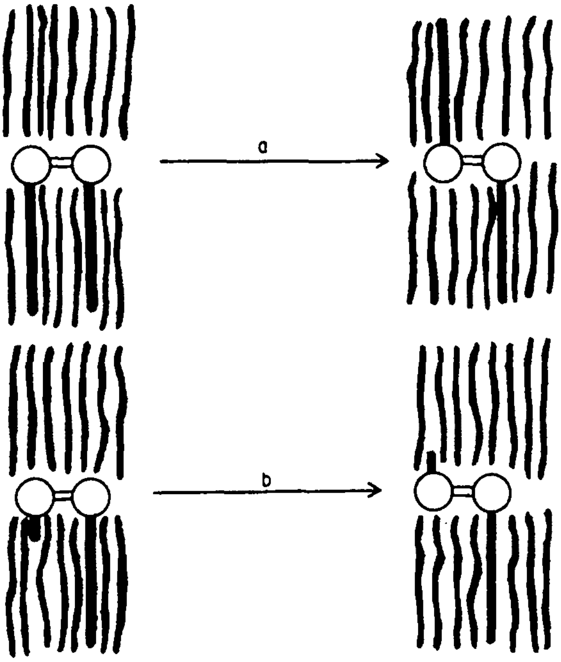
The influence of long chains on the rate of isomerization of the indigo moiety has been studied in the isotropic and smectic B phases of BS and in the cholesteric phase of a 60/26/14 (w/w/w) mixture of CO/CN/CHA.[86]

Single temperature measurements indicate that *cis*-**41b**, the bulkiest of the indigos studied, isomerizes 3–4 times more rapidly in cholesteric CO/CN/CHA than in toluene. The rate increase does not appear to be solvent order related since isotropic CO/CN/CHA allows isomerization to proceed *ca* three times as rapidly as in toluene. By contrast, the rates of isomerization of *cis*-**41a** or *cis*-**41d** in cholesteric CO/CN/CHA were found to be only about one-half of the corresponding rates in benzene. It is tempting to rationalize this limited data to differential solvent ordering effects in which the phenyl groups of **41b** cause the local environment in CO/CN/CHA to be disturbed and isotropic-like. However, further experimentation is required before this suggestion should be considered seriously.

Activation parameters for isomerization of *cis*-**41** in the various solvents (Table 11) are a much better diagnostic of the role of mesophase order. They indicate that cholesteric phase order has

Table 11. Activation parameters for the thermal *cis* to *trans* isomerization of **41** in various solvents[86]

41	Solvent (phase)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol-deg)
a	Benzene (isotropic)	23.8 ± 0.7	-1 ± 2
	CO/CN/CHA (cholesteric)	23.2 ± 0.8	-4 ± 3
b	Toluene (isotropic)	25.3 ± 0.4	-2 ± 1
c	Benzene (isotropic)	23.5 ± 0.3	-2 ± 1
	BS (isotropic)	21.0 ± 0.8	-8 ± 3
	(smectic B)	24.0 ± 1.6	$+3 \pm 11$
d	Benzene (isotropic)	22.2 ± 0.5	-6 ± 1
	BS (isotropic)	21.7 ± 0.6	-8 ± 2
	(smectic B)	31 ± 3	$+21 \pm 11$



Scheme 3. Cartoon representation of isomerization of (a) *cis*-**41c** and (b) *cis*-**41d** to the *trans* isomers in the smectic B phase of BS.

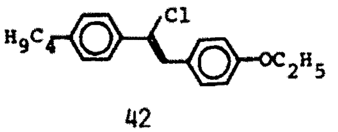
little, if any, influence on the isomerization of *cis*-**41a**. Comparison of the activation parameters for the *cis* isomers of **41a**, **41c**, and **41d** in smectic BS is intriguing.

As mentioned previously for **40**, a long substituent chain should aid the dye portion of a molecule to reside at or near a smectic layer interface: by intercalating itself in a smectic layer, the chain defines the location of the moiety to which it is attached (Scheme 3). The high polarity of the indigo group should exclude it from the hydrocarbon-like environment of the middle of a BS smectic layer, even in the absence of a long chain. The incompatibility between the indigo portion of **41** and BS is demonstrated by the inability to solubilize **41a**, the indigo with the shortest acyl chains, in smectic BS.

The stunning difference between the activation parameters for *cis*-**41c** and *cis*-**41d** in smectic BS implies that two anchoring chains exert a very strong influence over indigo isomerization but one does not. That the activation parameters for *cis*-**41d** in isotropic BS are normal (i.e. close to those in benzene or to those for *cis*-**41c** in isotropic BS) lends credence to the smectic phase numbers. Ganapathy *et al.*[86] interpreted these data to indicate that rotation of the indigo plates, themselves (a *cis* → *trans* isomerization), is unaffected by smectic BS: the *cis*-indigo moiety is sufficiently disturbing to its local environment near a layer interface to preclude the residual solvent order from inhibiting the shape changes which lead to the transition state. Movement of the stearoyl chains of **41d**, remote from the reactive site, *are* responsible for the large increases in the activation parameters measured in smectic BS. The anchoring effect illustrated in Scheme 3 suggests a new synthetic strategy for holding parts of molecules immobile while allowing others to change their conformations freely.

4. UNIMOLECULAR PHOTOCHEMICAL REACTIONS

As early as 1969, Haas *et al.* reported that UV irradiation of a mixture of CCl and cholesteryl iodide produces irreversible changes which can be used to form an image.[89] They did not investigate the photochemical processes involved. Reversible color change was achieved by Sackman[90] who followed the *trans* → *cis* photoisomerization (at $\lambda = 313$ nm) of azobenzene in a CN/CCl mixture by the selective reflectance of the solvent pitch band. The *trans* and *cis* isomers of the solute affect the pitch differently, allowing the changes in the wavelength maximum to serve as a quantitative measure of the extent of isomerization. In a similar approach, Haas *et al.*[91] used the photochemical



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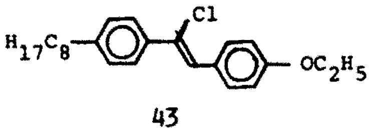
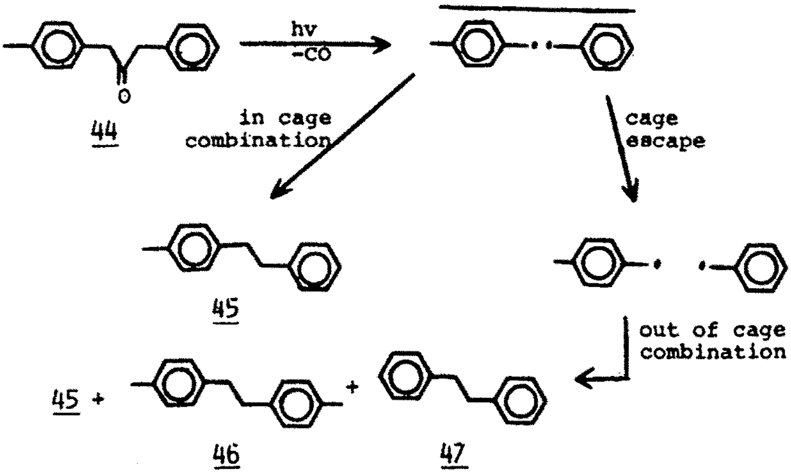


43

isomerization of mesomorphic *trans*-stilbenes (**42** and **43**), either alone or mixed with cholesteryl oleyl carbonate (COC), to cause depressions in the mesophase–isotropic phase transition temperatures. However, the authors did not address mechanistic questions involving the possible control of isomerization by a solvent matrix.



Scheme 4. In-cage and out-of-cage combinations of radicals from **44**.

The Norrish I photolysis of 1-(4-methylphenyl)-3-phenylpropan-2-one (**44**) produces benzyl and (*p*-tolyl)methyl radicals whose recombination can occur in-cage or out-of-cage (Scheme 4).[92] The fraction of in-cage reaction, F_c, is calculated according to eqn (24).[92]

$$F_c = \frac{[\mathbf{45}] - ([\mathbf{46}] + [\mathbf{47}])}{[\mathbf{45}] + [\mathbf{46}] + [\mathbf{47}]} \tag{24}$$

The fate of radical pairs from **44** produced in the solid, liquid-crystalline, and isotropic phases of 35/65 (w/w) CCl/CN, BCCN, or BS were examined by Hrovat *et al.*[93] Strong magnetic fields are known to influence F_c when **44** is irradiated in some solvent systems;[94] very small differences between experiments conducted at 0G and 3KG were observed in the cholesteric or isotropic phase of the CCl/CN and in the smectic B, nematic, or isotropic phase of BCCN.

Since the combination of radicals depends, in part, upon the rates of intersystem crossing of in-cage pairs, ^{12}C and ^{13}C (with nuclear spins of 0 and $\frac{1}{2}$, respectively) at the benzylic position influence product formation differently. At 30% conversion, the ^{13}C isotropic enrichment factor α[95] for recovered 1,3-diphenylpropan-2-one (**48**) was 1.09 ± 0.02 and 1.03 ± 0.01 in the smectic B (17°C) and isotropic (35°C) phases, respectively, of BS. These values should be compared with $\alpha = 1.04$ and 1.37 observed at room temperature in benzene and a cationic micelle, respectively.[92] Thus, the numbers from the mesophases are not extraordinary for solvents of high viscosity.

The F_c of each solvent with **44** is displayed in Fig. 8. Assuming that the radicals derived from **44** are somewhat inhibited from crossing smectic layer boundaries, preference for in-cage combinations in smectic BS can be rationalized. The ball-like shape of the radicals may allow them to escape the anisotropic diffusion enforced by the other ordered phases on more rod-like solutes. The results obtained to date on this system are promising. Longer homologs of **44** in BCCN and BS, especially, merit further investigation since the magnitude of the influence by both solvents has been found in other studies (*vide infra*) to be very sensitive to solute size and shape.

The photolysis of 2-methyl-2-nitrosopropane in mesophases[96] is mechanistically similar to the Norrish I reaction. It will be discussed in Section 6.

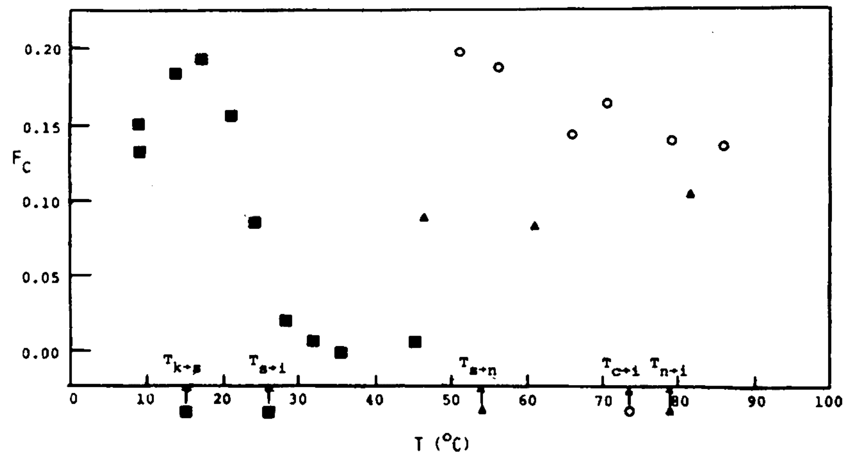


Fig. 8. Fraction of in-cage radical recombinations (F_c) from photolyses of **44** in BS (■), BCCN (▲), and CCl/CN (○) versus temperature. Phase transition temperatures are shown.[93] [Reprinted with permission of the American Chemical Society.]

5. PHOTOCYCLIZATION PROCESSES

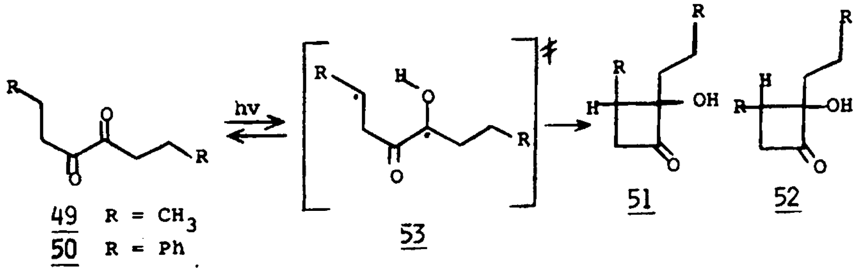
A second class of unimolecular photochemical processes in mesophases, those involving chain kinking or cyclizations, will be treated separately. These processes may be loosely classified as following the shape changes shown in Fig. 4a (A → D) of the Introduction.

The first attempt to observe restrictions of chain kinking by a liquid-crystalline matrix involved the Norrish II photorearrangement of α-diketones (**49** and **50**).[97] The sole products observed were the cyclobutanols (**51** and **52**). Since the intermediate 1,4-biradicals (**53**, Scheme 5) can close to yield either diastereomer, a first test of the specificity of solute-ordered solvent interactions is the **51**/**52** ratios. On this basis, the influence of solvent order cannot be judged as very important: almost equal amounts of **51** and **52** were obtained from both diketones in all mesophases examined.

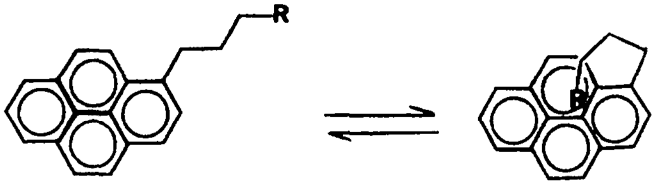
Another measure of the influence of solvent order is the quantum efficiency for product formation, Φ_p. In fact, Φ_p is influenced by temperature, solvent phase, and solvent structure. These changes can be ascribed to several factors: conformational constraints on the α-diketone, which affect its ability to adopt the kinked conformation (shown in Scheme 5) needed for intramolecular H-abstraction; changes in the triplet lifetime of the α-diketones (from which H-abstraction occurs); variations in the fraction of **53** which proceeds to product. Each of these must contribute to some extent to the overall results; the data are too sparse to allow definitive conclusions concerning the importance of each to be drawn, but suggest that the mesophase order alters the lability of solute chains.

Anderson *et al.* examined the conformational bending necessary to bring into collision the head and tail groups of 1,3-bis(1-pyrenyl)propane (P3P)[98] and *N*,*N*-dimethyl-4-[3-(1-pyrenyl)propyl]-aniline (**54**)[98,99] [i.e. a cyclization process as shown in eqn (25)] in a 59.5/15.6/24.9 (w/w/w) mixture of CO/CN/CCl(CM).

The dynamics of the process were followed by monitoring the temporal decay of fluorescence intensity of pyrenyl singlets which do (P3P and **54**) and do not (**55**) have the opportunity to



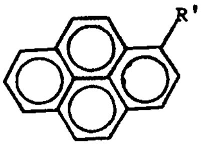
Scheme 5. Norrish II photocyclizations of **49** and **50**.



(25

P3P R = 1-pyrenyl

54 R = 4-(N,N-dimethylanilino)



55 R' = C_2H_5

56 R' = $C_{12}H_{25}$

encounter a quenching R group. The decay profiles, obtained with a time-correlated single photon counting technique, were analysed according to Scheme 6. It was assumed, based upon several factors (including the monoexponentiality of the decay curves), that k'_4 is much less than k'_3 or k'_5. The sums of $k'_1+k'_2$ were obtained from the inverse of the decay constants from **55** ($1/\tau_{55}$); $k'_1+k'_2+k'_3$ were calculated in the same way from P3P and **54** ($1/\tau_{(\text{P3P or 54})}$). Thus k'_3 can be determined uniquely from the difference of the inverses of the lifetimes as shown in Scheme 6.

$$\overparen{\text{Py}\quad\text{R}}\xrightarrow{h\nu}{}^1\overparen{\text{Py}\quad\text{R}}$$

$${}^1\overparen{\text{Py}\quad\text{R}}\xrightarrow{k'_1}\overparen{\text{Py}\quad\text{R}}+h\nu'$$

$${}^1\overparen{\text{Py}\quad\text{R}}\xrightarrow{k'_2}\overparen{\text{Py}\quad\text{R}}\text{ or }{}^3\overparen{\text{Py}\quad\text{R}}+\Delta$$

$${}^1\overparen{\text{Py}\quad\text{R}}\underset{k'_4}{\overset{k'_3}{\rightleftharpoons}}{}^1\overparen{(\text{Py}\ldots\text{R})}$$

$${}^1\overparen{(\text{Py}\ldots\text{R})}\xrightarrow{k'_5}\overparen{\text{Py}\quad\text{R}}+h\nu''\quad\text{or }\Delta$$

$$1/\tau_{55}=k'_1+k'_2$$

$$1/\tau_{(\text{P3P or 54})}=k'_1+k'_2+k'_3$$

$$1/\tau_{(\text{P3P or 54})}-1/\tau_{55}=k'_3$$

Scheme 6. Kinetic scheme for intramolecular pyrene excimer and exciplex formation.

Activation parameters for k'_3 derived from P3P and **54** were calculated in both the cholesteric and isotropic phases of CM. The results, summarized in Table 12, indicate that chain bending of

Table 12. Activation parameters for intramolecular quenching of pyrenyl singlets of 10^{-4} M P3P or **54** in CM[91,99]

	E'_3 (kcal/mol)		$\Delta S^{\ddagger}_3$ (cal/mol-deg)	
	Cholesteric	Isotropic	Cholesteric	Isotropic
P3P	10.5±0.4	10.1±0.2	1±1	0±0.5
54	10.8±0.2	7.9±0.5	6±1	−3±1

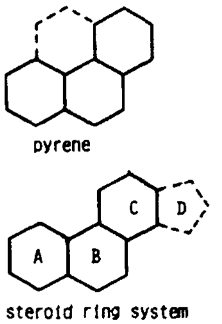


Fig. 9. Two-dimensional representations of pyrene and a steroid ring system. The common parts (rings A, B, and C) are shown in full lines. Parts which do not have a common projection are given dashed lines.

neither P3P nor **54** is influenced significantly by cholesteric order. Furthermore, the activation energies of the corresponding *intermolecular* quenching processes in CM are only slightly smaller than the E_3' reported in Table 12.[100,101] It was suggested that the bulky pyrenyl groups may have disturbed the environment near each solute to such an extent that the macroscopic order could not be sensed by P3P and **54**:[98] each solute is better viewed as a thread connecting two large discs rather than a somewhat perturbed alkane.

In spite of this characterization, the pyrenyl group bears some resemblance to a steroidal ring system (Fig. 9), and, therefore, from size and shape considerations, may be expected to associate preferentially with it rather than the alkyl chains on either end.

To test this hypothesis and to determine definitively the influence (or lack thereof) of cholesteric mesophase order on the dynamics of polymethylene chain cyclizations, Anderson and Weiss[12] and Sonnenschein and Weiss[13] examined intramolecular pyrenyl singlet quenching (and excimer formation) in the homologous series of α,ω-bis(1-pyrenyl)alkanes (P*n*P, where *n* is the number of alkyl carbons in the polymethylene chain). In isotropic solvents, the activation energies for chain cyclization of 'long' α,ω-diarylalkanes (measured via intramolecular electron exchange[102,103] or excimer formation[104,105]) are nearly constant within a series and only slightly higher than the calculated potential energy barrier for hindered rotation about a single carbon—carbon bond.[106] By using the methodology employed with P3P and **54**, including Scheme 6 and expressions analogous to its equations, the activation parameters for P3P and several other P*n*P (n = 5, 6, 7, 9, 10, 11, 12, 13, 22) were calculated in the cholesteric and isotropic phases of CM. All of the decay curves from which the constants were calculated are monoexponential. Except for P3P, 1-dodecylpyrene (**56**) was the model compound from which $k_1' + k_2'$ were derived.[107] The activation parameters from the P*n*P in CM, a 30/70 (w/w) mixture of CCl/CN, CO and BCCN are collected in Table 13.

These data and liquid crystal induced circular dichroism (lcicd) spectra obtained in CCl/CN demonstrate that cholesteric mesophase order does influence strongly the dynamics of P*n*P. In addition, the degree to which solvent influence is manifested depends upon the length of the P*n*P chain and its preferred association with one component of CM (as evidenced by the data taken in CCl/CN and CO). As with other α,ω-disubstituted alkane chain cyclization processes in isotropic media, the activation energies of the P*n*P in isotropic CM are nearly constant. However, in the cholesteric phase, seemingly non-systematic large variations occur.

A rough isokinetic relationship[108] exists for the P*n*P activation data obtained in isotropic CM. Quite surprisingly, an excellent correlation between $\Delta H_3^{\ddagger}$ and $\Delta S_3^{\ddagger}$ of P*n*P exists in the cholesteric phase of CM, also (Fig. 10). To explore the source of the activation parameter differences further, a Kramers treatment[109] of the data was undertaken. In this treatment, P*n*P quenching can be divided into a part which is intrinsic to pyrene excimer formation, one which is related to solvent friction, and another, which is dependent upon chain bending (E^*). It was found that E^* for all of the P*n*P in isotropic CM are very near the activation energy for rotation about a C—C bond.[110] This supports the contention that in isotropic media, the conformational dependency of intramolecular quenching in P*n*P has a length independent rate-limiting step (probably rotation about one bond).

In the cholesteric phase of CM, the values of E^* vary widely, depending upon the length of the P*n*P chain (Table 14). Anderson, Weiss and Sonnenschein[12,13] interpret these data as further evidence

Table 13. Activation parameters for fluorescence quenching of PnP in various anisotropic solvents[12,13]

PnP $n =$	Solvent	Phase	E'_3* (kcal/mol)	$\Delta S^{\ddagger}_3$* (cal/mol-deg)
3	CM	Cholesteric	10.5 ± 0.4	1 ± 1
		Isotropic	10.1 ± 0.2	0 ± 0.1
	BCCN	Nematic	5.9 ± 0.3	-11 ± 1
5	CM	Cholesteric	16.7 ± 1.9	16 ± 3
		Isotropic	9.8 ± 1.8	-5 ± 3
	CCl/CN	Cholesteric	17.1 ± 0.8	20 ± 3
	CO	Cholesteric	22.5 ± 2	36 ± 3
6	CM	Cholesteric	8.8 ± 0.6	-11 ± 3
		Isotropic	9.4 ± 2	-9.4 ± 6
7	CM	Cholesteric	No quenching observed	
		Isotropic	No quenching observed	
9	CM	Cholesteric	16.1 ± 1.0	16 ± 2
		Isotropic	8.9 ± 2.0	-6 ± 4
	CO	Cholesteric	27 ± 0.5	48 ± 3
10	CM	Cholesteric	5.7 ± 0.2	-16 ± 1
		Isotropic	11.7 ± 0.9	3 ± 2
	BCCN	Smectic	8.1 ± 0.8	-9 ± 3
		Nematic	7.1 ± 0.3	-11 ± 1
11	CM	Cholesteric	28 ± 1	53 ± 3
		Isotropic	12.1 ± 1.4	2.9 ± 2
12	CM	Cholesteric	25 ± 1.8	47 ± 3.5
		Isotropic	12.3 ± 0.7	4.3 ± 1
	CCl/CN	Cholesteric	15.1 ± 2.5	12 ± 1
	CO	Cholesteric	26.8 ± 2.3	51 ± 4
13	CM	Cholesteric	11.5 ± 0.5	3 ± 2
		Isotropic	11.8 ± 0.8	4 ± 2
22	CM	Cholesteric	16.1 ± 0.4	15 ± 1
		Isotropic	12.9 ± 0.5	6 ± 2
	BCCN	Nematic	9.8 ± 0.5	-3 ± 2

* Errors are expressed as one standard deviation.

that solvent order is influencing PnP conformational energies and the barriers which must be overcome to achieve the excimer geometry.

Sonnenschein[13] demonstrated conclusively that these effects are not due to subtle changes in cholesteric pitch (which might influence the mobility of PnP movements). Thus, P12P fluorescence quenching was examined at 55°C in various mixtures of CCl and CN which included very large changes in cholesteric pitch. The k'_3 values, obtained as before using **56** in the same mixtures as a model for $k'_1 + k'_2$, are displayed versus solvent pitch in Fig. 11. All of the k'_3 are within experimental error of each other.

In spite of the large effort given this problem, it is obvious that several important questions remain unanswered or only partially addressed. For instance, the preference of PnP to interact with

Table 14. E* of PnP in cholesteric CM[13]

PnP $n =$	E* (kcal/mol)
3	1.6
5	7.8
6	-0.1
9	7.2
10	-3.2
11	19.1
12	16.1
13	2.6
22	7.2

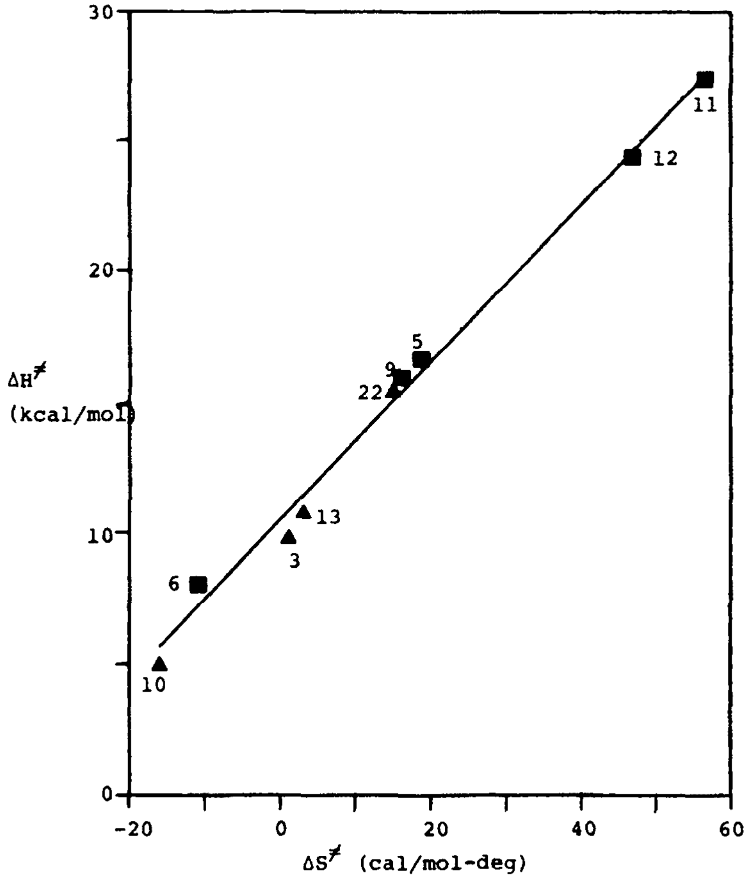


Fig. 10. Isokinetic plot of activation parameters for P*n*P intramolecular excimer formation in cholesteric CM.[12,13] Data in ref. 12 (▲) is converted to from E'_3 to $\Delta H^{\ddagger}_3$ by subtraction of RT (T = 310 K) from the former.

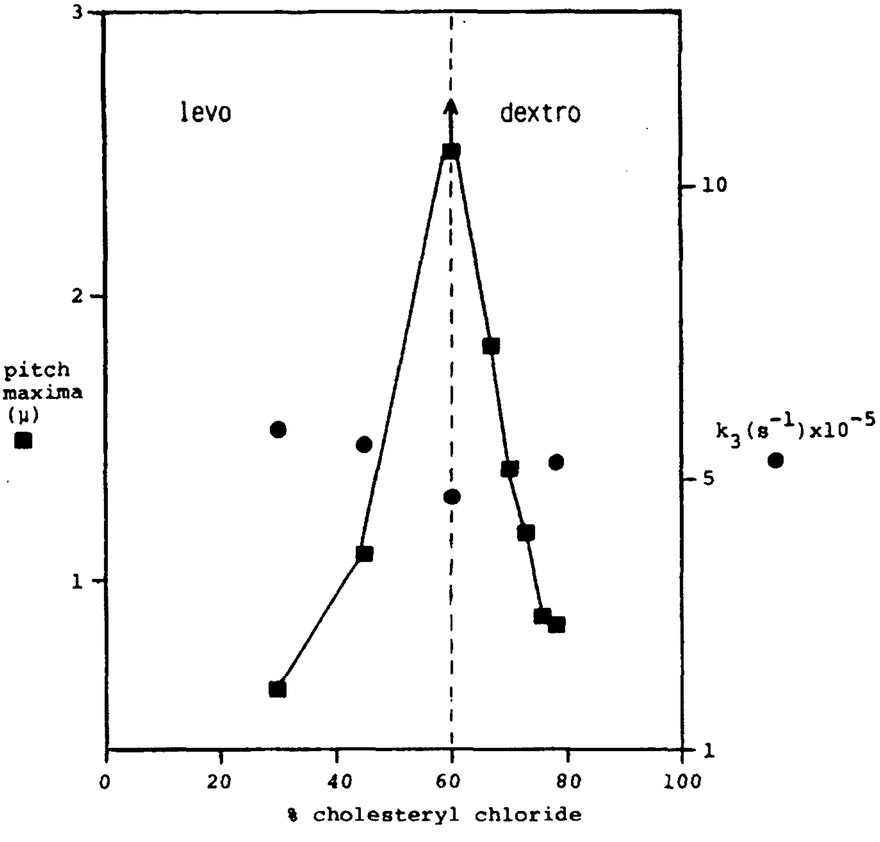
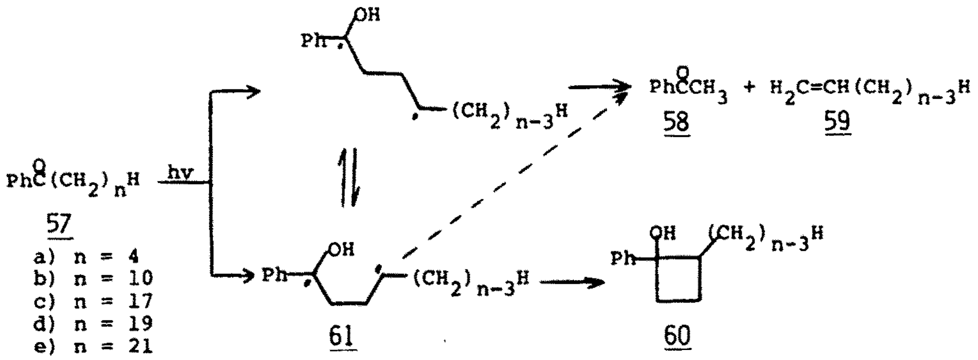


Fig. 11. Cholesteric pitch maxima (■) for CN/CCl mixtures and k'_3 values (●) for P12P at 50°C.[13] The pitch at 60% CCl was greater than the maximum of the instrumental range (2.5 μ). *Dextro* and *levo* refer to the twist direction of the pitch.

particular cholesteric molecules, the degree to which P*n*P molecules disturb their local environment, and the extent to which P*n*P molecules are extended before excitation all need to be explored further.

In a more systematic attempt to determine the influence of mesophases on Norrish II reactions,[97] Hrovat *et al.*[111] irradiated a series of alkylphenones (**57a–e**) in the condensed phases of BS[112] and in several isotropic solvents. The alkylphenones produce elimination products (E) **58** and **59** and cyclization products (C) **60** through different conformations of a common triplet 1,4-biradical intermediate **61** [eqn (26)].



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The ratio of E/C products (**58/60**) reflects the populations of **61t** and **61c** at the moment of their intersystem crossing to singlets and, therefore, the ability of an anisotropic matrix to influence chain motions of **61**. The total length of the ketones was chosen to span lengths much shorter than, about the same as, and longer than that of BS. Results of the photolyses are summarized in Table 15. It should be noted that heptadecane is a solid and BS is a smectic B mesophase at 20°C; both solvents are isotropic liquids at 30°C. In none of the non-mesomorphic solvents is a marked temperature effect on the **58/60** ratio observed. Only for those ketones whose lengths are near that of the BS solvent were large changes in product ratios between 20°C (smectic B) and 30°C (isotropic) observed. More complete profiles of the temperature dependence on the **58/60** ratios were reported for **57b** and **57d** (Fig. 12). They show clearly that the influence of solvent order on the reaction of **57** in both the smectic B phase of BS and its solid phases, which are organized like the smectic E phases, is large only when the solute is near in length to the solvent. The **58d/60d** increase is about constant throughout the smectic phase of BS but rises rapidly in the solid phase and appears to plateau again

Table 15. E/C product ratios* from **57** in several solvents[111]

		Solvent			
57		*n*-Heptane	*n*-Butyl acetate	*n*-Heptadecane	BS
a	30°C	2.3	4.2	1.9	3.2
	20°C	2.6	4.1	2.9	3.3
	20°C/30°C	1.2	1.0	1.5	1.0
b	30°C	0.8	2.0	1.3	1.7
	20°C	0.7	1.9	1.7	2.0
	20°C/30°C	0.9	0.9	1.3	1.2
c	30°C	1.1	2.0	1.0	3.0
	20°C	1.1	2.2	1.2	21
	20°C/30°C	1.0	1.1	1.2	7.0
d	30°C	1.8	2.0	1.0	1.9
	20°C	1.5	2.0	0.7	15
	20°C/30°C	0.8	1.0	0.7	7.9
e	30°C				1.3
	20°C				9.5
	20°C/30°C				7.5

* Values are not corrected for differences in detector response (error ± 10%).

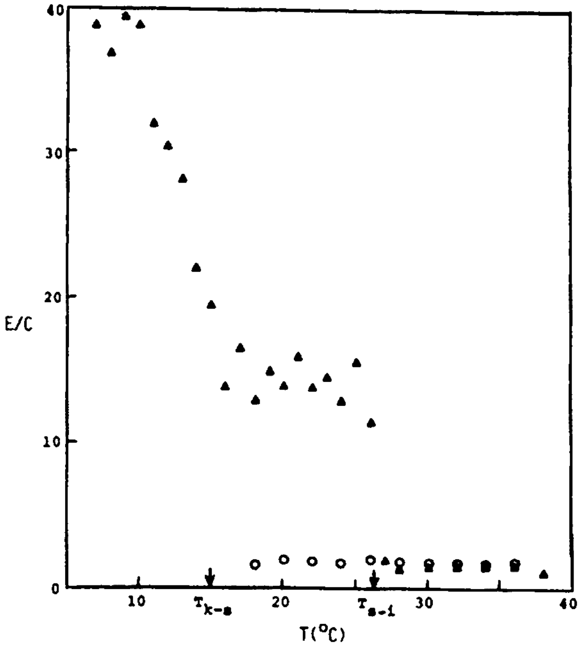
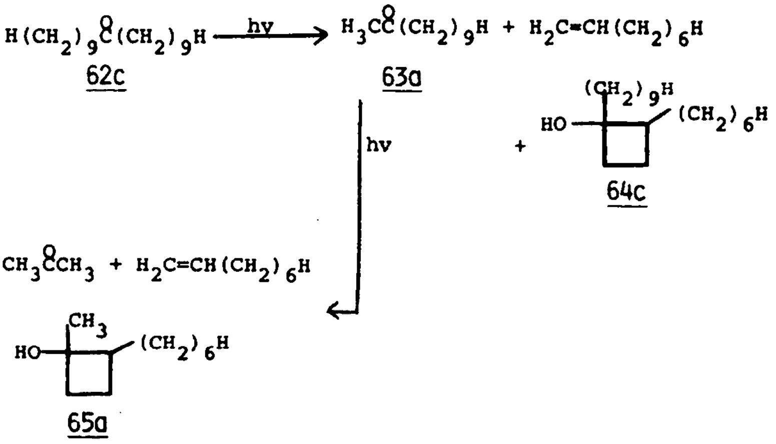


Fig. 12. Temperature dependence on the ratio of elimination (**58**) to cyclization (**60**) products for photolysis of **57b** (○) and **57d** (△) in BS.[111] Solvent transition temperatures are shown with arrows.

near the solid–solid phase transition.[112] The solid smectic E-like phases are somewhat similar in organization to the smectic B phase but less mobile and with fewer gauche defects along the polymethylene chains; as a consequence of the dampened rotation along the BS long axes, the solid layers are orthorhombically packed.

Hrovat *et al.*[111] explained the results in Table 15 and Fig. 12 on the basis of molecules like **57c**–**57e** replacing effectively solvent molecules in BS matrices. The shorter **57**, being incapable of occupying fully the space allocated a BS molecule, disrupt their environment and make it more fluid. Thus, the more ordered *and* selective cybotactic regions of **57c**–**57e** exercise greater control over solute motions. Since formation of **60** requires chain kinking while formation of **58** can occur from the preferred *all-trans* conformation of **61**, cyclization is attenuated greatly with **57c**–**57e**. Perhaps surprisingly, the triplet lifetime of **61** was found to be the same within experimental error in the smectic (20°C; $\tau = 70 \pm 5$ ns) and isotropic (30°C; $\tau = 64 \pm 5$ ns) phases of BS: **61t** and **61c** are not expected to exhibit the same triplet lifetime.[113] Yet, their relative populations are inferred to be very different in smectic and isotropic BS on the bases of product yields and solvent order.

Complementary results were obtained with two alkanones (**62c** and **63a**).[111] Irradiation of **62c** allowed both its E/C ratio and the *trans*/*cis* ratio of diastereomeric cyclobutanols from **62c** and **63a** (**64c** and **65a**), as shown in eqn (27), to be monitored. The ratios from **62c** favored elimination and



(27

trans-**64c** to a much greater extent in the very ordered smectic B phase of BS than in its isotropic phase. However, the cyclobutanol ratio from **63a** did not change with BS phase. These results suggested, again, the necessity of solute–solvent size and shape matching if solvent order is to be felt by a reacting solute. Although the results with **57a**, **57b**, and **63a** support the hypothesis that they create local disturbances to the BS smectic matrix, further evidence for this conclusion was clearly needed.

Treanor and Weiss[114] investigated in detail the dependence of Norrish II product selectivity on **62** and **63** chain lengths. Results from the 2-alkanone and *sym*-alkanone series are collected in Tables 16 and 17, respectively. At the concentrations of **62** and **63** employed ($\leqslant 1.4\%$ by weight), virtually no evidence for macroscopic disruption of solvent order was observed. The E/C and *trans*/*cis* cyclobutanol (*t*/*c*) ratios respond only to mesophase and solid BS order and only for those **62** whose extended lengths are near that of BS. The selectivity with **63** is greatest when its extended length is near that of the stearoyl portion of BS. These relationships are mirrored by the smectic → biphasic phase transition temperatures for 50% (by weight) of the ketones in BS (Fig. 13). Dipole–dipole

Table 16. Norrish II product ratios from **62** in BS[114]

62	Carbon chain length	Temperature (°C)	E/C	*t*/*c*
a	11	30	2.0±0.4	1.8±0.5
		20	1.8±0.4	1.5±0.5
		10	2.0±0.3	1.6±0.3
		0	2.0±0.3	2.0±0.4
b	15	RT*†	1.4±0.1	1.2±0.1
		30	1.9±0.5	2.4±0.6
		20	2.3±0.3	2.8±0.5
		10	3.2±0.6	3.5±0.4
		0	3.6±0.5	3.5±0.6
c	17	RT*†	1.8±0.1	1.3±0.1
		30	2.2±0.6	2.2±0.6
		20	3.2±0.8	10.8±1.6
		10	7.0±1.0	11.5±2.3
		0	10.0±2.5	6.8±0.3
d	19	RT*†	1.8±0.1	1.3±0.1
		30	2.0±0.3	1.8±0.2
		20	6.2±0.9	13.3±0.3
		10	10.0±2.3	11.3±0.9
		0	15.9±1.8	4.2±0.2
e	21	RT*†	1.8±0.2	1.2±0.1
		30	2.0±0.2	2.5±0.6
		20	5.5±1.0	14.1±0.1
		10	15.0±5.0	12.0±3.0
		0	>15	6.0±2.0
f	27	RT*†	2.0±0.1	1.3±0.1
		30	2.8±0.5	2.2±0.3
		20	3.2±0.5	7.2±0.5
		10	6.3±1.3	6.1±0.7
		0	7.5±1.3	4.0±0.3
g	29	30	2.7±0.7	2.2±0.3
		20	3.6±0.5	5.9±0.1
		10	2.9±1.1	7.0±0.3
		0	2.3±0.6	2.5±0.3
h	31	RT†‡	2.8±0.3	3.7±0.1
		42‡	2.8±0.2	3.6±0.3
		42	3.9±0.5	2.1±0.1
		20	3.0±0.5	5.5±0.5
		10	2.3±0.5	5.0±0.1
		0	1.7±0.6	3.1±0.3

* *t*-Butyl alcohol as solvent.
† At ambient room temperature.
‡ Hexane as solvent.

Table 17. Norrish II product ratios from **63** in BS[114]

63	Carbon chain length	Temperature (°C)	E/C	*t*/*c*
a	11	RT*†	2.3±0.3	2.0±0.2
		30	2.9±0.3	1.3±0.1
		20	3.1±0.3	1.2±0.1
		10	2.6±0.3	1.2±0.1
		0	3.6±0.6	1.2±0.1
b	13	RT*†	2.8±0.1	1.5±0.1
		30	3.5±0.4	1.5±0.1
		20	4.0±0.3	1.4±0.1
		10	4.2±0.4	1.3±0.1
		0	8.1±1.2	1.3±0.2
c	15	39*	2.9±0.1	1.2±0.1
		39‡	3.3±0.2	2.8±0.1
		30	3.6±0.2	1.3±0.1
		20	11.7±1.7	1.3±0.3
		10	19.8±1.7	1.8±0.1
		0	20.5±2.5	1.6±0.2
d	17	39*	2.7±0.3	1.3±0.1
		39‡	3.9±0.5	3.1±0.2
		30	3.7±0.4	1.5±0.1
		20	15.1±2.7	1.9±0.3
		10	27.4±3.2	1.9±0.3
		0	40.0±6.2	2.0±0.3
e	18	30	3.7±0.4	1.1±0.1
		20	14.8±2.3	1.6±0.2
		10	31.3±3.3	1.3±0.2
		0	42.3±7.0	1.7±0.2
f	19	39*	2.9±0.2	1.3±0.1
		30	4.1±0.2	1.3±0.2
		20	16.5±1.6	2.4±0.1
		10	22.8±3.8	2.5±0.1
		0	29.4±4.6	2.5±0.3
g	20	RT†‡	5.0±0.2	2.4±0.1
		30	3.9±0.5	1.0±0.1
		20	10.4±1.7	1.5±0.1
		10	18.5±3.0	1.5±0.2

* *t*-Butyl alcohol as solvent.
† At ambient room temperature.
‡ Hexane as solvent.

stabilized association between the carbonyl groups of **63** and the carboxyl groups of neighboring BS molecules were used to explain the results with the 2-alkanones: **63** longer than *ca* 19 carbons force either the carbonyl to be removed from the area near the carboxyl of BS or the ketone chain to kink or span a layer boundary. None of these options is energetically attractive to the system. The location of the carbonyl of **62**, in the center of the molecules, precludes carbonyl–carboxyl interactions unless somewhat unfavorable packing arrangements or conformations of the ketones obtain. The data support strongly a solubilization environment in which the ketone chains are fully extended and lie within a solvent layer parallel to the BS molecules. They are not consistent with reaction occurring from microcrystallites of solute since solid *n*-alkanones do not undergo Norrish II reactions.[114b,115]

More complete temperature profiles for product ratios from **62d** in BS versus temperature (and phase) are shown in Figs 14 and 15. That the two curves exhibit different shapes infers that BS solvent order influences differently the motions of the triplet hydroxyl-1,4-biradical intermediates which lead to elimination or cyclization (*transoid* ⇄ *cisoid* conformational changes) and to *trans*- or *cis*-cyclobutanols (diastereomeric conformational changes of the *cisoid* conformer).

The differences exhibited in Figs 14 and 15 between the solid smectic E-like phase of BS and its smectic B phase[116] are intriguing since their packing arrangements are very similar. To explore the

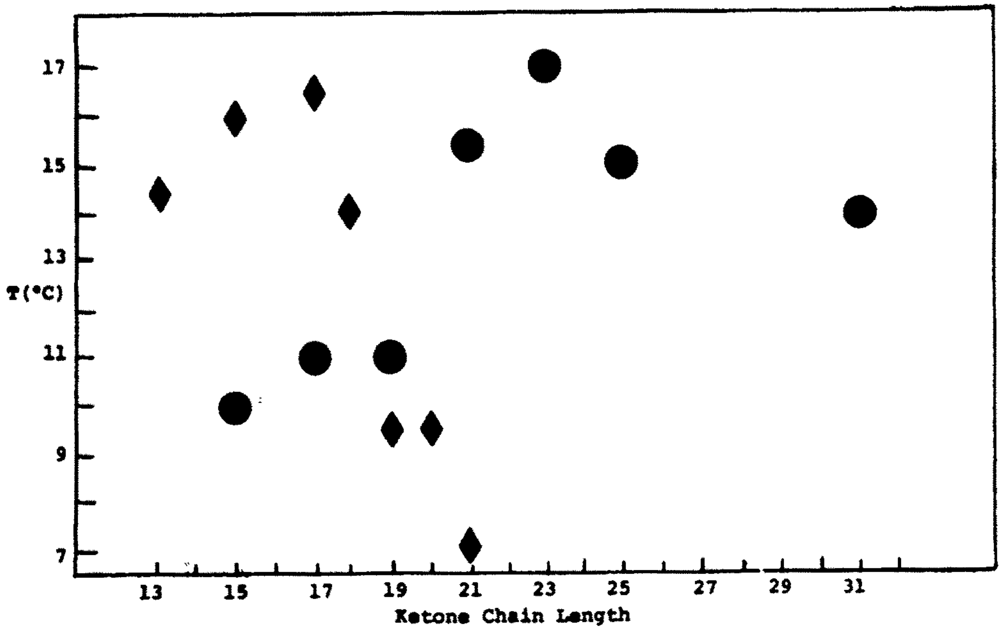


Fig. 13. Smectic → biphasic transition temperature for 50% (by weight) of **62** (○) and **63** (◆) in BS.[114] [Reprinted with permission of Pergamon Journals, Ltd.]

source of the differences, the Norrish II reactions of **62** and **63** (1% by weight) were examined in the isotropic and two solid phases of heneicosane ($C_{21}H_{44}$).[117] The organizations of the solid phases of heneicosane (phase I below 32.4°C[118] and phase II from 40.2°C to 32.5°C[119]) are very similar to the smectic E-like and smectic B packing, respectively, of BS.[118,119] Heneicosane also lacks a polar carboxyl group, so that specific ketone–solvent interactions are eliminated: product ratios from **62** and **63** should be determined almost exclusively by size and shape considerations.

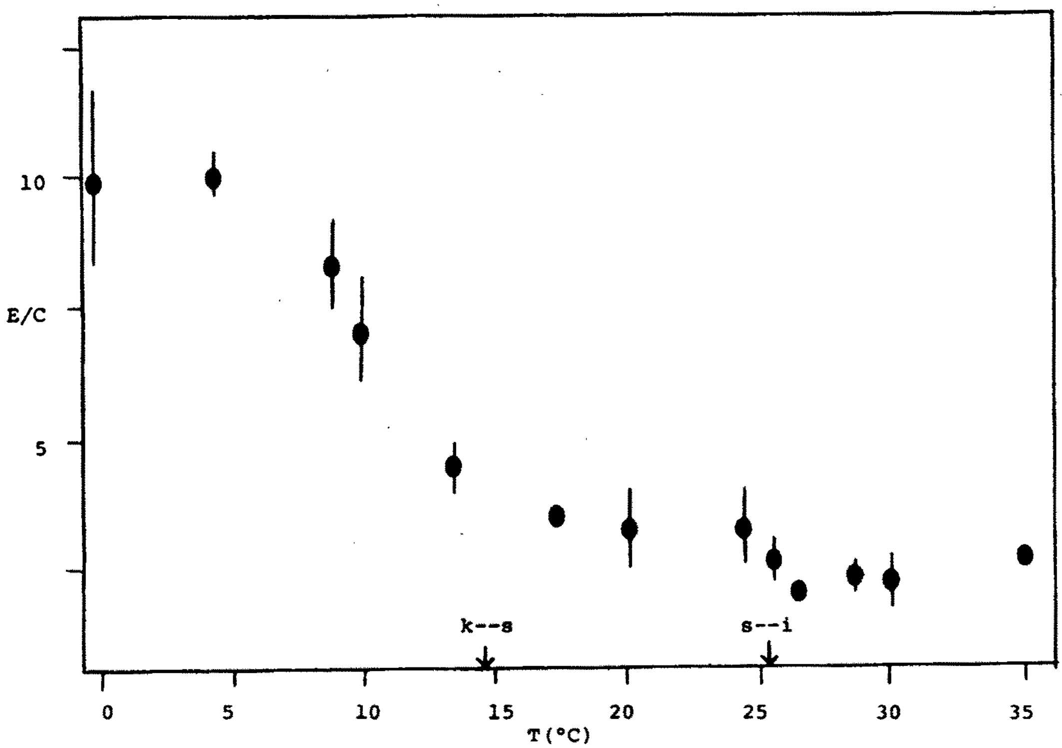


Fig. 14. E/C ratios from *ca* 1% (by weight) of **62c** in BS as a function of temperature.[114] Solvent transition temperatures are noted with arrows. [Reprinted with permission of Pergamon Journals, Ltd.]

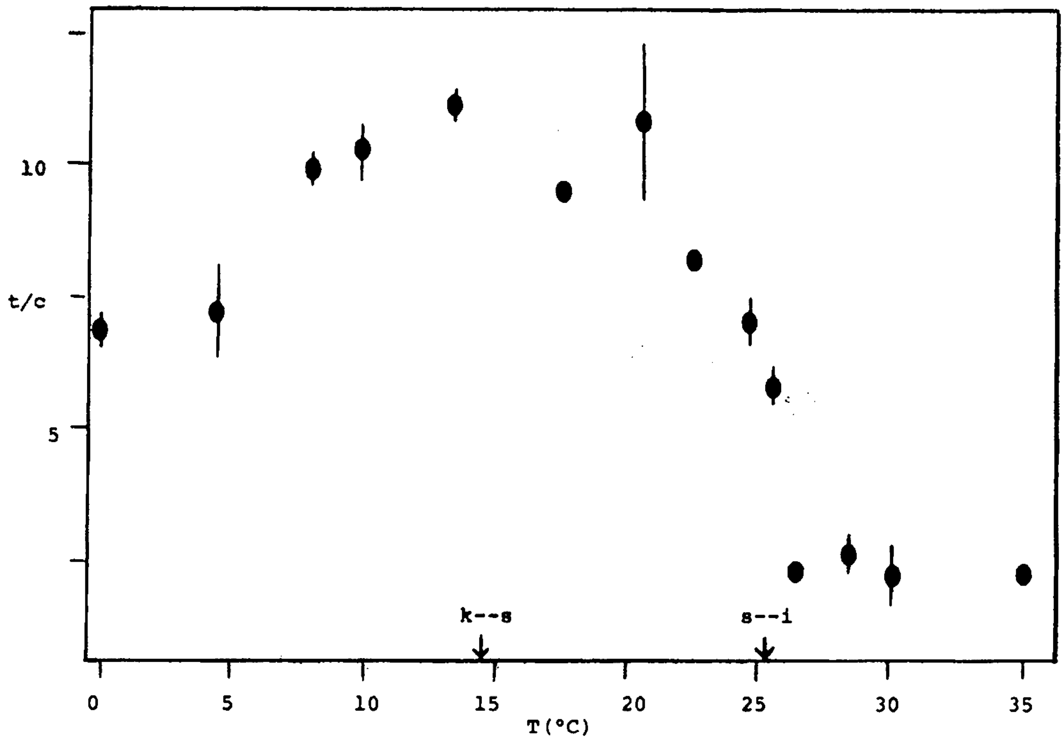


Fig. 15. *Trans/cis* cyclobutanol ratios from *ca* 1% (by weight) of **62c** in BS as a function of temperature.[114] Solvent transition temperatures are noted with arrows. [Reprinted with permission of Pergamon Journals, Ltd.]

The data in Table 18 indicate for phase I a very high selectivity of the E/C ratios from both **62** and **63** which match *exactly* the heneicosane chain length. The drop in E/C ratios for ketones which are slightly longer or shorter than heneicosane is especially abrupt in **62**. Surprisingly, very little, if any E/C selectivity occurred with the same ketones in phase II of heneicosane. As with BS, the kinking motions required to form the *cisoid* conformer of the hydroxy-1,4-biradicals must be less inhibited in the smectic B-like environment of phase II (which includes more *gauche* kinks of the solvent molecules)[118] than in the smectic E-like packing arrangement of phase I.

Table 18. Norrish II product ratios from 1% by weight of **62** and **63** in the isotropic (45°C), the hexagonal solid (35°C; phase II), and orthorhombic solid (25°C; phase I) phases of heneicosane[117]

Chain length of ketones	*T* (°C)	62		63	
		E/C	*t/c*	E/C	*t/c*
15	45	1.5±0.1	2.1±0.1	3.3±0.1	1.9±0.2
	35	1.8±0.4	1.8±0.1	3.7±0.3	2.4±0.2
	25	2.6±0.1	1.5±0.1	16.2±0.4	3.0±0.1
17	45	1.4±0.1	2.4±0.1	3.3±0.2	1.7±0.4
	35	2.4±0.1	5.9±0.1	4.6±0.7	3.4±0.2
	25	5.0±0.9	1.5±0.7	15.0±4.0	2.4±0.4
21	45	1.8±0.1	2.5±0.1	2.4±0.6	1.0±0.1
	35	3.5±0.1	24.9±3.0	5.7±1.3	2.5±0.2
	25	69.0±7.0	0.9±0.4	46.0±16.0	3.6±0.9
23	45	2.0±0.1	2.0±0.2	3.1±0.7	1.9±0.2
	35	2.9±0.1	10.8±0.5	1.6±0.3	2.4±0.2
	25	8.1±0.3	9.0±0.8	3.6±0.1	3.0±0.1
25	45	2.3±0.4	2.9±0.3		
	35	2.9±0.5	18.0±1.0		
	25	4.3±0.6	15.0±0.7		

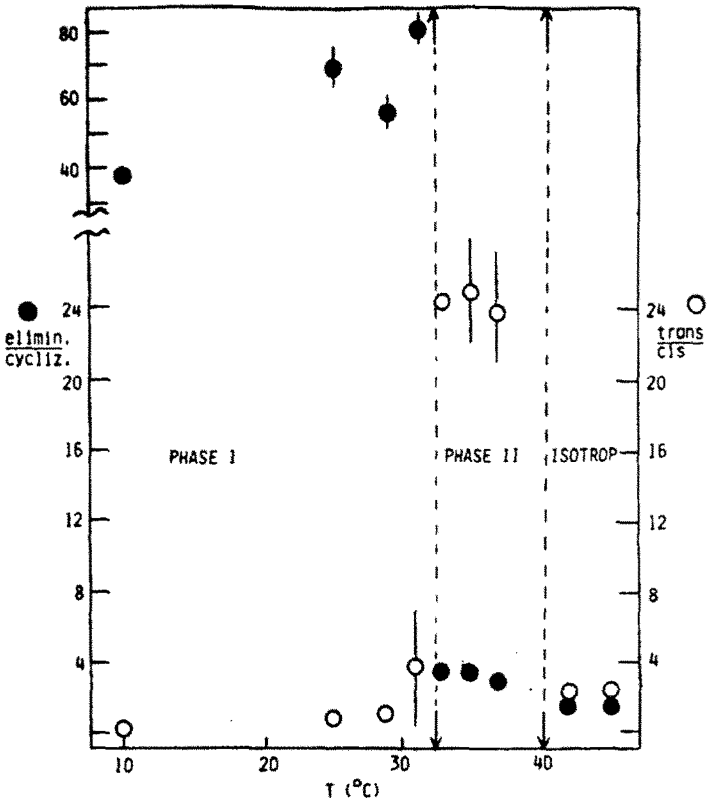


Fig. 16. Norrish II photoproduct ratios from 2% (by weight) **62e** in heneicosane versus temperature.[117] Phase transition temperatures are shown with arrows. [Reprinted with permission of the American Chemical Society.]

By contrast *t/c* product selectivity was noted only in phase I and only with the symmetrical ketones! The **62** longer than heneicosane did lead to some (as yet) unexplained *t/c* selectivity on phase I but no selectivity was detected from irradiation of any **63** in phase I or phase II. The latter result is, perhaps, not very surprising since *gauche* conformational defects are much more prevalent near the ends of heneicosane chains in the solid phases[118] and heneicosane lacks the attractive carboxyl 'anchor' of BS. In fact, the very small amounts of **64e** and the low ratio of its diastereomers, obtained from irradiations in phase I of heneicosane (Fig. 16) may arise from **62e** located in crystal defect sites which do not represent the environment of the vast majority of solutes. Regardless of its cause, the differences in product ratios between phase I and phase II are remarkable. They follow the qualitative trends observed for irradiation of **62c** in BS,[114] but are larger in magnitude.

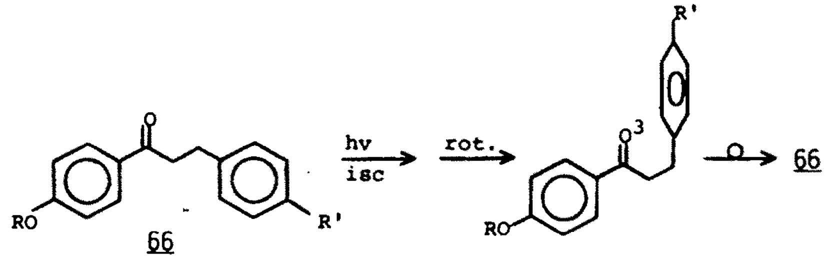
BCCN exhibits a slightly interdigitated smectic B-like mesophase[120] and a nematic phase. Several homologs exhibit smectic and nematic phases which resemble those of BCCN.[14a,120,121] For instance, the solid phases of both BCCN and *trans,trans*-4-ethyl[1,1′-bicyclohexyl]-4′-carbonitrile (ECCN) are layered and interdigitated, resembling closely a very immobile smectic phase.[14,121] However, ECCN has a tilted smectic phase with rhombohedral packing within layers.[120]

The activation energies of intramolecular P*n*P ($n = 3, 10, 22$) fluorescence quenching in BCCN reported in Table 13 show that solute chain bending can be influenced by the solvent's nematic order.[12] Only for P10P were non-curved Arrhenius plots for quenching in the smectic phase obtained. At the time when the experiments with P3P and P22P in smectic BCCN were performed, the possibility that the curvature of their Arrhenius plots[70] *may* have been due to undetected solvent-related factors was not considered.

Recently, Fung and Gangoda[122,123] found that small amounts of some simple solutes (e.g. benzene and dioxane) induce a novel phase in BCCN (*p*-phase) which cannot be detected by optical microscopy, but which is easily seen by ^{13}C or ^{2}H magnetic resonance spectroscopy. Treanor and Weiss[124] have determined that the phase consists of neat BCCN into which are interspersed highly organized (smectic-like) micropools which consist of *ca* two solvent molecules for each solute (Gangoda and Fung arrived at 1.7/1 of solvent/benzene).[123] Interestingly, some, but not all, of the molecules whose chemistry has been investigated in the mesophases of BCCN initiate *p*-phase formation. The temperaures of the *p*-phase–smectic transition vary with solute structure but are ⩽35°C for all solutes investigated thus far.[124b] For this reason, all data for solute reactions reported at <35°C in BCCN may require some reinterpretation.

The extent to which BCCN mesophases can influence chain bending was investigated in detail by Leigh[125,126] who followed the rates of intramolecular phosphorescence quenching of a series of *p*-alkoxy *β*-phenyl propiophenones (**66**) which resemble the solvent in size and shape. Comparison experiments with **66** were performed in the isotropic phase of BCCN and in the isotropic and mesophases of ECCN.

Intramolecular quenching of the excited triplets requires that the (presumably) extended conformations bend into a much bulkier shape which brings the *β*-phenyl and excited carbonyl into proximity [eqn (28)].[127] This motion should be resisted strongly by BCCN and ECCN if the solutes



(28

R =	R' =
CH_3	H
C_5H_{11}	H
C_8H_{17}	H
CH_3	C_6H_{13}
CH_3	cyclohexyl
C_5H_{11}	cyclohexyl
C_8H_{17}	cyclohexyl

are well-incorporated into the mesophase matrices. The activation parameters obtained by Leigh are collected in Table 19. Since the activation parameters for any of the **66** were the same for each of the phases of ECCN, only one entry is included in Table 19. The BCCN nematic values include data from the isotropic phase.

The data for **66a** are the most remarkable in Table 19. E_a and $\Delta S^‡$ are 10 kcal/mol and 30 cal/mol-deg, respectively, more positive in smectic BCCN than in its nematic phase. Thus it appears that **66a** is very well ordered in smectic BCCN. Consistent with previous observations, the nematic phase data for all **66** are very similar to the isotropic (ECCN) activation parameters. Unfortunately,

Table 19. Activation parameters for intramolecular triplet quenching of **66** in smectic or nematic BCCN and in ECCN[126]

			ECCN		BCCN (nematic)		BCCN (smectic)	
66	R =	R′ =	E_a (kcal/mol)	$\Delta S^‡$ (cal/mol-deg)	E_a (kcal/mol)	$\Delta S^‡$ (cal/mol-deg)	E_a (kcal/mol)	$\Delta S^‡$ (cal/mol-deg)
a	CH_3	H	5.2±0.3	−10.9±0.8	6.7±0.3	−6.7±0.8	16.7±1.3	24±4
b	C_5H_{11}	H	5.3±0.3	−11.8±1.3	6.4±0.6	−8.1±1.8	5.3±1.4	−11.4±4.6
c	C_8H_{17}	H	5.5±0.2	−10.7±0.5	6.2±0.3	−8.7±1.1	5.2±1.3	−11.8±4.1
d	CH_3	C_6H_{13}	5.8±0.5	−7.3±1.6	7.4±0.9	−4.1±1.5	7.1±2.5	−4±8
e	CH_3	cyclohexyl	6.6±0.4	−5.1±1.2	8.3±0.7	−0.3±1.5	9.9±3.1	5±10
f	C_5H_{11}	cyclohexyl	6.6±0.4	−5.9±1.3	8.6±0.6	−1.1±1.0	9.1±1.7	1±5
g	C_8H_{17}	cyclohexyl	6.4±0.6	−7.0±2.0	8.0±0.6	−2.5±1.9	9.8±0.9	3.4±2.8

Leigh did not report the activation parameters for the ethoxy and propyloxy homologs of **66a**. Presumably, the E_a and $\Delta S^\ddagger$ for **66f** and **66g** (as compared to **66b** and **66c**) indicate that the former solutes do experience some solvent order. However, they are more disruptive to their local environment than the smaller **66a**. In fact, Leigh has found spectroscopic evidence for association between the benzoyl chromophore of **66a** and the cyano group of BCCN.[126] In mesophases, this may serve as an anchor, forcing the rest of the solute molecule to adapt according to available space in the matrix.[114b] Yet to be addressed is why the smectic phase of ECCN does not exert a similar control to that of the slightly different smectic phase of BCCN.

Zimmermann *et al.*[128] employed the solid, smectic B, nematic, isotropic, and (unknowingly) the *p*-phase of BCCN to study the influence of solvent order on the Norrish II photochemistry of four alkylphenones (**67**–**70**) whose size and shape are similar to those of the solvent. The E/C ratios were monitored carefully. The results, presented graphically in Figs 17–20, include deuterium quadrupolar splittings ($\Delta\nu_{90}$; indicated as filled circles) for **67**–**70** which are predeuterated at the carbon alpha to the carbonyl.[124] In general terms, the larger is $\Delta\nu_{90}$, the greater is the order experienced by the C—D bonds[129] (and, presumably for **67**–**70**, the rest of the molecule).

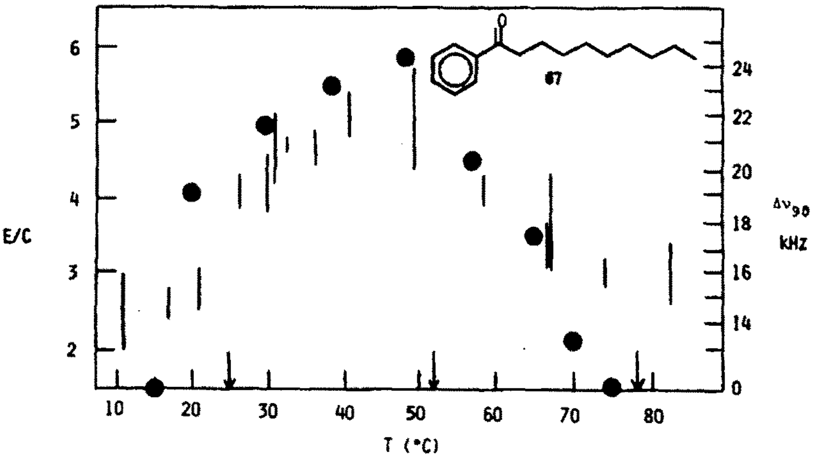


Fig. 17. E/C product ratios and deuterium quadrupolar splittings from **67** in BCCN.[124] The phase transition temperatures are marked with arrows. [Reprinted with permission of the American Chemical Society.]

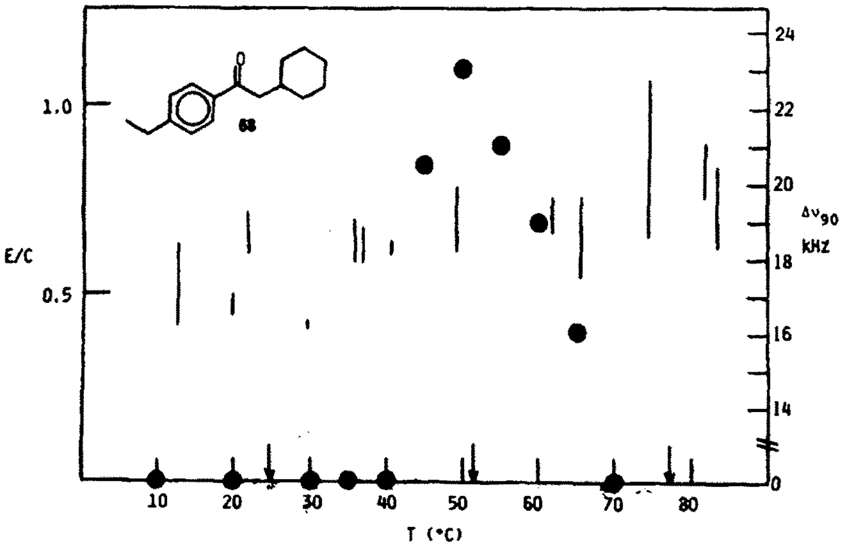


Fig. 18. E/C product ratios and deuterium quadrupolar splittings from **68** in BCCN.[124] The phase transition temperatures are marked with arrows. [Reprinted with permission of the American Chemical Society.]

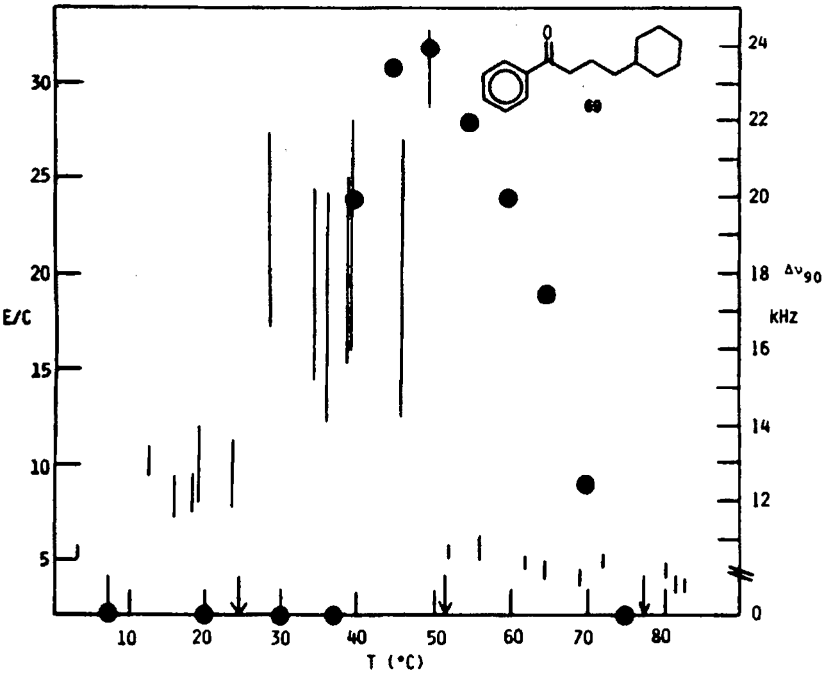


Fig. 19. E/C product ratios and deuterium quadrupolar splittings from **69** in BCCN.[124] The phase transition temperatures are marked with arrows. [Reprinted with permission of the American Chemical Society.]

As can be seen, there is no obvious correlation between the E/C ratios from **68**–**70** and $\Delta\nu_{90}$ values. The greater flexibility of **67**, both in terms of conformational and shape changes, is the probable source of its correlation. Further examples are required to test this hypothesis. The lower temperature point at which $\Delta\nu_{90}$ first reaches 0 Hz is taken to be the smectic-*p*-phase transition temperature. No discontinuities in the E/C ratios occur at this temperature (indicating that the *p*-

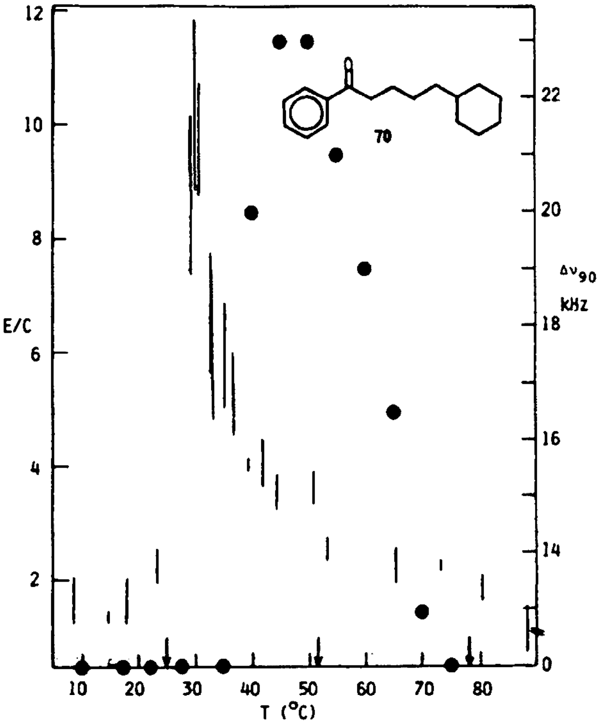


Fig. 20. E/C product ratios and deuterium quadrupolar splittings from **70** in BCCN.[124] The phase transition temperatures are marked with arrows. [Reprinted with permission of the American Chemical Society.]

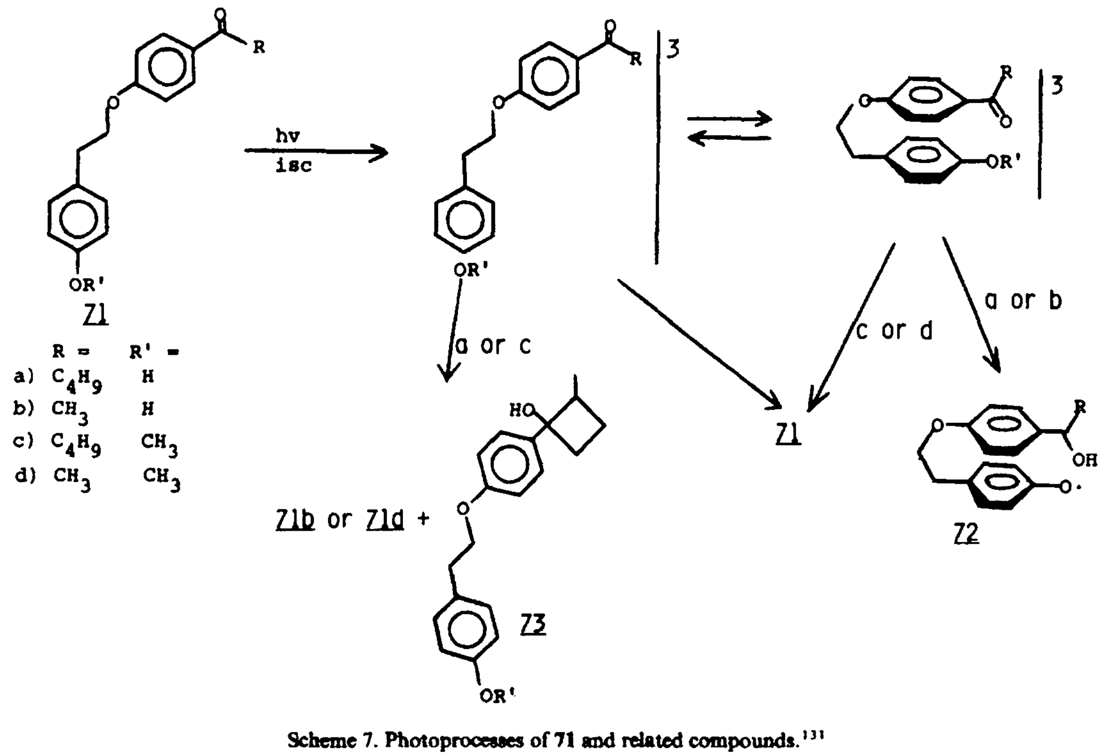
phase retains the smectic order of the bulk);[124a] if anything, the E/C ratios appear to track the macroscopically observed phase transitions. Except for **68**, the alkylphenones exhibit the greatest product selectivity in the smectic phase of BCCN: the *p*-methyl homolog of **68** has been shown to undergo the Norrish II reaction according to intramolecular constraints in its neat solid and in several isotropic solutions.[130] Thus, it is not surprising that **68** is imprevious to BCCN phase order also. The large differences in the E/C profiles for **67–70** demonstrate the sensitivity of solute structure to the influence of BCCN order on solute lability. A difference of only one methylene unit (**69** and **70**) leads to Norrish II selectivities whose phase responses and magnitudes are very dissimilar.

These differences contrast with the similarity among the $\Delta\nu_{90}$ curves for the same ketones (which show that the lability of the ketones depends upon the mobility of the solvent molecules themselves).

Further data concerning the relative control of solute chain bending and cyclization by smectic BCCN and ECCN was provided by Leigh and Jakobs.[131] They employed an ingenious system which allows remote hydrogen-atom abstraction to compete with Norrish II reactions (Scheme 7). The motions required of **71** to form the conformation necessary for hydrogen abstraction are similar to those for excimer formation in P3P.[12] However, the aromatic group of **71**, being much smaller than a pyrenyl ring system, disrupts BCCN solvent order to a lesser extent.

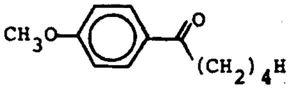
In isotropic solutions, formation of **72** from **73a** or **73b** occurs very efficiently and suppresses almost completely the Norrish II reactions of **71a**. Since **71c** undergoes the Norrish II reaction like *p*-methoxyvalerophenone (**74**), the lack of Norrish II products from **71a** cannot be attributed to charge-transfer or other photophysical interactions between the benzoyl triplets and the phenoxy groups. Time evolution of several of the transients in Scheme 7 was followed by nanosecond flash spectroscopy.

On the basis of optical microscopic investigations, both **71a** and **71c** were concluded to aggregate into ketone-rich nematic pools of BCCN which coexist with the smectic phase at temperatures which are well below the nematic–smectic phase transition temperature of the undoped solvent. These observations may require reinterpretation in light of the recent *p*-phase discoveries.[124] However, since similar concentrations of **71b**, **71d**, or **74** in BCCN did not induce optical patterns characteristic of a nematic phase at smectic phase temperatures, the bulk effects noted by Leigh and Jakobs[131] may be associated with classical disruption of solvent order by solutes.



Scheme 7. Photoprocesses of **71** and related compounds.[131]

Triplet lifetimes obtained for **71b** and **71d** in acetonitrile, the smectic phase of BCCN, and the nematic phase of a 2/1 (by weight) mixture of ECCN/BCCN are presented in Table 20. The extremely long lifetime of **71b** in smectic BCCN requires that the solvent matrix retard greatly the bending motions in Scheme 7 which lead to hydrogen abstraction. Even the nematic mixture (when compared with acetonitrile) is able to attenuate triplet quenching. The very small differences among the phases for the triplet lifetimes of **71d** reflect the very inefficient quenching of the benzoyl triplets by a methoxylphenyl group.



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Surprisingly, the E/C ratios from **71c** in several mesophases and methylcyclohexane exhibit no real differences. Only in the smectic phase of BCCN do the E/C and the *t*/*c* ratios of **74** exhibit any discernible solvent order related selectivity (Table 21). Thus, the combined data of Tables 20 and 21 indicate (as models in mesophases suggest) that the motions required to bring the two aromatic rings of **71** into a hydrogen abstraction (quenching) orientation are controlled much more than are the pentyl chain conformations of **71c** and **74**. Again, it should be noted that the orthorhombically packed smectic phase of ECCN is less selective than the hexagonally packed smectic phase of BCCN. In fact, from relative quantum efficiencies for the Norrish II reaction of **71a** and **71c**, the smectic phase of BCCN retards phenyl–phenyl overlap (i.e. hydrogen abstraction) *ca* 8 times more than does the smectic phase of ECCN.

These results and those cited from the work of others in this section demonstrate the promise and pitfalls of performing (unimolecular reactions in mesophases. When internally consistent comparisons of data have been gathered, mechanistically significant conclusions have followed. Clearly, there exists a very delicate balance between solvent order, solute structure, and intimate interactions between the two which determines the degree to which solute photochemical reactions will be affected by the solvent matrix. Before an *a priori* list of the important factors can be prepared and how each will influence a particular system is known quantitatively, much more data will be required.

Table 20. Triplet lifetimes of **71b** and **71d** in various solvents at 30°C[131]

	τ (μs)		
Ketone	CH_3CN	1/2 ECCN/BCCN (nematic)	BCCN (smectic)
71b	0.015	0.275	3.8
71d	2.3	5.6	11.0

Table 21. E/C* and *t*/*c* ratios from **71c** and **74** in several solvent systems at 30°C[131]

		Solvent				
Ketone	Ratio	CH_3CN	methylcyclohexane	1/2 ECCN/BCCN (nematic)	BCCN (smectic)	ECCN (smectic)
71c	E/C	6.4±0.5	15±2	20±3	19±2	17±2
74	E/C	4.4±0.3	4.2±0.4	6.1±0.2	9.2±0.3	4.7±0.3
	t/*c*	2.2±0.1	4.4±0.2	2.6±0.2	5.2±0.3	3.0±0.3

*The E/C ratios are not absolute since some decomposition of cyclobutanol occurred during analyses. However, comparisons of E/C ratios among the solvents are mechanistically useful.

6. BIMOLECULAR THERMAL REACTIONS

As mentioned in the Introduction, the first documented use of liquid crystals as reaction solvents was performed by Svedberg.[6] Since that time, several other examples of bimolecular reactions in mesophases have been performed.

Park and Labes[132] investigated the kinetics of Schiff base formation [eqn (29)] and amine exchange reactions of Schiff bases [eqn (30)] in a cholesteric solvent (CE) composed of 40% by weight of a 2/1.1/0.9 mixture of COC/CCl/CN and 60% by weight of 'Nematic Phase V' from Merck (a eutectic mixture of *p*′-ethyl-*p*-methoxyazoxybenzene and *p*′-*n*-butyl-*p*-methoxyazoxybenzene). By monitoring the shift of the pitch band maximum (which appears in the visible wavelength region) caused by reaction of chiral solutes, they were able to obtain rate constants and activation energies for the processes shown in eqns (29 and 30). Unfortunately, they did not investigate the kinetic properties of these reactions in an isotropic solvent; no mechanistic conclusions can be drawn from their data. However, it is somewhat surprising that the measured activation energies for eqn (29), especially (8.0 for **75a** and 6.1 kcal/mol for **75b**), are very low. The authors conjecture that undetected side reactions may have contributed to the observed changes in pitch.[132]

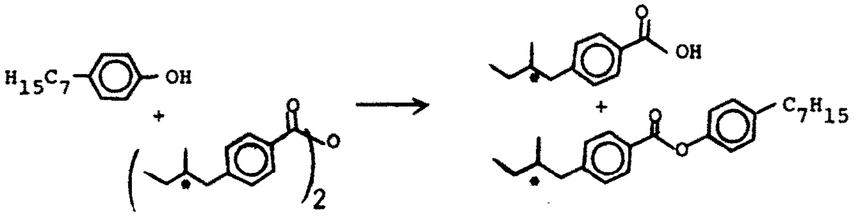
$$p\text{-}C_2H_5OC_6H_4CHO+\underset{\mathbf{75}}{H_2NR}\longrightarrow p\text{-}C_2H_5OC_6H_4CH{=}NR+N_2O \tag{29}$$

(a) R = (−)-α-phenethyl
(b) (−)-*p*-bromo-α-phenethyl

$$R'CH{=}NR+H_2NR''\longrightarrow R'CH{=}NR''+RNH_2 \tag{30}$$

(a) R = (+)-α-phenethyl, R′ = *p*-ethoxyphenyl, R″ = (−)-α-phenethyl
(b) R = (−)-α-*p*-bromophenethyl, R′ = *p*-ethoxyphenyl, R″ = (+)-α-phenethyl
(c) R = *p*-*n*-butylphenyl, R′ = *p*-ethoxyphenyl, R′ = (−)-α-phenethyl.

Okamoto and Labes[133] applied pitch band changes to measure the rate of formation of the ester from reaction of *p*-(*n*-heptyloxy)phenol and (+)-*p*-(2-methylbutyl)benzoic anhydride [eqn (31)] in a 40/60 by weight mixture of CN/*p*-pentylphenyl 2-chloro-4-(*p*-pentylbenzoyloxy)-



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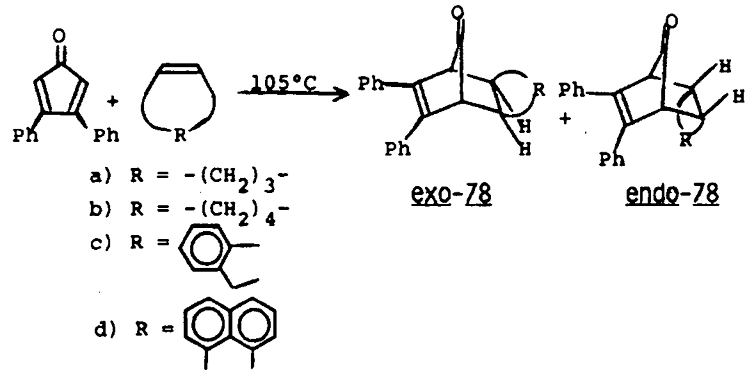
benzoate. The activation parameters obtained for this reaction ($\Delta H^{\ddagger} = 15.1 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -11.5 \pm 1.5$ cal/mol-deg are reasonable for a reaction of this sort in an isotropic solvent. In fact, contrary to Svedberg's reaction,[6] this esterification displayed no rate discontinuity at the cholesteric–isotropic phase transition: one straight line describes the Arrhenius plot for both phases.

The equilibration between 2-nitroso-2-methylpropane (**76**) and its dimer (**77**) has been examined in isotropic solvents and in the nematic phases of 4-methoxybenzylidene-4-butylaniline (MBBA).[96] At 25°C, $K_{eq} = ([76]^2/[77])$ follows the trend expected of a reaction in which separation of reacting partners is made more difficult in more viscous solvents: K_{eq} in MBBA is *ca* 10^{-2} the value in either benzene or heptane. The authors attributed the changes in K_{eq} to the shape of **77** being more easily incorporated in the nematic matrix than is the monomer **76**.

Photolysis of **76** is reported to be less efficient in the isotropic phase of MBBA than in its nematic phase.[96] The negative apparent activation energy calculated from initial rates in the nematic phase of MBBA and the lack of effect by another nematic solvent indicates that the source of the rate change is complex. Available experiments do not permit the various contributors to be dissected and analysed.

In the previous examples, the monitor of the bimolecular reactions is a function of the reaction itself, and the rates of solute diffusion through the solvent. By examining product ratios from the



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Diels–Alder reactions in eqn 32, Leigh was able to eliminate diffusion as a factor.[134] Leigh reasoned that the ratio of the two stereoisomeric adducts should be influenced by local solvent order to the extent that it affects the orientation of the collision complexes between the diene and dienophile. His results, summarized in Table 22, demonstrate that neither cholesteric nor smectic solvent order exerts an influence on the reaction comparable to diene-dienophile steric and electronic considerations. In retrospect, it is not surprising that no effect of solvent order was observed since neither the reactants nor products are expected to fit well into the mesophase matrices chosen.

A better engineered system has been reported recently by Leigh and Mitchell[135] who examined the thermal reactions between cholesta-5,7-dien-3β-yl acetate (**79**) and *N*-biphenylmaleimide (**80**). The isolated products are a mixture of Diels–Alder (**81**) and ene (**82** and **83**) adducts and an unidentified product (**84**).

Transition states for **81** and **82** require that **79** and **80** approach each other so that their long axes are nearly perpendicular. Formation of **83** can occur from a transition state which places the long axes of **79** and **80** nearly parallel. Thus, mesophase order is expected to encourage the transition state for **83** (and discourage those of **81** and **82**). Experiments in several solvents bear out the prediction (Table 23). Both the smectic B order of 4-(*trans*-4′-pentylcyclohexyl)-4′-(*trans*-propylcyclohexyl)biphenyl (S1544) and the cholesteric order of CBCl enhance the formation of **83**

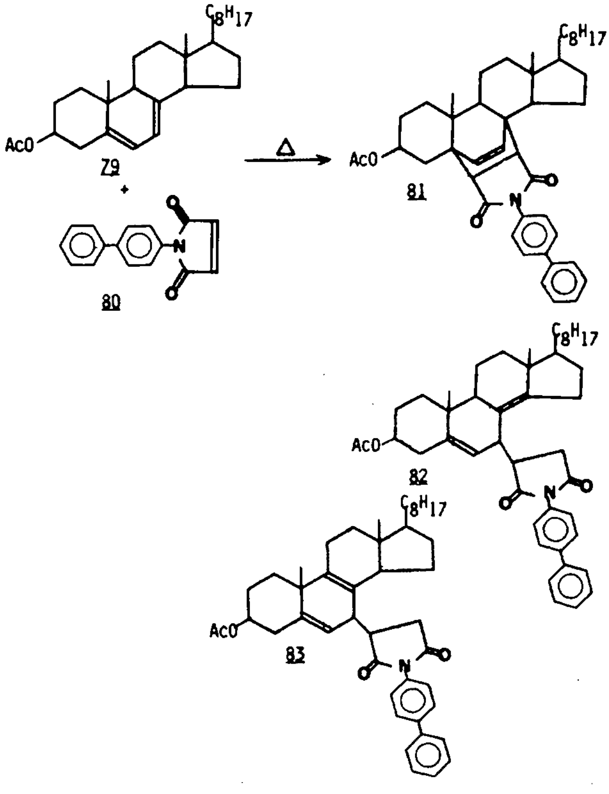

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Table 22. *Endo/exo* product ratios for the Diels–Alder reactions in equation 32[134]

Solvent (phase)	*endo/exo* of **78**			
	a	b	c	d
Benzene	0.91	2.6	4.5	8.3
CN (cholesteric)	0.93	2.6	4.5	8.5
(isotropic)	0.90	2.5	4.3	7.8
4-Ethyl-4′-(4-pentylcyclohexyl)biphenyl (smectic B)			4.6	

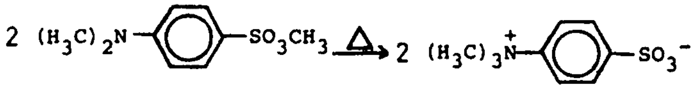
Table 23. Product yields and ratios from reaction of **79** and **80** in liquid-crystalline solvents at 200°C[135]

Solvent	Phase	Relative yields of products				
		81	**82**	**83**	**84**	(**81**+**82**)/**83**
Benzene	Isotropic	35	44	14	6	5.6
S1409	Isotropic	31	42.5	18.5	7.8	4.0
CB	Isotropic	31.1	42.1	16.8	9.5	4.4
CBCl	Cholesteric	21.2	33.3	32.3	13.0	1.7
S1544	Smectic B	20.7	31.3	39.2	8.8	1.3

at the expense of **81** and **82**. Although the effect is not large, it is clear and not easily attributable to factors other than solvent order. That a larger difference in product ratios between isotropic and meso solvents was not observed may be due to the disruptive influence of **79** and (especially) **80** to their *local* environments.

To date, Samori and coworkers have found the clearest example mesophase solvent control over a bimolecular reaction.[136] They showed first that intermolecular rearrangement of methyl *p*-(dimethylamino)benzenesulfonate (**85**) to *p*-(trimethylammonium)benzesulfonate (**86**), which is known to occur facilely in the neat crystal,[137] also occurs in some mesophases. In the very ordered smectic B phases of S1409 or S1544 of Merck, 1.5% by weight solutions of **85** led to relatively efficient rearrangement of **86**.[138] With even more forcing conditions, no formation of **86** was observed when the solvent was the nematic phase of BPCP. Samori concluded that the smectic phase favors face-to-face encounters between molecules of **85** (which are required for rearrangement to occur) but that nematic phases do not.[138]

Strong evidence for their hypothesis was found when the concentration of **85** was varied. The rate of reaction increased with higher initial concentration of **85** up to 6.8×10^{-2} M in smectic S1409. Above that concentration, the rearrangement rate *decreased* even though neat (crystalline) **85** exhibits the highest rearrangement rate: apparently, the disturbing influence of **85** on the smectic matrix (and, therefore, its ability to direct solute collision geometries) is more important than the greater collision probability.



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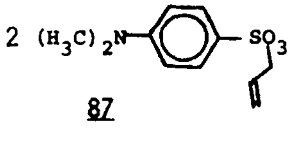
The same workers[139,140] then found that the allyl ester of **85** (**87**) undergoes the analogous rearrangement to yield **88** in smectic B phases, but not in nematic phases of the solvents above or in DCHC. The phase specific phenomenon is quite general.

Evidence for two solvation sites in smectic DCHC-*b* was obtained from linear dichroism measurements on **87**.[136] Whether they lead to different modes of solute reactivity is still a matter of conjecture.



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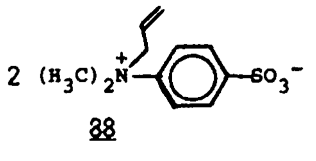

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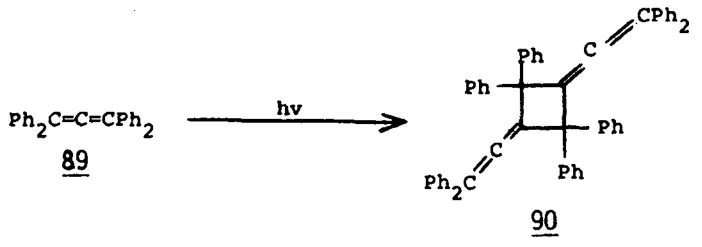
7. PHOTOCHEMICAL BIMOLECULAR PROCESSES

Tetraphenylbutatriene (**89**), dissolved in a compensated nematic phase (i.e. a cholesteric phase of infinite pitch) consisting of 1.95/1 (by weight) of CCl/cholesteryl laurate (CL) at 30°C, was shown by linear dichroism spectra to be oriented parallel to the long axes of the cholesteric molecules.[141] Upon irradiation of the solution, the sole product obtained was the dimer **90** [eqn (36)]. Irradiation of **89** in the isotropic (*ca* 80°C) and solid phases of CCl/CL or in the isotropic phase ($T \geqslant 40$°C) of the cholesteric mixture, to which had been added small amounts of diethylene glycol and dibutyl ether (to depress the phase transition temperature), led to no dimer. Since the linear dichroism spectra demonstrated that **89** are not aggregating to form microcrystals in the nematic phase, the authors proposed that the formation of **90** is due to an increase in the excited state lifetime of **89** and to the solvent order mediating collisional geometries between excited and ground state **89**.



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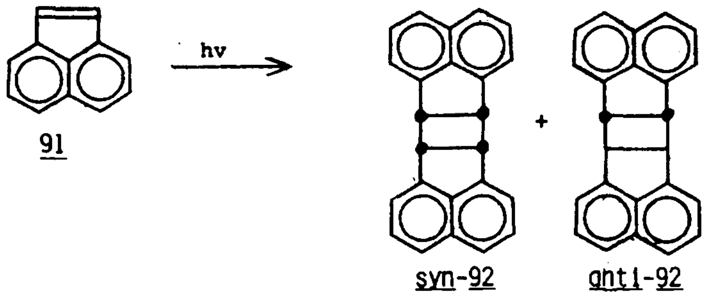

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Nerbonne and Weiss[142] examined in detail the influence of cholesteric phase order on the photodimerization of acenaphthylene (**91**, eqn 37).[143] They found that the distribution of *syn* and *anti* dimers (**92**) continues, as in isotropic solvents, to be controlled by the multiplicity of the excited state precursor.[143b] However, the efficiency of dimer formation is very dependent upon solvent phase, solute concentration, and the presence of disturbing molecules which do not interfere with the photochemistry.

As seen in Fig. 21, the quantum efficiency of dimerization (Φ_D) for 0.08 M **91** in BS and toluene vary similarly with temperature and are close in magnitude. No meaningful change in Φ_D occurred between the smectic (<25°C) and isotropic phases (>25°C) of BS.

By contrast, irradiation of the same concentration of **91** in a 1/1 (by weight) mixture of CHN/CHA led to Φ_D values which were *extremely* sensitive to solvent phase. In the isotropic phase of CHN/CHA, Φ_D is 2–3 times the value in toluene. Irradiation of 0.08 M **91** in the cholesteric phase (<48°C) increases the efficiency of formation of **92** by *ca* 10-fold and 20–25-fold over the values in toluene at the same temperature.

While it is not unreasonable that the BS smectic phase does not facilitate photodimerization—BS and **91** have very different molecular shapes—the large increase in Φ_D with CHN/CHA is quite surprising. There is at best a vague similarity between the plate-like **91** and the cholesteric esters of the solvent. In spite of this, the cholesteric phase appears to exert a significant control over the orientations and frequency of collisions of **91**: ignoring for simplicity's sake the influence of excited state multiplicity on Φ_D the rate of dimer formation can be expressed as $F_q \times F_c \times F_t$, the product of the frequency of excited **91** collisions with **91**, the fraction of those collisions which lead to **92**, and the excited lifetime of **91**, respectively. The dependency of Φ_D within the cholesteric phase, as shown

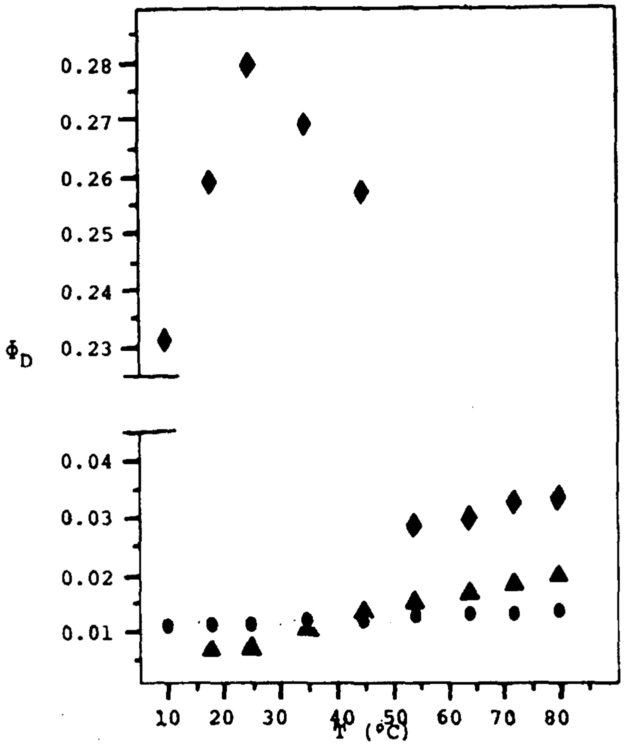


Fig. 21. Quantum efficiencies (Φ_D) for photodimerization of 0.08 M **91** in toluene (●), BS (▲); and a 1/1 (w/w) mixture of CHN/CHA (◆) as a function of temperature.[142b] [Reprinted with permission of the American Chemical Society.]

in Fig. 21, can be understood if F_q decreases and F_c and F_t increase as temperature decreases; below 25°C, the decreases in F_q cannot be compensated by the increases in F_c and F_t. The changes in F_t are expected to be smallest of the three variables.

To test this hypothesis, Nerbonne and Weiss added varying amounts of tetralin (a molecule which disrupts cholesteric order, increasing F_q and decreasing F_c, but which should not interfere with F_t) to the solutions of **91** in CHN/CHA. The data in Fig. 22 indicate that the greater solvent fluidity induced by tetralin is accompanied by an even greater chaos in collisions between molecules of **91**: Φ_D decreases as the concentration of tetralin increases.

That these results may be due, at least in part, to changes in cholesteric pitch, was indicated by the observation that at 25°C and the same initial concentration of **91**, Φ_D was over 8 times greater in a 70/30 mixture of CN/CCl (pitch $\simeq$ 2000 Å)[144] than in a 40/60 compensated nematic phase mixture of the same components (pitch $\rightarrow \infty$).[144]

Perhaps the best evidence against aggregation of **91** and for mesophase control over solute collisions being responsible for the reported changes in Φ_D was obtained from a study of the influence of initial solute concentration on dimerization efficiency in CHN/CHA. In an isotropic solvent, Φ_D should increase linearly with the concentration of **91** due to changes in frequency of collisions. Figure 23 shows that this is the case in isotropic CHN/CHA at 55°C. At 35°C, cholesteric CHN/CHA gives rise to Φ_D with a bizarre dependence on [**91**]: Φ_D is greatest at the lowest concentration of **91** employed! Were solute aggregation within the cholesteric phase responsible for the large Φ_D, it should not have decreased at larger solute concentrations. The decrease and subsequent increase in Φ_D with increasing [**91**] can be accommodated by a mechanistic model in which added **91**, much like added tetralin (Fig. 22), has a greater disruptive influence on solvent order *at low solute concentrations* than can be compensated by the increases in F_q. Above [**91**] $\simeq$ 0.08 M, the increase in F_q becomes greater than the decrease in F_c and Φ_D increases.[145]

A related photodimerization of 1,3-dimethylthymine (**93**) in solid, smectic, cholesteric, and isotropic phases was reported by Kunieda *et al.*[146] In polar isotropic solvents, four photodimers (**94**–**97**) are produced.[147] In less polar isotropic solvents, only **94** and **95** were detected in comparable

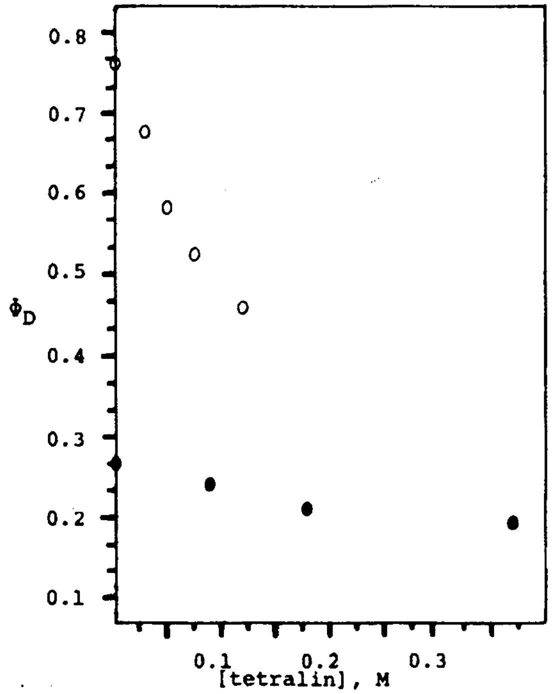


Fig. 22. Quantum efficiency (Φ_D) for photodimerization of 0.02 M (○) and 0.08 M (●) **91** in 1/1 (w/w) CHN/CHA versus the concentration of added tetralin.[142b] [Reprinted with permission of the American Chemical Society.]

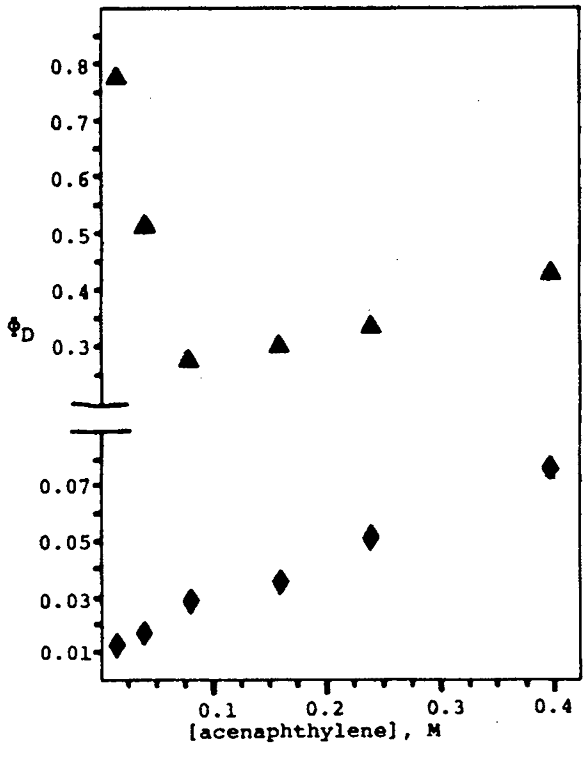
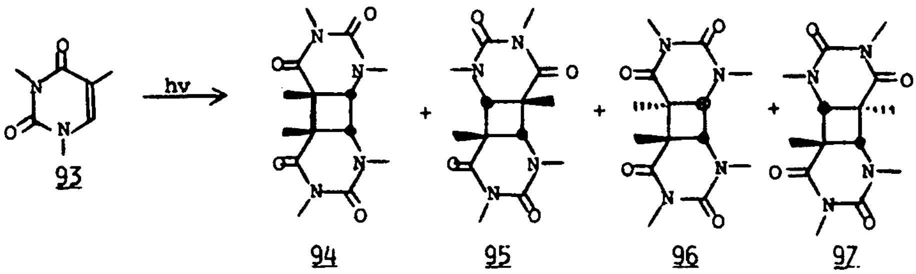


Fig. 23. Quantum efficiency (Φ_D) for the photodimerization of **91** in 1/1 (w/w) CHN/CHA at 35°C (▲) and 55°C (◆) as a function of the concentration of **91**.[142b] [Reprinted with permission of the American Chemical Society.]

Table 24. Photodimerization of **93** in various solvents[146]

Solvent	T (°C)	Phase	**94/95**
COC	−30	Solid	86/14
	10	Smectic	93/7
	23	Cholesteric	93/7
	43	Isotropic	71/29
Cholesteryl linoleate (CLI)	10	Solid	91/9
	30	Smectic	94/6
	43	Isotropic	77/23
BS	21	Smectic	94/6
	32	Isotropic	51/49
Dioxane	2	Solid	32/68

amounts (Table 24). Since high photoselectivity was observed in *all* the solid, cholesteric, and smectic phases employed, the origin of the product ratios is somewhat suspect: even the smectic phase of BS, whose constituent molecules differ from **93** in both size and shape, leads to a very high ratio of **94** to **95**. Regardless of the cause of this solvent-induced selectivity, it merits further study.



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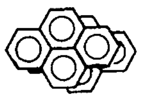
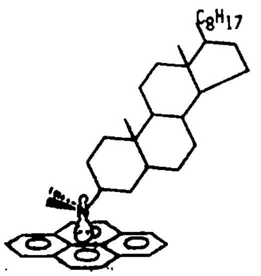
Anderson, Craig, and Weiss employed single photon counting techniques to follow the rate of fluorescence quenching (and excited state complex formation) of pyrene singlets by either pyrene (**98**)[101] or 5α-cholestan-3β-yldimethylamine (**99**)[100] in the isotropic and cholesteric phases of 59.5/15.6/24.9 (w/w/w) mixture of CO/CN/CCl. The quenching geometries for the pyrene excimer and the pyrene-**99** exciplex are very different. Whereas the excimer has the shape of two parallel plates (and should be formed by ^{1}**98**–**98** collisions whose orientations are like those leading to acenaphthylene dimers),[142] the exciplex is more similar to a rod intersecting a plate at a near-normal angle. This geometry allows overlap between the nitrogen lone-pair of electrons on **99** and the pi-system of **98** singlets.



excimer



exciplex

Table 25. Activation parameters for quenching pyrene singlets by **98** or **99** in CO/CN/CCl[100,101]

	98		**99**	
Quencher phase	Cholesteric	Isotropic	Cholesteric	Isotropic
E_a (kcal/mol)	8.9 ± 0.4	6.6 ± 0.6	9.9 ± 0.2	5.3 ± 0.1
$\Delta S^{\ddagger}$ (cal/mol-deg)	$+3 \pm 0.5$	-4 ± 0.5	$+5 \pm 0.6$	-10 ± 0.4

Dynamic Stern–Volmer plots[148] for pyrene fluorescence quenching by ($\lesssim 0.25$ M) **99** in CO/CN/CCl were curved, indicating that **99** causes a perceptible change in cholesteric solvent organization. Similar plots for pyrene fluorescence quenching by pyrene were linear at $\lesssim 0.20$ M pyrene. Several methods were employed to convert the experimental data into rate constants for quenching and then, to calculate activation parameters for quenching. The values reported in Table 25 are derived from Eyring and Arrhenius equations. They demonstrate that, as expected from the shapes of the excited state complexes, quenching by **99** is more difficult than by **98** and involves a larger disruption to solvent order. The differences between each parameter in the two phases (ΔE_a and $\Delta\Delta S^{\ddagger}$) for each quencher are more diagnostic than the absolute values. Since diffusion between two molecules of **98** or between **98** and **99** in one phase of CO/CN/CCl should be nearly identical, comparison between ΔE_a or $\Delta\Delta S^{\ddagger}$ for the two quenchers indicates the importance of solvent order to each process. Thus, ΔE_a (**98**) = 2.3 kcal/mol is significantly smaller than ΔE_a (**99**) = 4.6 kcal/mol: exciplex formation with **99** is energetically more disfavored than is excimer formation with **98** in the cholesteric phase of CO/CN/CCl. Similarly, the $\Delta\Delta S^{\ddagger}$ (**98**) = +7 cal/mol-deg and $\Delta\Delta S^{\ddagger}$ (**99**) = +15 cal/mol-deg are consistent with the exciplex being more disruptive to its local environment than the excimer.

Both Sackmann and Rehm[149] and Stegemeyer and coworkers[150] used fluorescence polarization measurements in liquid-crystalline solvents to determine that the direction of the transition moments in pyrene and its excimer are mutually perpendicular. They also observed that the sign of the circularly polarized fluorescence of several aromatic solutes could be correlated with the screw sense of the cholesteric matrices. Later, Sisido *et al.*[151] examined the circularly polarized fluorescence of several cholesteryl ω-arylalkanoates in their solid and neat cholesteric phases. One of their most interesting observations is summarized in Fig. 24. The ratio of excimer to monomer emission

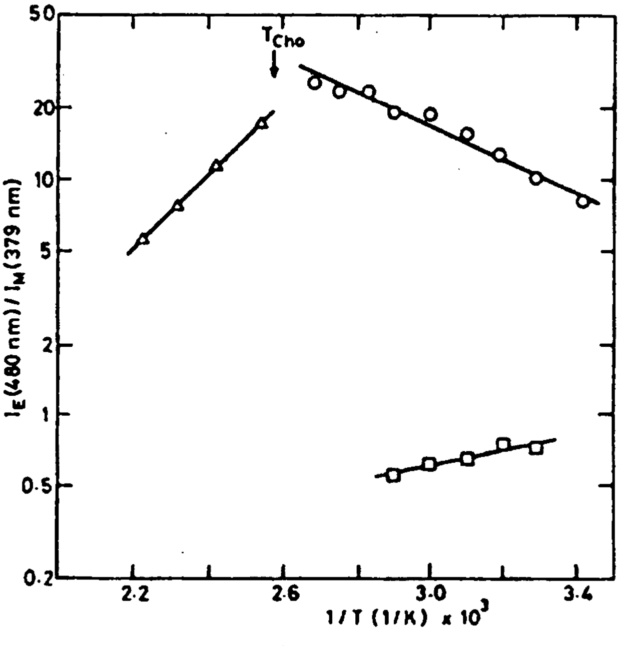


Fig. 24. I_E/I_M for pyrenyl luminescence from a 60/40 (w/w) mixture of 100/CPP versus temperature in the crystalline (□), cholesteric (○), and isotropic (△) phases.[151a] [Reprinted with permission of the American Chemical Society.]

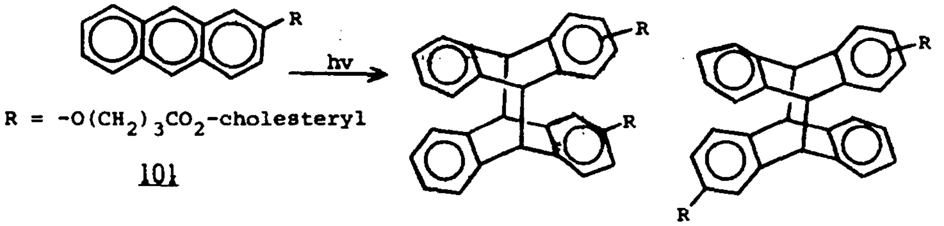
Table 26. Photodimer distributions from **101** in various phases[152b]

101 (wt%)	Solvent	Phase	T (°C)	**102** hh/ht	ht-**102** *syn*/*anti*
1.12	Dodecane	Gel	26.0	53/47	19/29
1.47	Dodecane	Gel	25.5	53/47	19/28
1.47	Toluene	Isotropic	25.5	46/54	17/37
Neat	—	Cholesteric	184.4	56/46	12/33
Neat	—	Cholesteric	183.5	55/45	13/33
Neat	—	Cholesteric	178.0	54/46	12/34
Neat	—	Isotropic	204.4	50/50	20/31
Neat	—	isotropic	206.7	47/53	17/36

intensities (I_E/I_M) was measured for the pyrenyl lumophores in a 60/40 mixture of cholesteryl 3-(1-pyrenyl)propanoate/cholesteryl 3-phenylpropanoate (**100**/CPP). In absolute terms, I_E/I_M is smaller in the crystalline phase than in the cholesteric phase. However, the cholesteric ratios increase whereas the solid state ratios decrease with increasing temperatures.

Anderson, Craig and Weiss made similar plots for pyrene in CO/CN/CCl.[101] They found that I_E/I_M in the cholesteric phase increased also, but more rapidly than in the **100**/CPP system. Furthermore, I_E/I_M continued to rise with **98** in the isotropic phase of CO/CN/CCl. That I_E/I_M decreased with increasing temperature in the isotropic phase of **100**/CPP may be due to increased excimer dissociation at the high temperatures (well above 100°C) where the isotropic phase exists: the origin of the differences between the isotropic data of Anderson *et al.*[101] and Sisido and coworkers[151a] can be traced to the photophysics of the pyrene excimer and not to differences between the arrangement of molecules in the respective isotropic phases. The same may not be true of the data for the cholesteric phases. The greater diffusional mobility and orientational freedom of **98** in cholesteric CO/CN/CCl allows it to attain appropriate excimer collisional geometries more easily than can **100** in its cholesteric mixture.

The chemical and physical interactions between pairs (and larger aggregates) of cholesteryl 4-(2-anthryloxyl)butyrate (**101**) have been investigated in its solid, cholesteric, neat isotropic, solution isotropic, and gel phases.[152] Absorption, excitation, and induced circular dichroism spectra of 0.8% (by weight) of **101** in its gel phase with dodecane confirm that the gelator molecules stack with their anthracenyl groups atop one another in a non-parallel arrangement. Connectivity of the anthracenyl at its 2-position to the cholesteryl group is necessary to attain liquid-crystallinity or gel formation since compounds analogous to **101** containing 9-substituted anthracenes form neither phase.[152b] The distribution of head-to-head/head-to-tail photodimers (hh/ht of **102**) and *syn*/*anti* ht **102**, were determined in each phase (Table 26). As can be seen, there appears to be little selectivity in and little difference between the distribution from the liquid-crystalline, gel, and neat isotropic phases (no dimer was detected from irradiation of solid **101**). Either the molecules of **101** pack without specific pair-wise interactions in these phases or, less likely, they are able to reorient themselves according to their photophysical preferences during the lifetime of the dimer precursors, the excited singlet state of **101** ($\tau < 20$ ns).[152b] The distribution obtained from irradiation of the isotropic toluene solution of **101** reflects the orientational preferences of ^{1}**101**–**101** collision partners when no solvent ordering constraints are imposed. Since it differs slightly from the other ratios, they must arise from systems in which the anthracenyl groups do experience some orientational restrictions.



R = -O(CH$_2$)$_3$CO$_2$-cholesteryl

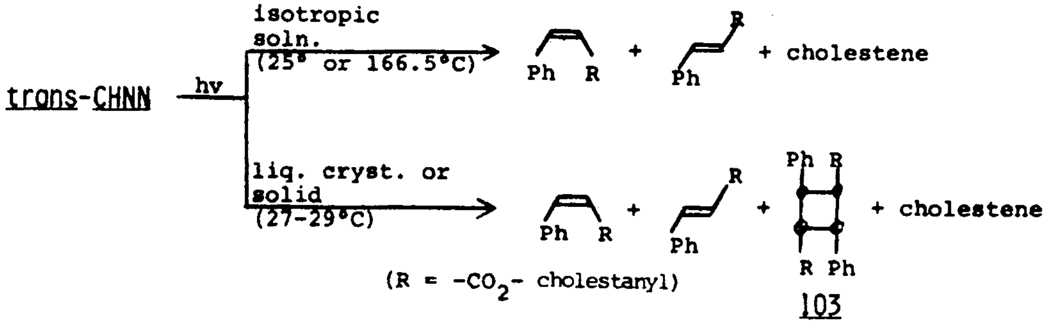
101

hh-102

ht-102

(39

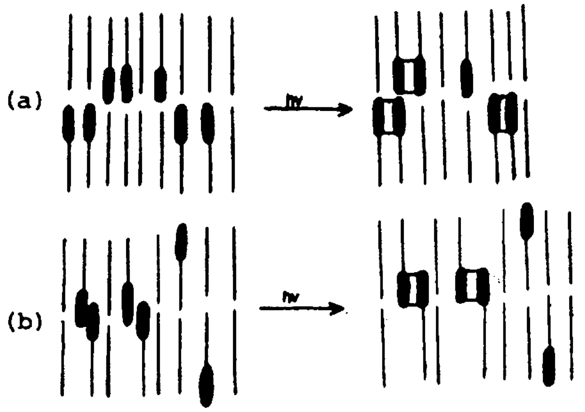
Tanaka *et al.*[153] and Ramesh and Weiss[154,155] have investigated the photodimerization of cinnamoyl groups in liquid-crystalline environments. When *trans*-CNN was irradiated at >300 nm from 25 to 225°C (spanning its solid, cholesteric, and isotropic liquid phases) in a KBr matrix,[153] it was converted to dimers whose structures were not determined. Qualitatively, the rate of the dimerization was slowest in the solid. Competing processes included formation of the *cis* isomer and cinnamic acid. Ramesh and Weiss[154] obtained evidence that irradiation of *trans*-CNN involves, at least partially, reaction of the C_5–C_6 double bond of the cholesteryl moiety. Thus, they investigated the photochemistry of 5α-cholestan-3β-yl *trans*-cinnamate (*trans*-CHNN) in its solid and cholesteric phases and in isotropic solutions (*n*-hexane and *n*-hexadecane). In the isotropic solutions, it was discovered that the major photochemical processes of *trans*-CHNN are photoelimination to yield *trans*-cinnamic acid and cholestene and *trans* ⇄ *cis* isomerization. In the neat ordered phases of *trans*-CHNN the photoelimination and isomerization are much less important than photodimerization of the cinnamoyl group [eqn (40)]. Only the α-truxillate diester (**103**) was detected by hplc and other analyses. It is the dimer expected if molecules of *trans*-CHNN are aligned in an anti-parallel, pair-wise fashion.



(40

Further evidence for this alignment and for partial interdigitation of *n*-alkyl *trans*-cinnamates (*t*-**104**) was obtained from their irradiation in the crystalline, smectic B, and isotropic phases of BS.[155] The alkyl chains of *t*-**104** were chosen to make them slightly shorter than, the same length as, and slightly longer than the extended length of BS. Up to 40% by weight of *t*-**104a** could be added to BS without significant depression of the smectic–isotropic phase transition temperature or induction of a biphasic (solid plus isotropic liquid) region. Both *t*-**104b** and *t*-**104c** depressed the smectic-isotropic phase transition temperature to a much greater extent; they could not be dissolved in BS at greater than 10% loading without inducing a biphasic region. Thus, *t*-**104a**, although longer than BS, is incorporated into the smectic matrix better than *t*-**104b** which is the same length as BS.

Given the results obtained with *trans*-CHNN, a logical interpretation is that the cinnamoyl groups of neighboring **104** are partially overlapping and in a head-to-tail arrangement: two partially overlapping *t*-**104a** molecules can have an extended length equal to twice a BS layer thickness (Scheme 8). If this hypothesis is correct, irradiation of **104** in smectic or solid BS should produce

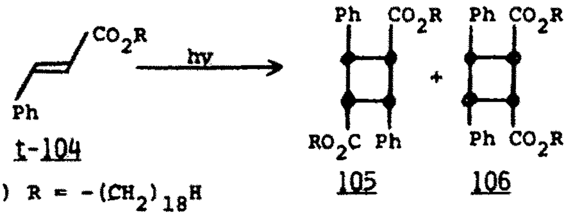


Scheme 8. Representation of the orientations of **104** in smectic or crystalline BS: (a) assumes alkyl cinnimates are constrained to one layer and yield only head-to-head photodimers; (b) assumes alkyl cinnamates are partially overlapping and yield only head-to-tail photodimers.[155] [Reprinted with permission of the American Chemical Society.]

Table 27. Photodimer ratios from *t*-**104** in various phases of BS[155]

t-**104**	wgt%	Phase (T, °C)	% conversion	**105**/**106**
a	20	Isotropic (32)	41	2.5±0.9
		Smectic (18)	12	8.0±0.6
		Solid (8)	9	8.0±0.6
	40	Isotropic (32)	17	2.3±0.1
		Smectic (18)	11	9.4±0.4
b	20	Isotropic (32)	40	3.3±0.7
		Smectic (18)	12	> 20
		Solid (8)	12	> 20
	40	Isotropic (32)	19	2.7±0.1
		Smectic (18)	14	> 20
c	10	Isotropic (32)	53	No dimer detected
		Smectic (18)	37	9.4±0.2

very large ratios of head-to-tail/head-to-head cyclobutane dimers. An alternative arrangement in which *t*-**104** molecules remain within the borders of one BS layer leads to the prediction of very low head-to-tail/head-to-head ratios. In fact, irradiation of neat, solid *t*-**104a** is known to produce exclusively head-to-tail, head-to-head, or no dimer depending upon the morphology of the crystal.[156] In all irradiations, only one head-to-tail dimer (**105**) and one head-to-head dimer (**106**) were observed at low percent conversions. Elimination and isomerization were competing processes whose importance increased with irradiation time. The results in Table 27 demonstrate that the **105**/**106** ratios *are* very large in the smectic and solid phases of BS; they are much smaller in the isotropic phase. Thus, even at very large concentrations of a solute which is similar in structure to the solvent, the ordered solvent matrices exert significant control over solute–solute interactions. It is interesting that in spite of *t*-**104a** being the more easily incorporated solute, *t*-**104b** and *t*-**104c** react more selectively in the ordered phases. The sensitivity of the BS ordered phases to solute shape and length is reminiscent of the results obtained with *n*-alkanones and *n*-alkylphenones as solutes (see Section 5).[111,114] It indicates that *both the compatability of the solute and an ordered matrix and the mobility of the solute in the ordered matrix affect its overall reactivity and selectivity.*



t-104 105 106 (41

a) R = $-(CH_2)_{18}H$
b) R = $-(CH_2)_{16}H$
c) R = $-(CH_2)_{14}H$

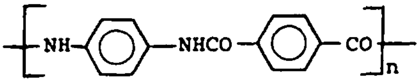
8. POLYMERIZATION OF SOLUTES

Research to synthesize polymers which exhibit liquid-crystalline properties has blossomed during the past several years.[157] There is every reason to believe that it will remain an area of intense investigation in the future. It is also likely that a great deal of the work devoted to polymerizations conducted in liquid crystals has not appeared in the open literature. It should be evaluated critically by someone more knowledgeable about the field and with greater access to all of its literature than this author.

Much of the available information concerning the influence of solvent order on polymerization processes of solutes is somewhat confusing. This may be a consequence, as noted by Mariani and coworkers,[158] that growing chains may (and probably frequently do) segregate themselves from an ordered host phase beyond a certain point in their polymerization; further polymerization occurs with the live ends in a much more disorganized environment. Thus, the length and tacticity of polymers obtained in mesophases may or may not reflect the influence of an ordered environment depending upon the polymer chain length, the nature and initial concentration of the monomers, and the structure of the mesophase.

Several results are sufficiently intriguing to warrant more effort in this area. For instance, Araya *et al.*[159] have found that polyacetylene, produced by introducing acetylene gas into a vessel coated with an oriented nematic mixture (1/1 ZLI-1476/ZLI-1477) containing a Ziegler–Natta catalyst [a mixture of $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$] at 18°C, is macroscopically oriented along the same direction as the solvent directors.

In another example of commercial importance, poly(*p*-phenylene terephthalamide) (**107**), can



107

be made into very high strength fibers (Dupont's Kevlar).[160] The *mechanical* details of the polymerization procedure determine the length and degree of polymer orientation. The strength of the polymer derives, in part, from its liquid-crystallinity which is responsible for inter-chain ordering.

9. ENERGY TRANSFER AND ASSOCIATION IN NEAT LIQUID-CRYSTALLINE PHASES

A fundamental requirement of electron-exchange energy transfer or complexation (excimer formation) between an excited state and a ground state molecule is that they be separated by no more than one or two solvent molecules.[161] For all intensive purposes, they must be collision partners. In neat isotropic media, a mapping of excitation energy migration looks like a random walk which terminates at an impurity quenching site or when an excited solvent molecule undergoes a process which leads to deactivation (like emission, internal conversion, phosphorescence, or reaction).

In mesophases, energy transfer along some directions, referenced to the orientations of the solvent directors, may be preferred over others; similarly, some molecular alignments may lead preferentially to excimer formation but others may inhibit complexation. Thus, liquid crystals open possibilities for observing one or two dimensional energy migration and for selective excimer formation. To date, much of the effort in this field has been focused on rod-like aromatic molecules (**108**–**111**) which form smectic A or nematic phases, discotic molecules (**112**–**114**) which form columnar phases, and their isotropic models. The meso and isotropic phases of **108**–**110** are known to consist of antiparallel molecular pairs which are dipole–dipole stabilized.[162,163]

The fluorescence characteristics of neat **108a** were examined by picosecond time-resolved techniques as a function of temperature in the crystalline, smectic A, nematic and isotropic phases.[164] As shown in Fig. 25, the fluorescence spectrum of **108a** is strongly phase (temperature) dependent.

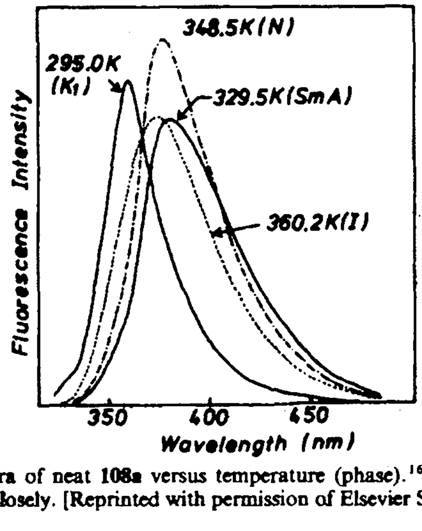
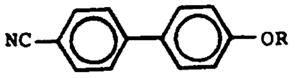
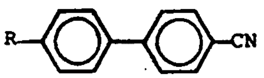


Fig. 25. Fluorescence spectra of neat **108a** versus temperature (phase).[164] The K_1 and I phase spectra resemble each other closely. [Reprinted with permission of Elsevier Science Publishers, B.V.]



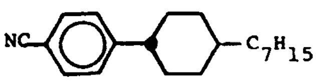
108

a) R = C_8H_{17}
b) R = C_3H_7

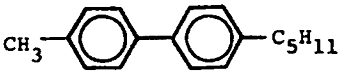


109

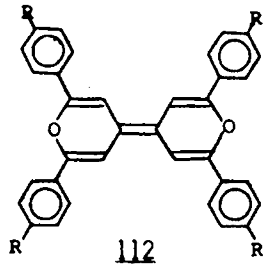
a) R = C_7H_{15}
b) R = C_8H_{17}
c) R = $C_{12}H_{25}$



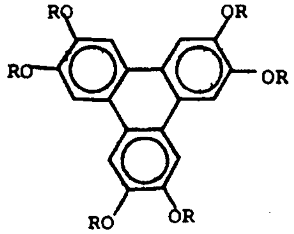
110



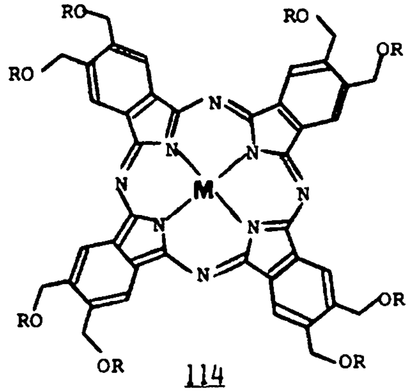
111



112
R = $C_{12}H_{25}$



113
R = $C_{12}H_{25}$



114

a) M = 2H
b) M = Cu(II)
R = $C_{12}H_{25}$

The lower temperature crystalline phase (K_1) spectrum was assigned to monomer emission and the higher temperature crystalline phase (K_2), smectic A, nematic, and isotropic spectra to excimer emission.[164] Steady-state emission intensity ratios at 380 nm and 360 nm, I_{380}/I_{360}, were measured for **108a** as a function of temperature (Fig. 26). They demonstrate that the smectic A phase can be extended on cooling to make a monotropic portion and that the excimer/monomer ratio is strongly dependent upon the phase.[165a] Similar observations have been made with **109** and **110**.[165b,166]

Gated emission spectra from the K_1 phase of **108a** showed no difference in shape between 0 and 691 ps time delays and resembled very closely the steady state spectrum. However, spectra from the smectic A phase at 56°C exhibited a time evolution from a shape which resembles that of the K_1 phase at 0 ps time delay to one which is very similar to the steady-state spectrum of the smectic A phase at *ca* 700 ps delay. By 200 ps delay, the 380 nm maximum already dominates the 360 nm maximum (i.e. excimer formation is nearly complete). Similar time-dependent behavior was observed in the nematic and isotropic phases of **108a** also.

Carefully analysed time correlated single-photon counting decay curves from **109** could be fit to a minimum of three exponential terms.[167] The decay constants are collected in Table 28.

From the wavelength dependence on the pre-exponential factors of the decay constants and the time evolution of the emission spectra, the authors concluded that three species, a monomer and

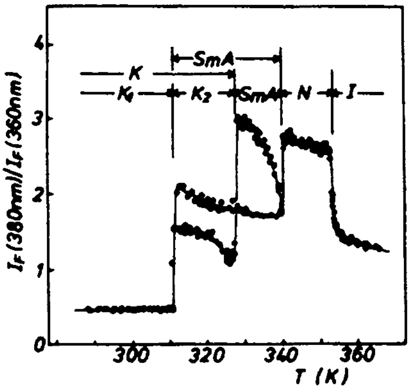


Fig. 26. I_{380}/I_{360} emission ratios from **108a** as a function of temperature (phase):[164] increasing temperature (●) and decreasing temperature (○) cycles. [Reprinted with permission of Elsevier Science Publishers, B.V.].

two excimers, are present:[167] the shortest decay constant was attributed to the monomer, the *ca* 3 ns decay to the head-to-head excimer,[163] and the longest decay constant to the head-to-tail excimer. This intriguing suggestion begs further verification.

An extended study of the excited state properties of neat **108–111** as a function of phase was performed by David and Baeyens-Volant.[165] They found that the excimer lifetime of **108a** is phase-dependent:[165a] $\tau = 10.7$ ns in the smectic phase (60°C); $\tau = 7.6$ ns in the nematic phase (72°C); τ of the **108b** excimer in its neat isotropic phase (75°C) is 7.7 ns. The lifetime of the **108a** singlet state is much shorter, 1.1 ns, in the smectic A phase of 4-pentylphenyl *trans*-4-pentylcyclohexanecarboxylate (PPPC). Markovitsi and Ide[167] performed similar studies on the alkylcyanobiphenyls **109a** and **109b**. Both molecules gave very similar structured steady-state fluorescence spectra in their crystalline phases. As with **108**, fluorescence in the isotropic and mesophases consisted of broad, structureless, red-shifted spectra. Time resolved emission spectra from **109b** in its crystalline and smectic A phases are shown in Fig. 27 (temperature not mentioned). In the crystalline phase, the emission spectra broaden with time, but do not undergo a perceptible shift in λ_{max}. The smectic phase spectra evolve from a short-time species with λ_{max} 350 nm to one with λ_{max} *ca* 380 nm after about 200 ns. Overall, the steady-state emission characteristics of **108a** and **108b** in their neat isotropic phases were very similar.

Subramanian and coworkers[166] performed steady-state experiments with **109c** which showed the presence of excimer and monomer emissions in the neat crystalline, smectic, and isotropic phases. The relative yield of excimer emission was greatest in the smectic phase due to the preordering effects of the smectic layers. As with **108a**, the excimer lifetimes were phase dependent: $\tau = 4$ ns (crystal); $\tau = 18$ ns (smectic); $\tau = 10$ ns (isotropic). Bayens-Volant and David[165b] reported $\tau = 21$ ns for **109b** in its smectic A phase (25°C), 16 ns in the nematic phase (33°C), and 9.6 ns in the neat isotropic phase (60°C). As a 2% solution in the smectic A phase of PPPC, **109b** monomer emission had $\tau = 1$ ns. Only monomer emission was observed from the crystal of **109b**, but both the smectic A and nematic phases yielded what appeared to be pure excimer emission. As expected, the isotropic phase emission consisted of a mixture of the monomer and excimer.

Table 28. Decay constants from neat **109a** and **109b** emissions at 440 nm as a function of phase[167]

109	Phase	T (°C)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
a	Nematic	35	0.1	2.8	19.7
	Isotropic	45	0.2	2.9	14.3
b	Smectic	26	0.1	2.6	21.4
	Nematic	36	0.2	3.3	19.4
	Isotropic	46	0.3	3.4	15.8

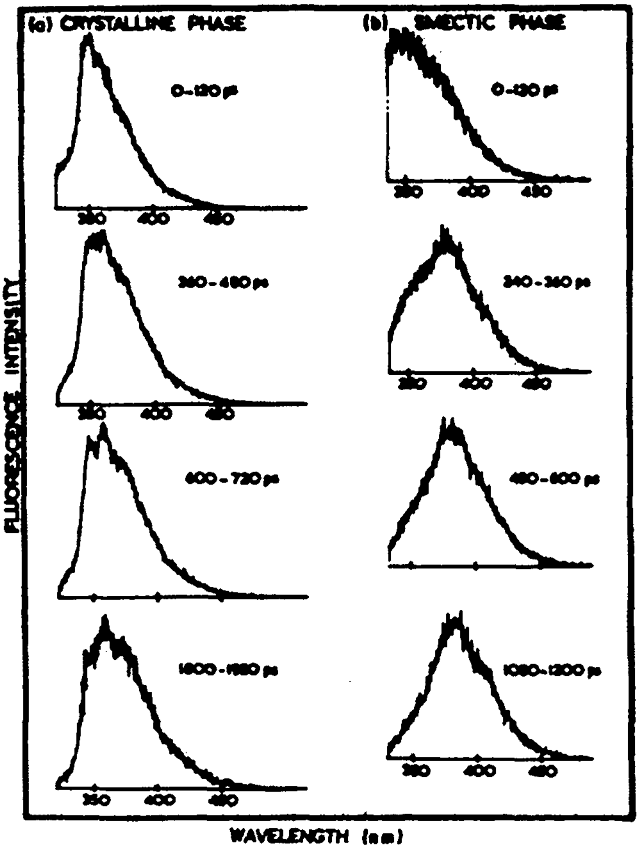


Fig. 27. Time resolved emission spectra from neat **109b** in its crystalline and smectic A phases.[167] λ_{excit} = 290 nm. [Reprinted with permission of *Journal de Chimie Physique*.]

Perhaps of greater importance were results from experiments which measured the rate of energy transfer from the excited singlet and excimer states of **108–111** to 1,8-diphenyl-1,3,5,7-octatetraene (**115**, a somewhat rod-like acceptor) or to perylene (**116**, a plate-like molecule).[165a] It was observed that both acceptors led to Stern–Volmer treatable quenching[168] in the mesophases and isotropic phases of the donors. The rate constants for **108–111** as a function of phase are summarized in Table 29.

Table 29. Rate constants for energy transfer from the excimer or monomer excited singlet state of **108–111** to **115** or **116**[165]

				$k_q \times 10^{-10}$ (l/mol-s)	
Donor	Excited	Acceptor	Phase	From static excitation	From flash excitation
108a	Excimer	**115**	Smectic A	7.8	5.1
	Excimer	**115**	Nematic	11	7.2
	Excimer	**116**	Nematic	2.6	
	Monomer	**115**	Smectic A*	110	
108b	Excimer	**115**	Isotropic	14	
109b	Excimer	**115**	Smectic A	2.84	0.92
	Excimer	**115**	Nematic	5.51	1.53
	Excimer	**115**	Isotropic	12.40	
	Monomer	**115**	Smectic A*	45.6	
110	Excimer	**115**	Nematic	1.64	0.80
111	Monomer	**115**	Isotropic	5.23	

* 2% donor (by weight) in PPPC.

The **108a** and **109b** monomer experiments were performed by dispersing the solutes and the acceptor **115** in the smectic A phase of PPPC. At one concentration of **115**, the fluorescence intensity of **108a** excimer (380 nm) was reduced by the same fractional amount in the neat smectic, nematic, and isotropic phases. The fact that **115** quenches **108a** as rapidly as does **116** was ascribed to the greater ordering of **115** in the host matrices.[165a]

In spite of the compatability of the data with Stern–Volmer kinetics, the rate constants in Table 29 are higher than the maximum allowed by self-diffusion. Thus, a simple collisional energy transfer cannot be responsible. Förster energy transfer,[169] which is allowed over larger separations between the donor and acceptor, is an unacceptable model, also. David and Baeyens-Volant[165] interpreted the very high apparent rate of energy transfer to an excitation migration mechanism devised by Voltz.[170] The combination of proximity among donor molecules and their alignment aids the hopping of excitation energy from molecule to molecule until a quencher is encountered.

Recently, Kato *et al.*[171] examined the intermediates obtained upon pulse radiolysis of the various phases of **109b**. Although the species have not been identified conclusively, a series of control experiments support the assignments of the authors. As with electronic excitation, the dynamic processes were strongly phase dependent. In the neat isotropic (47°C) and smectic A (27°C) phases, triplets (λ_{max} 380 nm) with half-lives of 1 ms and 10 ms, respectively, were detected. An additional absorption (λ_{max} 480 nm) with a half-life of 17 μs in the isotropic phase was ascribed to the cation of **109b**. In the nematic phase, an absorption (λ_{max} 550 nm) with a half-life of 2.5 ms was identified as the anion of **109b**.

Why the transients from electronic excitation and pulse radiolysis are so sensitive to the phase of **109b** is not yet understood completely. Molecular packing and viscosity differences must contribute. There is a clear need for future studies to determine how these operate.

Saeva, Reynolds, and Kaszczuk[172] were the first workers to exploit the stacking properties of a discotic liquid crystal (**112**)[173] as a means of inducing one-dimensional electron transfers. The analogous organization between electron-conducting organic crystals[174] and columnar phases, and the attractive redox properties of **112** make it well-suited for this type of study. Saeva *et al.* made the tetrafluoroborate and perchlorate salts of the electrochemically generated cation radicals of **112** (**112a** and **112b**, respectively). They were also able to form 1 : 1 molecular charge transfer complexes (**112c**) of **112** and 7,7,8,8-tetracyano-*p*-quinodimethane.

As shown in Table 30, **112a–c** form discotic and several crystalline phases. The enthalpies (ΔH) for discotic–isotropic and discotic–discotic transitions are relatively high, indicating significant interaction between neighboring molecules of **112**. Confirmation of this was found in the intense charge transfer band of **112c** from which an activation energy for electron self-exchange between **112** and its cation radical of *ca* 9.2 kcal/mol could be calculated. Unfortunately, **112c** exhibits low conductivity ($< 10^{-6}\ \Omega^{-1}\ cm^{-1}$) due to complete electron transfer having occurred between molecules within a stack.

Table 30. Phase transition characteristics of **112** and its salts[172]

Compound	T (°C)	ΔH (cal/mol)	ΔS (cal/mol-deg)	Transition	Mesophase range (deg)
112	34.5	3690	12.0	$K_1 \rightarrow K_2$	
	41	421	1.3	$K_2 \rightarrow K_3$	
	46	189	0.6	$K_3 \rightarrow K_4$	
	90	1780	4.9	$K_4 \rightarrow D_1$	59
	149	6390	15.2	$D_1 \rightarrow I$	
112a	95	4180	11.3	$K_1 \rightarrow K_2$	
	142.5	4340	10.4	$K_2 \rightarrow D_1$	
	155	5090	11.9	$D_1 \rightarrow D_2$	97.5
	~ 240 (dec)			$D_2 \rightarrow I$	
112b	106.5	4200	11.1	$K_1 \rightarrow K_2$	
	144.5	3820	9.1	$K_2 \rightarrow D_1$	
	157	4690	10.9	$D_1 \rightarrow D_2$	117
	261.5 (dec)			$D_2 \rightarrow I$	
112c	11	3710	13.1	$K_1 \rightarrow D_1$	
	34	2860	9.3	$D_1 \rightarrow K_2$	231.5
	242.5 (dec)			$D_2 \rightarrow I$	

[a] K = Crystal, D = discotic, I = isotropic.

Table 31. Excited state lifetimes from luminescences of 113 in various phase[175]

Phase	Temperature (°C)	τ_F* (ns)	τ_{DF}† (μs)	τ_P‡ (μs)
Isotropic (2×10^{-4} M 113 in heptane)	20	5.9 ± 0.6		
Crystal	20	7.4 ± 0.7	0.49 ± 0.02	1.13 ± 0.05
Columnar discotic	80	6.5 ± 0.7	0.45 ± 0.02	0.85 ± 0.05

* Prompt fluorescence.
† Delayed fluorescence.
‡ Phosphorescence.

One-dimensional excitation energy migration in columnar discotic phases has been observed by two groups recently. Markovitsi and coworkers[175] employed **113**, which exhibits an ordered hexagonal columnar mesophase between 68 and 97°C,[176] to investigate the dependence of directional energy transfer on solvent order. Triphenylene provides a convenient chromophore in **113** from which various types of luminescence can be observed. Given the fact that both the crystalline and discotic phases of **113** exist in molecular columns separated on center by *ca* 20 Å and for which molecular cores within a column are separated by 3.6 Å,[177] intracolumnar energy transfer can be crudely calculated to be 3×10^4 more probable by a Förster mechanism[169] and 10^7 greater by a collisional transfer (Dexter) mechanism[161a] than intercolumnar transfer. Thus, the observed energy transfer occurs almost exclusively within the column containing the chromophore originally excited. Fluorescence at 20°C (crystalline phase) and at 80°C (mesophase) from neat **113** is centered at 385 nm and gives no indication of excimer formation. The emission spectra do differ in that the vibronic structure of the crystalline phase disappears in the mesophase. In addition to the 'prompt' fluorescence from neat **113**, phosphorescence and a delayed component of fluorescence from excitation hopping between excited molecules in a column could be detected. Delayed fluorescence occurs only after two triplets interact (as nearest neighbors to form a singlet in a parity allowed process {eqns (42 and 43)]). Lifetimes of excited **113** from the various forms of luminescence are collected in Table 31. The dominance of delayed fluorescence over phosphorescence in the ordered phases of neat **113** is proof that energy migration within a column does occur and is an efficient process. Since τ_{DF} depends upon both the rate of excitation energy hopping and the population of triplets (the latter not being reported), the average residence time of triplet excitation energy on one molecule cannot be calculated.

$$^3\mathbf{113}+{}^3\mathbf{113}\rightarrow{}^1\mathbf{113}+\mathbf{113} \tag{42}$$

$$^1\mathbf{113}\rightarrow\mathbf{113}+h\nu \tag{43}$$

A different approach to measure one-dimensional energy transfer in columnar phases was adopted by Simon *et al.*[178] They employed the phthalocyanine **114a** into which was randomly dispersed $\geqslant$0.05 mol% of Cu(II) complexed **114a** (**114b**). The mesophases of **114** have hexagonally packed columns which are 31 Å apart (on center).[179] The solid phase at room temperature consists of orthorhombically packed columns which are tilted by 24°.[178]

At 16 mol% of **114b**, the fluorescence of **114a** is quenched almost completely at room temperature (solid phase). Fluorescence is easily observed from **114a** when **114b** is present at 0.05 mol%. The data for fluorescence intensity versus **114b** concentration can be used to calculate the average number of directed energy hops which occur upon excitation of each molecule of **114a**. In the solid phase, the hopping distance is calculated to be 100–200 Å. Upon heating **114a** containing 0.05 mol% **114b**, the fluorescence intensity suffers a sudden decrease in intensity which coincides with the crystalline-to-mesophase transition temperature. Apparently, the greater disorganization of the mesophase facilitates energy hopping between neighboring **114a**.

10. CONCLUSIONS

The research described in this Report has been accomplished through efforts of chemists, physicists, spectroscopists, and materials scientists. It demonstrates the utility of thermotropic liquid-crystalline solvents to direct some reactions and the sensitive relationship between mesophase solvent control and the compatability between solvent–solute shapes. Applications with lyotropic liquid crystals, although not discussed here, have led to equally important advances. Further progress with both liquid-crystalline types will require continued multidisciplinary work if two long-term objectives are to be attained. The first is to learn to dissect and interpret the various electronic and steric factors which determine how mesophases interact with a solute to alter its reactivity. The second is to be able to predict the influence exerted by liquid-crystalline media on reacting solutes (as well as the influence of solutes on *local* liquid-crystalline order).

It is hoped that this Report will stimulate others to help attain those objectives.

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