# Organic reactions in liquid crystalline solvents. 4. Nanosecond laser flash photolysis studies of intramolecular motions of rod-like solutes in liquid crystals

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This paper is dedicated to Professor Arthur N. Bourns

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The rates of triplet decay of a series of  $\beta$ -aryl-(4-alkoxypropiophenone)s in the smectic, nematic, and isotropic phases of 4'-butyl- and 4'-ethylbicyclohexyl-4-carbonitrile (BCCN and ECCN, respectively) have been measured over the 30–95°C temperature range by nanosecond laser flash photolysis. The rates of triplet decay for these probe molecules in fluid solution are governed by the rates of  $C\alpha$ —C $\beta$  bond rotation, which allows intramolecular quenching of the carbonyl triplet state by the  $\beta$ -aryl ring. The ketones are substituted with alkyl groups of varying length, shape, and flexibility in the *para* positions of the  $\beta$ -phenyl (H, n-hexyl, cyclohexyl) and benzoyl (meth-, n-pent-, and n-octoxy) rings. With the exception of  $\beta$ -phenyl-(4-methoxypropiophenone), for each ketone the Arrhenius parameters for triplet decay in the smectic phase of BCCN are similar to those in the nematic phase of the same solvent, and in all cases, the Arrhenius plots exhibit perfect continuity at the S—N transition temperature. A solvation model is tentatively advanced to explain these results. In the nematic phase of BCCN, the Arrhenius activation energy and entropy are significantly more positive than those in isotropic ECCN for all the ketones studied, but variations in the energetics of triplet decay in the nematic phase as a function of solute structure are parallelled in the isotropic solvent. Thus, the inhibiting effect of the nematic solvent on the bond rotations leading to intramolecular triplet quenching in these probes is attributed to the predominant influence of microviscosity (viscous drag) effects; the presence of solvent orientational order appears to have little or no effect on the intramolecular mobility of these results.

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Faisant appel à la photolyse flash au laser dans le domaine des nanosecondes et opérant à des températures allant de 30 à 95°C, on a mesuré les taux de dégénérescence des triplets d'une série de β-aryl alkoxy-4 propiophénones dans des phases smectiques, nématiques et isotropes des butyl-4' et éthyl-4' bicyclohexylcarbonitriles-4 (BCCN) et ECCN). Les taux de dégénérescence de ces molécules sondes dans des solutions fluides sont gouvernées par les vitesses de la rotation autour de la liaison  $C\alpha$ — $C\beta$  qui permet un piégeage intramoléculaire de l'état triplet du carbonyle par le cycle β-arylique. Les positions para des groupements phényle (H, n-hexyle, cyclohexyle) ou benzoyle (méthoxy, n-pentoxy ou n-octoxy) des cétones sont substitués par les groupements alkyles indiqués qui ont diverses longueurs, formes et flexibilités. A l'exception de la β-phényl méthoxy-4 propiophénone, les paramètres d'Arrhénius de chacune des cétones, pour la dégénérescence de l'état triplet dans la phase smectique du BCCN, sont les mêmes que ceux mesurés dans la phase nématique du même solvant; de plus, dans tous les cas, les courbes d'Arrhénius présentent toutes une continuité parfaite à la température de transition S-N. Sur une base préliminaire, on suggère un modèle de solvatation pour expliquer ces résultats. Pour toutes les cétones étudiées dans la phase nématique du BCCN, les énergies et les entropies d'activation d'Arrhénius sont toutes beaucoup plus positives que celles mesurées dans la phase isotrope du ECCN; toutefois, les variations dans les facteurs énergétiques de la dégénérescence de l'état triplet dans la phase nématique, en fonction de la structure soluté, sont parrallèlles à celles observées dans le solvant isotrope. Ainsi, l'effet inhibiteur du solvant nématique sur les rotations des liaisons, qui conduit à un piégeage intramoléculaire du triplet dans ces sondes, est attribué à l'effet prédominant des effets de microviscosité (attraction visqueuse); l'influence de l'ordre orientationnel du solvant semble n'avoir que peu ou pas d'effet sur la mobilité intramoléculaire de ces cétones. A la lumière de ces résultats, on discute des résultats et des conclusions d'études antérieures sur des réactions unimoléculaires dans des solvants nématiques.

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## Introduction

The effects of liquid crystalline order on the dynamics of uniand bimolecular reactions of dissolved solutes is an area of increasing interest. Several investigations have examined the possible effects of these media on cyclization reactions, both thermally (2) and photochemically (3) induced. The premise behind these investigations is that the conformational mobility of a reactive molecule dissolved in an orientationally ordered solvent might be restricted in favour of those conformations which "fit" the best into the surrounding solvent framework. Nematic and smectic liquid crystals are formed by compounds whose molecular shape is rod-like,<sup>2</sup> and the dominant feature of the ordering in these materials is that the long molecular axes of the constituent molecules are oriented parallel to one another, on the average. Thus, cyclization of a similarly oriented, rod-like solute molecule is expected to be inhibited in a liquid crystal, to the extent that extended or rod-like conformations are favoured over those which are more globular (or less rod-like) in shape, and that formation of the globular conformer and subsequent transition state for cyclization involves some local disruption of liquid crystalline order.

With a couple of exceptions (2e, 3e, f), the investigations reported to date have established only small or negligible effects of liquid crystalline solvents on the energetics of cyclization reactions. Several factors may be contributing to these results. The first (and most obvious) relates to the degree and rigidity of the orientational ordering in the various types of liquid crystals employed in these studies. Most have examined the effects of nematic or cholesteric liquid crystals on solute cyclization (2a-d, 3a-d). These are the most fluid types of liquid crystalline phase, and their relatively low degree of orientational

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<sup>&</sup>lt;sup>2</sup>For comprehensive descriptions of the nature and properties of liquid crystals and leading references, see ref. 4.

ordering and rigidity is apparently insufficient to significantly inhibit the conformational mobility of solutes. On the other hand, the smectic types are more crystalline in character (4), with the result that substantial effects on cyclization energetics can be observed in these types of mesophase (2e, f, 3e, f).

The second factor which presumably contributes to the ability of liquid crystals to affect solute cyclization is the structure of the solute itself (5). Bulky, globular solutes have a more disruptive effect on macroscopic liquid crystalline order (as measured by mesophase transition temperatures) than do rodlike solutes (2e, 3d, 5, 6), an effect which is presumably the result of microscopic (in the vicinity of the solute) disruption of solvent order (3e, 5). This local isotropization of the solute's environment effectively truncates the potential effects of the ordered solvent on the solute's conformational (3e) or configurational (5) mobility. Recent results from our laboratory suggest that for smectic phases, the molecular length of the solute in relation to the smectic layer thickness may be an important factor in determining the extent to which solvent order inhibits the conformational mobility of the solute (7). In general, it appears that liquid crystalline effects on solute intramolecular motions are greatest for solutes whose sizes and shapes are similar to that of the solvent molecules (3c-f, 7)

While it is clear that solute mobility can be affected to some extent in nematic and cholesteric liquid crystals, it is difficult to ascertain the nature of the effect. Considering the rather high bulk viscosities of these mesophases (8), the magnitude of the effect which is generally observed (<3 kcal/mol in  $E_a$ ; <5 eu in  $\Delta S^+$ ) might just as reasonably be attributed to microviscosity (viscous drag) effects as to the presence of solvent order. In principle, a distinction between the two effects should be possible by comparing the conformational mobilities of a series of probes of varying molecular lengths in isotropic and liquid crystalline solvents. For a suitable series of probes, microviscosity effects should be revealed by parallel behaviour of the probes in the two solvents, while solvent order effects should be revealed by varying changes in probe dynamics in the two solvents depending on the structures of the probes.

A number of techniques have been used to investigate solute molecular mobility in liquid crystals, including nmr (9), esr (10), fluorescence decay (3c-e, 11), and nanosecond laser flash photolysis (3f, 7) methods. In particular, the latter two techniques are the most useful for investigating intramolecular solute motions, since such motions can be monitored directly by examining the dynamics of intramolecular excited state quenching processes, such as intramolecular excimer or exciplex formation (3c-e) or triplet quenching (7). These experiments involve measuring the competition between normal, unimolecular decay of the initially excited end of a probe molecule and its quenching by a moiety at the other end. As long as the quenching step occurs irreversibly, and at a rate which exceeds both those of collapse of the quenching geometry prior to quenching and the competing unimolecular decay process, then the observed rate of excited state decay reflects the rate(s) of the conformational changes which are required in order for quenching to occur.

The time scale over which a particular probe system is useful depends primarily on the excited state lifetime of the isolated chromophore in the absence of quencher. For fluorescence decay methods, this limits the usable time range to 1-250 ns. While this appears to be adequate for nematic and cholesteric phases, difficulties arise in smectic solvents, where bond rotations occur on a time scale which is apparently of the

same order of magnitude (or perhaps longer) than the isolated lumophoric lifetime (3e). Nanosecond laser flash photolysis techniques allow the investigation of intrinsically longer-lived species, such as aromatic ketone triplet states, which affords more flexibility for monitoring the much slower rates of intramolecular quenching which may obtain in smectic phases.

Recently, we reported preliminary results of a nanosecond laser flash photolysis study of the effects of nematic and smectic solvent order on the triplet lifetime of  $\beta$ -phenyl-(4-methoxypropiophenone) (1*a*) (7).  $\beta$ -Phenyl ketones such as 1*a* owe their photoinertness (12, 13) and unusually short triplet lifetimes (13, 14) to intramolecular quenching of the carbonyl triplet state via exciplex interactions between the  $\beta$ -phenyl ring and the carbonyl group (reaction [1]) (13–15).



Attainment of the quenching geometry, which requires rotation about the C $\alpha$ —C $\beta$  bond (13–17), is severely inhibited in the smectic phase of *trans*, *trans*-4'-butylbicyclohexyl-4-carbonitrile (BCCN); the activation energy and entropy for triplet decay of 1a are 12 kcal/mol higher and 35 eu more positive, respectively, relative to their values in a model isotropic solvent (*trans*, *trans*-4'-ethylbicyclohexyl-4-carbonitrile, ECCN). In the nematic phase of BCCN,  $E_a$  and  $\Delta S^{\pm}$  were found to be 1.5 kcal/mol and 4 eu more positive, respectively, than their values in isotropic ECCN.



The similarity between the molecular shapes of 1a (in its *trans*-conformation) and BCCN-type analogues, and the ease with which solute structural features can be altered via appropriate substitution, make this system a seemingly ideal probe with which to examine how the conformational mobility of solutes in liquid crystals depends on solute length and substituent shape and flexibility. To this end, we have synthesized a series of  $\beta$ -aryl-(4-alkoxypropiophenone)s (1-3) and measured their triplet lifetimes as a function of temperature in the smectic, nematic, and isotropic phases of BCCN and ECCN by nanosecond laser flash photolysis. The results of this study are reported below.

#### Results

The substituted  $\beta$ -phenylpropiophenones (1-3) were prepared by condensation of 4-hydroxy- or 4-methoxyacetophenone with the appropriate *para*-substituted benzaldehyde (18), hydrogenation of the resulting  $\alpha$ , $\beta$ -unsaturated ketones over Raney nickel, and alkylation of the  $\beta$ -aryl-(4-hydroxypropio-



phenone) with the appropriate alkyl bromide or dialkyl sulfate. The ultraviolet absorption and phosphorescence emission spectra of each of these compounds are similar to those of the parent compound 1a.

Transition temperatures for BCCN, ECCN, and mixtures ca. 0.04 molal (1 mol%) in each of the ketones studied were measured by thermal microscopy and are listed in Table 1.

The ultraviolet absorption spectra of 1a in methylcyclohexane, acetonitrile, and isotropic BCCN are shown in Fig. 1. The spectra of this compound as non-oriented solutions in the nematic and smectic phases of BCCN (prepared by simple cooling of the isotropic melt) were indistinguishable from that in the isotropic phase.

Laser flash photolysis experiments were carried out using the pulses (337.1 nm, <10 mJ, ~8 ns) from a nitrogen laser for excitation, and monitoring transient absorptions using a system with nanosecond time response (19). Samples for these experiments were  $\sim 1.0 \mod \%$  solutions of the ketones in BCCN and ECCN, and were contained in Pyrex cells of 0.7 mm pathlength. Optical densities of the isotropic solutions were in the range of 0.15–0.20 at the excitation wavelength. Liquid crystalline samples were prepared by normal cooling from the isotropic melts. Smectic samples prepared in this way were typically somewhat opaque and caused considerable scattering of the monitoring light, which necessitated more extensive signal averaging (compared to nematic and isotropic samples) in order to obtain reproducible decay traces. Annealing these samples at 40°C for 2–7 days results in homeotropically aligned samples, which are much more suitable for transient absorption measurements within a limited temperature range (40  $\pm$  6°C). Above and below this temperature range, the glassy samples develop imperfections and turn opaque. Triplet lifetimes from annealed samples were identical to those obtained from unannealed ones, within experimental error. The former yield pseudoisotropic nematic phases upon warming; the characteristic turbid appearance of the nematic phase could be obtained by simple agitation of the sample cell.

Transient absorption spectra, recorded for 1b and 3a in the nematic phase of BCCN (~60°C), are shown in Fig. 2. These

TABLE 1. Transition temperatures for pure BCCN and ECCN and mixtures doped with  $1 \mod \% 1-3$  and MAP<sup>a</sup>

_	BCCN		ECCN		
Ketone	Sm–N	N–ľ	Sm-N	NI	
None	53.5-54	80	46-46.5	48.5	
<b>1</b> a	52.5-53	78.5-79	45-45.5	47.5-48	
<b>1</b> b	51.5-52	77-77.5	45-45.5	46.5-47	
1 <i>c</i>	51-52	77-77.5	45-45.5	46.5	
2	51.5-52.5	77-77.5	44.5-45.5	47-47.5	
<b>3</b> a	52-52.5	78-78.5	44.5-45.5	47.5	
<b>3</b> b	50.5-52	77-77.5	45-45.5	47-47.5	
<b>3</b> c	51-52	77-77.5	45.5-46	47-47.5	
MAP	51.5-52.5	78-78.5	45-45.5	47.5	

<sup>a</sup>Measured by thermal microscopy. Temperatures are in °C and are corrected.



FIG. 1. Ultraviolet absorption spectra of 1a in methylcyclohexane (---), acetonitrile (···), and the isotropic phase of BCCN (—).

spectra, as well as those of the other ketones studied (1a, c, 2, and 3b, c) agree well with that previously reported for the triplet state of 1a (17a, 20).

The triplet states of 1-3, monitored at 390 nm, decayed with clean first-order kinetics in every case. Representative decay traces, recorded for 1b and 3a in nematic BCCN (60°C), are included as inserts in Fig. 2. Generally, the transient absorptions decayed completely to baseline, although residual absorption did occur occasionally in the smectic phases. These absorptions were irreproducible and resulted in slightly larger errors in the calculated decay rates.

For each ketone, the triplet decay was monitored at several temperatures between 30 and 95°C in both BCCN and ECCN. Arrhenius plots of  $-\log \tau_T$  versus 1/T in the two solvents are shown in Figs. 3 and 4 for 1c and 3a, respectively. With the exception of 1a in BCCN (7), and possibly 3c in the same solvent, the data appear to fit to a single line in each case. Arrhenius parameters for triplet decay in the nematic and smectic phases of BCCN and the isotropic phase of ECCN,

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FIG. 2. Triplet-triplet absorption spectra of (a) 1b and (b) 3a in nematic BCCN, recorded at 58°C. Inserts: Representative decay traces, monitored at 390 nm for (a) 1b at 57°C and (b) 3a at 61°C.

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FIG. 3. Arrhenius plot  $(-\log \tau_T \text{ vs. } 1/T)$  for triplet decay of 1*c*, monitored at 390 nm, in the nematic and smectic phases of BCCN ( $\bullet$ ) and the isotropic and smectic phases of ECCN ( $\blacksquare$ ). Open symbols denote smectic phase, half-symbols denote nematic phase, and closed symbols denote isotropic phase results. Transition temperatures for the mixtures are indicated.

obtained from least squares analysis of the data for each ketone, are summarized in Table 2. Entropies of activation,  $\Delta S^{\pm}$ , were obtained from standard Eyring plots of the same data. The errors listed in Table 2 for  $E_a$ , log A, and  $\Delta S^{\pm}$  are listed as  $\pm 2\sigma$ (i.e. 95% confidence limits), as obtained from the least squares analyses. Table 2 also includes triplet lifetimes for each ketone



FIG. 4. Arrhenius plot  $(-\log \tau_T \text{ vs. } 1/T)$  for triplet decay of 3a, monitored at 390 nm, in the nematic and smectic phases of BCCN  $(\bigcirc)$  and the isotropic and smectic phases of ECCN  $(\bigcirc)$ . Open symbols denote smectic phase, half-symbols denote nematic phase, and closed symbols denote isotropic phase results. Transition temperatures for the mixtures are indicated.

in nematic and smectic BCCN and isotropic ECCN at 30 and 50°C, calculated from the corresponding Arrhenius parameters.

Owing to the limited temperature range over which we are able to obtain data in the isotropic phase of BCCN, we have employed ECCN as the model isotropic solvent with which to compare the behaviour of 1-3 in nematic and smectic BCCN. While ECCN is isotropic only above 48°C, the isotropic phase Arrhenius parameters reported in Table 2 were obtained from analysis of the ECCN data over the full temperature range studied (30-90°C). This treatment is justified on the basis that separate analysis of the smectic and isotropic phase data for this solvent yields identical Arrhenius parameters for each of the ketones studied. Similarly, the limited number of data points obtained in isotropic BCCN are indistinguishable from the nematic phase data in each case, and thus the two sets were combined and analysed as one to obtain the nematic phase Arrhenius parameters. For BCCN, separate calculations were performed for nematic and smectic phase data, even though in most cases (1b, c, 2, and 3a, b) triplet behaviour appears to be phase independent. This apparent phase independence may be the result of the somewhat greater scatter in the smectic phase data, caused by the usual semi-opaque nature of these samples.

Triplet lifetimes were also measured for 4-methoxyacetophenone (MAP) in the smectic, nematic, and isotropic phases of BCCN and ECCN by laser flash photolysis, and the results are plotted in Fig. 5. The factor of ca. 10 shorter lifetime of MAP in the isotropic and nematic phases of these solvents compared to those in smectic BCCN is presumably the result of more efficient impurity quenching in the former phases, reflecting their considerably lower viscosities relative to those of smectic BCCN (8).

### Discussion

The triplet lifetime of  $\beta$ -phenylpropiophenone in fluid solution at room temperature is exceedingly short (ca. 1 ns (14)), and it is now reasonably well established that this is the result of efficient intramolecular deactivation via exciplex interactions

TABLE 2. Activation parameters and extrapolated triplet lifetimes for the triplet decay<sup>*a*</sup> of 1-3 in the nematic<sup>*b*</sup> and smectic phases of BCCN and the isotropic phase of ECCN<sup>*c*</sup>

Ketone	Phase	$\tau_{T}^{60^{\circ}}$ (ns)	$\tau_T^{30^\circ}$ (ns)	$E_{\rm a}$ (kcal/mol)	$\log A(s^{-1})$	$\Delta S^{\pm}(\mathrm{eu})^d$
<u>1</u> a	Isot	34	74	$5.2\pm0.3$	$10.9\pm0.2$	$-10.9\pm0.8$
	Nem	41	113	$6.7\pm0.3$	11.8±0.2	-6.7±0.8
	Sm	28	346	$16.7\pm1.3$	18.5±1.1	24±4
1 <i>b</i>	Isot	46	100	$5.3\pm0.3$	10.8±0.2	-11.8±1.3
	Nem	53	138	$6.4\pm0.6$	11.5±0.3	-8.1±1.8
	Sm	54	120	$5.3\pm1.4$	10.8±1.0	-11.4±4.6
1 <i>c</i>	Isot	47	106	$5.5 \pm 0.2$	10.9±0.1	-10.7±0.5
	Nem	52	133	$6.2 \pm 0.3$	11.4±0.2	-8.7±1.1
	Sm	54	118	$5.2 \pm 1.3$	10.7±0.9	-11.8±4.1
2	Isot	14	34	$5.8\pm0.5$	11.7±0.4	-7.3±1.6
	Nem	19	58	7.4 $\pm0.9$	12.6±0.6	-4.1±1.5
	Sm	19	54	7.1 $\pm2.5$	12.4±1.8	-4±8
<b>3</b> a	Isot	16	44	6.6±0.4	12.1±0.3	$-5.1\pm1.2$
	Nem	22	77	8.3±0.7	13.1±0.4	$-0.3\pm1.5$
	Sm	19	85	9.9±3.1	14.2±2.1	$5\pm10$
<b>3</b> b	Isot	23	61	6.6±0.4	12.0±0.4	$-5.9\pm1.3$
	Nem	30	108	8.6±0.6	13.2±0.4	$-1.1\pm1.0$
	Sm	27	106	9.1±1.7	13.5±1.1	$1\pm5$
<b>3</b> c	Isot	22	58	6.4±0.6	11.8±0.5	-7.0±2.0
	Nem	31	104	8.0±0.6	12.7±0.4	-2.5±1.9
	Sm	28	123	9.8±0.9	14.0±0.8	3.4±2.8

<sup>a</sup>Measured by laser flash photolysis. Errors are quoted as  $\pm 2\sigma$ .

<sup>b</sup>Analyses performed using the data for both isotropic and nematic phases of this solvent.

<sup>c</sup>Analyses performed using the combined data for all phases of this solvent.

<sup>d</sup>Calculated from standard Eyring plots.

between the carbonyl group and the  $\beta$ -phenyl ring (14–16) (see reaction [1]). The activation energy for triplet decay of this molecule in fluid solution (2.3 kcal/mol (14)) is approximately that for rotation about the C $\alpha$ —C $\beta$  bond (14, 21); that these bond rotations are necessary for intramolecular quenching to occur is demonstrated by the fact that when the molecule is incorporated in zeolites (of such dimensions that the solute can reside in the channels only when it assumes the *trans*conformation), the triplet lifetime is extended to ca. 2 ms at room temperature and phosphorescence is observed (16).

Ketones such as 1–3 have lowest  $\pi,\pi^*$  triplet states (17*a*, 20), and the somewhat longer triplet lifetime and higher activation energy for triplet decay of 1*a* relative to that observed for  $\beta$ -phenylpropiophenone in fluid solution has lead to the conclusion that like the Norrish Type I and Type II reactions (22),  $\beta$ -phenyl quenching *requires* the proximity of the  $n,\pi^*$  state (17*a*). This introduces an extra energy requirement for the process in addition to that of the bond rotations involved in assuming the correct quenching geometry, viz., thermal population of the  $n,\pi^*$  triplet state. Accordingly, the activation energy for triplet decay of 1*a* in fluid solution (4.4 kcal/mol in toluene) and that of  $\beta$ -phenylpropiophenone in the same solvent (2.3 kcal/mol) corresponds roughly to the energy difference between the  $\pi,\pi^*$  and  $n,\pi^*$  triplet states of 1*a* (17*a*).

The triplet lifetime of 4-methoxyacetophenone (MAP) in BCCN and ECCN is 50-80 times greater than that of 1a under the same conditions of temperature and solvent phase, as comparison of the lifetime data in Table 2 and Fig. 5 shows. Furthermore, the fact that samples of 1a have been subjected to prolonged irradiation in these solvents with no apparent change in the appearance of the triplet decay profile or lifetime attests to the expected (14, 17b) photoinertness of these compounds. These results indicate that the observed triplet decay rates for 1-3 in liquid crystalline as well as isotropic solution are dominated by unimolecular decay processes, and that bimolecular quenching by adventitious impurities or hydrogen abstraction from the solvent is unimportant. As well, these results demonstrate that the observed Arrhenius parameters for triplet decay of 1-3 in the various phases of BCCN and ECCN reflect the energetics of those molecular motions which must occur in order for the correct geometry for  $\beta$ -phenyl quenching to be attained. These motions are, presumably, C $\alpha$ —C $\beta$  bond rotation (interconverting *trans*- and *gauche*-conformers) and C $\beta$ —C<sub>phenyl</sub> bond rotation (which brings the  $\beta$ -phenyl group into a position such that its  $\pi$ -system overlaps with the carbonyl n-orbital).

## Solvent properties

The dominant feature of the molecular ordering in liquid crystals is that the long molecular axes of the constituent molecules are oriented parallel to one another, on the average.<sup>2,3</sup> In nematic phases, this is the only type of ordering present, and hence these are the most fluid type of liquid crystalline phase. While molecular tumbling is on the whole anisotropic in these phases, the constituent molecules undergo nearly free rotation about their long molecular axes (24). In smectic phases, the constituent molecules are further arranged in layers in which the orientational vector is at some angle, or perpendicular, to the plane of the layer. Several types of smectic phases are known, and these are characterized according to the

<sup>&</sup>lt;sup>3</sup>For the sake of brevity, we confine our discussion to smectic, nematic, and cholesteric phases of rod-like mesogens. The molecular ordering in discotic liquid crystals is quite different. For a review of this type of liquid crystal, see ref. 23.



FIG. 5. Arrhenius plot  $(-\log \tau_T \text{ vs. } 1/T)$  for triplet decay of MAP, monitored at 390 nm, in the nematic and smectic phases of BCCN ( $\bullet$ ) and the isotropic and smectic phases of ECCN ( $\bullet$ ). Open symbols denote smectic phase, half-symbols denote nematic phase, and closed symbols denote isotropic phase results. Transition temperatures for the mixtures are indicated.

nature of the molecular packing within the layers (25). In smectic A phases for example, the packing within the layers is nematic-like; thus, this type of smectic phase might be expected to resemble a nematic phase with respect to its effects on the motions and unimolecular reactivity of dissolved solutes. The smectic B phase is more crystalline in nature; within the layers, the constituent molecules are hexagonally close-packed (25).

BCCN forms a single smectic phase between  $29-54^{\circ}$ C and a nematic phase between  $54-79^{\circ}$ C, while ECCN is smectic between  $28-44^{\circ}$ C, nematic between  $44-48^{\circ}$ C, and is an isotropic liquid at temperatures above  $48^{\circ}$ C (26). The smectic phases of these two compounds have not yet been conclusively assigned with respect to mesomorphic type. X-ray diffraction studies have been carried out with the homologous *trans, trans*-4'-propylbicyclohexyl-4-carbonitrile (PCCN), a polymorphic smectic (26), from which it has been established that the high temperature smectic modification of this compound is Sm B (27). Thermal microscopy (28, 29) and DSC investigations with mixtures of BCCN/PCCN and BCCN/ECCN indicate that BCCN forms a smectic phase of similar but higher order than the SmB phase of PCCN, and that the smectic phase of ECCN is of even higher order than that of BCCN (28).

Incorporation of a solute in a liquid crystal results in some degree of disruption of solvent order in the vicinity of the solute (2e, 3d, 5, 6), the extent of which depends on the structure of the solute in relation to that of the mesogen (6), and is reflected in the transition temperatures of the liquid crystalline mixture (6, 30). Rigid, rod-like solutes tend to be oriented in a liquid crystal with their long axes parallel to those of the solvent (31). Flexible molecules cause more disruption of local order, and may be oriented to a lesser extent than rigid solutes (9g). Nevertheless, while such solutes retain a high degree of conformational mobility in liquid crystals, the conformational distribution is altered relative to that in isotropic solvents in favour of those conformers which are most compatible with solvent ordering (9g).

The transition temperatures listed in Table 1 for the ketonedoped samples of BCCN and ECCN indicate that incorporation of 1 mol% of each of the ketones studied has pronounced effects on both the Sm  $\rightarrow$  N and N  $\rightarrow$  I transition temperatures of the two mesogens. n-Alkyl substituents at either end of 1*a* (compare 1*a* with 1*b*, *c* and 2) apparently result in somewhat greater disruption of local solvent order than a cyclohexyl substituent (cf. 1*a* and 3*a*) does. This is to be expected (6) considering the conformational motions available to the flexible alkyl chains compared to the relatively rigid cyclohexyl group, and the fact that the size and shape of the  $\beta$ -(4-cyclohexylphenyl) group in 3a-c is very similar to that of the solvent molecules.

The ultraviolet absorption spectra of 1a shown in Fig. 1 reveal that chromophore solvation in BCCN and ECCN is more like that in acetonitrile than in methylcyclohexane. Presumably, the fact that the position of the  $\pi,\pi^*$  absorption is shifted to longer wavelengths in acetonitrile from its position in methylcyclohexane while the  $n,\pi^*$  band is unaffected suggests that solvation in the nitrile solvents is such that there are strong interactions between the CN-group of the solvent and the benzoyl  $\pi$ -system.

# The behaviour of 1-3 in nematic BCCN

Variation in the length and flexibility of the alkoxy substituent (1a-c) has no effect on the Arrhenius parameters for triplet decay in either the nematic phase of BCCN or in isotropic ECCN, although the activation energy for decay in the nematic solvent  $(E_a^{\text{nem}})$  is consistently higher than that in the isotropic solvent  $(E_a^{\text{isot}})$ . The same trend is observed in the nematic and isotropic phase data for the homologous series 3a-c. This indicates that increasing the length of the alkoxy group with flexible substituents has no effect on the ability (albeit slight) of the nematic solvent to impede the bond rotations leading to  $\beta$ -phenyl quenching. Averaging the differences between  $E_a^{\text{nem}}$ and  $E_a^{\text{isot}}$  and between  $\Delta S^{\pm}$  values in the nematic and isotropic solvents over all the ketones studied yields  $\Delta E_a = 1.4 \pm 0.5 \text{ kcal/mol}$  and  $\Delta(\Delta S^{\pm}) = 3.9 \pm 1 \text{ eu}$ .

On the other hand, increasing the size of the  $\beta$ -aryl group within the series of 4-methoxy ketones 1a, 2, and 3a results in continuous increases in both  $E_a^{\text{nem}}$  and  $E_a^{\text{isot}}$ , and similar trends are observed in  $\Delta S^{\ddagger}$  (to more positive values). Along with the trends in the Arrhenius parameters observed for 1a-c and 3a-c, this suggests that solvation of the probes in these two solvents is such that solvent-solute interactions are strongest at the benzoyl end. This conclusion is supported by comparison of the uv absorption spectra of 1a in BCCN, acetonitrile, and methylcyclohexane. Thus, the benzoyl end of the ketone is apparently "anchored", and the  $\beta$ -aryl group constitutes the more mobile portion of the molecule. As the size of the mobile portion increases, the activation energy and entropy for intramolecular quenching tend to more positive values. This appears to be the case in both isotropic and nematic phases.

An explanation for the substituent effect on the energetics of  $\beta$ -phenyl quenching observed for 1*a*, 2, and 3*a* which is based on a substituent effect on the quenching step (i.e. that which occurs after the correct geometry has been attained) can be discounted. Substitution on the  $\beta$ -phenyl ring by electron-donating substituents might be expected to increase the rate of intramolecular quenching of the electron-deficient n,  $\pi^*$  triplet state. While the somewhat shorter triplet lifetimes of 2 and 3 compared to that of 1 in the isotropic solvent appear to be consistent with this, examination of the trends in  $E_a$  and  $\Delta S^{\ddagger}$  show that this cannot be the origin of the observed substituent effect on  $\tau_T$ . It is known that an increase in the activation energy

for an endothermic quenching process is accompanied by a *decrease* in the entropy of activation (a higher enthalpic requirement for quenching demands a tighter activated complex) (32). The trend to more positive  $\Delta S^{\pm}$  values as  $E_a^{isot}$  increases which is observed for 1*a*, 2, and 3*a* is clearly consistent with  $C\alpha$ — $C\beta$  and  $C\beta$ — $C_{phenyl}$  bond rotations being rate determining, since both will tend to more positive values as the viscous drag of the solvent on intramolecular motion increases. This provides further support for the explanation of the lack of a clear trend in the  $\tau_T$  values for a series of  $\beta$ -arylpropiophenones with lowest  $n, \pi^*$  triplet states (17*a*), from which it was concluded that bond rotations, and not the actual quenching process, form the rate determining step for  $\beta$ -phenyl quenching.

The effect of an ordered environment such as that found in liquid crystals on the intramolecular and diffusive mobility of solutes can be the result of microviscosity (viscous drag) effects or orientational ordering effects, or some combination of the two. Ultimately, the effects of high microviscosity and solvent orientational order on the Arrhenius parameters for solute motions are the same;  $E_a$  will increase and  $\Delta S^*$  will become more positive as molecular motions become more difficult and require greater displacement of the surrounding solvent matrix, whether it is ordered or not. Solvent microviscosity will heighten the barrier to conformational interconversions only as a result of effects on the transition state energy; it should have little or no effect on the relative energies of the ground state conformers. On the other hand, solvent orientational order will affect the energies of both the ground state conformers (9g) and the transition state for their interconversion (2e, 3c-e, 5, 6). In the present case, the presence of solvent order should stabilize the rod-like trans-conformer and destabilize the transition state for formation of the quenching (gauche-like) geometry.

It is important to note that the Arrhenius parameters for triplet decay of 1-3 obtained by the present method represent average values over all conformations present in solution. If microviscosity alone is responsible for the observed effects on the triplet decay of 1-3 in nematic BCCN, then parallel changes in activation parameters in the nematic and isotropic solvents with changes in solute structure should be observed. On the other hand, if solvent order plays the dominant role, then the difference between the activation parameters for triplet decay in nematic and isotropic phases should vary depending on solute structure, if the difference in conformational distribution between nematic and isotropic phases varies with solute structure. Clearly, the results obtained for 1-3 in nematic BCCN and isotropic ECCN indicate that microviscosity effects are almost entirely responsible for the slightly higher  $E_{\rm a}$  and more positive  $\Delta S^{\dagger}$  for solute bond rotations in the nematic phase. Either solute conformational energies are not altered enough in the nematic relative to isotropic phase to significantly contribute to the increase in activation parameters, or the changes do not vary appreciably throughout the series 1-3.

## The behaviour of 1-3 in smectic BCCN

The ability of the smectic phase of BCCN to inhibit  $\beta$ -phenyl quenching is strongly dependent on the structure of the probe (7). Inhibition is strong for probes which are shorter than (i.e. 1a) (7) or of a similar length to BCCN (28). For probes such as 1b and 1c, which are longer than BCCN, triplet decay is phase-independent (or almost so); this demands that the nature of the solvation of such probes in this smectic phase is much different than that experienced by 1a. The results imply that the

environment experienced by 1b and 1c in smectic BCCN is essentially isotropic (or perhaps nematic; *vide infra*) with respect to its effects on the conformational mobility of the solute, although *bulk* smectic order is preserved in the samples.

Other workers have observed analogous variations in solute behaviour in smectic solvents as a function of solute structure. The product distribution from the Norrish Type II reaction of phenylalkyl ketones in smectic n-butyl stearate varies guite dramatically with reactant length; the effect of smectic solvent order in this case is greatest when the reactive solute is similar in length to the mesogen, and falls off as the solute increases or decreases from this optimal length (3f). Electron spin resonance investigations of nitroxide spin probes in smectic phases have led to the suggestion that, depending on solute/solvent structural relationships, solutes can reside in either the relatively rigid, core portion of the layers or the more fluid, hydrocarbon interlayer region (10c, f), or be partitioned between the two (10b). Solute mobility is very different in these two regions. For small solutes, mobility can apparently be greater in Sm B phases than in the lower order SmA types (10b). This has been attributed to the solute residing in cavities in the hydrocarbon interlayer region, which become better-defined and afford less restriction to solute motion as the region increases in its overall rigidity.

BCCN is not a typical smectogen, in that the relatively short n-butyl end-chain does not allow for as much fluidity in the interlayer region as is usually the case in smectic phases (4). The Sm B phase of PCCN is regarded as being more crystalline in character than typical Sm B phases (27). This is the result of intercalation of the short n-propyl end-chains of one layer with nitrile groups in the next. For smectic BCCN, it thus seems unlikely that a solute which is unable to be incorporated unobtrusively *within* a smectic layer might reside instead in the interlayer region; there is simply just not enough room.

The perfect continuity in the Arrhenius plots for triplet decay of 1-3 at the S–N transition temperature may offer a clue as to the nature of the solvation of these probes in the smectic phases of both BCCN and ECCN, and allow a tentative explanation for the behaviour of 1-3 in these solvents. Normally, properties affected by diffusive mobility or viscosity are substantially altered at the S-N transition (4, 8b). The drastic change in the triplet lifetime of MAP at this transition (Fig. 5) is a perfect example of this behaviour; since the lifetime in this case is determined by impurity (e.g., oxygen) quenching, the large difference in the viscosities of the nematic and smectic phases (8) results in substantial differences in triplet lifetime in the two phases. The similar lifetimes above and below the bulk S–N transition temperature observed for 1-3 indicate that the microviscosity of the probes' local environment does not change detectably at the phase transition.

For all the probes studied except 1a, the results suggest that in the smectic phases of BCCN and ECCN, the local probe environment retains the order that was present in the nematic phase. Thus, the solvation shell for 1b-3c in these smectic phases might be viewed as a small, isotropized nematic "pool" surrounded by the bulk smectic phase. In each case, the effective microviscosity in the solvation shell depends on probe structural features. Probes with long, flexible substituents create more disorder and a less compact solvation shell, with microviscosity similar to that in the bulk nematic phase. Elongated probes with inflexible, solvent-like substituents (3) experience a slightly greater microviscosity since the overall shape change in proceeding to the quenching geometry is more pronounced. In the smectic phase of ECCN, these solvation pools may be intrinsically larger or better-defined than in BCCN, because the more crystalline-like interlayer packing renders the bulk smectic phase less miscible with the disordered regions surrounding the solute molecules. We note that the disordered microenvironment in a probe molecule's vicinity can only involve a few solvent molecules (certainly less than about ten) in order to maintain bulk smectic order at the high probe concentrations employed. The above description is essentially that of a mixed phase system, consisting of a ketone-rich nematic phase in coexistence with the smectic phase of the pure solvent.

In the case of 1a in BCCN, there is clearly a microscopic change in solvent phase which accompanies the bulk  $N \rightarrow S$ phase transition, but the difference in local microviscosity just below the transition is apparently negligible. This is surprising, considering the very much higher degree of order and rigidity present in the smectic phase of pure BCCN relative to the nematic (27, 28). Further experiments are clearly necessary in order to conclusively define the nature of the solvation of 1 in this phase.<sup>4</sup>

# Summary and conclusions

The Arrhenius parameters for triplet decay of a series of B-aryl-(4-alkoxypropiophenone)s reflect those of the simple conformational motions which allow intramolecular quenching of the carbonyl triplet state, and are significantly affected in the smectic and nematic phases of BCCN relative to their values in the isotropic phase of ECCN. The probes vary in the size and flexibility of substituents, and in their completely extended conformations, vary over a factor of two in length. Smectic solvent order results in large increases in  $E_a$  and  $\Delta S^{\dagger}$  for small, relatively compact probes, small increases for probes bearing a large inflexible substituent, and has no effect on the Arrhenius parameters for triplet decay of probes with flexible, long-chain alkyl substituents. The perfect continuity in the Arrhenius plots at the S-N transition temperature of BCCN suggests that for probes longer than the smectic layer thickness, their microenvironment in the smectic phase is similar to that in the nematic phase.

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In the nematic phase,  $E_a$  and  $\Delta S^{\ddagger}$  are consistently ca. 1.5 kcal/mol and 4 eu higher, respectively, than the corresponding values in the isotropic solvent. Variation of the alkoxy substituent has no effect on the Arrhenius parameters, while variation of the  $\beta$ -aryl substituent results in systematic increases with substituent size and rigidity. Parallel effects are observed in the isotropic phase, which leads to the conclusion that higher microviscosity, and not an orientational ordering effect, is responsible for the slight inhibition to solute conformational motion in the nematic phase relative to that in isotropic solvents.

From the present results, and previous studies of unimolecular reactions in nematic and cholesteric phases (2, 3), several conclusions can be derived with respect to the ability of these types of liquid crystals to inhibit intramolecular motion. It appears that the most one can expect in the way of an effect on the activation energy for such a process is about 3 kcal/mol, and it is likely that this is almost solely the result of microviscosity effects. Furthermore, an effect can only be expected when substantial changes in the *overall* shape of the molecule occur on the way to the transition state for reaction. The result that nematic solvents have no effect on the energetics of the Claisen rearrangement of cinnamyl phenyl ether (2c), for example, can be readily explained in this context; examination of molecular models shows that the bond rotations which interconvert the fully extended conformation of this molecule and that in the transition state for cyclization do not in fact alter the overall rod-like shape of the molecule appreciably. This same explanation can rationalize the small effects of cholesteric and compensated nematic solvents on the Norrish Type II reaction of  $\alpha$ -diketones (3a).

Further investigation of the balance between solute/solvent structural features and the ability of smectic phases to inhibit the intramolecular mobility of solutes is in progress and will be reported in the near future.

# Experimental

Melting points and transition temperatures were measured on a Reichert micro-hot stage microscope with polarizing lenses and are corrected. <sup>1</sup>H nmr spectra were recorded in deuterochloroform solution on a Varian EM390 nmr spectrometer, and are reported in parts per million downfield from TMS. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer, and are reported in wavenumbers, calibrated against the 1601.8 cm<sup>-1</sup> polystyrene absorption. Mass spectra were recorded on a VG Micromass 70-70F mass spectrometer, and exact masses have been calculated using an atomic mass of 12.00000 for carbon. Ultraviolet absorption spectra were recorded on a Hewlett Packard HP-8451 spectrometer.

Laser flash photolysis experiments employed the computerized facility which has been described in detail elsewhere (19), and the pulses (337.1 nm,  $\sim$ 8 ns, <10 mJ) of a nitrogen laser for excitation. Sample temperatures were recorded using a calibrated platinum thermometer, and are considered accurate to  $\pm 0.5^{\circ}$ C. Samples of 1-3 as  $\sim 1.0$  mol% solutions in BCCN and ECCN were contained in  $0.7 \text{ mm} \times 7 \text{ mm}$  rectangular Pyrex (Vitro Dynamics) sample cells. They were prepared by adding an aliquot of a standard solution of the ketone in dichloromethane to a cell by microlitre syringe, evaporating off the solvent with a stream of nitrogen, and then weighing the required amount of the mesogen into the cell. The samples were then either sealed with rubber septa and deoxygenated by bubbling dry nitrogen through the isotropic melts or subjected to three freezepump-thaw degassing cycles followed by sealing on a high vacuum line ( $10^{-3}$  Torr). Decay of laser-generated transients was monitored by uv absorption. The optical densities of the isotropic solutions were in the range 0.15-0.20 at 337 nm. While the isotropic solutions were optically clear at the transient monitoring wavelength (390-395 nm), and the nematic solutions almost so, the smectic samples generally had optical densities in the range 0.6-1.3 as a result of light scattering. For the smectic samples, decay traces represent the average of 40-60 shots, each corrected for background scattering from the excitation pulse. Annealing the smectic samples at 40°C for 2-7 days results in homeotropically aligned (i.e. glassy) samples, which have considerably better light transmission characteristics. The triplet lifetimes obtained using these samples do not differ significantly from the lifetimes obtained from the samples used immediately after cooling from the isotropic melts.

Methylcyclohexane (BDH Omnisolv), acetonitrile (Caledon HPLC), and dichloromethane (Caledon HPLC) were used as received. 4'-Butylbicyclohexyl-4-carbonitrile (BCCN; EM Licristal ZLI1538) and 4'-ethylbicyclohexyl-4-carbonitrile (ECCN; EM Licristal ZLI1537) were used as received from E. Merck, Co. 4-Methoxyacetophenone (Aldrich) used for laser flash photolysis experiments was recrystallized twice from methanol.

4-(n-Hexyl)benzaldehyde (bp 118-119°C, 3 mm Hg) and 4-cyclo-

<sup>&</sup>lt;sup>4</sup>NOTE ADDED IN PROOF: The 4-ethoxy and 4-propoxy derivatives of 1 also show phase dependent behaviour in BCCN. However, the break in the Arrhenius plot does not occur at the bulk  $N \rightarrow S$  transition temperature; rather it moves to progressively lower temperatures with increasing alkoxy chain length. The behaviour of the 4-<sup>n</sup> butoxy derivative is phase independent (27).

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIX WINDSOR on 11/19/14 For personal use only. hexylbenzaldehyde were prepared by formylation of 1-phenylhexane and cyclohexylbenzene (Aldrich), respectively, with hexamethylenetetramine in trifluoroacetic acid (33). The 4-cyclohexylbenzaldehyde that was obtained as a yellow oil after column chromatography of the crude reaction mixture on silica gel exhibited <sup>1</sup>H nmr, infrared, and mass spectra that were consistent with its structure. It was used without further purification or characterization.

The  $\beta$ -phenyl ketones 1a and 3a were prepared by condensing 4-methoxyacetophenone with benzaldehyde and 4-cyclohexylbenzaldehyde, respectively (18a), and hydrogenation of the resulting chalcone derivative over Raney nickel in ethyl acetate. Ketones 1b, c, 2, and 3b, c were prepared by condensing 4-hydroxyacetophenone with the appropriate 4-alkylbenzaldehyde (18b), hydrogenation of the resulting chalcone over Raney nickel in 10% sodium hydroxide, and finally alkylation of the  $\beta$ -aryl-4'-hydroxypropiophenone with 1-bromopentane, 1-bromooctane, or dimethyl sulfate and potassium carbonate in refluxing acetone (34). 3-(4-Methoxyphenyl)-1-phenylpropen-3-one (5a) had mp 105-106°C (lit. 101-103°C (1), 3-(4-hydroxyphenyl)-1-phenylpropen-3-one (4a) had mp 171-172°C (lit. 177.5°C (18b), 1-(4-methoxyphenyl)-3-phenylpropan-1-one (1a) had mp 96-97°C (lit. 96-97°C (18b)), and 1-(4-hydroxyphenyl)-3-phenylpropan-1-one (6a) had mp 104-105°C (lit. 104°C (18b)). Spectral data for the other ketones which were synthesized as precursors to 1-3 are as follows

3-(4-Hydroxyphenyl)-1-(4-<sup>n</sup>hexylphenyl)propen-3-one (4b) (from 4-hydroxyacetophenone and 4-<sup>n</sup>hexylphenyl)propen-3-one (4b) (from 4-hydroxyacetophenone and 4-<sup>n</sup>hexylphenzaldehyde) was recrystallized once from aqueous ethanol to afford light yellow needles, mp 108– 112°C. <sup>1</sup>H nmr:  $\delta 0.88(t, 3H)$ , 1.32(m, 6H), 1.61(m, 2H), 2.65(t, 2H), 6.89(br s, 1H), 7.00(d, 2H), 7.34(d, 2H), 7.53(d, 1H), 7.59(d, 2H), 7.87(d, 1H), 8.04(d, 2H). Ir (CCl<sub>4</sub>): 3608(w), 3415(m, br), 2960(w), 2925(m), 2855(w), 1667(m), 1653(m), 1598(s, sh), 1530(s, br), 1329(m), 1209(m), 1161(m), 980(m), 705(s, br). Mass: calcd. for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>, 308.1776; found, 308.1754.

*1-(4-Cyclohexylphenyl)-3-(4-hydroxyphenyl)propen-3-one (4c)* (from 4-hydroxyacetophenone and 4-cyclohexylbenzaldehyde) was recrystallized once from 95% ethanol to afford light yellow plates, mp 190–192°C. <sup>1</sup>H nmr:  $\delta$  1.40(m, 5H), 1.83(m, 5H), 2.46(m, 1H), 6.41(br s, 1H), 6.95(d, 2H), 7.27(d, 2H), 7.48(d, 1H), 7.58(d, 2H), 7.84(d, 1H), 8.03(d, 2H). Ir (KBr): 3100(br, s), 2918(m), 2840(m), 1646(m), 1595(s), 1552(s, sh), 1405(m), 1328(s), 1296(m), 1218(s), 1161(s), 1022(m), 980(m), 810(m), 579(w), 538(w). Mass: calcd. for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>, 306.1620; found, 306.1630.

*1-(4-Cyclohexylphenyl)-3-(4-methoxyphenyl)propen-3-one* (5c) (from 4-methoxyacetophenone and 4-cyclohexylbenzaldehyde) was chromatographed on silica gel (hexane/dichloromethane mixtures), and recrystallized once from 95% ethanol to afford light yellow plates, mp 95–96°C. <sup>1</sup>H nmr: δ 1.40(m, 5H), 1.83(m, 5H), 2.52(m, 1H), 3.89(s, 3H), 6.98(d, 2H), 7.37(d, 2H), 7.50(d, 1H), 7.59(d, 2H), 7.83(d, 1H), 8.07(d, 2H). Ir (CCl<sub>4</sub>): 3006(w), 2927(s), 2847(m), 1666(s), 1604(s, br), 1418(w), 1329(m), 1252(m), 1167(s), 1022(m). Mass: calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>, 320.1776; found, 320.1792.

3-(4-<sup>*n*</sup>hexylphenyl)-1-(4-hydroxyphenyl)propan-1-one (6b) (from 4b) was recrystallized from aqueous ethanol to yield a colourless solid, mp 94–95°C. <sup>1</sup>H nmr:  $\delta$  0.87(t, 3H), 1.30(m, 6H), 1.56(m, 2H), 2.57(t, 2H), 3.13(m, 4H), 6.33(br s, 1H), 6.90(d, 2H), 7.15(s, 4H), 7.94(d, 2H). Ir (CCl<sub>4</sub>): 3603(m), 3366(m, br), 3016(w), 2949(m), 2928(s), 2850(m), 1687(s), 1663(s), 1602(s, br), 1435(m), 1362(m), 1286(m), 1266(m), 1166(s). Mass: calcd. for C<sub>21</sub>H<sub>26</sub>O<sub>2</sub>, 310.1933; found, 310.1930.

3-(4-Cyclohexylphenyl)-1-(4-hydroxyphenyl)propan-1-one (6c) (from 4c) was recrystallized from aqueous ethanol to yield a colourless solid, mp 147–150°C. <sup>1</sup>H nmr:  $\delta$  1.37(m, 5H), 1.81(m, 5H), 2.42(m, 1H), 3.11(m, 4H), 6.31(s, 1H), 6.90(d, 2H), 7.16(s, 4H), 7.95(d, 2H). Ir (CCl<sub>4</sub>): 3608(m), 3372(m, br), 3010(w), 2928(s), 2850(m), 1688(s), 1667(m, sh), 1602(s, br), 1458(m), 1262(m), 1166(s). Mass: calcd. for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>, 308.1776; found, 308.1759.

#### Substituted $\beta$ -phenylpropiophenones 1-3

1-(4-Pentoxyphenyl)-3-phenylpropan-1-one (1b) (from 6a and 1bromopentane) was recrystallized twice from methanol to yield colourless plates, mp 63–64°C. <sup>1</sup>H nmr:  $\delta$  0.91(t, 3H), 1.42(m, 4H), 1.80(m, 2H), 3.15(m, 4H), 4.02(t, 2H), 6.94(d, 2H), 7.31(s, 5H), 7.99(d, 2H). Ir (CCl<sub>4</sub>): 3024(w), 2948(m), 2928(m), 2867(w), 1683(s), 1595(s, sh), 1532(s, br), 1303(m), 1338(m, br), 1306(w, sh), 1168(s), 978(m, br), 709(s, br). Mass: calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>, 296.1776; found, 296.1759.

*1-(4-Octoxyphenyl)-3-phenylpropan-1-one (1c)* (from **6***a* and 1bromooctane) was recrystallized twice from methanol to yield colourless plates, mp 48–49°C. <sup>1</sup>H nmr:  $\delta$  0.87(t, 3H), 1.31(m, 10H), 1.78(m, 2H), 3.13(m, 4H), 4.00(t, 2H), 6.90(d, 2H), 7.28(s, 5H), 7.94(d, 2H). The ir spectrum was similar to that of 1*b* except for minor differences in the C—H stretching region. Mass: calcd. for C<sub>23</sub>H<sub>30</sub>O<sub>2</sub>, 338.2246; found, 338.2289.

3-(4-<sup>*n*</sup>hexylphenyl)-1-(4-methoxyphenyl)propan-1-one (2) (from 6b and dimethylsulfate) was recrystallized twice from ethanol to yield colourless plates, mp 56–57°C. <sup>1</sup>H nmr:  $\delta$  0.87(t, 3H), 1.31(m, 6H), 1.53(m, 2H), 2.58(t, 2H), 3.12(m, 4H), 3.85(s, 3H), 6.92(d, 2H), 7.15(s, 4H), 7.97(d, 2H). Ir (CCl<sub>4</sub>): 3003(w), 2948(m), 2920(s), 2846(m), 1685(s), 1594(s, sh), 1535(s, br), 1462(w), 1416(w), 1357(w), 1302(m), 1244(s), 1165(s), 1030(m), 966(w), 706(s, br). Mass: calcd. for C<sub>22</sub>H<sub>28</sub>O<sub>2</sub>, 324.2090; found, 324.2067.

3-(4-Cyclohexylphenyl)-1-(4-methoxyphenyl)propan-1-one (3a) (from catalytic hydrogenation of 5c) was recrystallized twice from ethanol to yield colourless needles, mp 89–90°C. <sup>1</sup>H nmr:  $\delta$  1.40(m, 5H), 1.84(m, 5H), 2.43(m, 1H), 3.12(m, 4H), 3.84(s, 3H), 6.91(d, 2H), 7.17(s, 4H), 7.96(d, 2H). Ir (CCl<sub>4</sub>): 3080(w), 2925(s), 2851(s), 1683(s), 1594(m, sh), 1530(s, br), 1241(s), 1201(w), 1165(s), 1300(m), 966(w), 709(s, br). Mass: calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>, 322.1933; found, 322.1918.

3-(4-Cyclohexylphenyl)-1-(4-pentoxyphenyl)propan-1-one (3b) (from 6c and 1-bromopentane) was recrystallized twice from ethanol to yield colourless plates, mp 70–71°C. <sup>1</sup>H nmr:  $\delta$  0.92(t, 3H), 1.38(m, 9H), 1.81(m, 7H), 2.43(m, 1H), 3.13(m, 4H), 4.01(t, 2H), 6.92(d, 2H), 7.17(s, 4H), 7.94(d, 2H). The ir spectrum was similar to that of 3a except for minor differences in the 2800–3100 and 950–1050 cm<sup>-1</sup> regions. Mass: calcd. for C<sub>26</sub>H<sub>34</sub>O<sub>2</sub>, 378.2558; found, 378.2560.

3-(4-Cyclohexylphenyl)-1-(4-octoxyphenyl)propan-1-one (3c) (from 6c and 1-bromooctane) was recrystallized twice from ethanol to yield colourless plates, mp 63–64°C. <sup>1</sup>H nmr:  $\delta$  0.90(t, 3H), 1.32(m, 15H), 1.84(m, 7H), 2.47(m, 1H), 3.13(m, 4H), 4.02(t, 2H), 6.92(d, 2H), 7.18(s, 4H), 7.94(d, 2H). The ir spectrum was similar to those of 3a, b except for minor differences in the 2800–3100 and 950–1050 cm<sup>-1</sup> regions. Mass: calcd. for C<sub>29</sub>H<sub>40</sub>O<sub>2</sub>, 420.3028; found, 420.3037.

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