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ORGANIC REACTIONS IN LIQUID CRYSTALLINE SOLVENTS. 5. INTRAMOLECULAR PHENOLIC QUENCHING OF AROMATIC KETONE TRIPLETS AS A PROBE OF SOLUTE CONFORMATIONAL MOBILITY IN LIQUID CRYSTALS.

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ABSTRACT: The effects of liquid crystalline order on the conformational motions involved in end-to-end, intramolecular triplet quenching of aromatic ketones by a suitably situated phenolic moiety have been investigated. Triplet state quenching has been monitored using two independent probes: Norrish II fragmentation quantum yields of valeryl-substituted derivatives and direct lifetime measurements in methyl-substituted ketones, using the corresponding anisyl-substituted ketones as models for triplet state behaviour in the absence of phenolic quenching. Quantum yields for Norrish II fragmentation in the liquid crystalline solvents have been estimated using 4-methoxyvalerophenone (**MVP**) as the actinometer. The ability of liquid crystalline solvents to inhibit intramolecular phenolic quenching is dependent on both phase type and solute length. In one case, intramolecular quenching is completely suppressed in smectic phases, indicating that the conformational motions involved in achieving the quenching geometry are slowed by a factor of at least 10^3 relative to their rates in non-viscous, isotropic solvents. The Norrish II product ratios from photolysis of **MVP** in the liquid crystalline solvents are also affected dramatically by liquid crystalline order.

INTRODUCTION

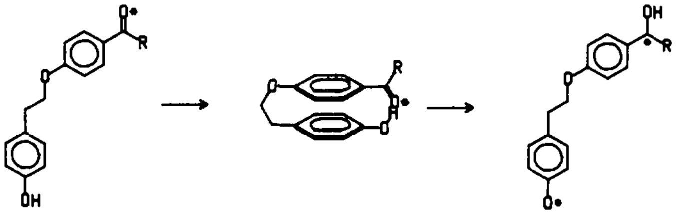
Liquid crystals are ordered fluids, with structures and properties intermediate between those of isotropic liquids and crystalline solids.[3] In liquid crystalline phases formed by rod-like "mesogens", the constituent molecules are oriented with their long axes parallel to one another, on average. This is the only degree of ordering present in nematic phases, which are the most fluid type of liquid crystal. In smectic phases, the constituent molecules are further arranged in layers with their long axes parallel to one another and perpendicular (or nearly so) to the plane of the layers. There are a variety of smectic types known, and these are classified according to the type of packing within the layers (e.g. hexagonal, orthorhombic, nematic, etc.) and the preferred angle of tilt between the long molecular axes and the layer planes.[4]

While the ability of liquid crystals to orient and restrict the diffusive mobility of dissolved solutes is well-recognized,[3,5] the effects of liquid crystalline order on the conformational mobility (and associated chemical reactivity) of solutes have only recently been demonstrated.[6-9] The ability of liquid crystals to affect motions of this type appears to be governed by a number of interrelated factors. In general, the effects are potentially the largest when the liquid crystal is highly ordered (e.g. smectic phases), when the solute's shape is similar to that of the mesogen (so that disruption of the solute's local environment is minimized), and when the process of interest involves substantial changes in the solute's shape as the transition state is approached.[7-9]

Intramolecular triplet quenching processes in aromatic ketones provide extremely useful probes for monitoring the conformational mobility of solutes in ordered media. Intramolecular excimer or exciplex formation in fluorescent molecules has, of course, been widely used to investigate molecular mobility in a variety of organized systems.[7,10] Aromatic ketone photochemistry complements fluorescent probes since the "intrinsic" excited state lifetime is much longer (allowing the investigation of much slower conformational motions) and ketones are usually smaller in size than typical fluorophores (and hence less disruptive of the medium). Furthermore, ketone excited state behaviour can be monitored either by direct methods such as triplet-triplet absorption or phosphorescence decay, or by indirect methods which depend on some aspect of carbonyl photochemistry.[11]

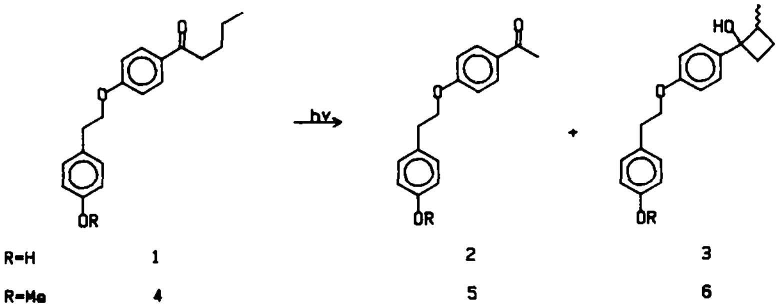
We wish to report the initial results of a study of the effects of smectic and nematic liquid crystalline solvents on an end-to-end cyclization process, involving quenching of an aromatic ketone triplet by remote hydrogen abstraction from a suitably situated phenolic moiety (Eq. 1).

(1)



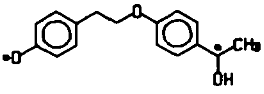
Both direct and indirect methods for monitoring triplet state quenching have been employed. In **1**, the efficiency of the Norrish Type II reaction serves as the diagnostic indicator of phenolic quenching, while in **2**, the triplet state lifetime has been measured directly by nanosecond laser flash photolysis:

(2)



There is considerable evidence to indicate that in fluid solution, intramolecular triplet quenching in **1** and **2** occurs with high efficiency.[12,13] First, the products expected from Norrish II reaction of **1** (viz. **2** and **3**) are not formed in detectable amounts upon photolysis in acetonitrile solution, even though **4** exhibits Norrish II reactivity similar to that of 4-methoxyvalerophenone (MVP) in the same solvent. Thus, the non-reactivity of **1** is due primarily to the presence of the remote phenolic hydrogen, and other quenching mechanisms such as donor-acceptor interactions between the reactive carbonyl triplet state and the electron-rich aryl group[14] at the other end of the molecule are relatively unimportant. Comparison of the transient spectroscopic behaviour of **2** and **5** has lead to the same conclusions, and in addition has provided direct evidence for the formation of the 1,13-phenoxy/ketyl biradical **7** from the triplet state of **2**.[12]

The short triplet lifetime observed for **2** in non-viscous solvents is the result of rapid phenolic hydrogen-abstraction, yielding biradical **7**:



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The substantial deuterium isotope effect on the triplet lifetime of **2** indicates that hydrogen atom transfer forms the rate determining step in the quenching process; the conformational motions involved in achieving the sandwich-like quenching geometry must therefore occur on a somewhat shorter time scale than this. These motions are expected to occur on a time scale of 1-3 nanoseconds in non-viscous solvents, on the basis of reported studies of intramolecular excimer formation in 1,3-diphenylpropane derivatives.[15]

Clearly, slowing down the conformational motions involved in phenolic quenching in **1** and **2** should result in an increase in triplet lifetime, and hence increased triplet state reactivity in **1**. Considering the magnitude of the effects of smectic and nematic liquid crystalline order which we have observed previously on considerably less severe solute conformational motions,[9b,c] it appeared likely that enormous effects on triplet lifetime and reactivity might be obtained with these molecules.

RESULTS

Solvent Properties

The liquid crystals employed in this work are 4'-butylbicyclohexyl-4-carbonitrile (**BCCN**) and the 4'-ethyl homolog (**ECCN**). These compounds both form enantiotropic smectic and nematic phases; for **BCCN**, the smectic and nematic phases exist between 29-54°C and 54-79°C, respectively, while for ECCN the corresponding temperature ranges are 28-44°C and 44-48°C.[16] X-ray diffraction data for the smectic phases of these two compounds have been recently reported.[17] Smectic **BCCN** has been assigned the bilayer Sm-B structure, similar to the high

BCCN: R=n-butyl
ECCN: R=ethyl

temperature smectic phases of the 4'-propyl (**PCCN**) and 4'-pentyl (**PeCCN**) homologs whose x-ray diffraction data were reported by Brownsey and Leadbetter.[18] The order in these phases is such that the molecules are hexagonally close-packed within the layers, with the long molecular axes oriented parallel to one another and perpendicular to the layer plane. The repeating distance defining the layer thickness (31Å for BCCN[17]) is somewhat less than twice the molecular length (17.5Å), consistent with the interdigitated bilayer structure proposed previously for **PCCH** and **PeCCH**.[18] While it is clear that **BCCH**'s smectic phase structure is *similar* to that of **PCCH**'s, miscibility studies indicate that the former forms a slightly more ordered smectic phase than **PCCH**.[19]

Smectic **ECCH** has a rhombohedral structure and is thought to be a higher-order smectic phase than that of **BCCH**.[17] The phase diagram for the **BCCH/ECCH** system is consistent with this relative ordering of the two smectic phases, in that smectic **BCCH** is immiscible with smectic **ECCH** and occurs at highertemperatures in mixtures where both phase-types exist.[19]

The nematic phase employed in the present study is that of a 2:1 (by weight) mixture of **ECCH** and **BCCH** (**EB**). This mixture forms enantiotropic smectic (**ECCH**-like) and nematic phases between 10-25°C and 25-57°C, respectively, and is an isotropic liquid above 57°C.[19]

Solubility of **1**-**4** in Smectic and Nematic **BCCH**

Incorporation of a solute in a liquid crystal results in disruption of the solvent matrix, to a degree which depends primarily on the similarities between the solute's structure and that of the mesogen.[6e,7c,8,9,20] A qualitative measure of the extent to which this occurs can be obtained from the transition temperatures of the solute-doped mesogen, and by visual inspection of the mixture through a polarizing microscope. Transition temperatures for 1 mol% mixtures of **MVP** and **1**-**4** in **BCCH**, measured by thermal microscopy, are collected in Table 1.

MVP causes very little disruption of either the smectic or nematic phases of **BCCH**, as is indicated by the only slight lowering of the Sm-N and N-I transition temperatures from those of the pure material. This result is the expected one considering the structure of this solute; it is three carbon atoms shorter than **BCCH** and is of similar breadth and flexibility. The mosaic microscopic texture of the smectic mixture is indistinguishable from that of the pure mesogen, and its formation upon cooling from the nematic phase proceeds rapidly and uniformly. Ketones **2** and **5** are of lengths similar to **BCCH**, and from the transition temperatures of the mixtures, it is clear that they disrupt smectic order to a greater extent than **MVP** does. In the case of **2**, formation of the mosaic smectic texture upon cooling from the nematic phase proceeds in a similar fashion to the **MVP** mixture, though over a somewhat broader temperature range. The cooling behaviour of the **5**-**BCCH** mixture is fundamentally different from this; formation of the mosaic texture proceeds more gradually in this case than in the others, the smectic phase appearing as serrated batonnets which gradually coalesce to form a mosaic texture. At temperatures within the transition range, the coexistence of monodomains is apparently complete.

The transition temperature ranges of the **1**- and **4**-**BCCH** mixtures are considerably broader, and the microscopic behaviour is analogous to that of the **5**-**BCCH** mixture, only more pronounced. Inspection of annealed (2 days at 35°C) samples at 30° distinctly reveals the presence of both smectic and nematic phases. In the 1 mol% mixtures, the samples are predominantly (90-95%) smectic, but as the bulk ketone concentration is increased (2-10%), the relative proportion of nematic phase increases. It thus appears that **1** and **4** are much less soluble in smectic **BCCH** than **MVP**, **2**, and **5** are, and reside largely in a ketone-rich nematic phase in equilibrium with the bulk **BCCH**-rich smectic phase. While the precise compositions of the two coexistent phases are not known, the suggestion that the ketones reside predominantly in nematic phases at 30°C is further indicated by their photochemical behaviour (vide infra). On the other hand, **MVP**, **2**, and **5** appear to be uniformly soluble in smectic **BCCN** (at 30°C, anyway), and cause disruption of local smectic order to a degree which correlates with their molecular lengths.

Table 1: Transition temperatures for 1 mol% aromatic ketone/**BCCN** mixtures.[a]

Ketone	Sm->N	N->I
none	53.5-54°	80°
MVP	51.5-52.5°	78.8-79.2°
1	46-51°	76-78°
2	51.5-52.5°	78.8-79°
4	48-52°	76-77.5°
5	50.5-52°	78.2-78.5°

[a] Measured in heating cycles by thermal microscopy.

Triplet Lifetimes of 2 and 5 in Liquid Crystalline Solvents

Triplet lifetimes for **2** and **5** in the smectic phases of **BCCN** and **ECCN** and in nematic **EB** were measured by nanosecond laser flash photolysis, monitoring transient absorptions after excitation with the pulses (337.1nm, 10ns, 80mJ) from a nitrogen laser.[21] Laser flash photolysis of annealed, deoxygenated, 1 mol% solutions of **2** and **5** in the two smectic solvents at 30°C gave rise to transients whose decay followed clean first-order kinetics, and which were assigned to the triplet states on the basis of their characteristic absorption spectra.[11,12,22] No evidence for formation of biradical **7** from **2** could be found in either solvent at this temperature. Similar experiments with **2** in nematic **EB** (0.2 mol%: ca. 0.005M) gave rise to more complex behaviour as a result of overlap (in both position and time) of absorptions assignable to triplet **2** and biradical **7**. Analysis of the first-order decay profiles at 390nm (where triplet absorption is strongest) and at 350nm (where biradical absorption is strongest) led to estimates of 275ns and 320 ns for the lifetimes of triplet **2** and biradical **7**, respectively. These values must be considered to be upper and lower limits (respectively), because of their similar magnitude and the degree to which the spectra of the two species overlap. At 30°C, similar results were obtained from 1 mol% solutions of **2** in **EB**, indicating that (bimolecular) self-quenching of the triplet state is negligible at this temperature (triplet lifetimes were comparatively shorter only at higher temperatures). Triplet lifetimes for **2** and **5** in these solvents and in acetonitrile[12] are collected in Table 2.

The Photochemistry of 1, 4, and MVP in Liquid Crystalline and Isotropic Solvents

The **UV** absorption spectra of **1**, **4**, and **MVP** (not shown) in nematic **EB** are similar to those recorded in acetonitrile solution, the π,π^* absorptions being shifted to longer wavelengths compared to their positions in methylcyclohexane. Similar features have been observed by us previously in the **UV** absorption spectra

Table 2: Triplet lifetimes for **2** and **5** in isotropic and liquid crystalline solvents at 30°C.[a]

Ketone	MeCN[b]	EB(nem)[c]	BCCN(sm)[d]
2	15	275	3800
5	2300	5600	11000

[a] Measured by nanosecond laser flash photolysis; lifetimes given in nanoseconds. Error is approximately ±10%.
[b] From Ref. 12.
[c] 0.2 mol% solutions, 3mm cells.
[d] 1 mol% solutions, 0.7mm cells.

of other *para*-alkoxyphenyl alkyl ketones in the meso- and isotropic phases of BCCN, compared to those in acetonitrile and methylcyclohexane.[9]

Deoxygenated, 1 mol% solutions of **1**, **4**, and MVP in smectic BCCN and ECCN, and 0.02M solutions of the same ketones in nematic EB, (isotropic) cyclohexane: ECCN (1:5 by wt: "EC"), and methylcyclohexane (MCH) were irradiated (312±10nm) in a merry-go-round apparatus. For each solvent, photolysis was continued for a period of time corresponding to 10-30% conversion of the MVP sample. The photolysates were analysed by vpc (MVP and **4**) and by hplc (in each case). The former analyses yielded fragmentation/cyclization (F/C) ratios for both ketones and relative yields of the diastereomeric (t/c) cyclobutanols from MVP in the four solvents studied. These data are listed in Table 3, along with the corresponding values obtained from photolysis of these ketones in acetonitrile solution.[12] The cyclobutanol(s) from **4** are thermally unstable under the gc conditions necessary for the analysis, so the calculated F/C ratios are not quantitative. The cyclobutanols from photolysis of MVP also partially decompose under the more severe GC conditions used for **4**, but the *percentage* decomposition does not vary with the amount injected. Thus, the F/C ratios reported for **4** are meaningful.

Table 3: Fragmentation/cyclization (F/C)[a] and trans/cis cyclobutanol (t/c) ratios from the Norrish II reactions of MVP and **4** in isotropic and Liquid Crystalline Solvents at 30°C.[b]

Ketone		MeCN[c]	MCH[d]	EC(isot)	EB(nem)	BCCN(sm)	ECCN(sm)
MVP	F/C	4.4±0.3	4.2±0.4	4.4±0.2	6.1±0.2	9.2±0.3	4.7±0.3
	t/c	2.2±0.1	4.4±0.2	2.2±0.2	2.6±0.2	5.2±0.3	3.0±0.3
4	F/C	6.4±0.5	15±2	16±2	20±3	19±2	17±2

[a] Ratios calculated using the total (t+c) cyclobutanol yield.
[b] Average of triplicate analyses from at least two photolysis runs. Relative vpc response factors were not determined.
[c] The data for **4** in this solvent are from ref. 12.
[d] Methylcyclohexane.

so long as we confine the discussion to a comparison of results for the different solvents studied. We have been unsuccessful in determining whether the single peak corresponding to cyclobutanol product(s) which elutes under our gc conditions (see Experimental) represents a single isomer or a mixture of the two.

Table 4 lists the relative Norrish II fragmentation yields for **1** and **4** in the various solvents studied, calculated in each case using the Norrish II fragmentation of **MVP** in the same solvent as the standard. This procedure represents an attempt to circumvent the problems associated with quantum yield determinations for photochemical reactions in liquid crystalline solvents which employ (isotropic) solution phase actinometers;[8a,d] viz. irreproducible sample light scattering/reflection and vastly different impurity quenching rates (a bulk viscosity effect) in liquid crystals compared to isotropic solvents. It has not been completely successful, as the errors in the smectic phase results are fairly large (±50%), even using annealed samples (unannealed samples are completely opaque, and the degree of reproducibility is much lower). There appear to be further difficulties with the smectic samples that render comparison with nematic and isotropic phase results difficult. These result from the differences in the solubility of **MVP**, **1** and **4** in the smectic phases, and will be discussed in more detail below. Because the solubilities of **1** and **4** in smectic **BCCN** are similar, **4** is in fact a better actinometer for **1** than **MVP** is; thus, the last series of entries in Table 4 lists the fragmentation yields from **1** relative to those from **4** in the same solvent. Qualitatively, Norrish II fragmentation of **MVP** proceeded at similar rates in all four solvents (and a factor of ~3 faster than in acetonitrile), while those of **1** and **4** followed the order **EB>BCCN>EC>>ECCN** and EB~EC>BCCN~ECCN, respectively.

Table 4: Relative quantum yields for Norrish II fragmentation of **1** and **4** in Isotropic and Liquid Crystalline Solvents.[a]

Ketone	MeCN[b]	**EC**(isot)[c]	**EB**(nem)[d]	**BCCN**(sm)	**ECCN**(Sm)
1	<.001	0.06±0.02	0.19±0.04	0.12±0.04	0.011±0.005
4	1.0±0.1	1.9±0.2	2.3±0.3	1.0±0.1	0.9±0.2
Φ_1/Φ_4	<.001	0.03±0.02	0.09±0.02	0.12±.04	0.015±0.005

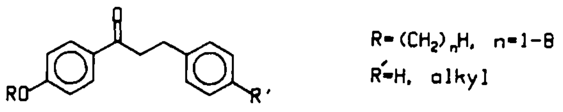
[a] 312±10nm irradiation, 30°C. Calculated relative to the yield of 4-methoxyacetophenone from **MVP** in the same solvent.
[b] Data from Reference 12.
[c] 5:1 **ECCN**:cyclohexane (by wt.).
[d] 2:1 **ECCN**:**BCCN** (by wt.).

DISCUSSION

Norrish II Reactivity of **MVP** and **4** in Isotropic and Liquid Crystalline Solvents

Weiss and coworkers have reported several thorough investigations of the Norrish II reactivity of aliphatic[8b,c,e] and aromatic[8a,b,d] ketones in the solid, meso-, and isotropic phases of n-butyl stearate[8a-c,e] and **BCCN**.[8d] The observation of substantial increases in fragmentation/cyclization (F/C) ratios in liquid crystalline relative to isotropic solvents of similar bulk polarity has been interpreted as reflecting the effects of the ordered medium on the kinetic behaviour of the cisoid- and transoid- 1,4-biradical intermediates;[8] biradical coupling to yield cyclobutanols is sterically more demanding than fragmentation, and involves conformational motions that are more strongly affected by the ordered solvent matrix. Solvent order effects on the behaviour of the cisoid biradical are also manifested in the ratio of diastereomeric cyclobutanols (t/c) formed, with higher proportions of the trans-isomer being formed as medium rigidity increases. Solvent polarity also affects Norrish II F/C and t/c product ratios, both increasing as solvent polarity decreases,[8,23] and this must always be accounted for in determining the contribution of medium rigidity to the observed product ratios. A number of workers have used Norrish II product ratios in similar fashion to probe the structure of, and solute/medium interactions in, ordered media.[24]

In smectic phases, the substantial effects on F/C and t/c product ratios that have been observed correlate with relative solute/mesogen structural features. The largest effects on biradical reactivity obtain when the ketone's structure is similar (in length and breadth) to that of the mesogen.[8] Variations in the magnitude of the effect on F/C and t/c ratios are extremely sensitive to solute length, often varying dramatically with changes in length of only one or two carbon atoms. We have observed similar relationships between solute length and the degree to which smectic phases restrict solute conformational mobility in studies of the triplet state behaviour of β-phenyl (4-alkoxypropiophenones) (**8**) in **BCCN**.[9] The other structural factor which appears to be important is the magnitude



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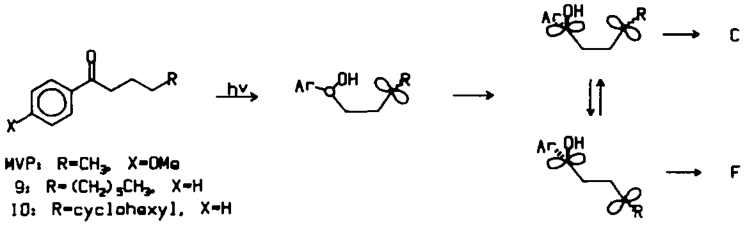
of the shape change which the solute must undergo in the course of the process of interest.[6e,8d,9a,b] All else being equal, the larger the shape change that accompanies the process, the more strongly it is inhibited in liquid crystalline solvents relative to isotropic ones.

Given these considerations, we were somewhat surprised to find that both the F/C and t/c product ratios from photolysis of **MVP** vary dramatically as a function of solvent phase (Table 3). The variations in these ratios with mesophase type parallel those which have been observed by Weiss and coworkers in other systems such as **9** and **10**.[8d] The conformational motions of the biradical that are necessary for product formation[7d,e,25] involve rotation about the $C_{ketyl}-C_{\alpha}$ and $C_{\alpha}-C_{\beta}$ bonds (Equation 3). The present results indicate either that these motions are affected by liquid crystalline order almost as much in the **MVP**-derived biradical as they are in those derived from **9** and **10**,[8d] or that local solvent polarity varies depending on the phase type. The latter possibility can be ruled out on the basis of the product ratios obtained from photolysis of **MVP** in **MeCN** and **MCH** (Table 3).

(3)



It seems most reasonable to suggest that **MVP** is simply more tightly solvated in the nematic and smectic phases than **9** and **10** are as a result of its smaller size. Hence, the biradical is subject to comparable restrictions to its conformational mobility, even though these motions involve much smaller shape changes than must occur in the biradicals derived from **9** and **10**.[8d] In smectic **BCCN**, it is possible that **MVP** is solvated in such a way that the valeroyl group is situated in the interdigitated, between-layer region of the solvent, although we have no evidence to support this.

The product ratios from photolysis of **MVP** in smectic **ECCN** indicate that this phase, in spite of the fact that it is more highly ordered (and hence more rigid) than smectic **BCCN**, exerts little or no influence on biradical dynamics beyond that which occurs in the nematic phase. Similar results have been obtained previously in our studies of **8** in **BCCN** and **ECCN**.[9b-d] Perhaps solutes in this phase experience greater mobility than in smectic **BCCN** because the higher crystallinity of the solvent matrix creates a better-defined "cavity", in which minor solute motions can proceed unrestricted.

The F/C ratios obtained from photolysis of **4** in the four solvents do not vary appreciably with solvent phase, indicating that the biradical experiences a similar environment (with respect to both polarity and microviscosity) in each of the four phase types. This would be the case if the ketone causes local "isotropization" of its solvation shell in the smectic and nematic phases. That **4** severely disrupts solvent order in the smectic and nematic phases of **BCCN** is clearly evident from the transition temperatures of the mixture. Comparison of the F/C ratios obtained in the mesogenic solvents with those in **MeCN** and **MCH** indicates that the biradical's environment is largely non-polar in these phases.

The relative quantum yields listed in Table 4 for Norrish II fragmentation of **4** indicate that Φ_{II} for **4** is similar to that for **MVP** in the smectic phases and a factor of 2-2.5 higher in isotropic **EC** and nematic **EB**. Since the F/C ratios obtained for **4** in these four solvents as well as the microscopic study of the **4**-**BCCN** mixture both suggest that this solute resides in virtually identical environments in each phase, identical Φ_{rel} values in the four solvents should be expected since fragmentation of **MVP** proceeds at a similar rate in each phase.

Perhaps it is the difference in sample quality between the smectic ones containing **4** and those containing **MVP** which is causing the apparent difference in quantum efficiency. While the smectic **MVP** samples were uniformly glassy in appearance, those containing **4** consisted of what appeared to be nematic droplets interspersed in the bulk smectic phase. Under our photolysis conditions, it is thus possible that **4** simply receives less excitation light than **MVP** does in the smectic phases, accounting for its apparently reduced reactivity compared to that in nematic or viscous isotropic solvents.

We do not yet understand the higher fragmentation yield exhibited by **4** in **BC** and **EB** (relative to **MVP**) compared to that in acetonitrile. The implication of these results is that **4** is of higher intrinsic reactivity than **MVP** in viscous media, presumably as a result of solvent-induced restrictions to its conformational mobility. This would indicate that in non-viscous solvents, there is slight quenching of the reactive triplet state via through-space interactions with the remote, electron-rich para-alkoxyphenyl ring. The triplet lifetime of **5** in acetonitrile solution (2.3 µs[12]) is consistent with this, since this is somewhat shorter than the triplet lifetimes of analogous compounds which do not have the potential for such interactions (e.g., 4-methoxyacetophenone under similar conditions: τ_T > 10 µs). The reason for the apparently higher intrinsic reactivity of **4** is not clear; it does not appear to derive from a substituent effect which raises the π,π^* state energy,(hence allowing more facile population of the reactive n,π^* state,[22b,26] as the phosphorescence emission spectra of **5** and **MAP** are identical.[12] We are investigating this aspect of the photochemistry of **4** and **5** in more detail.

Intramolecular Phenolic Quenching of Carbonyl Triplets in Liquid Crystalline Solvents

Incorporation of **2** in the smectic phase of either **BCCN** or **ECCN** results in virtually complete suppression of intramolecular phenolic quenching (Table 2). This means that the rate of the conformational motions involved in achieving the sandwich-like quenching complex have been slowed by a factor of over 10^3 in the smectic phases, relative to the value in non-viscous solvents. With the indication from the transition temperatures in Table 1 that **2** is uniformly soluble in smectic **BCCN** and disrupts solvent order only slightly, it is expected that **2** will be incorporated in the smectic phases in its fully extended conformation (preferentially) and with its long axis aligned parallel to neighbouring solvent molecules. The effect of smectic order on the conformational mobility of the solute is then the combined result of a relative lowering of the energy of the extended conformer and a very pronounced restriction to the motions involved in achieving the sandwich-like quenching geometry. Generally, liquid crystalline effects on reaction rates are masked somewhat owing to the opposing effect that increasing both the activation enthalpy and entropy has on the rate. An increased activation enthalpy is the result of solvent-induced restriction of the process, while the accompanying increase (i.e. to more positive values) in the activation entropy is the result of the increased disorder which is imparted on the solvent as the transition state is approached.[5e,6d,9] In the present case, it is apparent that the effect of smectic order on the activation enthalpy for cyclization far outweighs the entropy to be gained in the process.

In the nematic phase, intramolecular quenching is also impeded, but to a lesser extent than in the smectic phase. This is expected considering the pronounced differences in order and rigidity between the two phase types. The effect in the nematic phase may be due to solvent ordering, but without analogous results in viscous isotropic solvents, it is difficult to ascertain to what extent simple microviscosity effects contribute to the overall result. We have previously concluded that solvent microviscosity almost entirely accounts for the slight increases in the Arrhenius parameters for triplet decay of **8**,[9] but the shape changes involved in β-phenyl quenching are much less severe than those in the present case. Determination of the complete temperature dependence of the triplet state behaviour of **2** and **5** is the subject of future work.

The lifetimes of triplet **2** and biradical **7** are similar in the nematic phase, presumably as a result of the fact that the decay of both species is controlled by the rates of similar conformational motions. Both triplet quenching (*via* phenolic hydrogen abstraction) and biradical decay (*via* intersystem crossing[27])require end-to-end cyclization to a sandwich-like conformer. In acetonitrile solution, intersystem crossing controls the decay of biradical **7**,[12] since the conformational motions required to bring the two radical sites together occur on a much faster time scale (as evidenced by the deuterium isotope effect on the 15ns triplet lifetime[12]). Presumably, these conformational motions are impeded enough by solvent order and/or microviscosity in nematic EB that the rate of cyclization is slower than (or at least similar to) the rate of intersystem crossing, and end-to-end cyclization becomes the rate-determining step for biradical decay. Doubleday *et al*. have recently presented similar arguments to explain the viscosity- and temperature dependent decay of remote biradicals derived from Norrish I fragmentation of 2-phenylcycloalkanones.[28]

Our results for **1** in smectic BCCN and nematic EB are consistent with the earlier conclusion that this solute resides in a nematic phase within the (bulk) smectic solvent. As pointed out previously for **4**, the relative (to MVP) quantum yields listed in Table 4 for **1** in the two solvents are not correlatable because of problems with the smectic samples. Since similar problems were encountered with both **1** and **4**, it is more meaningful to use the fragmentation of **4** as the actinometer for **1** in a given solvent. These clearly demonstrate the similarity in the reactivity of **1** in nematic EB and the (bulk) smectic phase of BCCN.

If **1** resides in a ketone-rich nematic phase within the bulk smectic solvent, then one might expect self-quenching to reduce its apparent reactivity relative to that in the bulk nematic solvent, since bimolecular phenolic quenching of ketone triplets proceeds at the diffusion-controlled rate.[13] Our results indicate that self-quenching does not occur (more than ~10%) in the ketone rich nematic phase, in spite of the high concentration of **1** that must prevail. The effects of nematic solvents on the rate of γ-hydrogen abstraction in aromatic ketones is not known; however, assuming an upper limit of $1.5 \times 10^{6}\ s^{-1}$ (the value for MVP in fluid solution[21b]), and a lower limit of 0.2M for the effective concentration of **1** in the nematic "sub-phase", we calculate the rate of diffusion to be 10^{7}–10^{8} $M^{-1}s^{-1}$ or less, if 10% of the triplets are quenched bimolecularly. This value is reasonable, according to published determinations of diffusion rates in nematic phases.[29]

The higher Φ^1_{II}/Φ^4_{II} in EB compared to **EC** is probably attributable to the relatively higher viscosity of the nematic phase,[9] and its effect on the conformational motions leading to intramolecular quenching in **1**. Self-quenching should not be a contributing factor in the isotropic phase, since it does not occur in the case of **2** at a concentration of .003M in acetonitrile;[12] it is unlikely that diffusion rates in **EC**, a fairly viscous solvent, are less than a factor of ten slower than those in acetonitrile.

In smectic **ECCN**, Norrish II fragmentation of **1** is scarcely detectable, showing that the solute experiences a fairly low viscosity environment in which intramolecular quenching can proceed with only minor restriction. It is interesting that the mobility of **1** in this very highly ordered smectic phase is in fact greater than that in viscous isotropic solvents such as **EC**.

The pronounced differences in the behaviour of **1** and **2** in the two smectic phases are analogous to the variations in the triplet state behaviour of **8** as a function of substituent in these two solvents,[9] and corroborate the conclusion that the solubility and mobility of these molecules in the smectic phases is extremely sensitive to the length of the solute with respect to that of the mesogen. Ketone **2** is about the same length as β-phenyl-4-methoxypropiophenone (**8a**), whose conformational motions were found to be impeded substantially in **BCCN** throughout the temperature range of the bulk smectic phase. The effect of smectic solvent order on the conformational mobility of **2** is even greater, reflecting the more severe shape changes that this molecule must undergo in the course of intramolecular triplet quenching. Interestingly, **2** is similarly affected in smectic **ECCN**, in contrast to the behaviour of **8a** in this solvent.[9b] For smectic **ECCN** to inhibit conformational mobility in β-phenyl aromatic ketones, we have found that the solute needs to be further shortened from its length in **8a**.[30] Ketone **1** experiences only minor restrictions to its conformational mobility in smectic **BCCN** and **ECCN**, as a result of its inducing phase separation. Analogous results are obtained in the case of **8**, for solutes which are longer than **8c**.[9b,c]

Finally, the present results for **1** and **2** should be compared to the behaviour of α,ω-bis(pyrenyl)alkanes in liquid crystalline BCCN and cholesteric solvents, which has been studied by Weiss and coworkers.[7c,d] Intramolecular excimer formation in these compounds (1,3-bis(pyrenyl)propane in particular) involves similar conformational motions and sandwich-like quenching complexes as those in the present case, but they must occur over a considerably shorter time scale (300-400ns, the lifetime of the isolated fluorophore). Excimer formation does indeed proceed in these systems in smectic **BCCN**, although at somewhat reduced rates relative to nematic and isotropic solvents. Considering our results for **1** and **2**, the fact that excimer formation is observed in the pyrene systems indicates that the solutes severely disrupt local order in the smectic phase, although discrete phase separation may not occur at the low solute concentrations employed in the fluorescence measurements (if it did, one would expect similar solute behaviour in the bulk smectic and nematic phases). The isotropized local solute environment must have a very high microviscosity, presumably as a result of its intimate contact with the highly-ordered bulk environment.

We are continuing to investigate the delicate balance between the effects of liquid crystalline solvents on solute mobility and associated reactivity and relative solute/mesophase structural features.

EXPERIMENTAL

Melting points and transition temperatures were measured on a Bausch & Lomb 10X microscope, fitted with a brass hot-stage and polarizing filters (Spindler & Hoyer) and are corrected. Temperatures were measured using a Cole-Parmer Model 8110-10 Thermocouple Thermometer, the probe of which was embedded in the hot stage within 2mm of the viewing window.

Ultraviolet absorption spectra were recorded on a Hewlett Packard HP-8451 spectrometer, or a Perkin-Elmer Lambda-9 spectrometer equipped with a PE Model 3600 Data Station. Phosphorescence emission spectra were recorded on a Perkin-Elmer LS-5 spectrofluorimeter equipped with the associated phosphorescence attachment and Data Station, using 3-mm cylindrical quartz tubes.

Laser flash photolysis experiments employed the pulses (337.1 nm, 3-10 mJ, ca. 8 ns) from a Molectron UV-24 nitrogen laser for excitation, and the computer-controlled detection system that has been described in detail elsewhere.[21] Samples were contained in 0.3 x 7 mm rectangular cells built with Pyrex tubing (Vitro Dynamics) Samples were prepared by adding an aliquot of a standard solution of the ketone in dichloromethane to a cell by microlitre syringe, evaporating the solvent under a stream of nitrogen followed by baking in a 50° oven for a few hours, and then weighing the appropriate amount of the mesogen into the cell. Nitrogen was bubbled through the melted samples to ensure solution homogeneity, and they were finally deoxygenated with three freeze-pump-melt cycles (to 10^{-4} torr) and sealed. Smectic phase samples were then annealed in a 40°C oven for 7 days. The optical densities of the solutions at 337 nm were in the range 0.15-0.20. Decay of laser-generated transients was monitored by uv absorption, and transient lifetimes were calculated from traces obtained by averaging 10-50 shots, each corrected for background scattering of the excitation pulse.

Gas chromatographic separations employed a Varian Model 3700 gas chromatograph equipped with a flame ionization detector, 2mX1/8" stainless steel OV 17 (on 80/100 Supelcoport) or 30mX0.75mm 1 µm SPB-1 Microbore columns (Supelco, Inc), and a Hewlett-Packard Model 3393A and/or Varian CDS 111 integrator. High performance liquid chromatographic analyses were performed using a Gilson isocratic hplc system, consisting of a Model 302 pump (fitted with a 5 mL head), Model 802B manometric module, Holochrome variable wavelength detector, a Rheodyne Model 7125 loop injection valve, and a 0.46 cm Merck Hibar S160 (10 µm) analytical column. Ethyl acetate/hexane mixtures were used as eluants (0.5-1.0mL/min), and an analytical wavelength of 280nm was used throughout. The detector was interfaced to a Unitron microcomputer via an Adalab data acquisition/control card (Interactive Microware, Inc.), after amplification of the 0-10mV signal to 0-1V with an Adaamp analog amplifier. Chromatogram acquisition, storage, and integration was performed using the Chromatochart (Interactive Microware, Inc.) software package.

Acetonitrile (Caledon HPLC), dichloromethane (Caledon HPLC), ethyl acetate (BDH Reagent), hexane (Caledon HPLC), methylcyclohexane (BDH Omnisolv), and cyclohexane (Baker Photrex) were used as received. 4'-Butylbicyclohexyl-4-carbonitrile (**BCCN**; EM Licristal ZLI1538) and 4-ethylbicyclohexyl-4-carbonitrile (**BCCN**; EM Licristal ZLI1537) were used as received from E. Merck Co. Cyclohexylbenzene was used as received from Aldrich Chemical Co., and dimethyl isophthalate (Aldrich) was recrystallized from methanol (m.p. 67-68°C)).

4-Methoxyvalerophenone (**MVP**) was prepared by Friedel-Crafts acylation of anisole with valeroyl chloride and vacuum-distilled twice (b.p. 115°C, 2mm lit.[25a] 143°, 6mm). Ketones **1**, **2**, **4**, and **5** were prepared and purified according to our published procedure.[12]

Solutions for the transition temperature study were prepared by dissolving **BCCN** in appropriate aliquots of dichloromethane solutions of the ketones, and evaporating off the solvent under high vacuum. Samples were prepared on covered glass slides.

Solutions for quantitative photolyses were prepared (in the dark) by adding an aliquot of a standard dichloromethane solution of the ketone to a 5mm quartz tube, stripping the solvent under a stream of nitrogen, and adding the required amount of the mesogen. In some of the runs, the **MVP** samples also contained 0.25mol% (.005M) cyclohexylbenzene as an internal standard for vpc analysis. The tubes were sealed with rubber septa, deoxygenated by bubbling nitrogen through the isotropic phase (formed by heating, where necessary), and sealed with Parafilm. Smectic phase samples were then annealed at 40°C for 2-3 days. Irradiations were conducted in a merry-go-round apparatus immersed in a thermostatted (30±1°) water bath, with a 450W medium pressure Hanovia mercury lamp. The latter was suspended in a quartz immersion well, surrounded by an aqueous K_2CrO_4 (0.54g/l) /Na_2CO_3(2.0g/l) solution filter (1 cm pathlength) in a Pyrex vessel (312±10nm). The optical densities of the solutions (estimated from the UV absorption spectra) were ~1 at 312 nm, and varied between 0.8-2.5 throughout the bandwidth of the solution filter.

Solutions of **MVP**, 1, and 4 in smectic **BCCN** and **ECCN** (1.0mol%) and in **EB**, **EC**, and acetonitrile (0.02M) were prepared as above and irradiated together for a period of time corresponding to 10-30% conversion of the **MVP**/mesogen samples. The tubes were then opened and dichloromethane (200 µl) was added. Solutions containing **MVP** and 4 were analysed by vpc to determine t/c and F/C ratios. These ratios (Table 3) are the averages of triplicate analyses of two runs. The relative detector response for the fragmentation and cyclobutanol products was not determined.

Aliquots of a standard dichloromethane solution of dimethylisophthalate were added to the solutions of 1 and 4, and these were then analysed by hplc. Relative quantum yields were determined from the yields of **2** and **5** from 1 and 4, respectively (measured by hplc relative to dimethylisophthalate; relative detector responses calibrated) and from that of 4-methoxyacetophenone from **MVP** (measured by vpc relative to cyclohexylbenzene; detector response calibrated). In one run, analysis of all three reaction mixtures was carried out by hplc, using dimethylisophthalate as internal standard. Identical results were obtained, within experimental error. The results (Table 4) were obtained from the average of no fewer than triplicate analyses of three runs.

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