PHOTOCHEMICAL PROBES OF CONFORMATIONAL MOBILITY

IN THERMOTROPIC LIQUID CRYSTALS

by

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ABSTRACT

Phenyl ketone photochemistry has been used to probe the effects of thermotropic liquid crystals on the conformational mobility of dissolved solutes. In addition, concentration and temperature dependent deuterium (^{2}H) NMR spectroscopy studies of deuterated analogues of the probe ketones have afforded detailed information on the solubilisation behaviour of the solutes in the nematic and smectic liquid crystalline phases of various mesogens. Results from the ^{2}H NMR studies have allowed for the construction of binary phase diagrams of the solute/solvent mixtures and have provided a method for the accurate determination of the solubility limits of these probes in smectic phases.

The Norrish II reactions of butyrophenone (**BP**), valerophenone (**VP**), hexanophenone (**HP**), and γ-cyclohexylbutyrophenone (**CHBP**) have been carried out at 30°C as a function of concentration in the isotropic, nematic and smectic liquid crystalline phases of *trans,trans*-4'-alkyl-[1,1'-bicyclohexyl]-4-carbonitrile (**CCH-n**) liquid crystals. The distribution of fragmentation and cyclisation products from photolysis of these ketones in the nematic phase is similar to that obtained from photolysis in model isotropic solvents. The product distribution from photolysis of a homogeneous smectic phase solution of **BP** is also similar to that in the isotropic phase, but the fragmentation/cyclisation ratios from photolysis of homogeneous smectic phase solutions of **VP**, **HP**, and **CHBP** are significantly affected by the ordered environment. For ketone/mesogen mixtures of bulk solute concentration above the solubility limit, the observed effects of the smectic phase on the photochemistry of these solutes is lowered. This has been shown to be the result of a portion of the reactivity ensuing from

phase-separated nematic or isotropic phases which coexist with the smectic phase component in these cases. The magnitude of the effect on the reactivity of these solutes in the smectic phase of CCH-4 correlates with the size of the γ-substituent. The results seem to indicate that the necessity for specific size and shape structural features for the successful observation of effects in the smectic phase of this mesogen are not required. A solubilisation model has been proposed to account for the effects.

The rates of intramolecular triplet decay of β-phenyl-4-methoxy-propiophenone (1) in the isotropic and liquid crystalline phases of CCH-n, *trans*- 4-alkylcyclohexyl-*trans*-4'-alkyl-cyclohexylcarboxylate (OS-nm), and *trans,trans*-4'--alkyl-[1,1'-bicyclohexyl]-4-alkylether (CCH-nOm) mesogens have been investigated using nanosecond laser flash photolysis techniques. The average triplet lifetimes measured for homogeneous smectic solutions of 1 range from a factor of *ca.* two to four times longer than those in homologous nematic or isotropic phases at the same temperature. The magnitude of the change in lifetime that occurs at the nematic to smectic (N→Sm) phase transition is a function of the relative amount of order associated with each of the smectic phases. Despite the changes in lifetime which occur at the N→Sm transition temperatures, the differences in the Arrhenius parameters for triplet decay in the smectic and nematic/isotropic phases are small. A study of the photochemistry of a series of benzoyl- and β-aryl substituted derivatives of 1 in the CCH-n and CCH-nOm mesogens has shown that the nature of the effect on β-phenyl quenching is mainly the result of a change in the equilibrium constant for *trans/gauche* interconversion in the smectic phase compared to that in the nematic/isotropic phases. This latter study also investigated the effects of solute structure on the ability of thermotropic liquid crystals to control the conformational mobility of this probe. Slight variations in the structure of the alkoxy substituent reduces the ability of the smectic phase

to slow triplet deactivation, while substitution at the *para*-position of the β-phenyl ring magnify the effect of solvent order on the triplet lifetime. These results have been explained in terms of the ability of the ordered phases to solubilise these solutes.

In total, the results of these studies have allowed for a more complete understanding of the effects of highly ordered liquid crystalline phases on the solubilisation behaviour and on the conformational mobilities of dissolved solutes.

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CHAPTER 1

INTRODUCTION

1.1   Chemical Reactivity in Ordered Media

The investigation of chemical reactions in ordered environments is a relatively modern trend in organic chemistry. Traditionally, chemical reactions are performed using normal isotropic solvents, where motions of molecules remain (typically) quite random. Strategies usually employed by chemists to steer the selectivity of a reaction in these cases are a) to alter the electronic characteristics of a portion of the molecule, or b) to impede reaction at a particular centre or face of the molecule through steric factors. Another approach to controlling reactivity is to carry out chemical transformations in an organised environment where the medium is capable of imposing restrictions on the molecular and conformational motions of the included reactants. There are numerous advantages that can be gained by such an approach, and for chemists the main goal in studies of these type is to be able to control the regiochemical or stereochemical outcome of reactions of guest molecules. Control of reactivity in this way can occur either as a result of diverting the pathway of a reaction through a transition state that may be particularly compatible with the restrictions imposed by the ordered media, or as a result of limiting the way molecules can interact with their reactive partners. In the same manner the efficiency or rate of a particular reaction may also be affected.

The variety of studies of reactions in anisotropic environments is overwhelming and a number of reviews are available to familiarize the reader with studies

of this type.[1-5] The most familiar and most studied ordered media are *micelles, inclusion complexes* (in solution or the solid state) and *solid supports*. Examples include membranes, cyclodextrins, zeolites, silica or alumina surfaces, and crystalline solids. Another type of organised medium, which bridges the gap between the solid state and isotropic solution, is a unique class of compounds known as **liquid crystals.**[6-15] Liquid crystals are attractive ordered environments for investigation since the orientational order present in these media (*vide infra*) restricts the randomness of molecular motions associated with the isotropic state, but the rigidity present in a solid matrix is absent, thereby allowing some molecular mobility and conformational flexibility.

The nature of each type of ordered medium varies quite dramatically; however, all act to organise included reactants in ways, that under favourable circumstances, can affect their reactivity or mobility or both. Besides the numerous benefits to the chemist, host-guest complexes are also used as models for biological systems. Here, a better understanding of the remarkable efficiency and selectivity of biological reactions can be gained in the hope that we may one day be able to mimic nature in the laboratory.[1] In addition many studies, especially those on solid surfaces, are used as models for catalytic processes.[4] Understanding the roles these media play in orienting dissolved solutes and controlling their reactivity is still in its infancy. However, the ultimate goal is to gain a sufficient understanding of a particular system to enable one to predesign an experiment to achieve a desired outcome for a given application.

This thesis describes our contribution to the understanding of the nature of the effects that liquid crystals have on included solutes. For this purpose we have utilised photochemical probe molecules to gain information on the factors that affect conformational mobility and reactivity in liquid crystals. In the remainder of this chapter

an introduction to the unique properties of liquid crystals, and how they may potentially

alter reactivity of dissolved solutes, is given. This is followed by a description of the

probe methods which we have utilised in our efforts. Finally, a discussion of the impetus

for this work, which includes a brief review of some of the more successful studies

involving conformational control of reactivity in liquid crystalline solvents, is presented.

1.2   Thermotropic Liquid Crystals

It is important to discuss in general terms the structures and classifications of

liquid crystals before one can appreciate how liquid crystals act to orient dissolved solutes.

Liquid crystals (mesogens) have structures and properties intermediate between those of

an isotropic *liquid* and a *crystalline* solid.[6-15] In general, the molecules which form a

liquid crystalline phase (mesophase) possess orientational ordering, associated with a

crystalline state, but maintain a degree of translational mobility giving them some fluidity

that is associated with an isotropic state. Liquid crystals can be broadly divided, based on

a chemical standpoint, into the categories of *lyotropic* and *thermotropic* liquid crystals.

Lyotropic liquid crystals are generally formed from mixtures of an

amphiphilic compound and a controlled amount of a polar solvent. The types of phases

they form are dependent on the relative concentrations of each of the two or more

components and, to some extent, temperature. **Thermotropic liquid crystals are**

typically formed from a single component[16] and the mesophases are formed at

temperatures between those at which the isotropic and crystalline phases of the mesogen

exist. In this thesis we utilised thermotropic liquid crystals, therefore the discussion will

be limited to this category of mesogen.

Thermotropic liquid crystals are classified according to their molecular and phase structures.[6-15] In general, molecules which exhibit liquid crystallinity consist of a rigid core with flexible substituents. In a number of cases the mesogens contain polar functional groups as a terminal or central unit. The majority[17] of thermotropic liquid crystals are derived from rod-like molecules, whose molecular lengths are longer than their diameters, and are classified as *calamitic* mesogens. Mesogenic compounds which are large and disc-like are labelled as *discotic* liquid crystals. More recently, mesophases have been observed from molecules which have structural features of both rod-like and disc-like molecules. These so called "lath-like" species have been classified as *phasmadic* and are usually the precursors to the *sanidic* liquid crystalline polymers.[12] The remaining discussion will deal only with the phase types exhibited by calamitic mesogens since it is mesogens of this class that were used in this work.

The mesophases exhibited by calamitic liquid crystals fall into three major classes - nematic (N), cholesteric and smectic (Sm). These phase types differ in the nature and the degree of order that they possess. In general, the degree of order in the phases decreases as the temperature is raised from the crystalline phase (K) of the mesogen to the isotropic phase (I). The relative phase sequence observed as a function of temperature is shown pictorially in Figure 1.1. Liquid crystalline phases that can be formed by either heating the material from a more ordered phase or cooling from a less ordered phase are referred to as enantiotropic. Thermodynamically metastable mesophases (monotropic) can only be formed on cooling from a higher temperature phase.

Of the classes of liquid crystalline phase types, nematic phases are the least ordered. They are characterised by the long axes of the constituent molecules oriented in a parallel, or nearly parallel arrangement (see Figure 1.1). In nematic phases this is the

Nematic:
orientational order
no positional order

Smectic:
orientational and
positional order

Isotropic
Liquid (I)

T (°C)

Nematic (N)

Liquid
Crystalline

Smectic (Sm)

Crystalline
Solid (K)
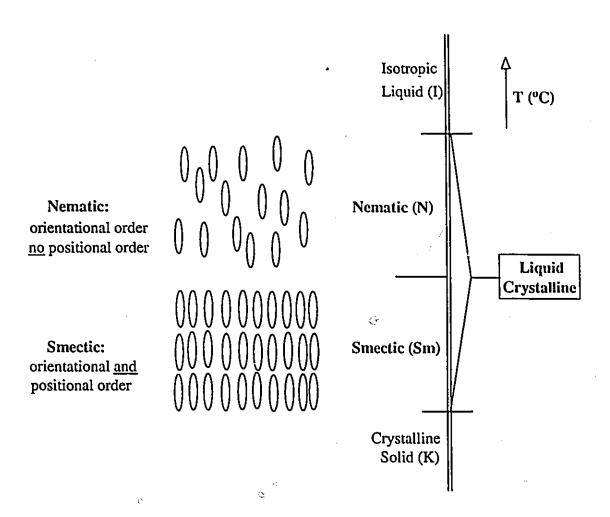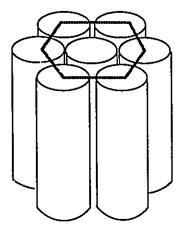
Figure 1.1. Idealised representation of the molecular orientation of a calamitic mesogen in the nematic and smectic liquid crystalline states. The relative order of the phase types as a function of temperature is also shown.

only degree of ordering present. While this phase type has very interesting properties because of its anisotropic ordering[13-15] it still possesses a large degree of rotational and translational mobility (still very fluid like). Except for a limited number of special cases[18] this phase structure changes to an isotropic liquid on heating. Cholesteric phases are formed by chiral mesogens (and, as their name implies, are frequently cholesterol derivatives), or by simple nematic phases doped with a chiral solute. They are considered a special type of nematic phase, since they have local nematic orientation of the molecules, but the orientation undergoes a <u>macroscopic</u> twist through the bulk sample. The period of this twist is typically on the order of several thousand Ångstroms, resulting in unique optical properties.[7,13] Smectic phases possess a higher degree of order than nematic (and cholesteric) phases do. In mesogens which exhibit both phase types, the smectic phase(s) generally exists at the lower temperature(s).[18] In addition to the <u>orientational</u> order present in the nematic phase, smectic phases have <u>positional</u> ordering with the molecules arranged in layers. The molecules may either be ordered or randomly situated within each layer. In addition, most smectic phases possess no long range positional ordering between layers. Therefore, they are often considered as two dimensional solids. There are a variety of smectic phases known,[6,7,9] classified based on the degree and type of packing within the layers, as well as the preferred angle of orientation of the mesogens with respect to the layer plane. Techniques used in the classification of the phase types include optical microscopy,[19] X-ray diffraction techniques,[11,20] differential scanning calorimetry,[19] and various spectroscopic techniques.[21]

Examples of the various types of smectic phases include the smectic A (Sm$_A$), smectic B (Sm$_B$), and smectic C (Sm$_C$) phases. The Sm$_A$ and Sm$_C$ phases are relatively

disordered smectic phases with the constituent molecules randomly situated within the layer plane. The distinguishing difference between the Sm_A and the Sm_C phases is that in the latter the molecules are tilted at an angle with respect to the layer plane, resulting in macroscopic optical activity. The key smectic phases utilized in the present study can be broadly designated as Sm_B phases.[6,11] The Sm_B structure is more highly ordered than those of the Sm_A and Sm_C phases. In smectic B phases the molecules are hexagonally close-packed in the layers (as illustrated in Figure 1.2), with the molecules arranged

Figure 1.2. Representation of the hexagonal packing in the Smectic B (Sm_B) phase. Each cylinder represents the area swept by a single molecule making up the phase.

perpendicular to the layered plane.[6-13] A further description of the order associated with the smectic phases used in this study will be given in the following section.

The unique ordering properties of liquid crystals can, in many cases, be controlled or induced with the application of magnetic or electric fields. This has allowed the technological exploitation of liquid crystals for a variety of applications, such as liquid crystal displays and other electro-optical devices, laser optics and mechanical engineering applications.[13-15] We are interested in liquid crystals as reaction solvents to utilise the

anisotropic nature of the mesophases of these materials to orient and subsequently control the motions and reactivity of dissolved solutes.

1.3   Thermotropic Liquid Crystals as Solvents for Photochemical Reactions

1.3.1   General Considerations

In order for liquid crystals to be suitable as solvents for investigating the effects of solvent order on aspects of chemical reactivity, there are a number of factors that must be considered. For use as photochemical reaction solvents, an obvious requirement is that the mesogens of choice be transparent to irradiation in the region where the probe molecules absorb or emit. Furthermore, the mesogen should not be efficient quenchers of the excited state of the probe solute. For practical purposes the mesogen should exhibit its liquid crystalline phases at temperatures close to ambient temperature. Since liquid crystals are being used as solvents, it is further advantageous that the mesogens employed be readily available at a reasonable cost in order to maximise the types and number of experiments possible.

In our experiments, where we are probing the influence of an ordered solvent on chemical reactivity, meaningful conclusions can only be made if comparisons to an isotropic phase of similar electronic properties is made. One is at an advantage when employing liquid crystals as the organised media since the phase can be changed by simply adjusting the temperature. Therefore, in many cases reactivity in the isotropic phase of the same mesogen is used for comparison. It is often more desirable to compare
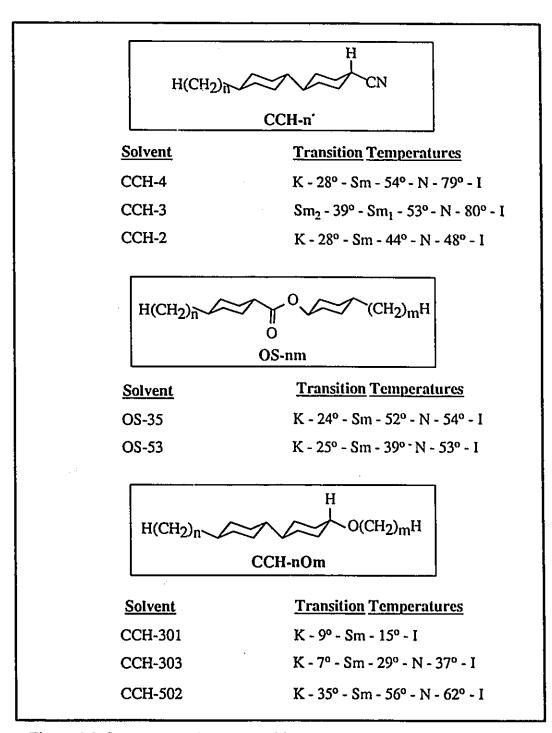
results at a single temperature. In these situations mixtures of similar mesogens, or mixtures of mesogens with other compounds of similar structure and polarity, can give rise to the desired model isotropic phases. The best model isotropic solvent is another member of the same family of mesogen which exists as an isotropic liquid over a similar temperature region where the material of interest is liquid crystalline. It is essential to have mesogens where one or more of these options are available to allow for proper interpretation of results.

Furthermore, if the goal of a study is to make general observations and conclusions regarding the effect of a particular phase type on the mechanistic and chemical details of a reaction, it is beneficial to be able to compare the results obtained in a number of different mesogens with similar liquid crystalline phases. Thus, one would require several series of liquid crystalline compounds whose individual members exhibit overlapping isotropic, nematic and smectic phase temperature ranges.

1.3.2   Liquid Crystals Used in this Study

We have found three families of mesogens that fulfil the above requirements and in addition, have fairly well-defined smectic phases. The mesogens used in this work are illustrated along with their phase transition temperatures in Figure 1.3 and are available commercially from E. Merck Inc..[22] The structure and phase characteristics of these materials have been fairly well established and a description of them follows.

The *trans,trans*-4'-alkylbicyclohexyl-4-carbonitrile (CCH-n) mesogens have found considerable use as solvents in U.V. absorption,[23] fluorescence spectroscopy,[24] and nuclear magnetic resonance (NMR) spectroscopy studies,[25-27] as well as for photochemical reactions.[14] The 4-butyl analog, CCH-4, has attracted the most attention because it exhibits enantiotropic smectic (Sm) and nematic (N) phases over broad temperature ranges close to room temperature: 28-54°C and 54-79°C, respectively.[28,29] The smectic phase of CCH-4 has been assigned the Crystal-B (Cr_B) structure based on X-ray diffraction data.[30] The order associated with the Cr_B structure is similar to that described for the conventional Sm_B phase, except there is additional layer-to-layer positional regularity.[9,11,31] The molecules in the Cr_B phase are arranged in a hexagonally closed packed _interdigitated_ _bilayer_ structure giving the phase some degree of three dimensional order and hence, the Crystal-B designation. The smectic phase of the 4-ethyl analog, CCH-2, has a rhombohedral structure,[30] which has been shown to have a higher degree of order than the Cr_B phase of CCH-4 on the basis of miscibility studies.[29] CCH-2 forms enantiotropic smectic and nematic phases between 28-44°C and 44-48°C, respectively.[28,29] A 2:1 mixture of CCH-2 and CCH-4, which we shall call "EB", forms a room temperature nematic phase between 25-54°C.[29] In addition, a 16 mol% solution of

CCH-n

Solvent	Transition Temperatures
CCH-4	K - 28° - Sm - 54° - N - 79° - I
CCH-3	Sm_2 - 39° - Sm_1 - 53° - N - 80° - I
CCH-2	K - 28° - Sm - 44° - N - 48° - I

OS-nm

Solvent	Transition Temperatures
OS-35	K - 24° - Sm - 52° - N - 54° - I
OS-53	K - 25° - Sm - 39° - N - 53° - I

CCH-nOm

Solvent	Transition Temperatures
CCH-301	K - 9° - Sm - 15° - I
CCH-303	K - 7° - Sm - 29° - N - 37° - I
CCH-502	K - 35° - Sm - 56° - N - 62° - I

Figure 1.3. Structures and phase transition temperatures of the liquid crystalline mesogens used as solvents in this work. Data from references 28 and 29.

cyclohexane in CCH-2 ("EC") is isotropic above 30°C. The last two mixtures have been utilised as model solvents in a number of our studies. The smectic phase of CCH-3 is somewhat less suitable as a reaction solvent since it forms a monotropic smectic phase below 53°C,[29,31b] however the nematic phase has been used utilised as a model solvent.

The *trans*-4-alkylcyclohexyl-*trans*-4'-alkylcyclohexylcarboxylate (OS-nm) mesogens[32] have found considerably less use as reaction solvents than has CCH-4[33-34] and have evidently only been used as a medium in a single photochemical study.[35] De Maria and co-workers have, on the basis of X-ray diffraction and optical microscopy studies, assigned the smectic phases of OS-35 and OS-53 as Sm_B.[33a] They have also suggested that the smectic phases of these mesogens possess some degree of long range positional ordering[33a] and, based on this observation, these phases might also be classified as Cr_B. Both OS-53 and OS-35 exhibit enantiotropic smectic and nematic phases over similar temperature ranges as the CCH-n mesogens[28,33a] (see Figure 1.3) which makes them useful solvents for comparison with results obtained with CCH-4.
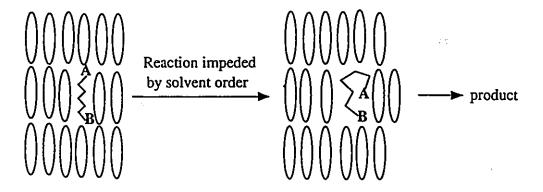
The *trans*-4-alkyl-1,1'-bicyclohexyl-*trans*-4'-alkylethers (CCH-nOm) are a relatively new class of liquid crystal[36] and have never been utilised as reaction solvents. The morphologies of the smectic phases of these mesogens have, to the best of our knowledge not been studied in as great detail as have the CCH-n or the OS-nm liquid crystals. CCH-502 and CCH-303 have however, been reported to exhibit enantiotropic Sm_B phases based on their textures observed in optical microscopy studies.[36] The former exhibits its smectic phase between 35-52°C,[28] and has been used most extensively in the present study. CCH-301 provides a useful model isotropic solvent with which to compare the results obtained in CCH-502 and CCH-303, since its isotropic phase exists over the entire smectic and nematic temperature regions of the other two mesogens.[28]

1.4   Chemistry of Guest Molecules in Liquid Crystals
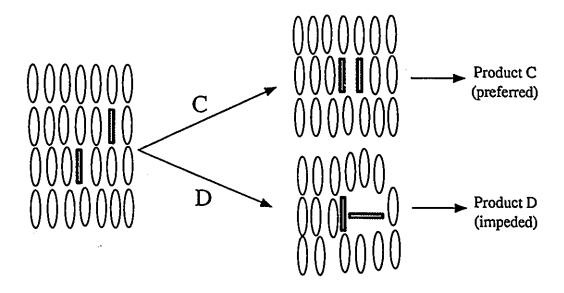
There has been a great deal of interest aimed at determining the effect that the anisotropic ordering in nematic and smectic liquid crystalline phases could have on the chemical reactivity of dissolved solutes.[2,37-39] The chemistry of reactants that are well oriented in a liquid crystalline matrix, and whose reactivity requires changes that are incompatible with the order imposed by the host, may be energetically unfavourable compared to the chemistry that occurs in an isotropic environment. Therefore, reactions which require either a specific orientation of the reactants or a change in conformation along its reaction coordinate are potentially alterable by liquid crystalline solvents.

These ideas are shown pictorially in Figures 1.4 and 1.5. For example, in a unimolecular reaction of a rod-like solute A-B, one might expect the solute to be incorporated into the host matrix in an extended conformation, since liquid crystals are known to orient solutes in a manner that is least disruptive to the mesophase's structure.[7,40] During the course of the reaction, if A-B requires some change in shape to achieve the transition state geometry or product, the ordered environment may act to impede this conformational motion (see Figure 1.4). The results of such impediments to these motions may be observed experimentally in numerous ways including rate changes, or in alterations of product distributions from that observed in an isotropic phase. The effectiveness of the solvent order in controlling reactivity is determined by its ability to discriminate between the reactant and the transition state geometries. Therefore, the larger the conformational change involved in a reaction, the greater are the expected constraints to reactivity. A bimolecular reaction between two rod-like solutes may also

Figure 1.4. Cartoon representation of how liquid crystalline solvent order might orient a solute and impede unimolecular reactivity by imposing restrictions on its mobility.

Figure 1.5. Cartoon representation of how liquid crystalline solvent order can be envisioned to control the orientational ordering during the course of a bimolecular reaction.

be affected by the orientational ordering ability of a liquid crystalline phase. If the solutes can react to form two products in an isotropic phase through two quite different transition state geometries (outlined by pathways C and D in Figure 1.5), it would be reasonable to expect that in the ordered environment of the liquid crystalline phase the reaction would preferentially proceed through the transition state which is most compatible with the host matrix.

There have been numerous contributions, involving a variety of reaction systems, which were designed to utilise the above ideas and exploit specific aspects of liquid crystalline morphology. Examples include thermally or photochemically induced geometric isomerisations,[41] sigmatropic rearrangements,[42] cycloadditions,[43-45] asymmetric induction reactions,[46] fragmentation reactions,[47,48] polymerisation reactions,[35,49] and numerous other processes.[37-39] With the exception of a few notable cases, most of the early examples reported showed either small or negligible effects of liquid crystalline order on reactivity. However, these studies did succeed in elucidating a number of factors which contribute to the ability of a liquid crystalline solvent to control chemical reactivity.

In many of these investigations it was suggested that the magnitude of the observed effects were correlated with the compatibility of the solute and solvent structures. For a liquid crystalline solvent to most effectively orient a reactant within its matrix the solute's structure should be such that it generate as little change as possible in the local order and packing of the liquid crystalline phase. Not surprisingly, a solute whose size or shape differs a great deal from that of the mesogen can cause disruption of the phase order to such an extent that little or no effect on reactivity is observed. In some cases, these effects can be seen at the macroscopic level in the observed phase transition

temperatures of the solute/mesogen mixture.

The nature and degree of the ordering present in liquid crystals are also factors which must be considered when attempting to use the constrained environments to control reactivity. The more weakly ordered nematic (and cholesteric) phases are thermodynamically closer to the isotropic phase than are the more highly ordered smectic phases. Consequently, they are able to incorporate larger quantities of a solute without substantial disruption of the nematic phase characteristics. However, because of the lower degree of ordering, and greater translational freedom associated with the nematic phases, they may not be able to impart a great deal of control over reactions; especially if the reaction involves fairly minor conformational or orientational changes. On the other hand, smectic phases, with their increased orientational and positional ordering, are better suited to controlling reactivity, but are less accommodating in terms of incorporation of the solute without changing the phase behaviour.

Many of the early studies were unsuccessful in observing liquid crystalline induced control over chemical reactivity because they neglected one or more of the above factors. However, even examples that were apparently well engineered, based on the above considerations, showed little or no effects on reactivity. For this reason it became apparent to us, and others, that a more systematic investigation into the nature of the effects on solute solubilisation and reactivity was required. Photochemistry and deuterium NMR spectroscopy offered two probe techniques, which appeared to be uniquely suited to gain valuable information on *solute/solvent interactions* in liquid crystals.

1.5   Photochemical Probes of Conformational Mobility

1.5.1   Advantages of Photochemistry

Photochemical reaction systems have found considerable use as probes to study the effects of organised or constrained environments on chemical transformations.[2-4] Studies of this sort in liquid crystals are no exception.[37-39] The general approach is to investigate the influence of the ordered medium on some photochemical or photophysical process which is well understood in solution. Once one has gained a sufficient understanding of how the ordered medium affects the photochemical process, the probe can then be used as a monitor to understand the morphology of similar ordered phases.

Photochemistry provides quite a versatile and powerful means of probing the mobility of a species within a constrained environment. A key reason is that there are numerous systems where the absorption of light can instantaneously create (or almost so)[50] a reactive intermediate whose chemistry is either completely, or at least partially, determined by its conformational dynamics.[51] In many cases the conformational restrictions imposed on the photochemical intermediate can either be <u>measured directly</u> by time resolved methods, or in other cases be <u>linked</u> to the structure of the observed products of the reaction. We have chosen aspects of ketone photochemistry as the probes in our studies. Ketone photochemistry offers a few distinct advantages over other photochemical systems, such as intramolecular fluorescence quenching probes.[52-54] The intrinsic lifetimes of excited state ketone triplets span timescales in the range of nanoseconds (ns) to milliseconds (ms), thus allowing investigation of a wide range of conformational motions. In contrast, the fluorescence quenching probes are limited to studying reactions

that occur on timescales faster than several hundred nanoseconds, as they are limited by the intrinsic singlet lifetime of the fluorophore. Another advantage in the use of ketone probe molecules is that their structures are generally **smaller** than typical fluorophores, and many systems can be found where the probe ketone is **similar in shape** (rod-like) to the mesogens employed. This makes them potentially less obtrusive to the order of the medium, which has been shown to be an important factor in studies of this type (*vide supra*).

In this thesis we have utilised two reactions in aromatic ketone photochemistry: the Norrish Type II reaction and intramolecular β-phenyl quenching of aromatic ketone triplets.

1.5.2 The Norrish Type II Reaction

The Norrish Type II reaction is one of the most extensively studied and best understood photoreactions in terms of its mechanism in solution.[55-62] The features of this reaction, including structure, temperature, and solvent polarity effects, have been well established and make this an extremely useful model reaction. The relevant mechanistic features of the reaction are outlined in Scheme 1.1.

In arylalkyl ketones the reaction proceeds exclusively from the lowest triplet excited state, which is formed after initial excitation of the ground state ketone and intersystem crossing (ISC). Formation of the 1,4 triplet biradical proceeds via an intramolecular γ-hydrogen abstraction from the n-π* triplet manifold.[55,56] Upon ISC to the singlet state the biradical can either undergo back hydrogen transfer to yield ground state ketone or proceed on to products. The products derived are either due to fragmentation

Scheme 1.1 .   The Triplet Norrish Type II Reaction of Arylalkyl Ketones.

"Fragmentation"

"Cyclisation"

(F) of the 1,4 biradical to yield the alkene and enol (and ultimately the acetophenone derivative), or cyclisation (C) of the biradical to either of the two cyclobutanol stereoisomers. For triplet biradicals, ISC to the singlet state is lifetime limiting. It is generally accepted[62] that the singlet species reacts in the conformation in which it was formed, since its lifetime is shorter than the time required for bond rotation.[63,64] The fragmentation to cyclisation product distribution (F/C ratio) is determined by a number of factors related to the conformational equilibrium and the kinetic behaviour of the 1,4-biradical intermediate.

With the aspects of this reaction so well understood in solution, the Norrish II reactions of alkyl and aromatic ketones have been used frequently to probe the structures and properties in a wide variety of organised media.[2] Norrish Type II reactivity is known to be strongly influenced by the conformational flexibility of the molecule,[51] and as such, the ordered structure of liquid crystalline phases may impart some constraints on the conformational dynamics of the dissolved solute and the resulting reactive intermediate. In liquid crystalline solvents it has been proposed that the transoid biradical conformers should be favoured over the cisoid and that the fragmentation pathway should be favoured *overall*, since it requires the least demanding changes in overall molecular shape.[65-72] Therefore, the relative Norrish II product ratios from a probe ketone dissolved in a mesophase, relative to a model solvent, can provide an **indirect** method for examining the effects of order on the conformational dynamics of the solute and the 1,4 biradical reactive intermediate. More specific information on how this probe system can be utilised, and the information that can be gained from it, will be outlined later in this chapter and is covered in Chapter 2 of this thesis.

1.5.3   Intramolecular β-Phenyl Quenching of Aromatic Ketone Triplets

The investigation of intramolecular triplet quenching of aromatic ketones is an additional system which can be employed to study the effects of ordered media on solute conformational motions. Ketones having aryl rings in the β-position, such as the one pictured in Scheme 1.2, have extremely short triplet lifetimes and low photochemical reactivity in isotropic solvents.[73-76] This has been shown to be due to efficient intramolecular deactivation of the excited n-π* carbonyl triplet state by through-space interactions with the β-phenyl ring.[73-76] β-phenylpropiophenone, for example, has a triplet state lifetime in isotropic solution at room temperature of *ca.* 1 ns.[75] To put this into perspective we can compare this to propiophenone (no β-substituent), whose triplet lifetime under similar conditions is found to be on the order of microseconds (μs).

It has been demonstrated that conformational effects play a significant role in the kinetics of the deactivation process. In ketones which contain the β-phenyl ring it has been well established that for quenching to occur, prior formation of a *gauche*-conformation whereby the β-phenyl ring is placed in a conformation that allows for favourable overlap with the carbonyl triplet, is required (see Scheme 1.2).[75-79] Ordered environments which impose geometrical constraints on the movement of the β-phenyl ring slow the deactivation process. In solid matrices such as zeolites, where only the *trans*-conformation of the probe is possible, the triplet lifetime of β-phenylpropiophenone is extended to *ca.* 2 ms at room temperature and phosphorescence is observed.[78] In a liquid crystalline matrix the ketone might be expected to preferentially exist in the elongated *trans*-conformer under best packing considerations (*vide supra*). Therefore, attainment of the required quenching geometry, which requires rotation about the C_α-C_β bond, in the

Scheme 1.2.   Intramolecular β-Phenyl Quenching of Aromatic Ketone Triplets.

X = H (β-phenylpropiophenone)

= OR

hv
ISC

k_d

k_q

Normal Decay
to Ground State

β-Phenyl Quenching
to Ground State

ordered phases might be severely inhibited. This would be reflected in longer triplet state lifetimes, which can be measured experimentally using nanosecond laser flash photolysis (NLFP) techniques.

Like the Norrish Type II reaction, β-phenyl quenching is known to involve the n-π* triplet excited state.[62] Unlike the unsubstituted analogs, β-phenyl ketones with *para*-alkoxy substituents on the benzoyl portion (e.g. X= OR in Scheme 1.2), have low lying π-π* triplet states. This results in (i) a stronger triplet-triplet absorption, and (ii) a longer observed triplet lifetime in isotropic solvents compared to the n-π* triplet ketones. The longer triplet lifetime is due to the added requirement for thermal population of the n-π* state prior to quenching.[76] This additional condition makes ketones of this sort better suited for studies aimed at monitoring the decay of the triplets at ambient temperatures, since unsubstituted β-phenyl ketones cannot be observed directly by NLFP at these temperatures.[75,76]

In our work, NLFP has been employed to directly monitor the rates of intramolecular triplet quenching of alkoxy-substituted ketones in various phases of liquid crystalline solvents. These experiments also provide Arrhenius parameters for triplet decay that potentially provide information on the effects of the medium on the *energetics* of the conformational motions involved in the β-phenyl quenching process. The β-phenyl ketone probe also allows one to study the effect of molecular length and substitution on the energetics and rates of this reaction in liquid crystals, since these compounds can be easily altered chemically by substitution on the β-phenyl or benzoyl ring. Further information on the use of this probe is available later in this chapter and the results of our studies are reported in Chapters 3 and 4.
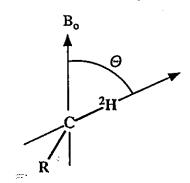
1.6 Deuterium NMR: A Probe of Orientational Ordering and Solute Environment in Liquid Crystals

Deuterium (^{2}H) NMR spectroscopy has proven to be a powerful tool for the investigation of molecular and conformational dynamics in biological systems.[80] This technique has also been extended to various studies involving liquid crystals and there are several comprehensive reviews that outline the theory and applications of this technique.[81-84]

Deuterium, being an atom with a nuclear spin equal to one, has a quadrupolar interaction which contributes to the overall magnetic interactions in the NMR experiment.[82] For a deuterated molecule whose motions are anisotropic, the quadrupolar interaction is often the dominant one.[81,82] This effect manifests itself experimentally as a quadrupolar splitting (Δv_Q) whose magnitude is given by Equation 1.1,[81,82] where (e^2qQ/h) is the quadrupolar coupling constant and Θ is the angle the C-^{2}H vector makes with the applied magnetic field (B_o) (see Figure 1.6). In a liquid crystal some of the molecular motions are rapid (but not random) on the NMR timescale. Therefore, the value of Θ constantly changes with time. Consequently, the magnitude of Δv_Q depends on the *time averaged* orientation of the C-^{2}H bonds with respect to the applied magnetic field (represented by, $<3 \cos^2\Theta - 1>$). The observed quadrupolar splitting provides information on the restrictions that phase order imposes on the motions of the C-^{2}H bonds, which can be related to the degree of orientational ordering associated with the molecule containing the C-^{2}H bond as a whole.[80-84]

The qualitative features of ^{2}H NMR spectra of a deuterated probe molecule included in a liquid crystal can provide valuable information on the order and environment

$$\Delta v_Q = \frac{3\,e^2\,qQ}{4h}\ (3\cos^2\Theta -1)$$

where, (e^2qQ/h) is the quadrupolar coupling constant.

[Eq. 1.1]

B$_o$

Figure 1.6. Schematic diagram illustrating the relationship between the C-^{2}H bond axis and the magnetic field director.

experienced by the solute. In the isotropic phase (and fluid solutions in general) the rapid and _random_ molecular motions average the ($<3\cos^2\Theta - 1>$) term to zero resulting in no quadrupolar splitting. Thus only a singlet is observed in the recorded spectrum (_i.e._ Δv_Q equals zero). One of the interesting features of liquid crystals are that nematic phases align either parallel or perpendicular to an applied magnetic field depending on the sign of the mesogen's diamagnetic anisotropy.[13,81-84] If the solute is ordered by the liquid crystalline matrix, the $<3\cos^2\Theta - 1>$ term will have a non-zero value and a well-defined quadrupolar doublet is observed for each non-equivalent deuteron. As the temperature is decreased and thermal motions become slower, the magnitude of the quadrupolar splitting generally increases. In the nematic phase, where there is still a large degree of freedom in the motions of the C-^{2}H bonds, the lines appear relatively sharp. If however, the order of the phase is sufficient to restrict the reorientation rates to timescales slow on the NMR timescale, lines will be broadened. This is due to the fact that more than a single

orientation of the C-^{2}H bond with respect to the magnetic field is "observed" during the experiment. In cases where the alignment of the mesogen persists into the smectic phase, effects of increased order and slower mobility on the anisotropic NMR behaviour can be expected, depending on the local order experienced by the solute.[83]

The degree of order experienced by a solute in a liquid crystal is a function of temperature, phase type, and (as we shall see) concentration of the probe molecule. By analysing the quadrupolar splittings and observed spectral features, ^{2}H NMR provides a useful tool with which to probe the solvation and temperature effects on the mesogen induced order experienced by a probe. We have developed a method to obtain information on the solubility and phase behaviour of the probes in the various mesophases using selectively deuterated analogs of the probe molecules. In addition, this technique can provide a qualitative indication of the bulk restrictions placed on the solute by the ordered environment.

Throughout this thesis numerous examples will illustrate the features of ^{2}H NMR in liquid crystalline solvents. In addition the difficulties associated with the interpretation of the ^{2}H NMR of dissolved solutes in liquid crystals, which in part has led to this present work, will be addressed.

1.7   Unimolecular Ketone Photochemical Reactions in Liquid Crystals

Mainly through the work of two research groups, ketone photochemistry has emerged as a useful tool to investigate the effects of liquid crystalline phases (especially smectic phases) on the conformational mobility of dissolved solutes. A short review of the key studies that have been reported will now be presented. For the most part, the studies that are discussed represent the best examples of liquid crystalline control of unimolecular reactions. These examples also serve to illustrate some of the difficulties that can arise when carrying out chemical reactions in liquid crystalline solvents. Some of these difficulties have provided the impetus for this thesis.

The first reported study to utilise ketone photochemistry to investigate the influence of liquid crystalline ordering on the conformational dynamics involved the Norrish II reaction as a probe. R. G. Weiss and coworkers reported the photochemistry of a number of phenylalkyl ketones (1-a-e) in the isotropic, smectic (Sm$_B$), and solid phases of n-butyl stearate (BS).[66] The smectic phase of BS was found to have an effect on the photochemistry of the ketones that were similar in overall length to that of BS (1-c-e). In

1 a: n = 4
  b: n = 10
  c: n = 17
  d: n = 19
  e: n = 21

BS

these cases, the F/C ratio increased in the smectic phase relative to the isotropic phase. The product ratios obtained for the smaller ketones (1-a,b) exhibited phase-independent behaviour. These results indicated that the ability of the smectic phase to control reactivity is largest when the solute and solvent are similar in molecular length. It was proposed that in these cases, solute-induced disruption of the solvent order is minimised and therefore solvent control of the reaction is maximised.

Analogous results were obtained for the reactions of 2- and *sym*-alkanones (2 and 3, respectively) in the same liquid crystal.[69] In these examples the lengths of the

ketones were varied from 11 to 31 carbons. In smectic BS, the F/C values were found to reach a maximum value when the ketones length matches that of BS (C_{17}-C_{21}) and then decrease as the solute is either shortened or lengthened from this optimum length. The effect was said to be the greatest when the solute can most easily fit into the solvent matrix without excessive reorganisation of the solvent molecules. This is proposed to occur when solute and solvent are of similar length. In addition, the maximum effects on the F/C ratios were found to be larger for 2 and 3 than for 1. Presumably, the phenyl ring on the latter acts in such a way as to disrupt the ordered phase. Results from the studies of 1-3 in BS illustrate the important relationship between solute and solvent **structural** **similarity** (size, shape, and length) and the degree to which the ordered matrix can influence the conformational motions leading to products.

In the same study, the F/C ratios were found to be more strongly affected by

the smectic phase for 2 than for 3. This suggested that there may in fact be differences on the reactivity depending on the location of the reactive centre in the smectic matrix. Weiss and coworkers proposed that in 3 the carbonyl would be situated in the more rigid inner-layer region between BS molecules resulting in a greater disruption to the local order than for 2, where the carbonyl is closer to the more fluid inter-layer region.

Recently, Weiss and coworkers have more closely investigated the relationship between the position of the carbonyl centre of the solute and how this affects the observed reactivity in the ordered phases of BS.[72] Specifically, they were interested in determining the dependence of the F/C product selectivity on the location of the carbonyl group of the solute within the smectic BS layer structure (*vide supra*[69]). In this study they utilised *para*-alkylalkanophenone derivatives (4), where the molecular length of the solute was held constant (at the optimal length) and the position of the benzoyl group was moved by varying the length of the alkyl chains. Their results indicate that the effect on Norrish

$$H(CH_2)_{\overline{m}} - \underset{}{\bigotimes} - \overset{O}{\underset{\|}{C}} (CH_2)_n H$$

4 : (m + n = 21)

II product selectivity correlates with the position of the *hydroxy of the 1,4- biradical* with the carboxyl group of one of the neighbouring solvent molecules. The authors suggest that the effect is largest for derivatives of 4 where the hydroxy group of the biradical intermediate is able to hydrogen bond to the carbonyl of the solvent, thus anchoring the biradical along a solvent layer. They propose that it is this interaction that provides the major source of the product selectivity. While their explanation for the selectivity in these

terms is more complicated than just simple hydrogen bonding effects, the results seem to

indicate that in these cases the solvent order may not play as large a role as the hydrogen

bonding interactions. Furthermore, these results may also suggest that there may be

distinct differences in the way each of the solutes are solubilised in the smectic phase of

BS.

Weiss and coworkers extended the Norrish II methodology to investigate the

mesophases of CCH-4. Their studies involved investigating the photochemistry of

decanophenone (5) and a series of cyclohexyl-substituted phenylalkyl ketones (6-8) as a

function of temperature in CCH-4.[67] These compounds were chosen since they are similar

5

6: $R = CH_2CH_3$; n = 1
7: R = H; n = 3
8: R = H; n = 4

in length (and shape) to CCH-4 and hence solute-induced disruption of the solvent order

might be minimised. In addition, the γ-hydrogen abstraction process and the *trans-gauche*

interconversion of the resulting triplet biradical (*vide supra*) involves appreciable

conformational motions of the alkyl portion of the molecule. Furthermore, the amplitude

of these motions vary to some extent throughout the series. Their results indicate there

was very little effect on the F/C ratio in the nematic phase compared to the isotropic phase

for each ketone. However, in the smectic phase of CCH-4 there was a dramatic effect on

the F/C ratio, particularly for **7** and **8**, whose F/C ratios increased by a factor of 3-6
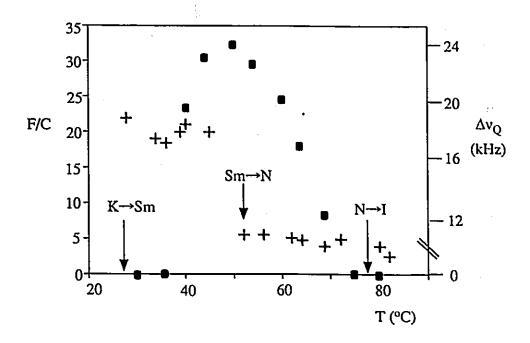
Figure 1.7. F/C product ratios (+) and Δv_Q values (□) versus temperature for **7** in CCH-4. Arrows indicate phase transition temperatures for CCH-4. Data adapted from reference 88.

compared to that in the isotropic phase. The F/C ratios obtained for **7** are shown in Figure 1.7 as a function of temperature. The results for **5** were somewhat less dramatic, with the F/C ratio in the smectic phase increasing by only *ca.* 1.5, and for **6** the F/C ratio was actually found to be lower in the smectic phase than in the nematic and isotropic phases. The large enhancements observed for **7** and **8** in the smectic phase were interpreted as due to these compounds being particularly compatible with the host matrix as a result of the cyclohexyl substituent. The cyclohexyl substituent also caused these probes to involve the more severe shape changes in the interconversions required in this reaction compared to **5** and **6**.

Our group's initial efforts at utilising photochemical reactions to study the effects of liquid crystalline phases on molecular mobility employed β-phenyl ketones of the type described earlier. In the original work, Leigh examined the photochemistry of 1 mol% samples of **9** and a number of derivatives (**10-15**) in the isotropic phase, and the nematic and smectic liquid crystalline phases of CCH-4 and CCH-2.[85] The rates of

9: X = H

10: X = CH$_2$(CH$_2$)$_4$CH$_3$

11: X = C$_6$H$_{11}$

12: R = CH$_2$(CH$_2$)$_3$CH$_3$; X = H

13: R = CH$_2$(CH$_2$)$_3$CH$_3$; X = C$_6$H$_{11}$

14: R = CH$_2$(CH$_2$)$_6$CH$_3$; X = H

15: R = CH$_2$(CH$_2$)$_6$CH$_3$; X = C$_6$H$_{11}$

intramolecular deactivation of the triplet were determined by monitoring the decay of the absorption of the triplet state using nanosecond laser flash photolysis techniques. The Arrhenius plot constructed from the data for a 1 mol% mixture of **9** with CCH-4 is shown in Figure 1.8. The large change in slope in the Arrhenius plot at the N→Sm phase transition temperature was interpreted as being a result of the significant increase in order associated with this phase change. Indeed, analysis showed that for **9** in CCH-4, the activation energy (E$_a$) and the entropy (ΔS‡) increased by *ca.* 12 kcal/mol and 35 e.u., respectively in the smectic phase, compared to the nematic and isotropic phases. At the time this represented one of the largest effects yet observed of liquid crystalline order on the *energetics* of an unimolecular reaction.

Arrhenius plots for similar mixtures of **9** in CCH-2 (included in Figure 1.8)
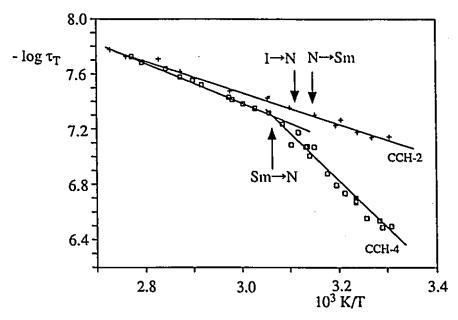
Figure 1.8. Arrhenius plot for the triplet decay of 9 as 1 mol % mixtures in CCH-4 (□) and CCH-2 (+). Data adapted from reference 85a.

indicate that the rate of triplet decay is phase-*independent* in this mesogen. This was somewhat surprising at the time, since the smectic phase of CCH-2 is a more highly ordered phase than that of CCH-4 and was expected to impede quenching to a greater extent. Furthermore, phase-independent Arrhenius behaviour for triplet decay was also exhibited for the other ketones (10-15) in both CCH-4 and CCH-2.[85] For the ketones substituted on the β-phenyl ring the *trans-gauche* interconversions required to achieve the quenching geometry might have been expected to be impeded to a greater extent in the smectic phase than the unsubstituted analogs, since the former require larger shape changes. Based on the Arrhenius behaviour of the individual mixtures Leigh concluded that the microenvironment for 10-15 in CCH-4 and 9-15 in CCH-2 must be similar to that in the nematic and isotropic phases. He correlated the results obtained with the relative

size of the probe in relation to the length of the mesogen. With compound 9, whose size is similar to that of CCH-4, the nature of the solvation in the smectic phase is such that β-phenyl quenching is inhibited. For 10-15 the probes' molecular lengths are longer than CCH-4 and are therefore incompatible with the ordered phase. The same rationale was used to explain the behaviour observed in CCH-2, however this mesogen is slightly shorter than CCH-4 and all probes were deemed too long to be effectively solubilised in this smectic phase.

Leigh and coworkers continued their studies on the ability of smectic phases to impede intramolecular quenching of ketone triplets by investigating the effects of the mesophases of CCH-n on the end-to-end phenolic hydrogen abstraction reaction of ketones 16 and 17.[86] In fluid isotropic solution, the triplet state of 16 has a short lifetime

16: R = H
16a: R = CH$_3$

17: R = H
17a: R = CH$_3$

(15 ns in acetonitrile at 23°C) as a result of efficient quenching of the carbonyl triplet by intramolecular phenolic-hydrogen abstraction via a sandwich-like conformer, as illustrated in Scheme 1.3.[87] In comparison the triplet lifetime of 16a, where hydrogen abstraction is not possible, is 2.3 μs under the same conditions. In smectic CCH-4 at 30°C, the triplet lifetime of 16 (as a 1 mol % solution) increased dramatically to 3.8 μs, indicating that the conformational motions involved in phenolic quenching are severely inhibited in this phase.

In the case of ketone 17, Norrish II reactivity of the valeryl ketone is almost

Scheme 1.3. Intramolecular quenching of ketone triplets by phenolic hydrogen abstraction.

16: R = -CH$_3$

17: R = -(CH$_2$)$_2$CH$_3$

[1]

completely suppressed in isotropic solution due to efficient intramolecular quenching. It was hoped that smectic CCH-4 could be utilised to enhance the Norrish II reactivity of **17** by suppressing the pathway for intramolecular quenching in a similar fashion as observed for **16**. The process was monitored by determining the quantum yield for Norrish II fragmentation in **17** relative to **17a** ($^{17}\phi_{II}/^{17a}\phi_{II}$). Compound **17a** is a useful model since intramolecular quenching can not contribute to loss of triplet reactivity. As expected, the relative quantum yield for Norrish II reactivity increased in the smectic phase of CCH-4 compared to isotropic solvents. Surprisingly though, the enhancement in reactivity was essentially the same as that obtained in the model nematic phase of EB. This result was explained on the basis of thermal microscopy experiments on mixtures of **17** and CCH-4. At the concentrations used in the photochemical experiments solute-rich nematic pools were observed interdispersed throughout the bulk smectic phase. This suggested that **17** was not soluble in the smectic phase of CCH-4 and existed in a phase-separated nematic environment. The similarities in the relative quantum yields in smectic CCH-4 and nematic EB is consistent with this suggestion, as reactivity ensues from similar

environments in the two mesogens. This conclusion is similar to the one given for the phase-independent Arrhenius behaviour for **10-15** in smectic CCH-4 and CCH-2, but in the earlier study microscopy experiments did not provide any direct evidence for phase separation. In contrast to the results with **17**, mixtures of **16** and CCH-4 *appeared* to be homogeneous in nature by thermal microscopy. The authors suggested that the contrast in solubilisation behaviour (and therefore in the photochemistry) between **16** and **17** in this study was due to the formers' structure being more compatible with the solvent matrix thereby being less disruptive.

In the studies which have been reviewed above, the ability of the smectic phase of the mesogen to affect reactivity has been linked to the structural similarity between the solute and solvent molecules. In cases where no or minimal effects are observed it has been proposed that the solute disrupts the liquid crystalline matrix. Leigh and coworkers have provided both direct (thermal microscopy studies of **17** in CCH-4) and indirect (Arrhenius behaviour of **10-15** in CCH-4) evidence that in these cases the solute experiences an environment similar to that in a nematic or isotropic phase. Following these earlier studies, research then turned to ^{2}H NMR spectroscopy of labelled solutes in an attempt to understand the solubilisation behaviour of the probe solutes in these phases.

Linking Photochemical Results with ^{2}H NMR Studies:

Evidence for Heterogeneous Solubilisation of the Probe Ketones

After their initial report on the Norrish II reactivity of **5-8** in CCH-4, Treanor and Weiss reported a deuterium NMR study of the α-deuterated analogs in the same

mesogen.[88] The magnitude of the quadrupolar splittings of mixtures of these ketones, at concentrations equal to those used in the photochemical experiments, were found to vary similarly as a function of temperature. Results obtained for 7 are shown overlapped with the plot of F/C ratios in Figure 1.7 above, as an example. This figure illustrates that while the F/C ratios for 7 (in fact, the same is true for all the ketones) did not vary appreciably throughout the smectic phase temperature region, the NMR behaviour changed dramatically over the same temperature range. Of special note is the replacement of the quadrupolar doublet by an isotropic singlet below 35°C, which is within the smectic phase temperature region. This phenomenon was found to be quite general for these compounds and indicates that the ketones experience an isotropic environment on the NMR timescale (*vide supra*). In spite of the isotropic NMR behaviour, the plots of the F/C ratios were continuous above and below this temperature in the smectic phase. In light of these findings, Weiss and coworkers had to modify their original interpretation[67] of the effect of the smectic phase on the photochemistry of these compounds to account for this unusual phase behaviour.

They attributed the isotropic singlet to a solute induced plastic or cubic phase (a "p"-phase) formed from a smectic solution.[88] Fung and Gangoda used the same rationalisation in an earlier report where they observed that 3-5 weight % mixtures of benzene or dioxane and CCH-4 exhibit partially isotropic ^{13}C NMR behaviour below 10°C.[25a] Similar isotropic NMR behaviour has also been observed using ^{1}H, ^{2}H, and ^{13}C NMR for a number of other solutes in CCH-4.[25,89] Based on these observations, Weiss envisioned the "p"-phase as consisting of microscopic pools of solute and CCH-4 clusters, which are macroscopically disordered, tumbling isotropically in neat CCH-4, to account for the NMR behaviour.[88] They further hypothesised these clusters must be

microscopically ordered phases, imparting similar effects on the ketones as the smectic phase, to account for the photochemical behaviour.[88]

In light of these results, Leigh and co-workers examined the α-deuterated analog of 9 in CCH-4 using ^{2}H NMR spectroscopy:[90] They observed that 1 mol% mixtures of 9 in CCH-4 exhibited similar NMR behaviour to that reported by Treanor and Weiss for ketones 5-8.[88] Even though the NMR behaviour in the nematic phase was unexceptional,[81-84] they were intrigued by the interesting spectral features below the bulk N→Sm transition temperature. For 9-α,α-d$_2$ the quadrupolar splitting decreases as the temperature is decreased below the onset of the bulk nematic to smectic phase transition, and is replaced by an isotropic singlet at 35°C. This is similar to that observed for the α-deuterated solutes previously mentioned (see Figure 1.7 for example). The spectral features observed in the 35-52°C temperature range, prior to the onset of the p-phase singlet, had been implied in the previous studies to represent the behaviour of the solute within the smectic phase.[25,88,89]

Leigh and co-workers, based on an extensive examination of the concentration dependence of the phase characteristics of mixtures of 9 and CCH-4 using ^{2}H NMR spectroscopy, thermal microscopy, and differential scanning calorimetry (D.S.C.), were able to describe the complete binary phase behaviour of mixtures of 9 in CCH-4.[90] They proposed that, in the case of 9, the observed ^{2}H NMR features below the N→Sm transition temperature were due to phase separation effects owing to the low solubility of this solute in the smectic phase of this mesogen. They suggested that within this temperature range the probe ketone resides in a solute rich nematic phase which coexisted with a solute depleted smectic phase. The compositions of the two phases in the biphasic region changes continuously with temperature. As the temperature is decreased, the nematic

phase component becomes more enriched in solute, thus decreasing the order on the solute which, in turn, gives rise to smaller quadrupolar splittings. They went on to suggest that this nematic, phase separated component reaches a critical concentration of solute and transforms into a viscous isotropic liquid or glass, which gives rise to the isotropic singlet in the ^2H NMR.

These *heterogeneous* solubilisation effects were further borne out by a more complete study of the NMR behaviour of 9-α,α-d_2 at concentrations lower than those used in the photochemical study. The same workers observed that a 0.5 mol% sample of 9 in CCH-4 exhibited ^2H NMR behaviour similar to that of the 1 mol% sample. However, in the case of a 0.2 mol% sample no deuterium NMR signals were observed between 50°C and 10°C. Below about 10°C "p-phase" formation was observed. They interpreted the absence of spectral features as indicating that the ketone is *homogeneously* solubilised in the smectic phase and that the signals in the smectic phase are either too broad, or the quadrupolar splitting too large, to be observed. Based on these experiments, the solubility limit of 9 in the smectic phase of CCH-4 was determined to be between 0.2 and 0.5 mol%; much lower than the concentrations used in their previous photochemical studies. From their results they concluded that p-phase formation could also ensue from the smectic phase solution.

Soon after the above work had appeared, the solubilisation behaviour of a number of acetophenone derivatives (18-20) in CCH-4 were reported by the same workers.[91,92] In this study they hoped to define the generality of their results with 9/CCH-4 mixtures and provide further examples of the NMR behaviour of solutes in the Cr_B phase of this mesogen. Overall, the general ^2H NMR behaviour of each of these solutes was very much the same as had been observed for the other solutes. The one key

18

19

20

exception is that an additional quadrupolar doublet is observed below the onset of the bulk N→Sm phase transition for each ketone. These signals were assigned to the ketone solubilised in the smectic phase. The ability to observe distinct ^{2}H NMR signals for the ketone residing in both a nematic and smectic phase environment at the same time, added credence to the biphasic model proposed for **9** in CCH-4.[90] Leigh and coworkers showed that the solubility limits of these ketones in the smectic phase of CCH-4 are lower than could be detected using traditional microscopy methods. They defined the solubility limits of each of these ketones as being the concentration where the nematic phase (or "p-phase") component in the NMR no longer exists in the smectic phase temperature regime. In addition, on the basis of their NMR, thermal microscopy and D.S.C. results with these solute/CCH-4 mixtures they identified the morphology of the solute induced p-phase as a highly concentrated, viscous *isotropic* liquid. This is in contradiction to the plastic or cubic phase as had been proposed previously.[25a,88,89]

From the results of the above two studies, Leigh and coworkers reinterpreted the original photochemical behaviour of **9** and its derivatives[85] to account for the heterogeneous solubilisation of this ketone in CCH-4.[90] The triplet lifetimes observed in

the smectic temperature range for 9 in the original report (see Figure 1.8), were proposed

to be average values of those due to the ketone in coexisting smectic and nematic

(between 54-35°C) and smectic and isotropic (below 35°C) solutions.[39] It was also

suggested that the phase independent triplet behaviour of 9-15 in CCH-2 and 10-15 in

CCH-4 may very well be due to similar solubility factors.[39] Furthermore, on the basis of

the similarities between the ^{2}H NMR behaviour of 9 in CCH-4 and those reported by

Weiss for ketones 5-8, Leigh *et al* suggested that the photochemical behaviour of ketones

5-8 in CCH-4 may be subject to heterogeneous solubilisation effects as well.[39,91] In fact, a

^{2}H NMR study on the concentration dependence of 7 in CCH-4 showed analogous

behaviour to that of 9.[91,92] At low concentration the nematic phase doublet of 7 in the

smectic phase temperature region disappears, leaving a spectrum devoid of any features.

Formation of the so called p-phase does not occur until well into the temperature region

were the mesogen is crystalline. This suggests that the solubility of this probe in the

smectic phase temperature region (<1.5mol%) is lower than that used by Weiss in the

photochemical experiments (>2mol%).[67]

1.8   Objectives of this Study

There is no doubt that the ordered phases of liquid crystalline mesogens can

have an effect on the outcome of thermal and photochemical reactions. The studies

involving ketone photochemistry, described above, are some of the better examples that

illustrate how liquid crystals can control reactivity and impart dramatic effects on the

conformational mobility of dissolved solutes. In these studies the results were often

linked to the relationship between the solute's structure to that of the mesogens. However,

the above review illustrates that predicting under which circumstances an effect will be observed and determining the nature of the solvents order on such motions is often a matter of conjecture.

The deuterium NMR studies of solutes in CCH-4 have far reaching implications on many of the reported studies involving probe molecules in liquid crystalline solvents. All previous studies involving solute/solvent interactions have basically assumed *homogeneous* solubilisation of the solute within the smectic phase. It is apparent from the preliminary ^{2}H NMR results that for solutes in CCH-4 the solubilisation behaviour is much more complex than originally thought. The chemical reactivity studies in CCH-4 which have been described have been carried out at compositions above their solubility limit, and therefore only a portion of the observed effects are due to solubilisation in the highly ordered smectic phase. The remainder, perhaps in some cases the majority, are a result of reactivity of the solute in coexisting nematic or isotropic phases. These studies have thus afforded only lower limits of the real magnitude of the effects that can be obtained in these highly ordered phases. In addition, it seems reasonable to assume that similar solubilisation problems may have unknowingly plagued many other solute/solvent interaction studies in highly ordered smectic and crystalline phases. The ramifications of this on the conclusions of the studies that have been carried out in other liquid crystalline solvents are obvious.

Before one can properly interpret the results of a chemical reactivity study in a liquid crystalline phase, a knowledge of the solubilisation behaviour of the solute in the mesogen of choice is required. One of the goals of this work was to develop a technique that could be used to provide an *accurate* indication of the solubility of probe solutes in smectic phases. To this end, the ^{2}H NMR behaviour of a variety of deuterated analogs of

our probe molecules in liquid crystalline solvents are described. A large portion of the work utilises CCH-n mesogens as solvents, since it is mesogens of this type with which a majority of the previous photochemical studies have been performed. Analysis of the results from the ^{2}H NMR studies allows for proper construction of solute/mesogen binary phase diagrams. These describe the phase behaviour of the reaction system at the "low" probe concentrations used in the chemical reactivity studies.

Once conditions of solute homogeneity are established, the photochemical behaviour of solutes involved in the Norrish II reaction, as well as intramolecular β-phenyl quenching in CCH-4 can be investigated. The aim is to determine the "true" effects of highly ordered smectic phases on these photochemical processes. These results are compared to those obtained under heterogeneous conditions to illustrate the misinterpretation that has occurred in the previous work because of a lack of understanding of nature of the solubilisation of the guest solutes.

We have also initiated a study to investigate the *generalisability* of the studies in the CCH-n mesogens to other families of mesogens with similar liquid crystalline phase types. Deuterium NMR and photochemical studies of the β-phenyl ketone probe in OS-nm and the CCH-nOm liquid crystals was undertaken so that comparisons can be made to the results obtained in CCH-4. The results have given a more encompassing view as to the nature of the solubilisation and the resulting solute/solvent interactions on the conformational mobility and reactivity in liquid crystals.

The power to predict the extent and nature of the general effects liquid crystals have on the reactivity of dissolved solutes or the causes of these effects is still quite limited. This may be due, in part, to the solubilisation phenomena eluded to above, complicating the conclusions drawn from all the previous work. Our studies represent a

systematic investigation that is aimed at understanding the effects liquid crystals have on the conformational mobility of dissolved solutes. With studies of this type it is hoped that in the future, one will be able to predict the effects so as to maximise the organisational benefits on the reactivity of dissolved solutes.

CHAPTER 2

THE NORRISH TYPE II PHOTOREACTIVITY AND
DEUTERIUM NMR SPECTROSCOPY OF
SIMPLE ALKANOPHENONES IN CCH-n LIQUID CRYSTALS

2.1   Introduction

This chapter describes the results of a photochemical and ^{2}H NMR study
which utilised simple alkanophenones to probe the effects of solvent order on molecular
mobility in CCH-n liquid crystals. The Norrish II reaction has previously been shown to
be useful to monitor the effects of liquid crystalline order.[65-71] Our group has used the
Norrish II reaction as a secondary probe to monitor the effects of CCH-n liquid crystalline
order on the conformational motions involved in intramolecular phenolic quenching of
aromatic ketone triplets.[86] In this latter study we employed *para*-methoxyvalerophenone
as a photochemical actinometer and observed that the F/C product distribution was altered
in the smectic phase of CCH-4 compared to that in the isotropic phase. This was
unexpected since the shape changes accompanying the conformational motions of the
1,4-biradical derived from this compound are much smaller than those in the compounds
utilised by Weiss in his studies in the same mesogen.[67,88] This suggested to us that large
solute shape changes, previously thought to be one of the main requirements in order for
the ordered phases to have an effect on reactivity, might not be a necessity. In addition,

O

CH₂(CH₂)ₙH → $CH_2(CH_2)_nH$

AP: n = 0
PP: n = 1
BP: n = 2
VP: n = 3
HP: n = 4

$CD_2(CH_2)_nH(D)$

α- deuterated

$CH_2(CH_2)_nH$

D_5

ring deuterated

our subsequent ^2H NMR results have indicated that the results of previously reported

Norrish II studies in the smectic phase (Cr_B) of CCH-4 are distorted because the reactions

were carried out under biphasic conditions.[90-92]

In this chapter we describe the results of a study in which the Norrish II

reactivity of butyrophenone (BP), valerophenone (VP), and hexanophenone (HP) have

been investigated in the liquid crystalline phases of CCH-4. The shape changes which

accompany *trans-gauche* interconversion in the 1,4-biradicals derived from γ-hydrogen

abstraction in these ketones are fairly minor, and hence may define the lower limit of the

effect the smectic (Cr_B) phase of CCH-4 has on the conformational mobilities of dissolved

solutes. The Norrish II photolysis data has been supplemented with a study of the

concentration and temperature dependence of the ^2H NMR spectra of the α- and ring

deuterated analogs of BP, VP, and HP in CCH-4, along with those of acetophenone (AP)

and propiophenone (PP). The ^2H NMR experiments provide valuable information on the

solubilisation of the ketones in the Cr_B phase of CCH-4, and on the ordering and mobility of these solutes within the liquid crystalline phases of CCH-4.

Also included in this chapter is an investigation of the concentration dependence on the Norrish II reactivity of γ-cyclohexylbutyrophenone (CHBP) in the smectic (Cr_B) phase of CCH-4 at 30°C. The results of this study define the true magnitude of the effect of the smectic (Cr_B) phase on the reactivity of this ketone, and can be compared to previously reported data which were obtained under biphasic conditions.[67,88] Furthermore, they illustrate the effect that phase separation has on the observed Norrish II reactivity of this probe in smectic phases, and provide a useful comparison to results obtained under similar conditions with the much smaller alkanophenones.

CHBP

2.2   <u>Deuterium NMR of Probe Ketones in CCH-4</u>

2.2.1   Preparation of Compounds

The α-deuterated ketones employed in this study were prepared from their all-protiated analogues by base catalysed deuterium exchange in alkaline deuterium oxide/dioxane solution. In all cases, the samples were found to be ≥ 90% deuterated in the α-position by ^1H NMR spectroscopy. The ring deuterated analogs were prepared by

Friedel-Crafts acylation of benzene-d_6 with the appropriate acid chloride and aluminum trichloride in carbon disulfide. All compounds were purified by repeated fractional distillation prior to use (see Chapter 6).

2.2.2 General Deuterium NMR Methods

The ketone/liquid crystal mixtures were prepared by adding the appropriate amount of neat solute to the mesogen and then heating the resulting mixtures to the isotropic phase for several minutes to ensure proper mixing. The samples were then transferred to 5mm NMR tubes.

Deuterium NMR spectra of the solute/CCH-4 mixtures were measured at 76.78 MHz on a Bruker AM500 NMR spectrometer on stationary samples using the quadrupolar echo pulse sequence.[93,94] Spectra were typically recorded between 20-84°C with the temperatures controllable to within ±0.2°C. The samples were first heated to the isotropic phase, and spectra were then recorded at 3-8°C intervals allowing both the probe and sample to equilibrate for 10-20 minutes at each temperature prior to data collection. Cooling from the isotropic phase ensured that the samples were uniformly oriented, since the nematic phase of CCH-4 is spontaneously aligned perpendicular to the applied magnetic field.[95] A few experiments were also performed on a different spectrometer at 41.3 MHz (where noted), using similar conditions to those noted above.[96,97]

2.3   Deuterium NMR Spectroscopy: Results and Discussion

2.3.1   Spectral Features of the Deuterated Probes
in the Isotropic and Nematic Phases of CCH-4.

The ^{2}H NMR spectra of the ketone/CCH-4 mixtures in the isotropic and
nematic phases are in all cases unexceptional.[80,82] In the isotropic phase the spectra are
characterised by a single narrow resonance. As the temperature is lowered below the
nematic to isotropic (N→I) transition temperature, the singlet is split into a quadrupolar
doublet for each non-equivalent deuterium present in the molecule, with a splitting equal
to Δv_Q. The temperature at which the bulk N→I phase transition occurs decreases with
increasing solute concentration. The general appearance of the nematic phase spectra are
in all cases characteristic of a well-oriented solute experiencing rapid anisotropic
reorientation.[80-84] The constituent molecules of the nematic phase align with their long
axes perpendicular to the magnetic field, because CCH-4 possess negative diamagnetic
anisotropy.[95] In the nematic phase the spectra of the α-deuterated ketones exhibit a
single, well-defined doublet. Two sets of doublets are observed for the ring-deuterated
ketones; a strong inner doublet flanked by a less intense doublet of greater splitting. This
is the expected result for two non-equivalent deuterons and the splittings observed have
been assigned as due to the *ortho/meta* and *para* deuterons respectively, based primarily
on the relative intensities of the two sets of signals. The linewidths of the signals in the
nematic phase spectra are on the order of 30-50 Hz. Examples of spectra for the
α-deuterated and ring-deuterated analogues of valerophenone (VP-αd$_2$ and VP-d$_5$) in the
nematic phase are shown in Figure 2.1 and are representative of the behaviour observed

for all the probe ketones. Although not observable on the scale shown in Figure 2.1, the inner doublet in the nematic phase spectra for all ring-deuterated ketones (except AP) consist of two separate splittings, separated by *ca*. 250-300 Hz, which we have assigned as being due to the *ortho* and *meta* deuterons.

As the temperature is lowered throughout the nematic phase, the Δv_Q for each doublet increases. This is indicative of an increase in the order experienced by the solute; as less thermal energy becomes available to the solvent molecules the mobility within the nematic phase decreases, thereby causing the mobility of the solute molecules to be reduced. Figures 2.2 and 2.3 illustrate the variation in Δv_Q in the nematic phase of CCH-4 as a function of temperature and concentration for VP-αd_2 and VP-d_5. The maximum splittings are always observed at the bulk nematic-smectic (N→Sm) phase transition temperature. The transition occurs closest to the N→Sm phase transition temperature of the pure mesogen for low concentrations of solute and occurs at progressively lower temperatures as the concentration of the solute is increased. The maximum splittings observed for each ketone in the nematic phase are listed in Table 2.1.

The magnitude of the splitting observed for each non-equivalent deuterium atom differs according to the differences in the time averaged angle each C-^{2}H bond makes with the magnetic field (*vide supra*). The maximum splittings observed for the α-deuterons of AP-HP range from 5.5-22.5 kHz, while those of the ring deuterons range from 6.5-11 kHz for the *ortho/meta* deuterons and from 32-44 kHz for the *para* deuterons. The splittings not only vary by deuteration site, but there is a general increase in the splitting as the alkanoyl chain length increases. The interpretation of this observation is discussed in section 2.3.4.
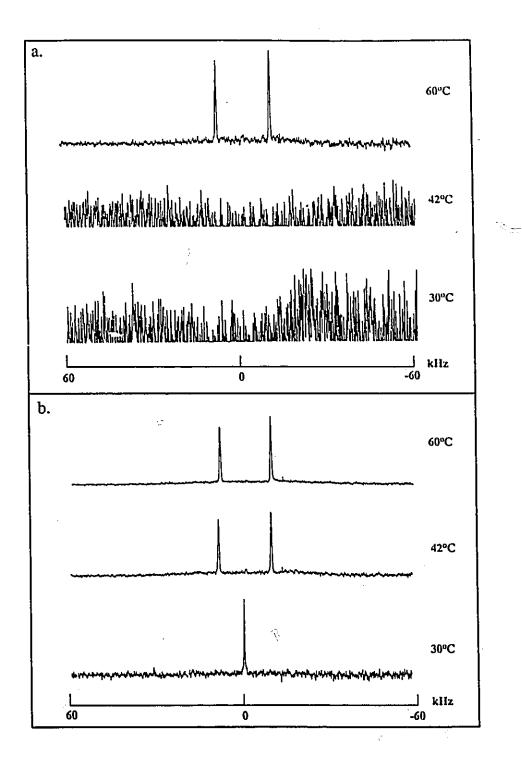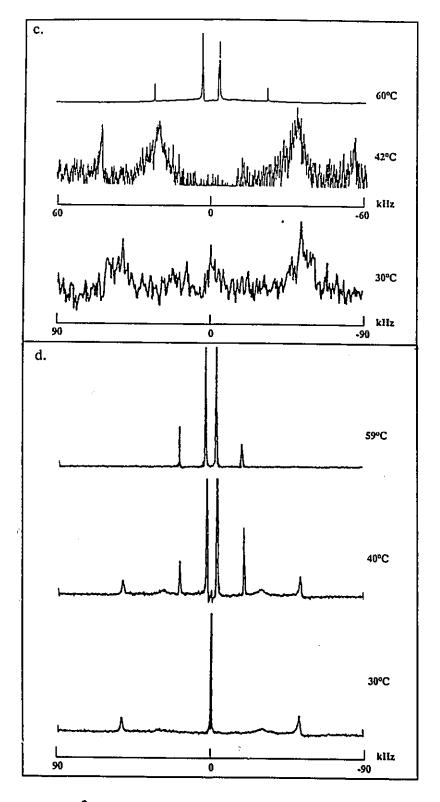
Figure 2.1a and b. ^{2}H NMR of α-deuterated VP in the nematic and smectic phases of CCH-4 as a function of temperature and concentration: (a) 1.0 mol % VP-αd$_2$ and (b) 3.0 mol % VP-αd$_2$. All spectra were recorded at 76.8 MHz.

Figure 2.1c and d. ^{2}H NMR of ring-deuterated VP in the nematic and smectic phases of CCH-4 as a function of temperature and concentration: (a) 1.0 mol % VP-d$_5$ and (b) 3.0 mol% VP-αd$_5$. The spectra in (d) and the 30°C spectrum in (c) were measured at 41.3 MHz.

2.3.2 ^{2}H NMR Spectra of the Deuterated Probes
in the Smectic Phase of CCH-4

The spectral behaviour observed below the bulk N→Sm transition is

dependent on deuteration site as well as solute concentration. The ring-deuterated ketones

exhibit quite unique spectral features below the N→Sm phase transition temperature

compared to the α-deuterated analogues. The results obtained for the α-deuterated probes

are discussed separately from those of the ring-deuterated probes, in order to illustrate the

progression of our understanding of the NMR behaviour and our interpretation of it in this

mesogen. General conclusions are then made based on what is observed from both types

of deuterated probes.

A. α-Deuterated Ketones

For higher concentration samples of the ketones in CCH-4 (≥3 mol%), the

Δv_Q decrease with temperature below the bulk N→Sm phase transition, and converge to

form a singlet at ca. 34°C (see Figure 2.2a). The linewidth of the singlet is similar to that

observed in the isotropic phase at higher temperatures (see Figure 2.1b). Similar

behaviour is observed for all other α-deuterated solutes in this mesogen (see

Introduction).[88-92] The origin of the apparent decrease in Δv_Q below the N→Sm phase

transition has been shown, for other solutes in CCH-4, to be due to biphasic solubilisation

effects.[90-92] Indeed, as the concentration of the ketones is lowered the ^{2}H NMR spectra in

the smectic phase change dramatically. For a 1 mol% mixture of VP-αd_2 the nematic

phase component disappears below 50°C and the NMR spectrum is devoid of features (see

Figure 2.2b). Examples of spectra showing this behaviour are included in Figure 2.1a.

We have interpreted these "non-spectra" as being characteristic of the ketone homogeneously solubilised in the smectic phase of CCH-4.[90-92] Recall that the absence of any spectral features for the α-deuterated ketones could either be due to the signals being too broad, or the splitting too large to be observed with our instrumentation. In order to ensure that the signals due to the α-deuterated VP in the smectic phase were not of such large splitting to be beyond the spectral width (170 kHz) offered by our spectrometer (76.8 MHz), we performed a few control experiments. The first control experiment consisted of altering the offset frequency of the spectrometer by up to 60 kHz from either side of the carrier frequency, which effectively allowed us to expand the spectral range and observe signals on either end of the original spectral window. We also employed the use of another spectrometer (41.3 MHz)[96,97] whose electronics are suited to observe a much larger spectral range (1MHz). In neither experiment were signals observed in the smectic phase temperature region that could be assigned to the ketone in the smectic phase.

Low concentration samples of HP-αd$_2$ behave similarly to VP-αd$_2$ in CCH-4. Mixtures of AP-αd$_3$, on the other hand, show distinct spectral features throughout the smectic phase temperature region. Observation of signals for AP-αd$_3$ and not for VP-αd$_2$ and HP-αd$_2$ is not surprising since the internal motion of the acetyl-d$_3$ group around its local C$_3$ axis is quite different than the motions of the α-C-d$_2$ functionality. Previous studies have shown that para-substituted acetophenone derivatives, deuterated on the acetyl portion, exhibit distinct spectral features assignable to the solute dissolved in the smectic phase of this mesogen.[91,92]

Interestingly, the low concentration samples of the α-deuterated derivatives of PP and BP also exhibit ^{2}H NMR spectral features below 50°C. Below the N$\rightarrow$Sm phase transition, new sets of doublets which are much more diffuse and of 1.5 times larger

splitting than in the nematic phase appear for both PP and BP. Representative examples

of the smectic phase spectra for AP-αd_3, PP-αd_2, and BP-αd_2 are shown in Figure 2.4.

The spectrum of AP-αd_3 resembles a powder pattern at the low temperature extreme.[81,82]

The signals for PP-αd_2 and BP-αd_2 persist below the temperature where the nematic

phase component disappears and becomes broader as the temperature is lowered. Below

ca. 35°C the signals are no longer observable and spectra reminiscent of low concentration

samples of VP-αd_2 and HP-αd_2 in the smectic phase are obtained. Broad signals with

quadrupolar splittings larger than those observed in the nematic phase are consistent with

the probe experiencing a greater degree of order and much slower reorientation rates.[98-101]

As such, the new doublets have been assigned to be due to signals from the ketone

solubilised in the smectic phase of CCH-4. These examples represent the first

αd_2-deuterated probes that exhibit detectable spectral features in the more highly ordered

smectic phase of CCH-4.

B. Ring Deuterated Ketones

The ^2H NMR behaviour of the ring deuterated ketones provide more detailed

information on the solubility behaviour and the mobility of these molecules in CCH-4.

Below the N→Sm phase transition, where the nematic phase doublet reaches its maximum

splitting, the 1.0 mol% samples of the ring-deuterated ketones in CCH-4 exhibit two new

doublets which coexist with the nematic phase doublets. Below ca. 48°C the nematic

phase doublets disappear, as they do for the α-deuterated ketones, but are replaced by two

new doublets. These new signals persist throughout the entire smectic phase temperature

region (see Figure 2.3b for an example). The new signals range from 2-8 times greater

splitting than the signals due to the solute in the nematic phase. For PP-HP-d_5 the spectra

consist of a broad doublet (4kHz width) with a splitting of $\Delta v_Q = 50$ kHz, due to the *ortho* and *meta* deuterons (*vide infra*) and a somewhat sharper doublet (1.5-2 kHz) of splitting $\Delta v_Q = 100$ kHz due to the *para* deuteron. For AP the spectral features are the same but the splittings are only 43 and 70 kHz, respectively. The spectra observed for 1 mol % mixtures of VP-d_5 in CCH-4 are shown in Figure 2.1c. Both sets of doublets become broader and more diffuse as the temperature is lowered in the smectic phase region and in all cases the outer doublet remains considerably sharper than the inner doublet. It is also observed that the linewidth of the inner doublet varies somewhat from ketone to ketone, broadening to a greater extent as the length of the alkanoyl chain length increases (*i.e.* the inner doublet remains easier to see for the shorter ketones as the temperature is lowered). Spectra recorded on the 41.3 MHz instrument are identical to those obtained on our instrument (76.8 MHz) except that the signals due to the ketone in the smectic phase below 35°C are somewhat easier to phase correctly because of the larger bandwidth of the 41.3 MHz spectrometer.[96]

The ^{2}H NMR features described above are consistent with the probe experiencing a greater degree of order and slower reorientation rates than is the case in the nematic phase, as would be expected for the probe dissolved in the highly ordered smectic phase.[98-101] The observation of new doublets in the smectic phase region for these probes (and PP-αd_2, BP-αd_2) indicates that the alignment of the liquid crystal in the nematic phase persists into the smectic phase region and that we are observing the spectra of oriented solutes in this phase. The maximum quadrupolar splittings observed for all ketones in the smectic phase of CCH-4 are tabulated in Table 2.1, along with the corresponding nematic phase values. In all cases, the differences in the reported Δv_Q values are measurable; *i.e.*, mixtures of any two similarly deuterated probes in CCH-4
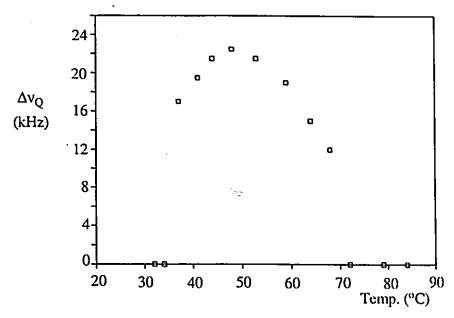
Figure 2.2a: Deuterium quadrupolar splitting *vs.* temperature for 3 mol % VP-αd_2 in CCH-4.
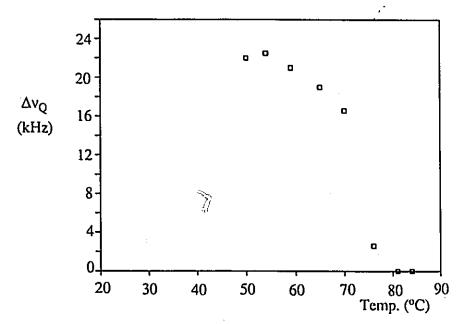
Figure 2.2b: Deuterium quadrupolar splitting *vs.* temperature for 1 mol % VP- αd_2 in CCH-4. No signals are observed below *ca.* 48°C.
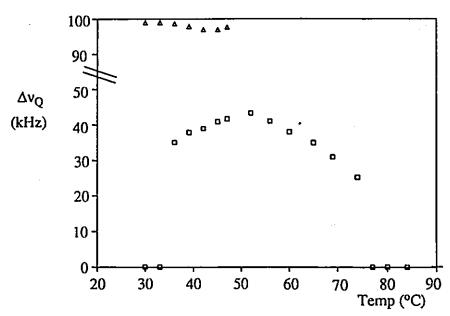
Figure 2.3a: Deuterium quadrupolar splittings (Δv_Q) *vs.* temperature for the *para*-deuteria in a 3 mol % sample of VP-d$_5$ in CCH-4. Key: (□), nematic phase splittings; (△), smectic phase splittings.
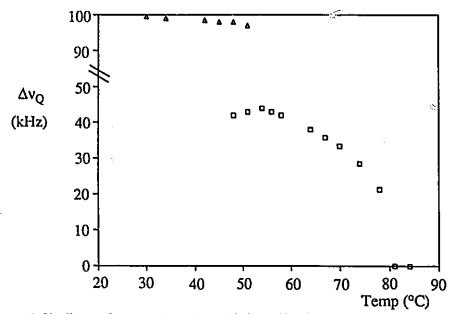
Figure 2.3b: Deuterium quadrupolar splittings (Δv_Q) *vs.* temperature for the *para*-deuteria in a 1 mol % sample of VP-d$_5$ in CCH-4. Key: (□), nematic phase splittings; (△), smectic phase splittings.

exhibit ^{2}H NMR spectra which contain clearly resolved signals for both probes in the mixture.

Although the ^{2}H NMR spectra of the higher concentration samples of the α-deuterated ketones exhibit spectra consistent with heterogeneous solubilisation, the NMR spectra of the ring-deuterated ketones at concentrations above *ca.* 3 mol % *clearly* demonstrate the biphasic nature of these samples. Below the onset of the N→Sm transition in the ^{2}H NMR experiments with the higher concentration samples of ring-deuterated ketones, the splittings of the nematic phase doublets decrease and finally collapse to a singlet at *ca.* 34°C. This is similar to what is observed for the α-deuterated ketones (compare Figure 2.2a to Figure 2.3a). However, the signals which are assignable to the ketone dissolved in the smectic phase coexist with these spectral components for the ring-deuterated ketones. Examples of spectra of biphasic samples (nematic and smectic or isotropic and smectic phases) are shown in Figure 2.1d. The variation in the observed splittings, as a function of temperature, for both the nematic and smectic phase components for the *para*-deuteron of **VP-d$_5$** are illustrated in Figure 2.3a. Analogous trends in the quadrupolar splittings (although of different magnitudes) are observed for the *ortho/meta* deuterons and are not shown. Biphasic spectra are also obtained for the lower concentration samples, although the temperature range over which the biphasic regions exist are much narrower. This is illustrated in Figure 2.3b, where splittings due to the ketone in the two phase environments coexist between 53-48°C. Below 48°C, the ketone exists solely in a smectic phase environment, as indicated by the absence of the nematic phase signals. In the higher concentration samples, the doublets due to the smectic phase component become more difficult to observe owing to their increased linewidth and the better signal to noise ratio of the nematic or isotropic signals. As mentioned previously,
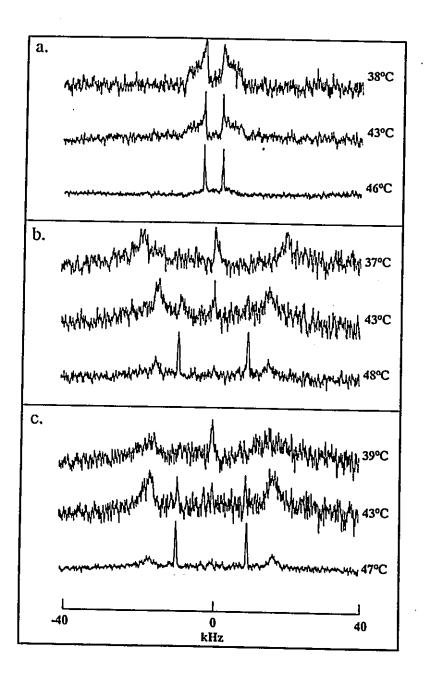
Figure 2.4. ^{2}H NMR spectra of (a) AP-αd$_3$ (0.67 mol %); (b) PP-αd$_2$ (1 mol %); (c) BP-αd$_2$ (1 mol %) in the smectic phase of CCH-4 betwen 48 and 37-38°C. Recorded at 76.8 MHz.

Table 2.1. ^{2}H quadrupolar splittings from NMR spectra of α- and ring-deuterated alkylphenones in the nematic and smectic (Cr$_B$) phases of CCH-4.[a]

Ketone	Phase	Δv_α (kHz)[b,c]	Δv_{para} (kHz)[b,d]	$\Delta v_{o/m}$ (kHz)[b,d]
AP	N	5.47	32.11	11.09
	Sm	11	70.5	43.0
PP	N	19.95	43.00	6.83
	Sm	29	93.5	51.2
BP	N	20.37	40.03	7.64
	Sm	32	94.7	53.4
VP	N	22.10	43.27	6.67
	Sm[e]	f	98.7	54.0
HP	N	22.52	42.74	6.81
	Sm[e]	f	98.3	52.2

a. Data recorded at 76.8 MHz, using 1.0 and 2.6 mol% solutions of the α- and ring-deuterated ketones, respectively. Errors in Δv_Q are ca. 10 Hz for the nematic phase. For the smectic phase, they are ca. 1kHz for Δv_α, ca. 0.5 kHz for $\Delta v_{o/m}$, and ca. 0.2 kHz for Δv_p. Key: N = nematic; Sm = smectic (Cr$_B$).

b. Only the absolute values of the magnitudes of the splittings are given.

c. Nematic phase spectra recorded at 50°C, smectic phase spectra at 43°C.

d. Nematic phase spectra recorded at 52°C, smectic phase spectra at 33°C.

e. Recorded at 36°C (VP) or 38°C (HP).

f. Unobservable. (see text)

the doublet due to the *para* deuteron is easier to observe than the signals due to the *ortho/meta* deuterons (for example, in Figure 2.1d the splittings due to the *ortho/meta* deuterons are barely resolvable from the baseline, while the outer doublet is clearly visible).

We have assigned the singlet which appears in the ^2H NMR spectra below *ca.* 34°C as due to the formation of a solute enriched ketone/mesogen isotropic phase, as we have for other solutes which we have investigated in this mesogen.[90-92] Evidence that the component giving rise to the singlet in the ^2H NMR spectrum is a mobile isotropic solution of ketone in CCH-4 is obtained from a ^{13}C NMR spectrum of the mixture of VP-d_5 in CCH-4 at 30°C, shown in Figure 2.5. Superimposed on the broad featureless absorption due to the smectic phase[27a,102] are sharp lines that can be assigned to both the ketone (VP-d_5) and CCH-4 in an isotropic environment, based on the chemical shifts of solution phase ^{13}C NMR spectra of the individual components. The signals due to VP-d_5 between 120 and 140 ppm are due to the aromatic protons and are broadened slightly by ^{13}C-^2H coupling. As was mentioned in Chapter 1, similar spectra were observed for benzene and dioxane[27] and other solutes[88,89] in CCH-4. However, in these cases the researchers had incorrectly assigned the sharp lines in the spectra as due to a solute induced plastic or cubic phase.[27,88,89] Our ^{13}C NMR experiments, coupled with our ^2H NMR results, support the suggestion that the solubilisation phenomena observed for the probe ketones in the present study is the same as had been previously observed, yet incorrectly assigned, in other studies involving solutes in this mesogen.

The ability to observe distinct ^2H NMR signals in the smectic phase temperature region for low concentration samples of both the ring-deuterated probes and for PP-αd_2 and BP-αd_2 corroborates our proposal that the absence of signals for the

5 mol % VP-d$_5$ in CCH-4

30°C
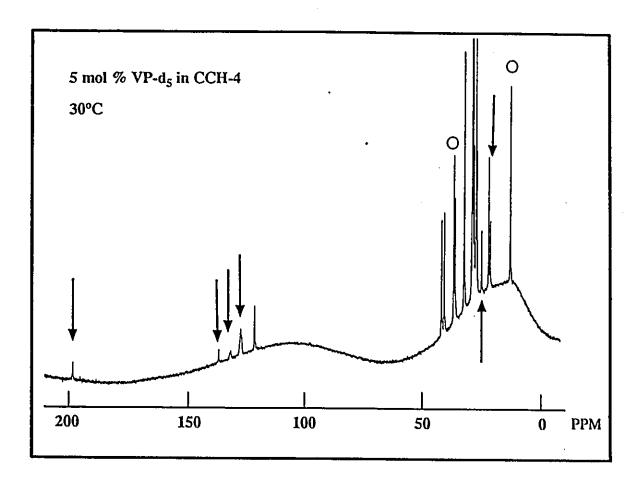
Figure 2.5. ^{13}C NMR spectrum of a 5.0 mol% sample of VP-d$_5$ in CCH-4 at 30°C, recorded at 125.7 MHz. The signals designated by arrows (↓) are due to VP-d$_5$, while the remainder are due to CCH-4. Two other signals from the ketone, designated by circles (O), overlap with solvent signals.

α-deuterated ketones in other studies[88,90-92] is characteristic of smectic phase solubilisation. Likewise, given the similarities between the ^{2}H NMR behaviour of the higher concentration α-deuterated samples observed in this study with those previously reported,[27,88-92] we believe the unique ^{2}H NMR behaviour observed in the latter studies are due to similar solubilisation behaviour as that shown explicitly above for **AP-HP**. The formation of nematic/smectic and isotropic/smectic biphasic systems appears to be a general phenomenon in this mesogen for samples whose solute concentration is above the solubility limit.

The use of α-deuterated analogues of the probe ketones in ^{2}H NMR studies is appealing because of their ease of preparation and the possibility of obtaining information regarding solute ordering and mobility at a site very close to the reaction center in the Norrish II reaction. They were an unfortunate choice in the earlier studies however,[88,90-92] since the spectra in the smectic phase are misleading, which has led to errors in the subsequent interpretation of the photochemical and solubilisation behaviour of the probe solutes in this mesogen. [27,67,86-92] The results obtained from the ring-deuterated compounds are much more informative and better enable the correct interpretation of the phase behaviour of our probe molecules[90-92] and that of other probe systems[67,88] which have or will be studied.

2.3.3 Determination of Probe Solubility Limits
in Smectic Phases

With a clearer understanding of the ^{2}H NMR features exhibited by solutes in the various liquid crystalline phases of CCH-4, accurate solubility limits can be determined for each of the probes in this mesogen. At a particular temperature, the solubility limit is defined as the maximum bulk concentration of solute for which a homogeneous solution is obtained. Knowledge of the solubility limits of the various probes in the smectic phase is necessary for the photochemical studies to ensure that one understands the bulk morphology of the mixture being utilised. In particular, it is important that when investigating the effects of the smectic phase of CCH-4 on the reactivity of a solute, a mixture whose composition is of a *homogeneous* smectic phase solution is used.

Our method of determining the solubility limits for each ketone in the smectic (Cr_B) phase of CCH-4 involves determination of the temperature below which the nematic (or isotropic) phase component is absent from the ^{2}H NMR spectrum for a particular sample composition, and only features characteristic of the ketone within the smectic phase are observed. The experiment is then repeated for a series of samples of different compositions to observe the concentration dependence of the phase transition temperatures. The results of such a concentration and temperature dependence study for VP are tabulated in Table 2.2. The data from a complete study, such as the one shown in Table 2.2, allows for the construction of the low concentration region of the binary-phase diagram of the ketone/CCH-4 mixture. Figure 2.6 shows a generalised phase diagram, constructed from the data in Table 2.2 for VP/CCH-4. The general form of this phase

Table 2.2. Phase transition temperatures as a function of concentration
of VP in CCH-4.[a]

Concentration (mol %)	Transition Temperatures (°C)[b]			
	$T_{N \to I}$[c]	$T_{N \to Sm + N}$[c]	$T_{Sm + N \to I}$[c]	$T_{Sm + N \to Sm}$[c,d]
0.6	79	53	e	51
1.0	79	53	e	48
1.5	79	52	e	42
2.0	78	51	e	40
2.3	77	50	e	36
2.6	75	49	e	32
3.0	71	47	33	f
5.0	69	45	33	f

a. Determined from ^{2}H NMR spectroscopy.
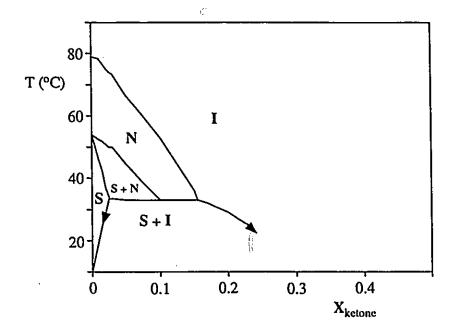
b. Transition temperatures are typically ± 1°C.

c. I = isotropic; N = nematic; Sm = smectic.

d. Temperature represents solubility limit for VP at each concentartion.

e. No nematic to isotropic phase transition observed. Smectic to isotropic transition below 20°C.

f. Sample remains biphasic throughout the entire smectic phase temperature region.

Figure 2.6. Generalised temperature/composition binary phase diagram for ketone/CCH-4 mixtures. The portion of the diagram below $X_{ketone} = 0.05$ was constructed from ^2H NMR data for VP-d_5 and VP- αd_2 in CCH-4.
Key: I = isotropic; N = nematic; S = smectic (Cr_B).

diagram is similar for all the ketones in this study. The portions of the phase diagram where we have no ^{2}H NMR data (above 5 mol%) have been generalised from the phase diagrams of other ketone/CCH-4 mixtures that have been studied by our group.[90,91,103] Phase transition temperatures for mixtures of ketone and CCH-4 above 5 mol % can be determined visually through thermal microscopy studies. Below 5 mol %, the microscopy studies are generally unreliable for observations of the complex phase behaviour exhibited by the solute, and it is at low concentrations where the power of the ^{2}H NMR technique is most useful.

Analysis of the phase diagram allows the determination of the solubility limits in the smectic phase throughout the 28-53°C temperature range. The solubilities in the smectic phase at 30°C and 45°C of each of the deuterated ketones determined <u>directly</u> from analysis of their NMR behaviour, are reported in Table 2.3. Those of BP, VP, and HP have been determined most accurately since they are the ones utilised in the photochemical study. The solubilities of AP and PP were estimated from the relative intensities of the signals due to the nematic and smectic phase components in the spectra recorded for 0.6, 1.0 and 2.6 mol % samples. According to our interpretation of the ^{2}H NMR spectra of the α- and ring deuterated solutes in the smectic phase of CCH-4, the solubility limits determined by our method should be independent of site of deuteration. This was shown explicitly with VP, whose solubility limits were determined from the spectral behaviour of both the α- and ring deuterated derivatives.

From the data in Table 2.3 it appears as if the solubility limits increase precipitously with ketone alkyl chain length, and then level off to similar values for BP, VP, and HP at the lower temperature range of the smectic phase. We have previously estimated the solubility limit of the much larger CHBP at 30°C, based on the ^{2}H NMR

Table 2.3. Solubility limits of alkylphenones in the smectic (Cr_B) phase
of CCH-4 at 30 °C and 45 °C.[a]

Ketone	30°C	45°C
AP	1 - 1.5[b]	< 0.6[b]
PP	1.5 - 2[c]	≈ 0.8[c]
BP	2.3	≈ 0.8
VP	2.6	1.0
HP	2.2	1.3

a. Estimated by ^{2}H NMR spectroscopy (see text). Errors are roughly 10%.

b. Estimate is based on behaviour of 0.6, 1.0 and 2.6 mol% samples only.

c. Estimate is based on behaviour of 1.0 and 2.6 mol% samples only.

behaviour of the α-deuterated analog, to be roughly the same value (*ca.* 2 mol%) as the solubility limits of **BP**, **VP**, and **HP**.[91,92] Interestingly, the solubilities of the smaller probes (**AP** and **PP**) are much lower than that of the other ketones. The solubility limits of other acetophenone derivatives were also estimated to be quite low (0.6-1.0 mol%) at 30°C in CCH-4.[91,92] It appears as if the solubility limits of probes in this mesogen increase as the alkyl content of the molecule increases in relation to the aromatic content. Further examples that illustrate this effect are discussed in Chapter 3 and 4.

2.3.4 Mobility Information From ^{2}H NMR Behaviour

Besides the invaluable information on solubility and phase behaviour which is offered by ^{2}H NMR spectroscopy, qualitative information on the mobility of the solutes in mesogenic phases can also be obtained if we have data for a series of similar compounds over the same temperature and concentration ranges (as we do here).

Qualitative information on the reorientational motions of the phenyl ring in the smectic (Cr_B) phase of CCH-4 can be obtained from the observed quadrupolar splittings of the *ortho/meta* and *para* deuterons. It is known that alkylphenones[90-92,95] (and other alkylaromatics)[25a] will tend to align in this liquid crystal with the long molecular axis parallel to the mesophase director (M_z), which is perpendicular to the applied magnetic field. Furthermore, these alkylphenones align with a preference for the plane of the phenyl ring being perpendicular to the applied magnetic field direction (B_o).[104,105] A coordinate axis system describing this orientation is shown in Figure 2.7.

For a solute that reorients with a 3-fold or higher symmetry about the long molecular axis, the maximum quadrupolar splittings are obtained when the molecular axis
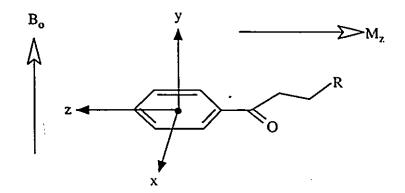
Figure 2.7. Coordinate system illustrating the alignment of the alkanophenones in CCH-4.

(z-axis) is rigidly aligned along the smectic phase director (M_z).[80,83] The quadrupolar splittings for the ring deuterons obtained by this model are given by Equation 2.1.[106] This equation is similar to Equation 1.1 with the exception that the angular dependence term in Equation 1.1 is now written as a product of two terms. The first term varies with Θ, the angle between the solute molecular axis (M_z) and the magnetic field (B_0). The second term varies with β, the angle subtended by the C-^{2}H bond and the molecular axis. For a solute oriented in CCH-4, Θ can be taken to be essentially $90°$[95] (as described in Figure 2.7). Therefore, the maximum splittings predicted from Equation 2.1 are 1.? kHz and 17.3 kHz for the for the *para* ($\beta = 0°$) and *ortho/meta* deuterons ($|\beta| = 60°$), respectively. Any motion of the z-axis of the solute with respect to the mesophase director will result in both splittings being reduced from their maximum values. By comparing the maximum splittings observed (Table 2.1) to the calculated values we see that the splittings for the *para* deuterons are in all cases less than 138 kHz; however, the splittings for the *ortho/meta* deuterons are much greater than the maximum splitting predicted by this model. These observations suggest that rapid reorientation about a 3-fold or higher symmetry axis of the phenyl ring does not take place in the smectic phase of CCH-4. It is

$$\Delta v_{Qi}{}^{max} = \frac{3\,e^2\,q\,Q}{2\,h} \quad \frac{3\cos^2\Theta - 1}{2} \quad \frac{3\cos^2\beta - 1}{2} \qquad\qquad \text{[Eq. 2.1]}$$

where $(e^2\,q\,Q/h)$ *is taken to be ca. 185 kHz for aromatic deuterons.*[107]

possible that either the phenyl ring reorients about 2-fold axis or more likely, by small angle librations in the highly ordered smectic phase.

Evidence for small angle librations about the long molecular axis are given by the spectral features observed for the ring deuterons in the smectic phase. The C-^{2}H bonds aligned along the long molecular axis (*i.e. para* deuterons) will be less sensitive to small angle librations occurring about this axis. The variation in the $(\cos^2\beta)$ term is larger as the angle deviates from $\beta = 60°$ (*ortho/meta* deuterons) than its does for changes from $\beta = 0°$ (*para* deuteron). This is consistent with the observation that the signals due to the *para* deuterons remain sharper than the signals for the *ortho/meta* deuterons, which broaden dramatically as the temperature is lowered throughout the smectic phase. The assignment of the signals in the ^{2}H NMR to the *para* and *ortho/meta* deuterons that were originally assigned (*vide supra*) in the nematic phase based on their relative intensities also fit with the model we have proposed for the orientation of the solute in the liquid crystal. The largest quadrupolar splittings are expected for cases where the C-^{2}H bond is aligned along the long molecular axis, and in our case these correspond to the *para* deuterons.

Additional information can also be obtained from spectra of the series of α-deuterated ketones (AP-HP) in the smectic phase of CCH-4. For ketones which show signals assignable to the ketone solubilised in the smectic phase (α-deuterated AP, PP,

and **BP**), the spectra exhibit a marked increase in linewidth with increasing alkyl chain length and decreasing temperature (see Figure 2.4). This behaviour is indicative of a decrease in the C-^{2}H bond reorientation rates as these parameters are varied. If the C-^{2}H bond reorientation rates are slowed to the point where they are similar in magnitude to the quadrupolar splitting (*ca*. 180 kHz), they will no longer be observable.[108] We believe this to be the case for **VP** and **HP**, and in fact, for all other αd_2-deuterated phenylalkyl ketones that we have studied in the smectic phase of CCH-4.[90-92] If the reorientation rates are slowed beyond the 180 kHz range the spectral components are expected to reappear.[108] Therefore, the results of our series, along with the other ketones we have studied, indicate that there is a levelling off in the C_α-^{2}H (H) reorientation rate that occurs as the α-substituents are increased in size or length. The C_α-^{2}H bond reorientations which are probed in the ^{2}H NMR spectra may be either conformational motions of the alkyl chain or **bulk** molecular motions. However, the earlier conclusion that the phenyl rings are subject to only small angle librations over the same timescale, suggests that the motions probed by the C_α deuterons are due primarily to conformational changes.

A saturation effect also appears to occur in the magnitude of the quadrupolar splittings in the ^{2}H NMR spectra of the α- and ring-deuterated ketones. Variation in the magnitude of the quadrupolar splitting at a single temperature, for a given concentration of solute, throughout a homologous series of solutes, is proportional to the degree of ordering the solutes experience. For the α-deuterated ketones in the nematic phase there is a rapid increase in the $\Delta\nu_\alpha$ as the alkyl chain length increases through the shorter chain members of the series (**AP-BP**). It then levels off at a maximum of *ca*. 23 kHz for the longer chain lengths (**VP** and **HP**) (see Table 2.1). Interestingly, the deuterium NMR spectra for other α-deuterated solutes in CCH-4, which we[90-92] and others[88] have measured, all exhibit

maximum splittings of *ca*. 24-25 kHz in the nematic phase of this mesogen regardless of their overall structure (*vide infra*). An identical trend is also exhibited by the *para* and *ortho/meta* deuterium splittings in the spectra of the ring deuterated ketones in the nematic and smectic phases (see Table 2.1). These trends in the quadrupolar splittings and the spectral features of the α- and ring deuterated solutes (*vide supra*), suggest there is a structural effect on the average **ordering** experienced by solutes of this sort in this liquid crystal. These features are consistent with levelling of in the effectiveness of the alkanoyl functionality in *anchoring* the phenyl ring and the α-carbon as the alkanoyl chain is lengthened. Whether or not this ordering effect manifests itself in the photoreactivity of these solutes in the smectic phase of CCH-4, is the focus of the remainder of this chapter.

2.4   Norrish Type II Photoreactivity in CCH-4

2.4.1   General Methods

Mixtures of ketones in the various liquid crystalline phases for the photolysis experiments were prepared by weighing the appropriate amounts of ketone and mesogen (*ca.*150 mg total) into a vial which was then heated to the isotropic phase to ensure complete mixing. The mixtures were then placed in 5 m.m.-o.d. quartz tubes and sealed with rubber septa. The samples were heated to the isotropic phase again and deoxygenated with dry nitrogen for 5-10 minutes. The samples were placed in a thermostated water bath at 30°C and irradiated at 312 ± 15 nm to 5-20% conversion. Control experiments indicate that the product distribution obtained from photolysis of the mixtures were essentially independent of extent of conversion below *ca.* 30%. Samples of 0.1 M ketone in a number of typical isotropic solvents were handled in a similar manner to samples in liquid crystalline solvents.

After irradiation, the tubes were opened and the contents were dissolved in dichloromethane and analysed in triplicate by vapour-phase chromatography (v.p.c.). Product ratios were determined from v.p.c. analysis of at least two runs for each sample. Procedures used for the identification of products are given in Chapter 6. In all cases only products due to the Norrish II reaction were observable; there was no evidence for the formation of benzaldehyde (a Norrish I product) or any other product in significant yield (≥ 2 %).

2.4.2   **Effects of Liquid Crystalline Phases on the**

Product Distributions in the Norrish II Reaction

The steady state irradiations of **BP**, **VP**, and **HP** were carried out at 30°C

under various conditions, so that the photochemistry of each ketone could be examined in

a number of different phase environments. Photolysis of 0.6 mol% mixtures of ketone in

CCH-4 were performed to investigate the effect of the smectic phase of this mesogen on

the photoreactivity of the probes. Similar experiments were also carried out with 5 mol %

mixtures of the ketone in CCH-4, since NMR results indicate that at this concentration the

solutes exist as *heterogeneous* mixtures segregated between the smectic phase and a

viscous isotropic phase. In addition, product ratio studies were performed a) on 0.6 and

5.0 mol % solutions of ketone in EB (a 2:1 mixture of CCH-2:CCH-4), which is a model

nematic phase at 30°C,[29] b) on 0.6 mol % solutions in the viscous isotropic phase of EC (a

1:6 weight % mixture of cyclohexane:CCH-2) and, c) on 40 mol % mixtures of ketone in

CCH-4 (isotropic at 30°C (see Figure 2.6)). For comparison, product ratios were

determined for 0.1 M solutions of the alkanophenones in methylcyclohexane (MCH;

non-polar), acetonitrile (CH$_3$CN; polar aprotic), methanol (MeOH; polar protic), and

tert-butanol (*t*-BuOH; polar protic). Results of the product ratio studies

[acetophenone/total cyclobutanols, (F/C) and *trans-/cis*-cyclobutanol, (*t/c*)] for **BP**, **VP**,

and **HP**, as outlined in Scheme 2.1, are summarised in Table 2.4.

The results obtained for the non-viscous isotropic solvents agree closely with

those previously reported.[60,61] In all solvents there is typically a preference for

Scheme 2.1. Products observed by v.p.c. on irradiation of BP, VP, HP and CHBP. Ratio of acetophenone/(total CB) gave F/C ratios. See Table 2.4.

BP: R = H
VP: R = CH₃
HP: R = CH₂CH₃
CHBP: R = C₆H₁₁

acetophenone (+ alkene)

trans-CB   cis-CB

fragmentation over cyclisation and a slight preference for the *trans*-cyclobutanol (CB) over the *cis*-CB, due presumably to steric factors involved in the formation of the *cis*-CB. As expected, increased selectivity for fragmentation over cyclisation was observed in the polar protic solvents (MeOH and *t*-BuOH) compared to the aprotic solvents. This has been rationalised as due to the ability of the solvent molecules to hydrogen bond to the hydroxyl functionality of the biradical, sterically crowding that center and impeding cyclisation.[60,61,109] This same reasoning has been used to describe the generally higher quantum yields of reaction[59,61b] and the longer triplet biradical lifetimes[63] that are observed in polar protic solvents. Results obtained from studies in the isotropic solvents provide useful information on typical solvent effects on product ratios. They were also valuable in the v.p.c. identification of photoproducts for the various ketones, since the

traces were simplified due to the absence of peaks resulting from the liquid crystalline solvent.

Photolysis in Model Isotropic Solvents

The photolysis of 40 mol % ketone/CCH-4 mixtures and solutions of the ketones in EC define the effect of solvent viscosity on product distribution. The 40 mol % mixtures also model the reactivity of the ketones in the phase-separated isotropic component of the 5 mol % ketone/CCH-4 mixtures at 30°C. We estimate (based on the phase diagram in Figure 2.6) that at this temperature the composition of the isotropic component in the biphasic 5 mol % ketone/CCH-4 mixtures to be *ca.* 40 % ketone in CCH-4.

The product distributions from photolysis in the model isotropic solvents are similar to one another and compare most closely with the results obtained in the non-viscous, polar protic solvents (MeOH and *t*-BuOH). The effect in the viscous isotropic solvents is not the result of an increase in solvent polarity however, since EC and the 40 mol % mixtures are, at best, only weakly polar. Presumably, these are less polar than acetonitrile, which shows a lower F/C ratio than the polar protic solvents. There is little information available on the effects of solvent viscosity on product distributions in the Norrish II reaction, with the exception of studies in the isotropic phases of thermotropic liquid crystals.[66-71] Solvents of high viscosity are known to have negligible effects on the lifetimes of biradicals derived from the Norrish II reaction,[63] however the factors involved in controlling biradical lifetimes are somewhat different than those that determine the product distribution.[110,111] It is known that Norrish II product quantum yields, and F/C ratios from alkanophenones, generally increase in isotropic solvents with

increasing ketone concentration.[56] Wagner and coworkers have suggested that this is most likely due to specific solvation of the hydroxyl group of the biradical by ground state ketone through hydrogen bonding, which affects reactivity in a similar manner as hydroxylic solvents.[59] These effects may in fact be magnified in the 40 mol % mixtures by the higher viscosity of this solution, and be reflected in the slightly larger product ratios in this solution compared to those in EC.

Photolysis in the Model Nematic Phase, EB

In the model nematic phase of EB, photolysis of BP, VP, and HP gives product ratios that are comparable to those obtained in the viscous isotropic solvents. Furthermore, no concentration effects are observed for the ketones between 0.6 and 5 mol %. The ^2H NMR features of the α- and ring-deuterated analogues of the ketones in the nematic phases of CCH-4 and EB indicate that the reorientational motions of these solutes are rapid on the NMR timescale, but are not isotropic in nature. The observed product ratios indicate that the mobility of the alkyl chain in the 1,4- biradical intermediate is high enough that the reactivity of the species is unaffected by nematic solvent order. The absence of an effect in the nematic phase is not unexpected considering the small conformational motions involved in the reaction and the relatively weak order associated with this phase type. Similar results have been obtained for other Norrish II reactions in nematic and cholesteric liquid crystalline solutions.[65-67,88,112]

Photolysis in the Smectic Phase of CCH-4

The results for the photolysis of the ketones as mixtures in the smectic phase of CCH-4 are far more interesting than those in the model nematic and isotropic phases.

Table 2.4. Fragmentation/cyclization (F/C)[a] and *trans/cis*-cyclobutanol (*t/c*) product ratios from photolysis of butyrophenone (BP), valerophenone (VP), and hexanophenone (HP) in liquid crystalline and isotropic solvents at 30°C.[b]

Solvent	Concentration[d] (phase)	BP F/C	VP F/C	VP *t/c*	HP F/C	HP *t/c*
CCH-4	0.6 (Sm)	8.6 ± 0.8	9.2 ± 0.4	6.30 ± 0.04	12.3 ± 1.6	6.6 ± 0.4
CCH-4	5.0 (Sm + I)	9.6 ± 0.8	7.4 ± 0.2	3.3 ± 0.1	9.1 ± 1.0	3.4 ± 1.4
EB[c]	0.6 (N)	9.7 ± 1.1	6.1 ± 0.6	2.07 ± 0.06	6.5 ± 1.1	1.4 ± 0.2
EB[c]	5.0 (N)	8.9 ± 1.8	6.2 ± 0.4	2.2 ± 0.1	6.5 ± 1.4	2.2 ± 0.8
CCH-4	40 (I)	7.8 ± 0.3	6.0 ± 2.0	2.00 ± 0.04	5.6 ± 1.0	2.00 ± 0.02
EC[c]	0.6 (I)	8.5 ± 1.0	5.0 ± 1.0	2.0 ± 0.1	4.8 ± 0.6	2.1 ± 0.1
MCH[c]	0.1 M	5.6 ± 0.4	2.50 ± 0.06	4.0 ± 0.1	2.0 ± 0.1	4.0 ± 0.1
CH₃CN[c]	0.1 M	5.8 ± 0.4	3.10 ± 0.01	1.40 ± 0.02	3.0 ± 0.1	1.30 ± 0.02
MeOH[c]	0.1 M	10.6 ± 0.6	5.0 ± 0.3	1.44 ± 0.02	4.6 ± 0.3	1.41 ± 0.04
t-BuOH[c]	0.1 M	8.0 ± 0.6	4.26 ± 0.08	1.35 ± 0.06	3.9 ± 0.2	1.32 ± 0.04

a. Fragmentation/cyclization (F/C) ratios represent the ratio of acetophenone to isomeric cyclobutanols from photolysis of the three ketones at 312 ± 15 nm. Product ratios quoted are the average from two samples, each analysed in triplicate by vpc. The FID detector was not calibrated for differences in response factors. Errors are quoted as ± two standard deviations from the mean.

b. Sm, smectic (Cr$_B$); N, nematic; I, isotropic.

c. EB: 2:1 CCH-2/CCH-4; EC: 6:1 CCH-2/cyclohexane; MCH: methylcyclohexane; CH₃CN: acetonitrile; MeOH: methanol; t-BuOH: *tert*-butanol.

d. mol %; unless otherwise noted.

For 0.6 mol % samples of ketone in CCH-4, where the probe ketone is known to be homogeneously solubilised in the smectic (Cr$_B$) phase of CCH-4, the F/C and t/c values for VP and HP both increase dramatically compared to the values obtained in the nematic and isotropic phases. The F/C ratio for the photolysis of 0.6 mol % mixtures of BP in CCH-4 on the other hand, is essentially identical to that measured in the nematic (EB) and isotropic (EC) liquid crystalline phases (see Table 2.4). The alterations in the product distributions for VP and HP are due to an effect of the order imposed on the reaction dynamics of the solutes by the ordered solvent matrix. The increase in the F/C ratio cannot be attributed to differences in local solvent polarity at the site of the reaction for smectic compared to isotropic solvents, since specific interactions of our solutes with the cyano portion of the mesogen are not expected to have any greater effect on the product ratios than is observed in methylcyclohexane or acetonitrile.

Using ^{2}H NMR techniques we have concluded that 5 mol % mixtures of BP, VP, and HP in the smectic phase of CCH-4 are heterogeneous in nature throughout the smectic phase temperature region. At 30°C the samples exist as mixtures of both smectic and isotropic components. From the solubility limits at 30°C (see Table 2.3), it is estimated that the solutes are approximately equally distributed between a smectic solution (comprising the majority of the sample) whose concentration will be equal to the solubility limit and a minor amount of an isotropic solution dispersed throughout the smectic phase (consisting of the amount of ketone in excess of the solubility limit as a 20-40% mixture in CCH-4). The product ratios obtained from photolysis of 5 mol % mixtures of VP and HP reflect the biphasic nature of these samples. The F/C and t/c ratios are intermediate between the values obtained in the homogeneous smectic phase environment (0.6 mol % samples in CCH-4) and the isotropic environment of 40 mol %

mixtures of the ketone in CCH-4 (see Table 2.4).

Similar concentration dependence on product ratios is also observed in the photolysis of **CHBP**. The Norrish II product ratios obtained from photolysis of **CHBP** as a function of concentration of ketone in CCH-4 are given in Table 2.5. The corresponding phases in which the ketone exists at each concentration, as determined by ^{2}H NMR,[91,92] are also given, as are the product ratios in a few typical isotropic solvents. The results for the lower concentration samples reflect the *true* ability of the smectic phase to control the Norrish II reactivity of this probe. This should be compared to that which has previously been reported, and which was performed under biphasic conditions (*vide supra*).[67,88] The present results indicate that at compositions above that where the isotropic phase is observable by NMR (*ca.* 1.4 mol %), the F/C and t/c ratios gradually decrease. This is representative of a *greater* proportion of the reactivity ensuing from the phase-separated isotropic component of the mixture as the concentration of ketone is increased above its solubility limit. The product ratios continue to decrease until about 9.5 mol %, where the product distribution is similar to the 40 mol % mixture which is completely isotropic at 30°C. Presumably no effect is observed with the 9.5 mol % sample since the majority of the reactivity observed occurs from ketone solubilised in the isotropic component of the biphasic mixture.

The measured product ratios in the 5 mol % samples of **BP-HP**, and those of **CHBP** above its solubility limit, are weighted averages reflecting reaction of the ketone in the two different environments in which it is solubilised. In principle, for a given ketone/CCH-4 mixture whose composition is biphasic in nature, it should be possible to quantitate the relative proportion of reactivity from each phase type based on the *solubility limits* determined by ^{2}H NMR and the *phase specific product ratios*. The latter are

Table 2.5. Concentration effects on the Norrish Type II product ratios from photolysis of **CHBP** in CCH-4 and in isotropic solvents at 30°C.[a]

Concentration (mol %)	Phase[b]	.F/C[c]	t/c[d]
0.58	Sm	14.2 ± 2.8	7.4 ± 3.2
0.67	Sm	11.1 ± 0.8	6.8 ± 0.8
1.0	Sm	12.0 ± 1.6	5.2 ± 1.8
1.4	Sm + (I)	9.3 ± 1.2	5.0 ± 1.0
2.4	Sm + I	8.2 ± 0.8	3.0 ± 0.6
4.8	Sm + I	6.3 ± 0.1	2.6 ± 0.2
9.5	Sm + I	4.8 ± 0.7	2.0 ± 0.1
39.7	I	4.5 ± 1.0	1.7 ± 0.1
C_6H_6[e]		1.9 ± 0.2	3.3 ± 0.2
t- BuOH[e]		3.5 ± 0.3	1.1 ± 0.1
CH_3CN[e]		3.4 ± 1.0	1.5 ± 0.1

a. Results obtained from vapour phase chromatography analysis of mixtures photolysed at 312 ± 15nm. Product ratios are the average of at least two runs analysed in triplicate. Errors quoted are twice the standard deviation from the mean. All samples were deoxygenated with dry nitrogen in their isotropic phase.

b. Phase characteristics determined from the ^2H NMR behaviour of mixtures of CHBP-αd_2 and CCH-4. See references 91 and 92 for details. Key: Sm = smectic (Cr_B); I = isotropic.

c. Ratio of acetophenone/ (trans + cis) cyclobutanols from photolysis.

d. Ratio of trans-/cis- cyclobutanols from photolysis.

e. Deoxygenated 0.1M solutions.

defined by the product distribution obtained in the homogeneous smectic phase solution (from samples whose compositions are below the solubility limit) and the 40 mol % mixtures, which represent reactivity in the viscous isotropic phase. For 5 mol % samples of VP and HP for example, we would estimate that the measured product ratios reflect the average of ketone proportioned equally between the two phase types; the product ratios observed roughly reflect this approximation. However, this interpretation of the data does not take into account the possible differences in the quantum yields for product formation in the two phase types. Quantum yields in the smectic liquid crystals might be expected to be quite different from those in isotropic phases. Determination of quantum yields in the smectic phase or in heterogeneous mixtures are complicated due to light scattering effects[86,88] and the difficulty of obtaining an actinometer whose reactivity is well defined in the smectic phase. Some of these difficulties may be surpassed by combining the actinometer and probe molecule in the same sample. This however, causes additional problems since one must consider the overall solubility properties of the mixture, which one might expect to be different than the individual solubility limits of each component. The information obtained from such studies would be of interest and we have taken steps to design such a system.[113] However, for the purposes of this study quantum yield studies were deemed unwarranted.

The Norrish II reactivity of BP-HP and CHBP in CCH-4, were studied at the temperature where the solubility limits of the ketones in the smectic phase are the largest. The present work has shown that the portion of ketone in excess of the solubility limit acts to truncate the apparent effects which the smectic phase has on the reactivity of dissolved solutes. Such deviations from true smectic phase behaviour are expected to be larger at higher temperatures and be observable with lower ketone concentrations as the

temperature increases. This is because solubility limits in the smectic phase decrease with increasing temperature and proportionally larger amounts of the solutes are solubilised in the nematic (or isotropic) phase which coexists with the smectic phase.

2.4.3 Factors that Affect the Norrish II Reactivity in the Smectic Phase

The various factors that control the product distribution obtained in the Norrish II reaction in isotropic solvents are well understood[55,56] and a cursory introduction to this reaction has been given in Chapter 1. In liquid crystalline solvents the factors that contribute to the product distributions are more complex and are a function of the effects of the medium on the conformational equilibrium of the triplet 1,4-biradical intermediates, the kinetic distribution of products obtained from each conformer, and other intimate solvent-solute interactions that control the nature of the local environment of the probe ketone.

Mechanistic Considerations
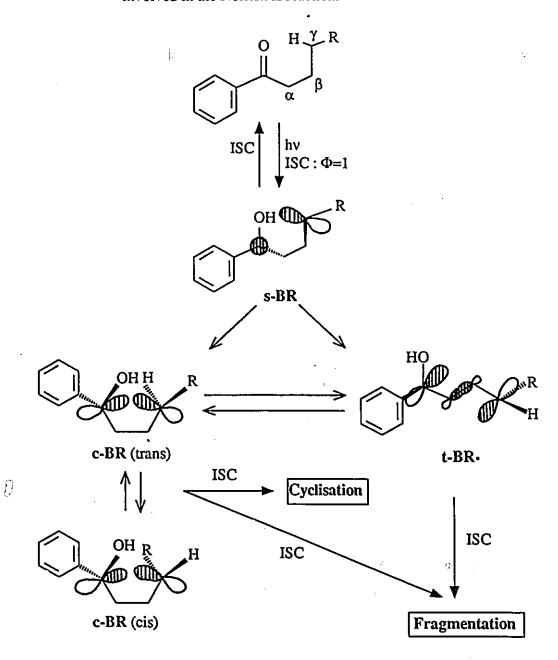
In aromatic ketones, γ-hydrogen abstraction proceeds from the n-π^* triplet state to generate a triplet 1,4 biradical. This biradical is initially formed in a skewed conformation (s-BR), in which the γ-p-orbital is essentially parallel to, and the benzylic p-orbital perpendicular to, the C_α-C_β bond. This is illustrated in Scheme 2.2. Due to orbital overlap considerations, two families of 1,4-biradical conformers are considered to

be important in the formation of products: the transoid biradical (t-BR) and the cisoid biradicals (c-BR), both of which are derived from the s-BR via rotations around the central C_α-C_β σ-bond or the carbonyl and C_α bond. The requirement for favourable orbital overlap precludes cyclisation from the transoid biradical and only fragmentation can occur. Cyclisation must occur from a cisoid biradical which may also undergo the fragmentation process, in principle. It has been shown that in cases where severe internal steric constraints inhibit overlap of the singly occupied orbitals in the c-BR,[114] or when ring strain makes cyclisation impossible,[62,115] the fragmentation process can dominate. The extent of fragmentation derived from a cisoid biradical is controlled by the extent of overlap of the p-orbital with the C_α-C_β σ-bond that is being broken and the relative efficiency of the other processes.[116] In a recent study, Caldwell *et al* showed that a conformationally-locked cisoid biradical undergoes cyclisation as the preferred pathway to products.[117] In addition, it has been demonstrated that in the solid state, in the absence of large steric constraints in the molecule, biradicals held in a conformation favourable for ring closure proceed to cyclisation products almost exclusively.[116,118] Therefore, it appears that in the absence of any intramolecular steric constraints, the majority of fragmentation products arise from the t-BR.

Product formation from the biradical is preceded by intersystem crossing (ISC) to the singlet state, whose lifetime is too short to allow any further bond rotations[64,110,119] (especially in viscous solvents). The reaction therefore, ensues from the conformer which was formed on ISC.[110,119] The triplet lifetimes of the 1,4-biradical intermediates of alkanophenones, like the ones used in this study, are known to range from 30-120 ns in hydrocarbon solvents, and are slightly longer in protic solvents.[63,120,121] These lifetimes are of sufficient length for the biradical to achieve conformational

Scheme 2.2: Conformational interconversions of the biradical intermediates involved in the Norrish II reaction.
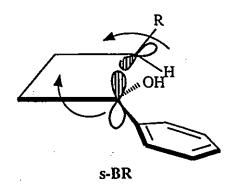
equilibrium in solution prior to ISC. While little information is known on the lifetime of biradicals in liquid crystalline solvents,[66,86] high solvent viscosity has been shown to have little effect on Norrish II biradical lifetimes.[63] Given the relatively long lifetimes of the triplet biradicals, conformational equilibrium may be established in the liquid crystalline phases prior to ISC. This is undoubtedly the case in the nematic phases, where reactivity mirrors that observed in isotropic phases - where there is no solvent order.

When considering the above mentioned conformational motions in an ordered environment one must consider the mobility of the solute within the space occupied by the reactant and the region surrounding it. The response of the local solvent shell to the molecular motions of the guest solute and how it, in turn, controls those motions, play key roles in the outcome of reactions carried out in ordered environments. Molecules making up the smectic phase are not immobilised, as in a crystalline solid, but allow for molecular movement and flexibility. Therefore, even well-ordered solutes are expected to have some degree of rotational and conformational freedom. Based on the mechanistic features described in the preceding paragraphs, and the differences in the required motions of the s-BR to achieve a geometry for reaction, one can begin to appreciate how an ordered liquid crystalline environment may steer the reaction of such solutes by altering the equilibrium of the reactive conformers.

2.4.4   Rationale for Observed Selectivity:

Why is Fragmentation Preferred?

The increased preference for fragmentation in the Norrish II reactivity of VP,

HP, and CHBP in smectic CCH-4 compared to model nematic/isotropic solvents is

probably not a result of the cleavage process being enhanced in the former, but a result of

a decrease in the pathway to cyclisation due to restrictions imposed by the ordered matrix.

To achieve the geometry for cyclisation, considerable movement of the ketyl *or* alkyl

portion of the 1,4-biradical in the initially formed s-BR is necessary (see Scheme 2.3).

Such motions are expected to require a large volume to be swept out in the local solvent

shell and therefore be unfavourable due to the constrained environment of the surrounding

solvent.

Scheme 2.3. Representation of the motions involved in the formation
of c-BR from s-BR. Adapted from reference 122a.

s-BR

The alternative pathway available to the s-BR is conversion to the t-BR. In

the smectic phase, the motions leading to the t-BR, while they can also involve fairly large

motions (as implied in scheme 2.2), should be favoured over those leading to the c-BR

since the shape of the former should be least disruptive to the surrounding solvent matrix. Thus, the biradical should be expected to proceed to fragmentation products since it is the least sterically demanding pathway. Conversion from the s-BR to the t-BR can also be achieved with only small changes in reaction volume. This would be true if it is the alkyl chain which undergoes the conformational change, while the ancillary substituents are held fairly rigidly. These conformational motions have been termed as "crankshaft" motions[66,67] and involve simple twisting of the alkyl chain. The crankshaft motion is illustrated in cartoon form in Scheme 2.4. Similar motions have also been proposed in geometric isomerisations of the alkyl portion of polyenes.[122b] The crankshaft motions of the 1,4 biradical are most likely not the key conformational changes involved in the biradical interconversions in typical (non-constrained) solution since it is a high-energy pathway. However, they may be important in the restricted environment of smectic (Cr_B) CCH-4. Thus, in the smectic phase environment the *equilibrium* between the two reactive

Scheme 2.4. Cartoon representation of the "crankshaft" motions that may be involved in interconverting the s-BR to the t-BR.

P = phenyl moiety (constant in size)
R = alkyl moeity (variable in size throughout series)

conformers may be *directed in favour of the t-BR* since it can be formed with the least amount of disruption to the solvent order. Once the transoid biradical is formed it can only undergo fragmentation (*vide supra*). The increased F/C ratios observed in the

smectic phase are consistent with a greater proportion of the reaction ensuing from the t-BR and therefore it appears as if the solvent is affecting the equilibrium of the biradical conformers prior to reaction. Results presented later in this thesis will support this proposal.

Deuterium NMR results may provide indirect information on the conformational mobility of the 1,4-biradical intermediate if its motions can be related to the motions of the ground state ketone. Direct comparisons between the NMR and the photochemical results cannot be made since the two techniques probe different motions over different timescales. The Norrish II data reflect specific conformational motions involving the entire 1,4-biradical intermediate that occur on the 10-150 ns timescale, while the ^{2}H NMR spectral behaviour reflect ground-state C-^{2}H bond reorientations that are subject to quite different motions and occur over a much longer timescale (ca. 10μs). However, we can make some qualitative comparisons between the mobility of the ground state ketone (offered by ^{2}H NMR) with the conformational mobility of the 1,4 biradical intermediate. Deuterium NMR evidence indicates that the phenyl ring is essentially immobilised in the timescale of the experiment. This is consistent with the proposal that the interconversion of the s-BR to either the c-BR or the t-BR would preferentially involve motions of the alkyl portion of the probes and not the phenyl-ketyl moiety.

2.4.5 The Effect of Smectic CCH-4 on the Photoreactivity of Alkanophenones as a Function of Chain Length

Although the product ratios provide evidence that the smectic phase of CCH-4 affects the conformational distribution of the biradical intermediates, the exact nature of the effect on the reactivity of the alkanophenones is still rather uncertain. Regardless of these uncertainties, certain conclusions can be made based on the variations in the reactivity within the series of compounds in the smectic phase of CCH-4. The degree to which the F/C ratios are affected appears to increase as the size of the γ-substituent increases. This is illustrated graphically for **BP, VP, HP,** and **CHBP** in Figure 2.8; which plots as a function of γ-substituent size, the ratios of the F/C values from photolysis of the 0.6 mol % mixtures in CCH-4 and those obtained in the model isotropic phases. Such a plot <u>removes</u> any differences in product ratios that can be attributed to factors which are common to both phase types and provides a clearer indication of the relative enhancement obtained in the smectic phase. Also included in Figure 2.8 is a data point for decanophenone **(DP)**. This value was calculated from the product distribution data previously reported for **DP** in CCH-4 at 30° (smectic) and 80°C (isotropic).[67] From the solubility limits determined for the ketones in this study and the F/C ratios and ^{2}H NMR data reported for 1.5 mol % mixtures of **DP** and **DP-**αd_2 in CCH-4,[67,88] the reported value was obtained from a biphasic sample. However, we estimate that the $[(F/C)^{Sm}/(F/C)^I]$ reported in Figure 2.8 is only 10- 30 % off the true value which would be obtained from a homogeneous smectic phase solution.

In spite of the fact that the ^{2}H NMR results indicate that motions of the alkyl chain and phenyl portion of **BP** are similar to those of **VP** and **HP** in the smectic phase of

$$\frac{(F/C)^{Sm}}{(F/C)^I}$$

Ketone:	BP	VP	HP	DP	CHBP
γ-Substituent:	H	CH_3	CH_2CH_3	$(CH_2)_5CH_3$	C_6H_{11}
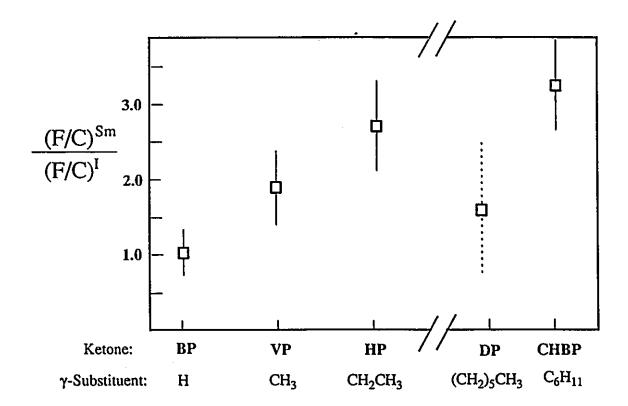
Figure 2.8. Plot illustrating the variation in F/C ratios as a function of the γ-substituent from photolysis of **BP**, **VP**, **HP**, and **CHBP** as 0.6 mol % solutions in the smectic phase of CCH-4 relative to the ratios obtained in the viscous isotropic phase of the 40 mol % solutions. The value for **DP** in the smectic phase was taken from reference 67 and was obtained under biphasic conditions. By our estimates the value is within 10-30 %of the true value (see text). The error shown for **DP** was calculated from the errors in the measurements and does not include the error associated with the biphasic nature of the sample.

CCH-4, especially at the lower temperatures, there is no *measurable* effect of the smectic phase on the Norrish II reactivity of this compound. Apparently, the conformational dynamics controlling the reactivity of BP involve motions that are too diminutive to be affected. The smectic phase matrix presumably cannot distinguish between the shapes of the c-BR and the t-BR in a way that would lead to changes in observed reactivity. Furthermore, it is intriguing that the relative F/C ratios obtained for VP and HP are similar to those obtained for the larger and bulkier CHBP and DP. The shape changes along the alkyl chain required in the reaction of VP and HP seem to require fairly innocuous motions, while those for CHBP and DP might be expected to be larger because of the increased length and steric bulk in these solutes. As such, more enhanced F/C ratios might have been expected for the latter ketones than was observed. In fact there appears to be a levelling off of the effect of smectic CCH-4 on the F/C ratios as the substituent increases beyond a certain size. Recall that a similar plateauing effect also occurs with a number of the ^{2}H NMR features for this series of compounds (*vide supra*). The two sets of independent data both point to distinct differences in the mobility of the smaller ketones (AP, PP, and BP) compared to those of the longer or bulkier ketones (VP, HP, and CHBP) in the smectic phase of CCH-4. Both techniques seem to indicate that increases in the alkanoyl chain length tend to aid in immobilising the remainder of the solute in the ordered environment of this mesogen. The apparent levelling off that occurs with substituent in the photochemical (and ^{2}H NMR) results can also be explained by the solvation model illustrated in Scheme 2.4. Once a R-group is present that is of sufficient size to act as an anchor for the alkyl chain, further increases in the size of the substituent will no longer have any effect on the ability of the alkyl chain to undergo the crankshaft type motions that are involved in the biradical interconversion.

Solutes, with large γ-substituents, chosen so as to *maximise* the shape changes in the conformational motions involved in the Norrish II reaction, may in fact have the added effect of disrupting the ordered matrix around the solute and provide a slightly less ordered local environment around the site of the reaction. The overall results for such probes appear, from the results presented in this study, to be essentially the same (or even smaller) than those observed for the much smaller probes that would involve fairly minor conformational motions. The latter, more compact probes, may allow for a much **tighter packing** of solutes in the smectic phase and a much more rigid local environment. Therefore, fairly minor structural changes in the series in going from **BP-HP** may result in only small changes in the intrinsic nature of solvation in the solvent matrix but large effects on the sensitivity of the solvent to the conformational changes involved in the reaction. Whatever the source is for the observed effects the similarity in the results for **HP** and **VP** to those of **CHBP** and **DP** suggests that the size of the γ-substituent is not a particularly important factor in controlling Norrish II reactivity in this mesogen, as was once thought.[37-39]

Selectivity in the Cyclisation Pathway

The factors that contribute to enhanced product selectivity (F/C) for **VP**, **HP**, and **CHBP** in the smectic phase of **CCH-4**, compared to the nematic and isotropic phases, are the result of the pathway to cyclisation being unfavoured. In turn, there is also some discrimination between the pathways to the two cyclobutanol diastereomers. We observe, in all cases, that when cyclisation does occur it does so with a preference for the *trans*-CB over the *cis*-CB in the smectic phase. We attribute this selectivity to differences in the size and shape of the c-BR conformers which lead to the two products. The *cis*-CB, where

the phenyl and alkyl substituents are *cis* to one another, is more bulky and spherical in shape than the *trans*-CB, which is more like the ground state ketone in overall shape. The *cis*-biradical precursors are expected to be similar in shape to the products they are forming. Therefore, the c-BR conformer leading to the *trans*-CB (being less bulky) will be more compatible with the surrounding liquid crystalline environment than the c-BR which leads to the *cis*-CB. The results presented here suggest that the mesogen directs the reactivity to the product that will be most easily solvated. Similar preferences for the formation of the *trans*-cyclobutanol isomer have been observed in other studies in liquid crystals[66,68-72] as well as other ordered environments.[2] Interestingly, the magnitude of the *t/c* cyclobutanol ratios, while also being enhanced in the smectic phase, appear to be independent of γ-substituent for **VP**, **HP**, and **CHBP** and do not follow a trend as do the F/C ratios shown in Figure 2.8

2.5   Summary and Ramifications of this Study

The ^{2}H NMR results presented here have provided valuable information on the solubilisation behaviour of phenyl ketones in the nematic and smectic liquid crystalline phases of CCH-4. The ring deuterated analogues of the guest solutes have provided the first examples of distinct ^{2}H NMR features that could be assigned to solubilisation of a chemical probe molecule in the smectic (Cr_B) phase of this mesogen. This has allowed for precise determinations of the solubility limits of **AP-HP** in the smectic phase of CCH-4.

The results of the Norrish II photoreactivity studies of homogeneous smectic phase solutions of **BP-HP** have shown that the necessity for specific size and shape structural features for the successful observation of effects in the smectic phase, as eluded

to in the introduction chapter, are not necessarily a general requirement. We believe that this study defines the lower limit of the ability of this mesogen to control conformational motions. The present results indicate that the smectic phase does not impart any noticeable effects on conformational mobility in the reactivity of **BP**, but it does have measurable effects on the reactivity of only slightly larger solutes that involve minor conformational motions.

The ability to directly observe the probe molecules in a smectic phase environment has simplified the interpretation of the ^{2}H NMR behaviour observed for α-deuterated analogues and has given <u>direct</u> evidence for the biphasic nature of ketone/mesogen mixtures of composition above the solubility limit. We have shown that the portion of ketone above the solubility limit, which resides in a phase separated nematic or isotropic phase, acts to lower the observed effect which the liquid crystal has on the reactivity of dissolved solutes. By comparison of NMR results obtained from the ring-deuterated analogues to the α-deuterated analogs, and by correlating them with previous NMR studies of α-deuterated solutes in this mesogen, we conclude that the solubilisation behaviour observed for the probes in this study is a general phenomenon for aromatic ketones in the smectic phase of CCH-4. We have shown this explicitly by the concentration dependence on the photochemistry of **CHBP** at 30°C in CCH-4. This latter work has defined the true ability of the smectic phase of CCH-4 to alter the photochemistry of this probe, which had previously been reported under biphasic conditions.

We have shown that ^{2}H NMR is a useful tool to monitor the local phase environment of a dissolved solute. Perhaps the more substantial ramification of this work is the broad applicability of our ^{2}H NMR technique for investigation of the solubilisation

behaviour of probes in ordered solvents. In Weiss's studies of the Norrish II photolysis of several long chain alkanones and alkylphenones in the Sm_B phase of n-butyl stearate (BS)[68,69,72] he found that F/C ratios reached a maximum for ketones which were similar in length to BS and fell off as the solute was either shortened or lengthened from the optimum length. It was concluded that ketones whose length or structure deviate from that of the mesogen disrupt the local ordered environment around the reactive center, leading to lower F/C ratios for these ketones. This may be the case. However, without a firm indication of the variations in the solubility of the probes in the smectic phase with structure it is difficult to accept this conclusion without considerable caution. Clearly, determination of the solubility behaviour of each of the probes may aid in determining if solute length (in relation to solvent length) is the sole source of the observed effects.

In spite of the results presented in this chapter (which have been published[105]), examples continue to be reported by other workers where the ^2H NMR spectra of probe solutes in ordered phases are misinterpreted. Recently, Weiss and co-workers reported findings on the influences of smectic phases on the Norrish II photochemistry of perfluoroheptyl octyl ketone.[123] Their studies employed perfluorodecyl decane as the mesogen. This liquid crystal exhibits two smectic phases which have been identified as smectic G phases.[124,125] The morphology of the smectic G phase is very similar to that of the smectic B phase,[124,125] which has been described previously (see Chapter 1). At the concentrations utilised, the ^2H NMR spectra of the α-deuterated derivative of their probe molecule exhibited only a singlet in the smectic phase temperature region. Even with this result, they found it surprising that there was a lack of significant control on the Norrish II product selectivity in the highly ordered smectic phases. They rationalised their results by suggesting that the environment experienced by the reaction centre is microscopically

disordered (given by the isotropic signal in the NMR) even though the guest molecule is well ordered within the smectic phase matrices. Of course, by analogy with our work, we believe that minor control over selectivity in the reaction is a direct result of phase separation of the ketone into an isotropic environment, similar to what is observed for high concentrations of solutes in the smectic phase of CCH-4. Clearly, these workers should reevaluate their results and perform a more thorough study of the concentration dependence of the ^{2}H NMR and the photochemistry of this probe in these mesophases. Closer examination may show that the solubility of their probe in these mesogens may be much lower than the concentrations used.

The solubility behaviour of the phenyl alkyl ketones in the smectic phase of CCH-4 is truly more complex than previously thought. The probes used in this work have illustrated the importance of thorough concentration dependent ^{2}H NMR studies of any probe system used to investigate the effects of ordered phases of liquid crystalline solvents on reactivity. The Norrish II reaction is a useful monitor to observe whether the smectic phase of a mesogen has any effect on the conformational dynamics of a dissolved solute. However, the specific nature of the responsible solute-solvent interaction is difficult to obtain. This is partly due to the complexity of the reaction, as well as the fact that we are monitoring the end result of any interaction and not the effect on the biradical intermediate itself. For this reason little quantitative information on the mobility and reactivity of the reactive intermediate is obtainable. We therefore turned our attention to the β-phenyl quenching probe from which we could monitor the effects of restriction of motions on the excited state triplet directly and obtain quantitative information on the mobility of such probes in the smectic phases of liquid crystalline mesogens. This is the focus of the remainder of this thesis.

CHAPTER 3

INTRAMOLECULAR TRIPLET DEACTIVATION OF β-PHENYL-4-METHOXYPROPIOPHNONE: A DIRECT PROBE OF CONFORMATIONAL MOBILITY IN THE MESOGENIC PHASES OF CCH-n, OS-nm, AND CCH-nOm LIQUID CRYSTALS

3.1   Introduction

Following our investigation of the effect of liquid crystalline phases on the conformational dynamics of simple alkanophenones using the Norrish II reaction as a monitor we turned our attention to the use of β-phenyl-4-methoxypropiophenone (1) as a probe of conformational mobility in CCH-n liquid crystals. By determining the conformation dependent triplet lifetime of this solute in mesogenic solvents using nanosecond laser flash photolysis (NLFP) techniques, it is possible to probe more precisely the effect of ordered phases on discrete molecular motions of dissolved solutes.

Preliminary investigations of the photochemistry of 1 in CCH-n liquid crystals showed interesting phase dependent Arrhenius behaviour for triplet deactivation in the mesogenic phases of CCH-4, but phase independent behaviour in CCH-2 (see Chapter 1 for details).[85] The results of subsequent ^{2}H NMR studies on the α-deuterated derivative of 1 (1-αd$_2$)[90,92] and those of related molecules[91,105] indicated that the original studies

1 ·

utilised samples whose solute concentrations are above the solubility limits. Therefore, the preliminary photochemical study was performed under conditions where the solute experienced complex solubilisation phenomena and thus provided an inaccurate indication of the ability of the smectic phases of these mesogens to control the mobility of **1**.

In this chapter, we report the results of a study which defines the *true* effect of the liquid crystalline phases of the CCH-n mesogens on the triplet state behaviour of **1**. The work includes detailed investigations of the concentration and temperature dependence of the ^{2}H NMR spectra of a number of deuterium labelled analogs of **1** (**1**-αd_2, **1**-Od_3 and **1**-βd_5) in the CCH-n liquid crystalline phases. These experiments allow qualitative information to be gained on the mobility of this probe in the smectic phases, and allow an accurate determination of the solubility limits of **1** in these mesogens. In addition, triplet lifetime data from homogeneous solutions (of composition well below the solubility limits) were measured and are compared to those obtained under heterogeneous solubilisation conditions.

For further comparison, these studies have been extended to the OS-nm and CCH-nOm liquid crystals. These experiments allowed for the investigation of the generalisability of the photochemical results obtained in the mesogenic phases of CCH-n to those of other families of liquid crystals. This allows more general conclusions to be made regarding the mode of solubilisation of aromatic ketones in highly ordered smectic

1- αd$_2$

1-Od$_3$

1-βd$_5$

phases, and the effects of these phases on the conformational mobility of the probe molecule.

PART A: Deuterium NMR Spectra of 1 in CCH-n, OS-nm and CCH-nOm Liquid Crystalline Solvents

3.2 Results and Discussion

3.2.1 Preparation of Compounds

Compound 1 and β-phenyl-4-hydroxypropiophenone were prepared from 4-methoxy- or 4-hydroxyacetophenone and benzaldehyde using a previously reported procedure.[76]

The α-deuterated derivative of 1 was prepared from the all protiated analog in the same manner as those in Chapter 2. The methoxy-deuterated derivative (1-Od$_3$) was prepared by Williamson etherification of β-phenyl-4-hydroxypropiophenone with

iodomethane-d_3 and potassium carbonate in refluxing acetone. Compound 1-βd_5 was synthesized from 4-methoxyacetophenone and benzaldehyde-d_5 by the procedure used for preparation of the undeuterated analog. Benzaldehyde-d_5 was prepared from bromobenzene-d_5 and N-formyl-morpholine by a modification of the method of Olah and co-workers.[126] All compounds were purified by repeated recrystallisation from aqueous ethanol prior to use. Further experimental details are given in Chapter 6.

3.2.2 General Considerations

Samples of mixtures of the deuterated analogs of 1 in the various mesogens were prepared in a manner similar to that described in Chapter 2. Deuterium NMR spectra were recorded (using the method employed in Chapter 2) at 76.8 MHz, at various temperatures throughout the 0-84°C temperature range using the quadrupolar echo pulse sequence.[93,94] A few experiments with CCH-4 mixtures (where noted) were also carried out at 61.4 MHz, using a home built 400 MHz solid state spectrometer.[127]

Like the CCH-n mesogens, the OS-nm and CCH-nOm have negative diamagnetic anisotropies.[128] Thus, nematic phase samples are aligned spontaneously by the spectrometer with the mesogen's long axis perpendicular to the magnetic field. This simplifies comparisons of the recorded quadrupolar splittings for the various liquid crystalline solutions. It is important to recall that each of the mesogens being discussed exhibit their liquid crystalline phases over somewhat different temperature ranges (see Figure 1.3).

3.2.3 ^{2}H NMR Spectral Features of 1 in the
Isotropic and Nematic Phases

The ^{2}H NMR behaviour of the deuterated analogs of 1 (1-αd$_2$, 1-Od$_3$, and 1-βd$_5$) as mixtures in the isotropic and nematic phases of each mesogen was qualitatively similar to that observed for the alkanophenone/CCH-4 mixtures described in Chapter 2. The isotropic phase spectrum for each mixture always consists of a single deuterium resonance. On lowering the temperature below the I→N transition temperature, the singlet splits into one or more well-defined quadrupolar doublets depending on the number of non-equivalent deuterons in the molecule. The maximum quadrupolar splittings vary according to the site of deuteration and the mesogen. In every case, the maximum splittings are observed at the bulk N→Sm transition temperature, where the order in the nematic phase is the greatest. The trends observed for the individual mesogens (with respect to variations in the magnitude of the splittings as a function of temperature and the effect of increased solute concentration on the I→N transition temperature) are similar in all cases to those described at length in Chapter 2.

Both the α- and methoxy- deuterated derivatives show a single narrow quadrupolar doublet in the nematic phase of each of the respective liquid crystals. The nematic phase splittings for 1-Od$_3$ range from 2.9 to 7.7 kHz in the various mesogens studied and are always smaller in magnitude than the splittings for 1-αd$_2$, which range from 14.3 to 25.2 kHz. The smaller splitting for 1-Od$_3$ is consistent with the more rapid motions available around the C$_3$ axis of the methoxy portion compared to the motions available to the alkyl chain portion of the molecule. The nematic phase signals for 1-βd$_5$

are very similar to those of the alkanophenone-d_5 derivatives reported in Chapter 2. In each of the nematic phases, 1-βd_5 exhibits two sets of doublets: a strong inner doublet due to the *ortho* and *meta* deuterons, and a weaker outer doublet, with much larger splitting, due to the *para* deuteron. The maximum splittings observed for the two types of phenyl deuterons, as well as the maximum splittings for 1-αd_2 and 1-Od_3 in each of the mesogenic solvents, are included in Table 3.1. In addition, selected examples of nematic phase spectra of these deuterated probes in a number of different mesogens are shown in Figures 3.1, 3.2, 3.3, and 3.4. The large differences in splittings observed between the *ortho/meta* and *para* deuterons in each solvent indicates that the probe solute is preferentially oriented in the nematic phase with the *para* C-^{2}H bond on the β-phenyl ring parallel to the orientation of the solvent molecules , which is perpendicular to the magnetic field. As has been described in the previous chapter, the quadrupolar splitting is expected to be at a maximum for deuterons in this orientation.

The nematic phase spectra of the deuterated analogs of 1 are very similar in each of the mesogenic solvents and their interpretation is straightforward. There are also many similarities in the NMR behaviour of these probes in the smectic phases of the various mesogens. However, since the spectra observed also exhibit interesting differences, each of the phase types will be discussed individually in the following section.

3.2.4 ^{2}H NMR Spectra of 1 in the Smectic Phases

(i) CCH-4 and CCH-2

The concentration dependence of the ^{2}H NMR behaviour of 1-αd$_2$ in CCH-4 has been discussed in Chapter 1. The results of that earlier study has led, in part, to the portion of this thesis which was aimed at gaining a better understanding of the solubility behaviour of ketones in the smectic phase of CCH-4. The temperature dependence observed in the NMR spectra of 1 mol % mixtures of 1-αd$_2$ in CCH-4 are similar to that described for higher concentration samples of VP and HP-αd$_2$ in the previous chapter. Low concentration samples of 1-αd$_2$ are also similar to those of VP and HP-αd$_2$, and are devoid of spectral features in the smectic phase temperature region. This latter result has been shown to be indicative of homogeneous smectic phase solubilisation for this ketone. However, under no circumstances has any direct spectral evidence for 1 solubilised in the smectic phase been obtained. From our results in Chapter 2, it was evident that changing the site of deuteration may aid in giving a clearer indication of the solubilisation behaviour of 1 in the smectic phase of CCH-4. The obvious choice for an alternate position to deuterate, and the simplest from a synthetic standpoint, is the alkoxy portion of the molecule.

Below the bulk N$\rightarrow$Sm phase transition temperature, the ^{2}H NMR of mixtures of 1-Od$_3$ in CCH-4 (K-28-Sm-54-N-79-I)[28,29] show a second broader double resonance with a splitting about 2.5 times larger than that of the nematic phase doublet (see Table 3.1 for actual value). This new doublet broadens as the temperature is lowered, but remains

visible at all temperatures. These general characteristics are consistent with the ketone experiencing a more highly-ordered environment, and have thus been assigned to **1** solubilised in smectic CCH-4. Spectra of 1 mol % mixtures of 1-Od_3 in CCH-4 (the concentration used in the original photochemical experiments[85]) verify our previous conclusions, which were based on variable-concentration ^{2}H NMR studies with the α-deuterated derivative coupled with thermal microscopy and D.S.C. experiments.[90] At 1 mol %, the sample is biphasic throughout the complete 30-53°C temperature range of the smectic phase. Between 53 and 34°C, the nematic phase doublet splitting continuously decreases with temperature (as we have seen with 1-αd_2), and coexists with the doublet assigned to the smectic phase component. Below 34°C, the nematic phase doublet is replaced by an isotropic singlet, indicating that the ketone exists in both a smectic and isotropic environment below this temperature. By carefully controlling the temperature in the vicinity of the (N + Sm)$\rightarrow$ (I + Sm) phase transition temperature, spectra showing the ketone residing in all three types of environment are observed. This indicates the presence of a eutectic in the phase diagram of the mixture in CCH-4. Biphasic spectra of 1-Od_3 at various temperatures between 48-30°C are shown in Figure 3.1a.

The relative proportions of **1** existing in the two phase environments are, as we have previously described, dependent on the solubility limit of the ketone in the smectic phase at a particular temperature. The observation of distinct smectic phase signals allows for a more accurate determination of the solubility limits of **1** in the smectic phase of CCH-4. The solubility limits were established by adjusting the sample concentration until only spectra of homogeneous smectic solutions of **1** were obtained, as described in Chapter 2. The ^{2}H NMR experiments also allowed for the construction of the binary phase diagram of 1/CCH-4 mixtures in the region where the mole fraction of **1** is below 5
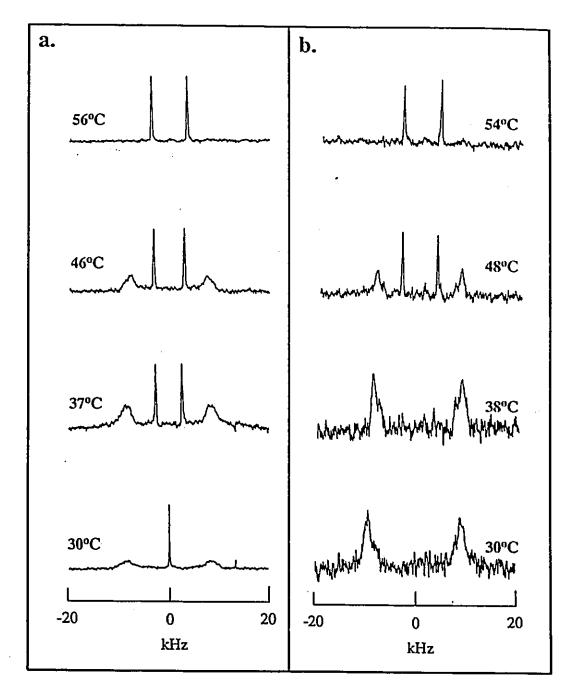
Figure 3.1. ^{2}H NMR spectra of mixtures of (a) 1 mol % and (b) 0.25 mol % 1-Od$_3$ in CCH-4, recorded at 78.8 MHz at various temperatures between 84-29^{0}C. Spectra in (a) illustrate the biphasic nature of the sample throughout the smectic phase temperature region, while those in (b) show an example of homogeneous solubilisation in the smectic phase.
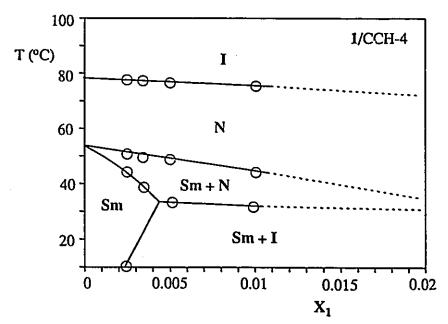
Figure 3.2. Partial composition/temperature binary phase diagram for 1/CCH-4 constructed from ^{2}H NMR data. Actual data shown.
Key: I = isotropic; N = nematic; Sm = smectic.

mol %. A portion of the composition/temperature phase diagram for 1/CCH-4 mixtures (below 2 mol %) is shown in Figure 3.2. The phase diagram is qualitatively similar to that shown for VP/CCH-4 mixtures shown in Chapter 2. A 0.5 mol % mixture of 1-Od$_3$/CCH-4 behaves similarly to the 1 mol % mixture. However, a 0.25 mol % sample is homogeneous between 46° and 10°C, as revealed in the NMR spectra by the presence of only the quadrupolar doublet assigned to 1 in the smectic phase (see Figure 3.1b). The persistence of the smectic phase spectrum at temperatures below 28°C is due to supercooling of the Sm→K transition.[29] Between 46° and 53°C the sample is biphasic, as shown by the presence of both the nematic and smectic phase spectral components. The biphasic behaviour extends further into the smectic phase temperature region as the concentration of the ketone in the sample is increased above the solubility limit. For example, in a 0.34 mol % sample, the nematic phase component persists down to 38°C before the sample becomes monophasic. The solubility limit increases with decreasing temperature and is estimated to be approximately 0.4 mol % at 30°C and 0.25 at 45°C. For the purpose of variable-temperature studies in the photochemical experiments, a concentration of 1 in each liquid crystal is required such that the probe remained homogeneously soluble throughout the majority of the smectic phase temperature region of the pure mesogen. In this chapter, the composition of the mixture that meets this requirement is defined as the solubility limit. For 1 in CCH-4, this value was determined to be between 0.2 and 0.25 mol %.

Spectra of 1 mol % samples of 1-αd$_2$ in CCH-2 (K-28-Sm-44-N-48-I)[28,29] were found to be significantly different than those observed with CCH-4. As the temperature is lowered below the bulk N→Sm phase transition, mixtures of 1 in CCH-2 form a Sm + I mixture without intermediate formation of a N + Sm biphasic mixture. As

with CCH-4, no spectral features assignable to a smectic phase component are observable. At the time, we believed that the absence of spectral features for the smectic phase component was due to similar factors as given earlier for the same observation in CCH-4. We therefore studied the spectra of 1-Od_3 in CCH-2 in the hope of observing the smectic phase component and define a solubility limit of 1 in this mesogen. However, even samples of 1-Od_3 at compositions as low as 0.1 mol % show only an isotropic singlet between 20-44°C (i.e. below the N→Sm transition) and no other features assignable to a smectic phase component (see Figure 3.3). This indicates that the solubility of 1 in the smectic phase of CCH-2 is <u>substantially</u> lower than 0.1 mol %. At this concentration (and above) the majority of the probe must exist in a phase-separated isotropic environment which coexists with the bulk smectic phase. The smectic phase component must be such a minor portion that it can not be observed in ^{2}H NMR experiments. Additional NMR experiments with samples of lower solute concentration were not attempted because of sensitivity problems. Given that the smectic phase of CCH-2 is of higher order than the smectic phase of CCH-4, the lower solubility limit of 1 in the former is not unexpected. What is surprising is that the solubility limit in CCH-2 is evidently so low that the portion of the ketone in the smectic phase cannot be observed even at 0.1 mol %.

Earlier, it was illustrated how ^{2}H NMR could be used to obtain qualitative information on the mobility of a probe molecule within the smectic phase. In this regard, the smectic phase spectra of 1-Od_3 do not give useful information on the mobility of that portion of the molecule which is involved in the photochemical reaction. For this reason, we investigated the NMR behaviour of $1\text{-}\beta d_5$. For low concentration samples of $1\text{-}\beta d_5$ in CCH-4, the sharp lines due to the nematic phase are gradually replaced by a doublet of *ca.* 10 kHz splitting and a linewidth of several kilohertz at temperatures below the bulk
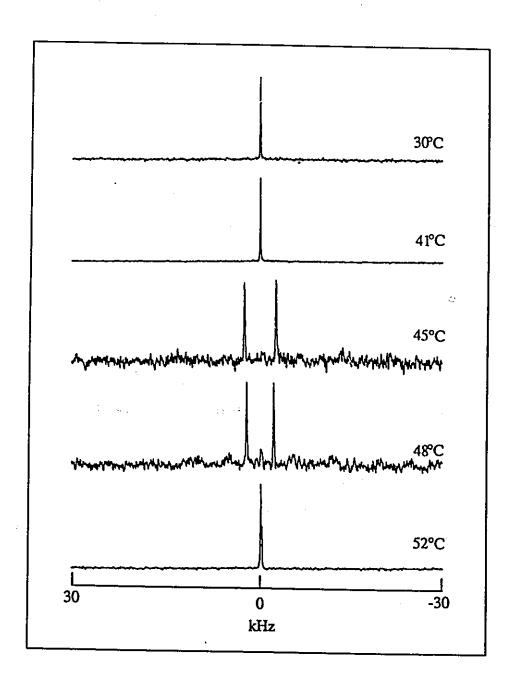
Figure 3.3. ^2H NMR spectra of a 0.1 mol % mixture of 1-Od$_3$ in CCH-2 measured at 78.8 MHz at temperatures between 50 and 30°C.

N→Sm transition. The quadrupolar doublet broadens as the temperature is lowered, and gradually becomes a broad featureless absorption which spans about 35 kHz (see Figure 3.4a). This behaviour is consistent with the β-phenyl portion of the molecule experiencing a highly ordered environment and slow reorientation rates on the NMR timescale.

We worried that this broad featureless absorption could be due to a *random* orientation of the probe in the smectic phase. We therefore repeated the experiment with a 0.21 mol % sample at 61.4 MHz on a home built 400 MHz solid state spectrometer at a single temperature in the smectic phase. Under these conditions, the spectrum of 1-βd$_5$ shows a broad absorption with a splitting of 10.5 kHz (as was observed on the 500 MHz spectrometer) flanked by a weaker doublet with a splitting of 84.0 kHz, and is similar in appearance to the smectic phase spectra of the ring deuterated ketones described in Chapter 2. The outer doublet, which is presumably due to the *para* deuteron, is of approximately two times greater splitting than in the nematic phase, and was not observed on the 500 MHz spectrometer. The better resolution obtained with the 400 MHz spectrometer is a result of its shorter 90° pulse width and a higher accumulated signal to noise ratio. The inner doublet, assigned to the *ortho/meta* deuterons, is of approximately five times larger splitting than in the nematic phase. The spectrum observed suggests that the β-phenyl ring is well oriented in smectic CCH-4, with a preference for the *para* C-^{2}H bond to be aligned perpendicular to the magnetic field; furthermore it is subject to slow reorientation rates on the NMR timescale.

The spectrum obtained for 1-βd$_5$ on the 400 MHz spectrometer in the smectic phase of CCH-4 was recorded after cooling the sample from the nematic phase. In the original arrangement of the sample tube and the magnet, the sample is oriented with the liquid crystal aligned perpendicular to the magnetic field (the same as on the 500 MHz

spectrometer). Another spectrum was recorded at the same temperature, but with the sample tube rotated 90° within the probe of the instrument.[129] Since the smectic phases of liquid crystals maintain their alignment from the nematic phase and are very slow to reorient,[82,91,105] this second experiment should afford a spectrum characteristic of the probe in a parallel alignment with respect to the magnetic field direction. Indeed, the appearance of the spectrum is dramatically different than the previous one, giving further evidence that the solute is well-oriented within smectic CCH-4.[130] If the sample was randomly ordered in the smectic phase, the spectrum would not be expected to change appreciably as the sample alignment is altered.[130]

An experiment was also performed using a 0.21 mol % sample of benzoyl ring-deuterated 1 (1-Acd). The nematic phase spectra consist of two quadrupolar doublets

1-Acd

of equal intensity with splittings of 1.8 and 10.4 kHz. These correspond to the two non-equivalent deuterons on the ring. The nematic phase component disappears at a similar temperature to those of the other deuterated probes in samples of similar composition. Below this temperature the spectra were featureless, indicating that the reorientation rates of these deuterons must be slowed to a similar rate as the α-deuterons. Recall that no spectral features will be observable when the reorientation rates are of similar magnitude to the quadrupolar coupling constant.[108]

Taken as a whole, the results of the ^{2}H NMR studies of the four deuterated probes in CCH-4 indicate that the probe molecule is well oriented in both the nematic and

smectic phases. In addition, the results obtained for the homogeneous smectic phase solutions show that the solute experiences a great deal of order and restricted motion at all positions within the molecule. Our results in CCH-4 also prove that our method of determining the solubility limit is indeed independent of the site of deuteration, since similar results were observed for mixtures of each of the deuterated probes.

(ii) OS-53 and OS-35

The ^{2}H NMR spectra of 1-αd$_2$, 1-Od$_2$, and 1-βd$_5$ were measured in OS-53 (K-25-Sm-39-N-53-I)[28,29] and OS-35 (K-24-Sm-53-N-80-I).[28,29] The spectra were found to be qualitatively similar to those in CCH-4, as expected since the OS-nm liquid crystals also possess negative diamagnetic anisotropy[128] and are believed to have the same morphology as CCH-4 (see Chapter 1).[33,131] The quadrupolar splittings observed for each probe in the OS-nm liquid crystals at various temperatures are summarised in Table 3.1. The spectral features observed for 1 as a function of concentration and temperature in both OS-35 and OS-53 (see discussion below) allowed for construction of a portion of the binary phase diagram for each 1/OS-nm mixture. That constructed from the ^{2}H NMR data for 1/OS-35 mixtures is shown in Figure 3.6a. Again, the overall phase diagram is very similar to that shown previously for 1 in CCH-4 and VP in CCH-4.

At temperatures below that of the bulk N→Sm phase transition, samples of the three deuterated analogs all exhibit features in the NMR spectrum that are assignable to the probe in a smectic phase environment. Using the deuterated probes, 1 was found to form homogeneous smectic phase solutions between 4-35°C and 10-46°C for OS-53 and OS-35 respectively, when the sample compositions are 0.1 mol % (the Sm→K transitions
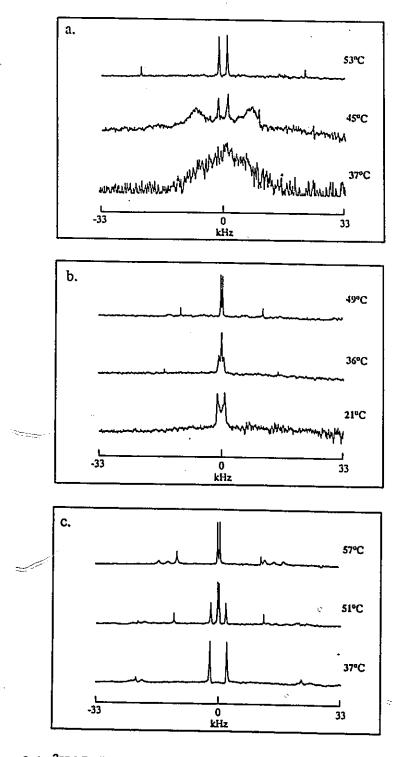
Figure 3.4. ^{2}H NMR spectra of 1-βd$_5$ as a (a) 0.21 mol % mixture in CCH-4; (b) 0.1 mol % mixture in OS-35; (c) 0.5 mol % mixture in CCH-502 illustrating the features observed in the nematic, biphasic and smectic temperature regions of each mesogen.

Figure 3.5. ^{2}H NMR spectra of 1-αd$_2$ as a (a) 0.58 mol % mixture in OS-53 and (b) 0.5 mol % mixture in CCH-502. The spectra illustrate the features observed in the nematic, biphasic and sm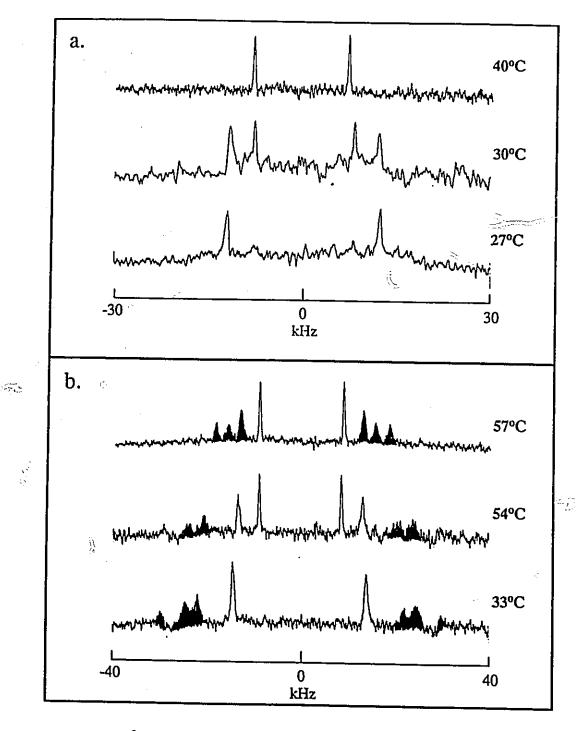ectic temperature regions of each mesogen. Peaks shaded in (b) are due to a deuterated impurity in the liquid crystal. See text.

of both mesogens supercool substantially). At temperatures above the onset of sample homogeneity and below the N→Sm phase transition temperature of the pure mesogen, spectra exhibiting heterogeneous solubilisation behaviour (N + Sm) are observed. A few examples of spectra showing these general features are shown in Figures 3.4b and 3.5a.

Compound 1-αd$_2$ shows no detectable spectral features in monophasic smectic phase solutions in OS-35. On the other hand, samples of 1-αd$_2$ in smectic OS-53 exhibit a quadrupolar doublet with splitting of *ca.* 33 kHz. Examples of spectra recorded for 1-αd$_2$ in OS-53 are shown in Figure 3.5a. The absence of observable features in the spectra of 1-αd$_2$ in the smectic phase of OS-35 is presumably due to similar factors as the behaviour of this probe in CCH-4. Interestingly, spectra of VP-αd$_2$ show distinctive smectic phase quadrupolar doublets in both OS-nm liquid crystals. The reorientation rates of C-^{2}H bonds of VP-αd$_2$ in the OS-nm mesogens must be faster than in CCH-4, and faster than those in 1-αd$_2$ in OS-35 to account for the fact that a signal is observed. In both OS-nm mesogens, spectra of 1-Od$_3$ exhibit similar features to those observed in CCH-4, but the quadrupolar splittings are comparatively smaller.

Spectra of 0.1 mol % samples of 1-βd$_5$ in OS-35 and OS-53 below the bulk Sm→N transition temperature show the formation of a single broad quadrupolar doublet of slightly larger splitting than is observed for the *ortho/meta* deuterons in the nematic phase. The signal observed in OS-35 has a splitting of 3.9 kHz and an example is shown in Figure 3.4b. In OS-53, the smectic phase signal has a smaller splitting (1.6 kHz) and has the appearance of a powder pattern.[82] However, the signal in OS-53 can not be due to a crystalline sample since the spectra of the methoxy deuterated and α-deuterated samples clearly indicate that the solute is well-oriented in the smectic phase. The doublet observed for 1-βd$_5$ in OS-53 and OS-35 is, we believe, due to the *ortho/meta* deuterons, even

though there is no evidence in either case of a less intense signal of even larger splitting that could be assigned to the *para* deuteron. Samples of the ring-deuterated analogs of AP-HP in the liquid crystalline phases of OS-53[132] exhibit spectra similar to 1-βd$_5$ with the exception that in the former, weak signals due to the *para*-deuterons could be observed. Work on the ring- deuterated alkanophenones involved samples whose compositions were six times greater than those involving 1; we attribute the absence of signals for the *para* deuterons in 1 to the low signal to noise ratio that we were able to accumulate.

Deuterated samples of 1 at concentrations greater than 0.1 mol % in either OS-nm mesogen exhibit wider biphasic temperature regions. Solutions of 0.58 mol % 1-αd$_2$ in OS-53 remain nematic to 32°C, are biphasic (N + Sm) between 32-27°C, and are homogeneously smectic below 26°C. The solubility limits for 1 in this mesogen are therefore approximately 0.58 mol % at the lower end of its smectic phase temperature region, and 0.1 mol % at the upper end. No evidence for formation of a phase-separated isotropic phase is observed until the sample is cooled to below 4°C. When the sample concentration is increased further, the phase-separated nematic phase component persists to lower temperature and still no evidence for the phase separated isotropic phase is observed.

The phase behaviour of higher concentration mixtures in OS-35 are slightly more complicated (see Figure 3.6a). Spectra of 1-Od$_3$ as a 0.25 mol % mixture and of 1-αd$_2$ as a 0.58 mol % mixture indicate that at compositions above the solubility limit, the samples remained nematic to about 46°C and are biphasic (N + Sm) to 43°C, where the nematic phase component collapses to form an isotropic phase. The isotropic component of the spectrum slowly decreases in intensity until 29°C where a spectrum indicative of a
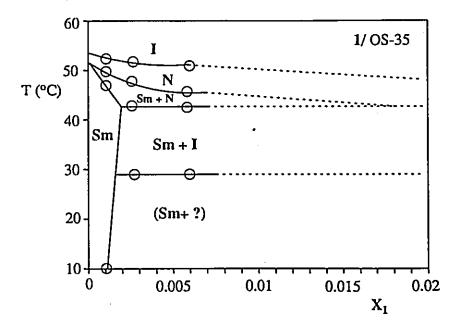
homogeneous smectic phase solution is observed. These results suggest the presence of a eutectic in the binary phase diagram of 1 in OS-35.

A comparison of results obtained in the OS-nm mesogens to those in CCH-4 show that the observed behaviour is in general qualitatively similar. However, the phase behaviour is condensed to a smaller concentration range in the OS-nm mesogens (compare Figures 3.2 and 3.6a). Furthermore, the magnitude of the quadrupolar splittings in the OS-nm series are always smaller than in CCH-4 (see Table 3.1). This may indicate that the solute is somewhat less ordered in OS-nm than in the corresponding phases of CCH-4. Since both mesogens are thought to be of similar morphology, the difference in the apparent order must be due to the ability of each mesogen to effectively solubilise the solute within its matrix. The solubility limit of 1 in the OS-nm mesogens, being approximately one half that measured in CCH-4, also supports this idea. The OS-nm liquid crystals are less able to incorporate the solute within its smectic phase lattice without disruption of the local order. The series of alkanophenones have also been determined to have much lower solubility limits in the OS-nm mesogens.[132] The solubility of these compounds were found to be approximately 0.6 mol % at 30°C. This low solubility precluded studies of the Norrish II reactivity of these probes in the OS-nm mesogen.
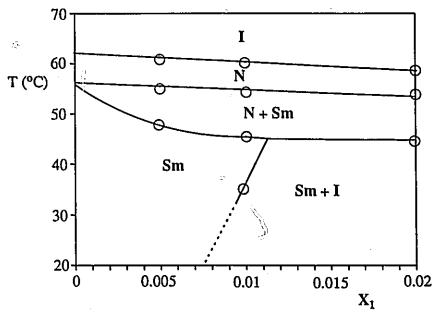
(iii) CCH-502 and CCH-303

Smectic phase signals, distinctive from those due to the probe in the nematic phase, are observed for mixtures of 1-αd$_2$, 1-Od$_3$, 1-βd$_5$, and 1-Acd in CCH-502 (K -35- Sm -56- N -62- I).[28,29] This allowed for an accurate determination of the phase behaviour of 1 in the smectic phase of this mesogen. A portion of the binary phase diagram for

Figure 3.6a. Partial composition/temperature binary phase diagram for 1/OS-35 constructed from ^{2}H NMR data. Actual data points shown.

Figure 3.6b. Partial composition/temperature binary phase diagram for 1/CCH-502 constructed from ^{2}H NMR data. Actual data points shown.

1/CCH-502 mixtures constructed from the ^{2}H NMR data is shown in Figure 3.6b. This mesogen appears to be able to incorporate large quantities of solute without obvious disruption to the bulk phase behaviour. This is in contrast to what is observed for 1 in CCH-4 and OS-nm mesogens (compare Figures 3.6b with Figures 3.2 and 3.6a).

Samples of high concentration of the deuterated probes gives evidence for phase separation phenomena. A 2 mol % sample of 1 consists of the ketone solubilised in the smectic phase coexisting with a phase-separated nematic phase between 54-45°C, and a phase-separated isotropic phase below 45°C. Samples of the deuterated derivatives of 1 as 0.5 mol % mixtures are homogeneously solubilised in the smectic phase below 48°C. The Sm→K phase transition supercools substantially (< 16°C). The smectic phase splittings for these probes are listed in Table 3.1. Examples of spectra measured with 0.5 mol % samples of 1-αd$_2$ and 1-βd$_5$ are shown in Figures 3.4c and 3.5c, respectively. In these figures there are extra signals in the wings of the spectra. These have been determined to be due to deuterated impurities in the liquid crystal, or due to the liquid crystal itself (i.e. they were present in similar spectra recorded with samples of pure mesogen).

The smectic phase signals are all characterised by a larger quadrupolar splitting than in the nematic phase; consistent with the probe experiencing a more ordered environment. Interestingly, the linewidths observed for each probe in the smectic phase are only slightly larger than those observed in the nematic phase (see Figure 3.4c and 3.5c for examples). The narrower linewidths are in stark contrast to those observed in the other mesogens studied, and are especially striking in the case of the β-phenyl-d$_5$ derivative (see Figure 3.4 for comparisons). In the NMR spectra of homogeneous solutions of the α- and ring-deuterated analogs of AP-HP[132] in CCH-502, the linewidths of the smectic phase

signals are also similar to those of the nematic phase signals. The results suggest that the probe molecules undergo fairly rapid reorientation in the smectic phase environment of CCH-502. They also suggest that the smectic phase of this mesogen is much less ordered than those of CCH-4 and the OS-nm liquid crystals.

In the case of CCH-303 (K-13-Sm-64-I),[28,29] the solubility of 1 and the NMR behaviour of the α- and methoxy deuterated analogs more closely resemble those observed with the CCH-4 and OS-nm mesogens. Solubility limit determination employed 1-Od_3, since no signals are observed for the α-deuterated analog in the smectic phase of this mesogen. Samples of $1\text{-}\alpha\text{d}_2$ and 1-Od_3 as 0.5 mol % mixtures (the solubility limit in CCH-502) indicate the sample to be biphasic (Sm + I) above 28°C, but homogeneous (Sm) below this temperature. No nematic phase exists for CCH-303 and thus no N + Sm biphasic region is observed. Deuterium NMR spectra of a 0.1 mol % mixture in the smectic phase indicate the sample to be homogeneous over the 15-49°C range, biphasic (Sm + I) between 49-56°C, and isotropic above 56°C. The solubility limit of 1 in smectic CCH-303 is therefore at least five times lower than that in CCH-502. The smectic phase of pure CCH-303 extends to 64°C, therefore the actual solubility limit of 1 by our definition, is actually lower than 0.1 mol %. However, samples below this concentration are not suitable for photochemical experiments.

It appears as if the smectic phase of CCH-303 is a more highly ordered one than CCH-502 and thus not a simple Sm_B phase as has been reported.[36] The similarities in NMR and solubility behaviour of 1 in CCH-303 to those of 1 in CCH-4 and the OS-nm liquid crystals suggest that CCH-303 may be more similar in morphology to these mesogens than to CCH-502.

Table 3.1 Quadrupolar splittings from ^{2}H NMR spectra of deuterated analogues of 1 in the nematic and smectic phases of CCH-n, OS-nm and CCH-nOm liquid crystals.[a]

Liquid Crystal	Phase	α-d_2	Od_3	β-d_5	
				ortho/meta	*para*
CCH-4[g]	N[b]	25.2	7.7	2.1	43.5
	Sm[c]	d	19.4	10.5[e]	84.0[e]
CCH-2	N[b]	18.8	5.1	f	f
OS-53	N[b]	22.2	4.4	0.2	28.7
	Sm[c]	33.0	6.5	1.6	d
OS-35	N[b]	14.3	2.9	0.4	19.1
	Sm[c]	d	7.3	3.9	d
CCH-303[h]	Sm[c]	d	4.2	f	f
CCH-502[i]	N[b]	17.3	3.5	0.5	24.0
	Sm[c]	27.1	5.2	4.4	45.0

a. Recorded at 76.8 MHz, using the quadrupolar echo pulse sequence. Errors in splitting are ca. ± 0.1 kHz.

b. N = nematic; spectra were recorded 1-2°C above the S-N transition temperature.

c. Sm = smectic; spectra were recorded at 30°C.

d. No signals observable.

e. Recorded at 61.4 MHz, 37°C.

f. Not recorded.

g. Splittings for 1-Acd in CCH-4 were 10.6 and 1.8 kHz in the N phase and were not observed in the Sm phase.

h. No nematic phase present.

i. Splittings for 1-Acd in CCH-502 were 5.0 and 0.85 kHz in the N phase and a single unresolvable doublet of 4.9 kHz in the Sm phase.

PART B: <u>Nanosecond Laser Flash Photolysis Studies of 1</u>

<u>in the Liquid Crystalline Phases of CCH-n OS-nm,</u>

<u>and CCH-nOm Mesogens</u>

<u>3.3</u>   <u>Results</u>

3.3.1   **Sample Preparation and General Technique**

Nanosecond laser flash photolysis (NLFP) experiments were carried out using the pulses from an excimer laser filled with N_2/He (337 nm; 6 ns, 5 mJ) or Xe/HCl/H_2/He (308 nm; $\leq$ 12ns,40 mJ) mixtures. Transient absorptions were monitored using a microcomputer controlled detection system which has been described in detail.[133] In the investigation of the photochemistry of 1 in homogeneous smectic phase solutions of each mesogen, samples of bulk solute concentration equal to or less than the solubility limit were utilised. A summary of the solubility limits of 1 in the smectic phase of each solvent, determined from ^{2}H NMR studies (*vide supra*), is given in Table 3.2. Low concentration samples were prepared as we have described for other solute/mesogen mixtures and then sealed in 3 X 7 mm^2 Suprasil quartz T-cells (path length 3 mm) on a high vacuum line, after degassing with at least 5 freeze-pump-thaw cycles. Typically, the sealed samples were allowed to anneal in an oven for several days at 37-38°C. Prior to the start of an experiment, samples were then slowly cooled to the lower temperature limit of the particular smectic phase. Samples handled in this manner were homeotropically aligned (*i.e.* glassy) and were much more suitable for transient absorption measurements than samples which were allowed to anneal at room temperature, or cooled rapidly from the nematic phase. The latter two methods gave samples that were turbid or opaque,

making light transmission through the sample difficult. In some cases, samples left at room temperature for long periods of time crystallised (*vide infra*).

All solute/solvent mixtures yielded intense transient absorptions, with a λ_{max} of approximately 385 nm, upon laser excitation. The transient absorption spectrum recorded for the 0.25 mol % mixture of **1** in the smectic phase of CCH-4 at 30°C, is shown in Figure 3.7, and is typical of what was observed for mixtures of **1** in all mesogens. The spectra agree well with those previously reported for **1** in typical isotropic solvents[74,76] and are assignable to the triplet state of **1**.[13,135] A typical NLFP experiment involves monitoring the change in optical density of the transient absorption, at a particular wavelength, as a function of time. In these particular studies, this involved monitoring the decay of the triplet-triplet absorption spectrum of **1** at $\lambda = 385$ nm, and averaging the data obtained from a number of individual experiments. Computer analysis of the averaged data yields the rate constant for decay (k_{decay}), which can be used to calculate the triplet lifetime, τ_T, of **1**. This experiment was then performed at various temperatures throughout the liquid crystalline and isotropic phases of each mesogen (more details are given below). Experiments were also carried out in nitrogen purged 1×10^{-3}M solutions of **1** in a number of typical isotropic solvents.

3.3.2 Photochemistry of 1 in the Liquid Crystalline Phases of CCH-n Mesogens.

NLFP experiments were performed on 0.25 mol % mixtures of **1** in the smectic and nematic phases of CCH-4. Experiments were also carried out with 1.0 mol % mixtures of **1** with CCH-2, CCH-3 and EB, which served as model nematic and isotropic
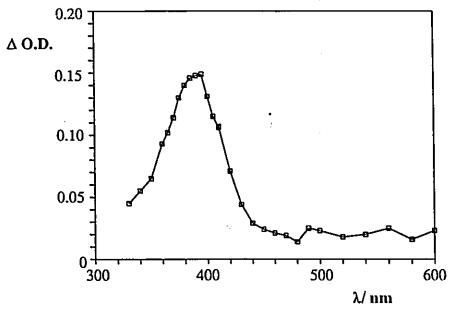
Table 3.2. Summary of the solubility limits determined for **1** in the smectic phases of CCH-4, CCH-2, OS-35, OS-53, CCH-303 and CCH-502.[a]

Solvent	Solubility Limit[b] (mol %)
CCH-4	0.2- 0.25
CCH-2	$\ll 0.1$
OS-35	≈ 0.1
OS-53	≈ 0.1
CCH-303	< 0.1
CCH-502	0.5

a. Determined from ^{2}H NMR studies on $1\text{-}\alpha d_2$, $1\text{-}Od_3$, and $1\text{-}\beta d_5$ as mixtures in each of the various mesogens.

b. Solubility limits for this table are defined as the composition at which the sample remains homogeneous throughout the majority of the smectic phase, and are approximate.

Figure 3.7. Triplet-triplet transient absorption spectrum of a 0.25 mol % mixture of **1** in CCH-4, recorded in the smectic phase at 32°C. The spectrum was recorded between 40-120 ns after 308 nm excitation.
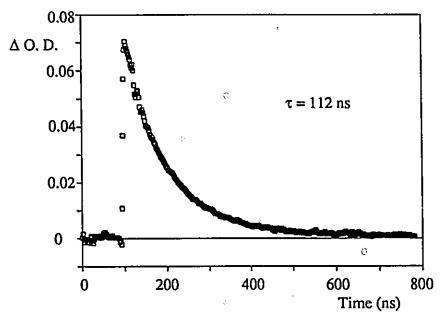

Figure 3.8. Representative decay trace from NLFP of a degassed 1.0 mol % sample of **1** in EB at 30°C.

phases. The 1 mol % mixtures were prepared in a similar fashion to the lower concentration samples, except they were sealed in 0.7 X 7 mm^2 Pyrex cells.
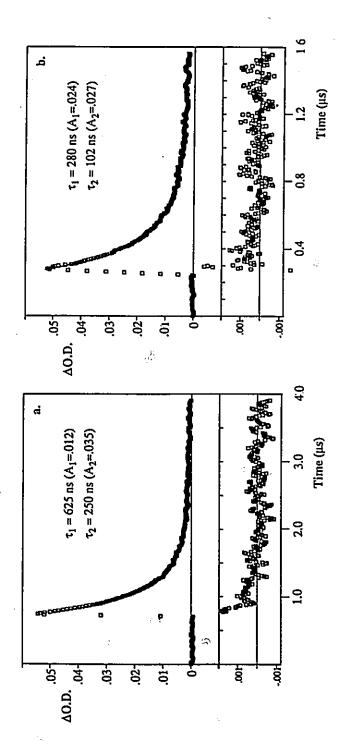
The triplet state of 1 in the nematic and isotropic phases of CCH-2, CCH-3, CCH-4, and EB decayed with clean first order kinetics in every case. Figure 3.8 shows a representative decay trace obtained from a 1 mol % sample of 1 in EB. In some cases, the traces had a slight bit of residual absorption, but it never accounted for more than 5 % of the maximum transient optical density and was generally not reproducible. In all cases with the CCH-n mesogens (and in fact with all liquid crystals utilised in this study) the triplet lifetime and transient optical density of 1 did not change significantly, even after several thousand laser pulses, indicating the photoinertness of this probe.

In the case of the 0.25 mol % 1/CCH-4 sample, the triplet decayed with what appeared to be multi-exponential kinetics at all temperatures throughout the smectic phase region. Representative decay traces for this sample at 30.4°C and 45.8°C are shown in Figure 3.9. The data was fit to two-exponential decays using a curve-fitting procedure. A plot of the residuals obtained from such an analysis is included with the two decay traces in Figure 3.9. The lifetimes obtained, and the relative contribution of each component to the overall optical density of the transient, from the biexponential analyses, are listed in the right hand corner of each trace in the same Figure. Control experiments, in which the laser power was adjusted, were performed to rule out the possibility that there were contributions to the decays in the smectic phase due to bimolecular triplet processes.[136] The fit to two exponentials did not improve at lower laser power and therefore bimolecular triplet processes were not responsible for the observed kinetics. Examination of the residuals obtained from the two-component analyses indicate that the fit of the data to two exponentials improves as the temperature is increased in the smectic phase region.

Upon heating the samples into the nematic phase the decays become clean first order. It was also observed that the fit to two-exponentials is poor for the data points at the beginning of each trace measured in the smectic phase. This may be due to a contribution from a short lived component not accounted for in the analysis, and/or due to an over correction for background fluorescence that occurs with the liquid crystalline samples under our conditions. Curve-fitting to a larger number of exponentials was not attempted since the quality of data available from NLFP experiments does not allow for an accurate fit of the data to a multi-exponential. Due to this complication, and the overall quality of the data we can obtain, the relative contributions of each of the components obtained in the biexponential analysis vary erratically throughout the smectic phase. For this reason the data was fit, using a least squares routine, to a single exponential decay to extract average triplet lifetimes for 1 in the smectic phase of CCH-4. These analyses used a minimum of 100 data points and gave linear correlation coefficients of 0.99 or better in every case. The triplet lifetimes obtained using this method agreed, within experimental error, to the average lifetime calculated from the two components obtained in the two-exponential analyses.

From the temperature dependence of the average triplet lifetimes Arrhenius plots (of the log of the rate constant for triplet decay (log k_{decay} or -log τ_T) *versus* inverse temperature (1/T)) were constructed. The Arrhenius plot for the 0.25 mol % 1/CCH-4 mixture is shown in Figure 3.10. The (upper) nematic and isotropic phase portion of this figure was supplemented with data from a 1 mol % sample of 1 in CCH-4. The turbidity of unoriented nematic phases led to low light transmission through the longer path length of the lower concentration sample, which resulted in poor quality decays compared to those from the 1 mol % samples. Data from the 1 mol % sample were superimposable on
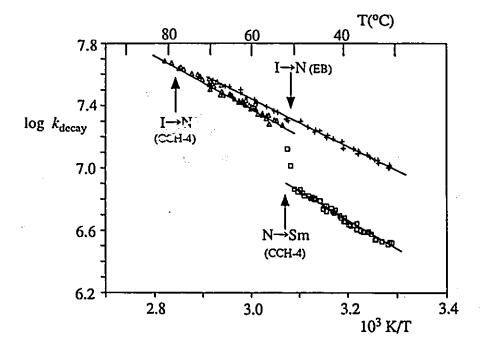
Figure 3.9. Representative decay traces from nanosecond laser flash photolysis of a degassed 0.25 mol % solution of **1** in CCH-4 at (a) 30.4°C and (b) 45.8°C. A plot of the residuals from two-exponential curve-fitting of the data is included for each trace, as are the values obtained from those analyses.

data from the 0.25 mol % sample above 50°C. Also included in this plot are the data

obtained from the 1 mol % sample of 1 in EB, which is nematic between 25-54°C and

isotropic above 54°C. This solvent mixture allows for a direct comparison of the triplet

lifetime of 1 in the smectic phase of CCH-4 to that in a nematic phase of similar polarity

at any temperature. Arrhenius plots were also constructed from data obtained from 1 mol

% mixtures of 1 in CCH-2 and CCH-3. These plots are similar to those observed for 1 in

EB and exhibit no discontinuity at the N→I transition temperatures.

Each Arrhenius plot consists of data obtained from both heating and cooling

the samples from either end of the temperature range of the particular phase. Lifetimes

determined at a particular temperature are independent of whether that temperature was

approached from a higher or a lower value. One exception is found for data in the

Arrhenius plot for 1 in the smectic phase of CCH-4. On heating the sample from 30°C,

data consistent with 1 in a homogeneous smectic phase solution is obtained up to 49°C,

before evidence for a phase transition is observed. Deuterium NMR results, on the other

hand, determined by cooling the sample from the nematic, show the sample to be biphasic

(N + Sm) to as low as 46°C. Slight variations in temperature for a phase transition

between heating or cooling a sample are not unusual and may account for this

discrepancy.[29] Another explanation may be that at 0.25 mol% the portion of ketone

residing in the nematic phase environment between 46-49°C is too low to significantly

contribute to the observed decay trace.

Activation parameters[137,138] (E_a and log A) for triplet decay, in the nematic

and smectic phases of CCH-4, and the nematic and isotropic phases of EB, CCH-3, and

CCH-2, were calculated from least-squares analysis of the rate constants for decay

according to the Arrhenius equation, and are summarised in Table 3.3. Entropies of

Figure 3.10. Arrhenius plots for the triplet decay of **1** in CCH-n liquid crystals. The arrows point to the phase transition temperatures of the pure mesogens. Key: □, 0.25 mol % **1** in CCH-4, smectic phase; Δ, 1.0 mol % **1** in CCH-4, nematic and isotropic phases; +, 1.0 mol % **1** in EB, nematic and isotropic phases.

activation, $\Delta S^{\ddagger}$, obtained from the intercept of Eyring plots[137,138] of the same data, are

also included in Table 3.3. In addition, Table 3.3 includes triplet lifetimes for 1 at 30°C in

each of the phase types; in some cases (where noted) these were estimated by

extrapolation of the Arrhenius plots of higher temperature data.

Samples of 0.25 mol % 1 in CCH-4 which were allowed to sit at room

temperature became opaque and were unsuitable for laser flash experiments. However, a

sample left at room temperature for several weeks became fairly transparent and permitted

flash experiments to be performed. Data obtained at 23°C, by monitoring the decay of the

transient absorption at 385 nm, exhibited mixed kinetics and consisted mainly of a long

lived component with a lifetime of approximately 8-9 μs (see Figure 3.11). The transient

absorption spectrum confirmed that the decay is that of the triplet state of 1. The triplet

lifetime shortened slightly as the temperature was raised until *ca.* 29-30°C, where the

lifetime dropped dramatically to a value which was within experimental error of those

measured at the same temperature for a sample originally annealed at 38°C. The large

change in the rate constant for decay at 30°C occurs at a temperature which corresponds to

the K→Sm transition temperature of CCH-4. In this case, the quality of traces recorded

above 30°C was poor due to sample opaqueness.

Laser flash photolysis experiments were also carried out for 0.1 and 0.01 mol

% samples of 1 in purified CCH-2. Owing to the low concentration of solute in the

samples, 308 nm pulses from the excimer laser were utilised. Decay traces from the 0.1

mol % sample were analysed using first order decay kinetics and were found to be phase

independent, with lifetimes identical to those measured for the 1.0 mol % sample of 1 in

CCH-2. Deuterium NMR experiments suggest that the solubility limit of 1 in CCH-2 is

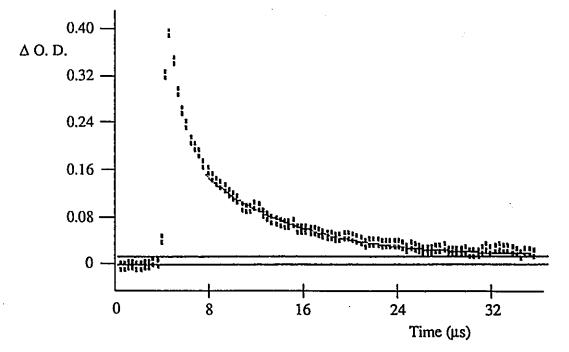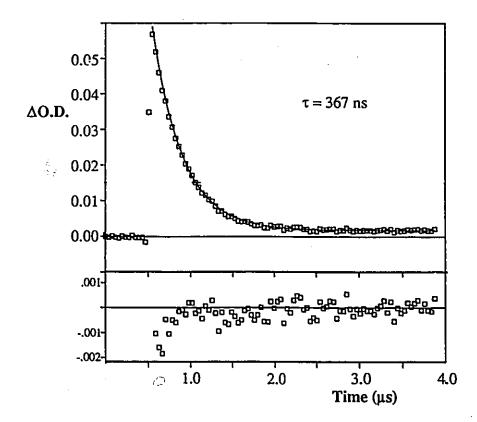much less than 0.1 mol %, although the exact solubility limit could not be determined

Figure 3.11. Representative decay trace from NLFP of a degassed
0.25 mol % sample of **1** in the crystalline phase of CCH-4.
Sample was annealed at room temperature.

(*vide supra*). In an attempt to determine whether the smectic phase of CCH-2 has a similar effect on the lifetime of 1 as the smectic phase of CCH-4 does, experiments were performed with a 0.01 mol % sample. This concentration of 1 in CCH-2 represented the lowest value that could conveniently be used for NLFP experiments under our conditions. The extremely low optical density of this sample at the excitation wavelength results in weak transients, giving rather poor quality traces which were further complicated by light scattering effects. The decay traces obtained appeared to consist of at least two components, with the long lived component analysing for a lifetime of more than 1 μs. However, errors associated with the analyses (in some cases as large as 60 %) did not allow for the accomplishment of an accurate Arrhenius study.

3.3.3   Photochemistry of 1 in the Liquid Crystalline Phases of OS-nm Mesogens

Laser flash photolysis experiments were also carried out using 0.1 mol % mixtures of 1 in OS-53 and OS-35. Due to the low bulk sample concentrations, the 308 nm laser was again used in order to obtain transients of reasonable intensity. Samples of 1 in the OS-nm mesogens were found to be better suited for laser flash experiments than those in the CCH-n mesogens, since they readily formed homeotropically aligned smectic phases that allow for better light transmission and fewer difficulties from light scattering. In addition, samples could be supercooled well below the Sm→K transition of the pure mesogen without crystallisation of the sample, allowing for a larger effective smectic phase temperature region over which to observe the photochemistry.

Figure 3.12. Representative decay trace from NLFP of a degassed 0.1 mol % solution of **1** in OS-53 at 9.5°C. A plot of the residuals from single exponetial least squares analysis of the data is included.

Triplet decays for solutions of **1** in the smectic <u>and</u> nematic phases of OS-35 and OS-53 were found to follow clean first order kinetics with only a slight amount of residual absorption in some cases. A representative decay trace is shown in Figure 3.12, which also includes a plot of the residuals from a single exponential least squares analysis of the data. The analyses of the data to a single exponential decay led to correlation coefficients of 0.99 or better in every case. As was observed for the traces from **1** in the smectic phase of CCH-4, the fit to the analysis is poorer at the beginning of the decay. In the case of OS-nm liquid crystals, this slight deviation could almost certainly be ascribed to insufficient correction for fluorescence in the raw data, giving poor quality, early data points. The analyses of the data to first order kinetics give the same results within experimental error, whether or not these early data points are included.

Figures 3.13a and b show Arrhenius plots of data obtained from a complete temperature study of the kinetics of **1** in OS-53 and OS-35, respectively. Once again the upper, nematic/isotropic portion of each plot includes data from a higher concentration sample (0.58 mol %) of **1**. The data obtained with the 0.58 mol % samples are indistinguishable from data obtained from lower concentration samples in this region. Gaps in the Arrhenius plots at the Sm→N transitions are due to our inability to obtain data in these regions, because the 0.1 mol % samples turn opaque during the phase transition (where the sample is biphasic), impeding light transmission through the sample. Standard least squares analysis of the data according to the Arrhenius and Eyring equations yield activation parameters for the triplet decay of **1** in each phase of the two mesogens. These are summarised in Table 3.3. The triplet lifetimes determined for **1** at 30°C are also included. A model solvent which exhibits nematic or isotropic phases between 23-50°C was not available; therefore, values for lifetimes in the more mobile phases at 30°C were

extrapolated from the Arrhenius plot for the higher temperature nematic phase data.

Laser flash photolysis experiments were also conducted with the 0.58 mol % samples in the smectic phase temperature region of each mesogen. The ^{2}H NMR studies of samples of this composition suggest that 1 is *heterogeneously* solubilised throughout the bulk smectic phases in these cases (*vide supra*). The Arrhenius behaviour of these mixtures is similar to that observed for the 1 mol % mixture of 1 in CCH-4 in its smectic phase temperature region (see Figure 1.7).[85] 3.14 shows the Arrhenius plot obtained from triplet lifetime data for the 0.58 mol % mixture of 1 in OS-53; that obtained in OS-35 is similar to that of the OS-53 plot and is not shown. The apparent activation parameters calculated from the decay in the smectic phase temperature region for the higher concentration samples are given in Table 3.4.

3.3.4   Photochemistry of 1 in the Liquid Crystalline Phases of CCH-nOm Mesogens

Triplet lifetimes of 1 as 0.5 mol % mixtures in CCH-502 and CCH-301 (Sm-15-I) were measured by NLFP (337 nm) as a function of temperature. The triplet-triplet absorption spectra of 1 in these mesogens are similar to that shown in Figure 3.7, having a λ_{max} at 385 nm. Decay traces in CCH-502 and CCH-301 followed clean first order kinetics in all cases (least squares fitting to a single exponential gave correlation coefficients of 0.99 or better), with only a slight amount (< 5% of the maximum transient absorption) of residual absorption observed in some cases.

Arrhenius plots constructed from the data for 0.5 mol % solutions of 1 in CCH-502 and CCH-301 are shown in Figure 3.15. Data in the nematic and isotropic
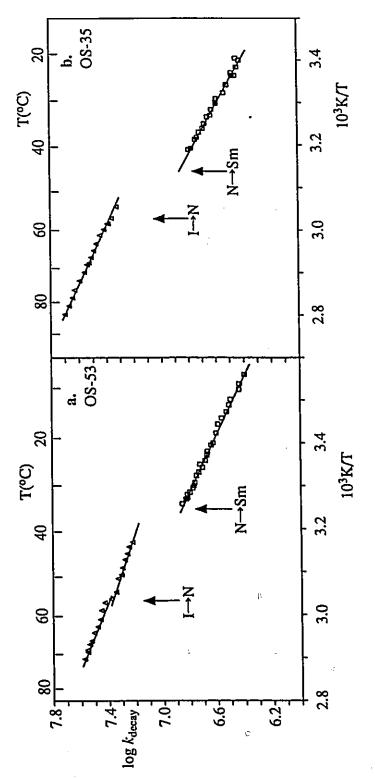
Figure 3.13. Arrhenius plots for the triplet decay of 1 in (a) OS-53 and (b) OS-35 liquid crystals. Key: □, 0.1 mol % sample, smectic phase data; △, 0.1 mol % and 0.58 mol % samples, nematic and isotropic phase data.
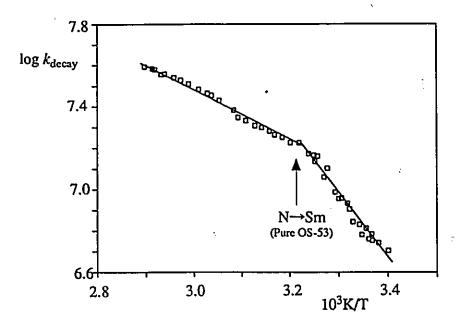
Figure 3.14. Arrhenius plot for the triplet decay of **1** as a 0.58 mol %
solution in OS-53. Below the N→Sm transition temperature the sample has
been shown by ^{2}H NMR to be biphasic in nature (see text).

Table 3.4. Activation parameters for the triplet decay of **1** as 0.58 mol %
mixtures in the smectic phase temperature regions of OS-53 and OS-35 and
as a 1 mol% mixture in the smectic phase temperature region of CCH-4.[a,b]

Solvent	E_a (kcal mol^{-1})	log A (s^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
OS-53	14.6 ± 1.1	17.6 ± 0.8	19.8 ± 1.1
OS-35	16.4 ± 1.7	18.5 ± 1.2	23.9 ± 1.8
CCH-4	16.7 ± 1.3	18.5 ± 1.1	24 ± 4

a. Concentration of the samples were 0.58 mol % **1** in each of the mesogens. Samples
   were determined to be biphasic throughout the temperature range used in the calculations
   by ^{2}H NMR spectroscopy (see text). Errors are quoted as ±2σ.

b. Data for **1** in CCH-4 is taken from reference 85; the Arrhenius behaviour was confirmed in this study.

phases of CCH-502 include points obtained using a 1 mol % sample. Arrhenius and Eyring activation parameters for the triplet decay of **1** in the smectic and nematic phases of CCH-502 and in CCH-301 (isotropic) are summarised, along with the triplet lifetimes measured at 30°C, in Table 3.3.

Similar experiments were also performed with a 0.1 mol % mixture of **1** in CCH-303, using 308 nm pulses. Smectic phase samples of this concentration have been shown by ^{2}H NMR to be homogeneous at the temperatures below 49°C (*vide supra*). Decay traces obtained were mono-exponential in the isotropic phase, but appeared to be multi-exponential in the smectic phase region. The quality of the traces for the smectic phase was rather poor due to the low concentration of solute and to light scattering from the sample. Lifetimes of **1** in the smectic phase of CCH-303 were found to be greater than two times those measured for **1** in CCH-301 at the same temperature.
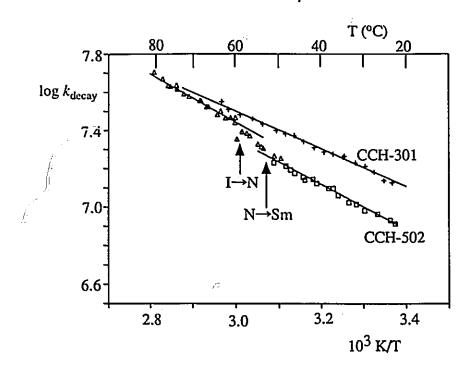
Figure 3.15. Arrhenius plots for triplet decay of 1 in CCH-nOm liquid crystals. Key: □, 0.5 mol % in CCH-502, smectic phase; Δ, 0.5 mol % in CCH-502, nematic and isotropic phases; +, 0.5 mol % in CCH-301, model isotropic phase.

Table 3.3. Activation parameters and triplet lifetimes for homogeneous solutions of **1** in liquid crystalline and isotropic solvents. [a]

Solvent	Phase[b]	E_a (kcal/mol)	$\log A$ (s^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})	$\tau_{30^{\circ}C}$ (ns)
CCH-4	Sm[c]	8.8 ± 0.4	12.8 ± 0.2	-2.1 ± 0.1	346
	N[d]	8.0 ± 0.4	12.6 ± 0.3	-3.0 ± 0.1	150
EB	N/I[d]	7.0 ± 0.1	12.0 ± 0.1	-5.8 ± 0.1	112
CCH-2	I[d]	6.0 ± 0.1	11.4 ± 0.1	-8.6 ± 0.1	78[i]
CCH-3	N/I[d]	6.8 ± 0.3	11.9 ± 0.1	-6.2 ± 0.2	105[i]
OS-53	Sm[e]	6.7 ± 0.2	11.6 ± 0.1	-7.4 ± 0.1	165
	N/I[f]	5.8 ± 0.3	11.3 ± 0.2	-9.2 ± 0.2	73[i]
OS-35	Sm[e]	7.9 ± 0.4	12.3 ± 0.3	-4.3 ± 0.3	259
	N/I[f]	6.8 ± 0.2	11.9 ± 0.2	-6.6 ± 0.1	96[i]
CCH-502	Sm[g]	5.3 ± 0.3	10.8 ± 0.2	-11.6 ± 0.3	104
	N/I[g]	6.0 ± 0.4	11.4 ± 0.2	-8.8 ± 0.3	90[i]
CCH-301	I[g]	4.5 ± 0.2	10.5 ± 0.1	-12.7 ± 0.2	61
CH$_3$CN	I[h]	4.7 ± 0.1	10.8 ± 0.1	-11.5 ± 0.1	40

a. Errors in Arrhenius parameters are quoted as $\pm 2\sigma$. Errors in lifetimes are ca. 10%.
b. Key : Sm= smectic; N = nematic; I = isotropic.
c. Sample composition = 0.25 mol%. d. Sample composition = 1.0 mol %. e. Sample composition = 0.1 mol %.
f. Sample composition = 0.58 mol %. g. Sample composition = 0.5 mol %. h. Sample composition = 0.001M.
i. Extrapolated from Arrhenius Plot.

3.4   Discussion

3.4.1   Effect of Nematic Phase Ordering on

Triplet Decay of 1

The rate of intramolecular triplet decay of 1 through β-phenyl quenching

(Equation 3.1) is slower in the various nematic and mesogenic isotropic phases than in

typical isotropic solvents. The lifetime of 1 does not vary significantly as a function of

[Eq. 3.1]

solvent polarity (see Table 3.5) except in protic solvents. These can hydrogen bond to the

carbonyl group, and the lifetime increases significantly. In the case of methanol and

tert-butyl alcohol, hydrogen bonding restricts access of the β-phenyl ring to the carbonyl

resulting in a slower rate of deactivation. A similar rationale has been advanced to explain

the higher F/C product ratios and increased quantum yield of the Norrish II reaction of

alkanophenones in hydroxylic solvents (see Chapter 2).[55,56,63] There is a slight

lengthening of the lifetime of 1 in ethereal solvents (tetrahydrofuran (THF) and diethyl

ether), although the change is not as large as in the hydroxylic solvents. The lifetime of 1

in the nematic and isotropic phases of the mesogens is at least two times longer (except in

CCH-301) than is observed in non-viscous aprotic solvents. Presumably this is due to

microviscosity effects. The fact that solvent viscosity plays a role in determining the

Table 3.5. Triplet lifetime of **1** in typical isotropic solvents, measured at room temperature.[a]

Solvent	lifetime $(\tau_{23\,^{\circ}C})$[b] (ns)
acetonitrile	56
cyclohexane	52
ethyl acetate	54
diethyl ether	63
tetrahydrofuran	70
methanol	245
t-butyl alcohol[c]	373

a. All decay traces monitored at 385 nm following 337 nm excitation of nitrogen purged solutions.

b. Errors in lifetimes are typically 5-10%

c. Measured at 26°C.

lifetime of the triplet verifies that conformational dynamics are an important factor contributing to triplet state deactivation in **1**.

For a given mesogenic solvent (with the exception of OS-53 and perhaps CCH-502) there is no discernible discontinuity in the Arrhenius line at the N→I phase transition temperatures. From this we conclude that the nematic phase solvent order does not impart any detectable orientational effects on intramolecular quenching in **1** in these mesogens. This is in spite of the fact that the ^2H NMR spectra of the deuterated analogs of **1** in the nematic phase of each mesogen, show that the motions of **1** are anisotropic. The discontinuity observed in the Arrhenius plot for **1** in OS-53 is the first such example

of a nematic phase having any observable effects on the conformational motions of this probe. However, the effect is quite small and may be an artifact of the data analysis. The apparent discontinuity observed for the Arrhenius plot of 1 in CCH-502 is due to the poor quality of data obtainable in the narrow nematic phase temperature range of this mesogen. The lack of an effect in the nematic phase compared to the isotropic phase is a general observation for all liquid crystalline solvents in this series, and is a similar result to what was observed in the Norrish II reactivity in the nematic phases of CCH-n liquid crystals (see Chapter 2).[105]

Differences in triplet lifetime and activation parameters in the nematic and isotropic phases, throughout the series of mesogens, may be accounted for by differences in solvent viscosity, since viscosity is expected to vary to some extent by mesogen type. In the isotropic phase of CCH-301, which has no orientational ordering ability, the lifetime of 1 increases by *ca.* 20 ns compared to the majority of aprotic solvents; however, it is essentially the same as that measured in THF. Since the polarity of CCH-301 is expected to be intermediate between that of cyclohexane and THF, it is likely that this is due to a combination of solvent polarity and microviscosity effects. In the nematic and isotropic phases of the other solvents, 1 exhibits longer triplet lifetimes and higher activation parameters than in acetonitrile or cyclohexane. This is presumably due entirely to viscosity effects. Contributions from adventitious quenching impurities cannot be completely ruled out for minor variations in activation parameters and measured lifetimes between mesogenic solvents of similar structure (e.g. EB, CCH-2, CCH-3, CCH-4). However, similar Arrhenius behaviour was also observed in scrupulously purified mesogens, indicating that the major difference is indeed due to variations in microviscosity.

3.4.2   Effect of Smectic Phase Ordering on the Photochemistry of 1

The Arrhenius plots obtained from the homogeneous smectic phase solutions of 1 in the liquid crystalline phases of CCH-4, OS-53, and OS-35 show that the rate constant for triplet decay is significantly smaller in smectic relative to nematic or isotropic phases. While the effect in CCH-502 is not as dramatic, the relative form of the Arrhenius plot is similar to those of the other mesogens. The precipitous lifetime enhancement which accompanies formation of the smectic phase of each mesogen is believed to reflect sudden changes in the motional restrictions placed upon the solute, by the more highly ordered environment. This impedes the triplet state from achieving the conformation required for intramolecular quenching. For a single liquid crystal, the effect is *not* due to a sudden change in the local polarity experienced by the chromophore, brought about by a specific solubilisation site in the matrix of the smectic phase. Such changes in polarity would be observable as a shift in the static UV absorption spectra of samples of 1 in the various phase types. *No* measurable change in UV absorption accompanies the Sm→N phase transition in any case. In addition, solvent polarity has been shown to have little effect on the triplet lifetime of 1 except in hydrogen bonding solvents (see Table 3.5).

The lifetime of 1 in the smectic phase of CCH-4 can be compared to the lifetime in the crystalline phase of the same mesogen. The lifetime observed in the latter phase is approximately 10-20 times longer than the lifetime at the low temperature end of the smectic phase. The lifetime of 1 in the crystalline phase is more in line with what would be expected for complete immobilisation of the probe (*i.e.* β-phenyl quenching

completely inhibited). This can be demonstrated by comparing the triplet lifetime of **1** under these conditions ($\tau = 8$ μs) to that of 4-methoxypropiophenone ($\tau_T = 3.5$ μs in isotropic solution) in which β-phenyl quenching is not possible. Therefore, in the smectic phase of CCH-4 (and those of the various other mesogens) the solute must still be undergoing molecular motions which lead to β-phenyl quenching.

Concentration Dependence of Arrhenius Parameters
For Triplet Decay of 1

The Arrhenius behaviour observed for the 0.25 mol % solution of **1** in CCH-4 (Figure 3.10) represents the "true" effects that the smectic phase of this liquid crystal has on the conformational mobility of this probe molecule, and contrasts sharply with the results obtained previously for **1** using a 1 mol % sample (Figure 1.7).[85] These results confirm our earlier suggestion, based on ^{2}H NMR evidence (see Part A), that the latter reflect the _heterogeneous_ nature of the 1 mol % sample. In this mixture, the ketone is solubilised in _both_ the smectic phase and in a more mobile nematic or isotropic phase throughout the entire smectic phase temperature region (see NMR discussion and Figure 3.1). The triplet lifetimes reported in the earlier study were therefore weighted averages of the ketone distributed between the two coexisting phase environments. This distribution varies with temperature, as the solubility limit of **1** in the smectic phase changes. This is reflected in the triplet lifetimes, which span from the nematic phase line at the high temperature extreme (where the ketone is largely in a nematic environment), to the true smectic phase line at the low temperature extreme (where the majority of the ketone is solubilised in the smectic phase). The results obtained with the higher concentration (0.58

mol %) samples of 1 in the OS-nm mesogens (see Figure 3.14 and Table 3.4) show that distortions of this type are general. In retrospect, the large change in slope of the Arrhenius plot, yet small change in rate constant for decay, that accompanies the N→Sm phase transition in the higher concentration samples should have aroused more suspicion in the original study, considering the higher degree of order and rigidity that is associated with this change of phase.

In the original study, [85] the triplet decay of a 1 mol % sample of 1 in CCH-2 was reported to be phase *independent*, with no discontinuity in the Arrhenius line at the N→Sm phase transition (see Figure 1.7). At the time, it was proposed that this indicates that the smectic phase of this mesogen imparts very little restraint on the conformational mobility of 1. In fact, the present NMR studies have shown that the solubility limit is well below 0.1 mol % throughout the entire smectic phase temperature region. The coincidence of the Arrhenius lifetime data for the 0.1 mol % sample with those for the 1 mol % sample shows that in both mixtures, the bulk of the solute is solubilised in a highly concentrated phase-separated isotropic phase which coexists with the smectic phase of composition > 99.9 mol % CCH-2. The mobility of 1 in the isotropic liquid phase must be similar to that experienced in the nematic and *bulk* isotropic phase (at lower concentrations) to account for the phase-independent triplet state behaviour. The qualitative indication that the 0.01 mol % sample exhibits much longer lifetimes ($\tau_T \approx 1$ μs) in the smectic phase temperature region compared to the 0.1 mol % sample suggests that the smectic phase of CCH-2 does indeed restrict the mobility of the probe solute in a manner similar to the other highly ordered smectic phases. The absence of a discontinuity at the Sm→N transition for the 0.1 mol % (or higher) samples is due to the fact that the amount of solute solubilised in the more ordered phase of CCH-2 is too low for the

smectic phase component to contribute significantly to the observed decays. The lifetime for **1** in smectic CCH-2 is intermediate between the lifetimes obtained in the Cr_B and crystalline phases of CCH-4. This is consistent with the proposal that CCH-2 forms a more highly ordered smectic phase than CCH-4.[29] ·

3.4.3 Comparisons of the Triplet Decay of 1 in the Various Smectic Phases

The similarities in the appearance of the Arrhenius plots for homogeneous solutions of **1** in the various solvents, shown in Figures 3.10, 3.139, and 3.15, indicate that the effect of the smectic phase on triplet decay rate is quite general. While each plot exhibits a change in the rate of triplet decay at the N→Sm transition, the magnitude of this change varies quite dramatically from mesogen to mesogen, as exemplified by the triplet lifetime data summarised in Table 3.6. Since diffusion through the smectic phases is much slower than the measured rates of triplet decay,[7,13,139] it is unlikely that bimolecular quenching of the triplets by impurities contributes to the variations in lifetimes between smectic phases. The difference in the rate constant for decay in the smectic phase compared to the corresponding nematic/isotropic phase ranges from a factor of 1.7 in CCH-502 to *ca.* 2.5-4 in CCH-4 and OS-nm mesogens. These values reflect the differences between the conformational dynamics of the probe in the smectic and isotropic/nematic media. At a given temperature however, direct comparisons of the lifetimes of **1** in the various smectic phases is not an accurate reflection of the relative amount of order present in each mesogen. This is related to the fact that each solvent exhibits its mesophases over different temperature ranges. A plot of log k_{decay} *versus*

reduced temperature ($T_{Sm \rightarrow N}$ - T) can be constructed to alleviate this complication. The reduced temperature parameter measures the difference between the actual sample temperature and the Sm→N phase transition temperature for each liquid crystal. Any bias in the lifetimes that arise due to differences in the smectic phase temperature regions are removed by effectively placing them all on the same temperature scale. Therefore, the plot describes the temperature dependence of liquid crystalline order. Figure 3.16 shows a plot of log k_{decay} *versus* reduced temperature, combining the data obtained for **1** in smectic CCH-4, OS-53, OS-35, and CCH-502. The $T_{Sm \rightarrow N}$ values used in the calculation of reduced temperature were defined as 1°C below the midpoint of the Sm→N transition range for the mixtures, as determined from the ^{2}H NMR studies. The lifetime of **1** in each of the smectic phases at a reduced temperature of 10°C (an arbitrary value) are tabulated in Table 3.6.

By comparing data from the reduced temperature plots and the corresponding lifetimes (τ_{RT}) more meaningful comparisons of the effect that smectic phases have on the rate of triplet deactivation of **1** can be made. For example, while the lifetime data of **1** in the smectic phases of the two OS-nm liquid crystals varied by approximately 100 ns at any given temperature, the two sets of reduced temperature data are virtually identical and fall on the same line. The coincidence of this data indicates that the factors that are responsible for determining the rate of triplet decay in these smectic phases - solvent order and local solvent polarity- are the same for these two mesogens. The line defined by the data from the smectic phase of CCH-4 is displaced by *ca.* 45 ns from those defined for OS-53 and OS-35. The apparent difference between the OS-nm mesogens and CCH-4 may be due to the solute experiencing a greater degree of <u>order</u> or greater <u>local solvent polarity</u>, or both, in the smectic phase of CCH-4. The fact that the nematic and isotropic

Table 3.6. Triplet lifetimes of **1** (a) measured in the various smectic
phases at 30°C and (b) determined from the reduced temperature
plot of log k_{decay} vs. reduced temperature.[a]

Smectic Phase	$\tau_{30°C}$ (ns)[b]	$\tau_{RT=10°C}$ (ns)[c]
CCH-4	346	234
OS-53	165	187
OS-35	259	187
CCH-502	104	79

a. Average triplet lifetimes. Errors are roughly 5-10%.

b. Triplet lifetime of 1 taken from Table 3.3

c. Triplet lifetime of 1 at a reduced temperature (RT) of 10°C.

data in 1/CCH-4 mixtures are also displaced similarly from 1/OS-nm mixtures suggests
that the difference in the two classes of smectic phases may be due primarily to solvent
polarity differences.

The phase dependence of the Arrhenius behaviour for **1** in CCH-502 is
markedly less dramatic than that observed with the other mesogens. The raw data clearly
indicate that the rate of triplet decay is slowed in the smectic phase of CCH-502 compared
to the nematic and model isotropic (CCH-301) phases. However, the lifetime of **1** at any
point along the reduced temperature line for CCH-502 is a factor of 2-3 shorter than in
CCH-4 or OS-nm liquid crystals. This deviation is too large to be attributed solely to
solvent polarity effects. We believe that it is a reflection of the lower degree of order
associated with the smectic phase of this mesogen compared to those of CCH-4 and the
OS-nm liquid crystals. The ^{2}H NMR features of **1** in the smectic phase of CCH-502 are
also consistent with the conclusion that the probe is subject to a lesser degree of order in

Figure 3.16. Plot of log k_{decay} *versus* reduced temperature ($T_{Sm \to N}$ - T) for the triplet decay of 1 in the smectic phases of CCH-4, OS-nm and CCH-502 liquid crystals. Key: □, 0.25 mol % 1 in CCH-4; Δ, 0.1 mol % 1 in OS-53; +, 0.1 mol % 1 in OS-35; +, 0.5 mol % 1 in CCH-502. $T_{Sm \to N}$ is taken to be 48.5°C for CCH-4, 36°C for OS-53, 48°C for OS-35, and 49°C for CCH-502 (see text for details).

this smectic phase compared to the others (*vide supra*). It seems apparent that the Sm_B phase of CCH-502 cannot restrict the conformational motions that are involved in the quenching process of this probe to as great an extent as the more highly ordered Cr_B phases of CCH-4 and OS-nm. Compound 1 must be more rigidly held in the matrix of the latter two compounds.

The near coincidence of the reduced temperature plots for CCH-4 and the OS-nm mesogens seem to indicate that 1 is solubilised similarly in the Cr_B phases of the three mesogens, resulting in comparable effects on the quenching dynamics of this solute. The effect of the smectic phase of CCH-303 on the triplet lifetime of the solute is closer to that observed for CCH-4 and OS-nm. Overall, the observed photochemistry in each of the CCH-nOm mesogens corroborate the indication from the solubility limits and the features of the ^2H NMR quadrupolar doublets (*vide supra*) that CCH-303 forms a more highly ordered smectic phase than CCH-502. The higher solubility limit for 1 in the smectic phase of CCH-502 is congruent with the lower amount of order associated with the phase morphology and the resulting effect on the photochemistry of 1 in this phase. This does not hold true for CCH-4 and the OS-nm mesogens. The magnitude of the effect on the photochemistry of 1 appears greatest in CCH-4, even though the solubility limit is approximately twice that in OS-nm liquid crystals. It appears that the factors which determine the ability of a mesogen to solubilise a solute are not only a function of phase morphology, but also the chemical structure of the solvent and its' relationship to how the solute is incorporated into the matrix.

The triplet decay traces of 1 in the smectic (Cr_B) phases of CCH-4 do not follow clean first order decay kinetics but follow multi-exponential (or at the very least biexponential) kinetics. This may indicate that the ketone is solubilised in this mesogen in

a *distribution of conformations* within the liquid crystalline lattice or in a *distribution of sites*, each with slightly different effects on the conformational mobility of the solute. As the temperature is raised in the smectic phase, the fit to biexponential kinetics improves, suggesting that the distribution of lifetimes in the highly ordered phase becomes narrower as the phase transition is approached. This is the expected result as thermal motions of the solute and solvent molecules increase with temperature. For the Arrhenius plot of 1 in CCH-4, decay traces were fit to mono-exponential decay kinetics. Since the data could be fairly well modeled using this simple first order treatment, the distribution of lifetimes spans only a factor of two or three. Simple computer simulation shows that the sum of two independent first order decays, obtained from transient absorption data, are indistinguishable from a single decay for differences up to a factor of approximately four in the triplet decay rates of the components. This is nicely illustrated for the cases of first order triplet decays obtained from higher concentration samples of 1 in the smectic phases of CCH-4 and OS-nm liquid crystals. In these samples the decays might be expected to be biexponential because they are the sum of two first order decays: that from the ketone in the smectic phase with that of the ketone in the phase separated nematic (or isotropic) region. Throughout the bulk smectic phase these samples exhibit reasonably clean first order decay traces, since the lifetimes in the two components of the mixture differ by a factor of 2-4 (see Table 3.3). Presumably, the lifetime distribution of 1 in the smectic phases of OS-nm and CCH-502 are narrower than in CCH-4 and the decay profiles are more successfully modeled by first order kinetics.

3.4.4.   Phase Dependence of Reaction Energetics

The order associated with the smectic phase might be envisioned to alter the energetics of the conformationally dependent triplet quenching in 1 a number of ways. First, the ordered matrix might be expected to incorporate the solute specifically in its all *trans*-conformer, based on best packing considerations. This would have the effect of stabilising this conformer in relation to isotropic solvents. Second, the quenching conformer would be destabilised in the smectic phase due to the necessity of disrupting the surrounding local environment to achieve the required gauche-like geometry.[78,79] Both of these features would have the effect of raising the activation energy barrier (E_a) for *trans/gauche* conversion and increasing the entropic term in the smectic phase compared to that in the nematic/isotropic phase.

Table 3.3 shows that the activation parameters for triplet decay in the smectic phases of each of the mesogens is altered in the predicted way from those observed for acetonitrile solutions. The relative magnitudes of the differences between smectic and isotropic (acetonitrile) phase Arrhenius parameters parallel the differences in "reduced lifetime" data for the various mesogens (*i.e.* the difference is greatest for CCH-4 and smallest for CCH-502). Curiously however, the changes observed in the activation parameters in each of the smectic phases are **paralleled** in the corresponding nematic/isotropic phases. Thus, the substantial decrease in the rate of triplet decay for 1 that occurs at the N→Sm transition temperatures of each mesogen is the result of very small alterations in activation parameters between the two liquid crystalline phase types. Table 3.7 summarises the differences between the Arrhenius and Eyring parameters for triplet decay in the smectic and nematic/isotropic phases of each mesogen. These

Table 3.7. Differences between the smectic and nematic/isotropic activation parameters for triplet decay of **1** in CCH-4, OS-nm and CCH-502.[a]

	CCH-4	OS-53	OS-35	CCH-502[d]
ΔE_a[b] (kcal/mol)	0.8 ± 0.8	0.9 ± 0.5	1.1 ± 0.5	0.8 ± 0.5
$\Delta(\Delta S^{\neq})$[c] (calK^{-1} mol^{-1})	1.1 ± 0.2	1.8 ± 0.3	2.3 ± 0.4	1.1 ± 0.5

a. The data used in the calculations is tabulated in Table 3.3.
b. Activation energy determined in smectic phase minus that in the nematic/isotropic phase.
c. Entropy of activation determined in smectic phase minus that in the nematic/isotropic phase.
d. Data in smectic phase of CCH-502 minus data in CCH-301.

variations are very much smaller than those observed for the higher concentration samples of **1** in CCH-4[85] and OS-nm (Table 3.4) and reflect the *true* effect which the smectic phases have on the energetics of this reaction.
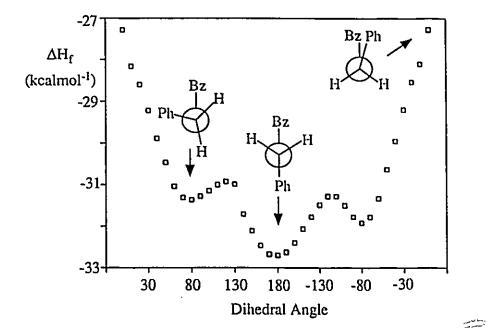
The ΔE_a and $\Delta(\Delta S^{\neq})$ values are too small to allow any definitive conclusions as to whether the observed differences in the rate of intramolecular triplet decay in **1** between the two phase types are the result of entropic or enthalpic factors, or some combination of the two. Nevertheless, a few generalisations can be made.

The results summarised in Table 3.7 indicate that the smectic phases impart only slight restrictions on the energetics of β-phenyl quenching in **1**. The simplest explanation of this would be that the solute is poorly constrained in the smectic phases and able to undergo fairly unrestricted molecular motions, in spite of the large degree of order associated with the smectic phases.

A second explanation is that the solute is <u>well</u> <u>constrained</u> in the smectic phase matrix, but need undergo only small amplitude conformational changes to reach the quenching geometry. This would be true if the probe solute was rigidly solvated in the ordered matrix in a conformation, or a *distribution* of similar conformations, in which the β-phenyl ring and the carbonyl functionality are already in a geometry close to that required for quenching. Semi-empirical (AM1) dihedral angle driver calculations were performed for **1** [140] and the results are summarised in Figure 3.17. The data indicate that there exists *gauche* conformations which are only slightly less stable than the lowest energy, all *trans*-conformation. The low energy *gauche*-conformer is very similar in *overall* shape, and occupies only a slightly larger volume, than the *trans*-conformer. In this conformer β-phenyl quenching can occur with relatively small amplitude motions of the β-phenyl ring. Such a model might not require the probe to achieve the totally eclipsed geometry in order for quenching to occur. It may be that there is a range of geometries that possess sufficient overlap of the β-phenyl π-system with the carbonyl n-orbital to allow quenching to occur.

The above two explanations assume that the rate determining step for β-phenyl quenching in the ordered liquid crystalline environments involves conformational motions, and not the actual quenching process which occurs once the optimum geometry(ies) has (have) been reached. Recall from Chapter 1 that β-phenyl quenching requires the n,π* triplet state of the carbonyl. β-Phenyl ketones, which are unsubstituted on the benzoyl ring, have lowest n,π* triplet states and in non-viscous isotropic solutions have lifetimes <1 ns. The extremely short triplet lifetimes, and the fact that the lifetimes are relatively insensitive to substituents on the β-phenyl ring, are consistent with conformational motions being rate-determining in these cases. On the other hand, *para*-alkoxy substituted

Figure 3.17. Heat of formation energy *versus* dihedral angle calculated for **1** using AM1.[140] Newman type projections are shown to represent the minimum and maximum conformations. Energies are not absolute but only relative. Key: Bz = *para*-methoxybenzoyl group; Ph=phenyl.

β-phenyl ketones such as 1 have lowest π,π^* triplet states. The triplet lifetime of 1 is extended compared to the unsubstituted analog in non-viscous isotropic solutions (see Table 3.5), reflecting the necessity for prior thermal population of the n,π^* triplet state. In this case, it is believed that the rate-determining step for triplet decay is the actual quenching process (which includes thermal population of the n,π^* state) and not the conformational interconversions.

Therefore, a third possible explanation for the observed results for 1 is that in the smectic liquid crystalline phases, the β-phenyl quenching process remains the rate-determining step for triplet decay, and the overall decrease in the triplet decay rate is due to an alteration in the *conformational distribution* of the solute in favour of the lower energy *trans*-conformer. Since the interconversion of conformers occurs prior to the quenching step, slight variations in the equilibrium constant for conformer population may translate to a substantial change in the rate of triplet decay, but result in only small changes in the activation parameters. In this model, the rate of *trans→gauche* conversion in the smectic phase must be greater than *ca.* $2 \times 10^7 s^{-1}$. Unfortunately, the ^2H NMR results in each of the smectic phases are consistent with any of the above possible explanations of the laser flash photolysis data. Both techniques indicate that 1 experiences a greater degree of order in each of the smectic phases compared to the corresponding nematic and isotropic phases. In particular, the ^2H NMR data indicates that the β-phenyl ring is subject to slower reorientation rates in the smectic phases. However, the timescale over which these reorientations is measured is much longer than the triplet decay rate and no quantitative information regarding these rates are available. Studies directed at distinguishing between the different possibilities in terms of a solubilisation model in smectic liquid crystalline solvents are the subject of Chapter 4, and the experimental

rationale will be discussed in more detail there.

3.5   Summary and Ramifications of this Work

The deuterium NMR studies of the selectively deuterated analogs of **1** in the smectic phases of CCH-4 and CCH-2 have shown unequivocally that the previously reported photochemical behaviour of **1** in these phases were the result of phase separation phenomena, which occurs throughout the bulk smectic phase temperature ranges. Furthermore, we have shown that the *overall* binary phase characteristics of **1** are <u>similar</u> in all the mesogens studied, with differences occurring only due to the actual solubility limit of the probe in each of the phases. These experiments have also illustrated that our method of determining solubility limits is quite general, although in some cases more than a single deuterated probe may be required to sufficiently describe a system. In a more qualitative fashion, the ^{2}H NMR features exhibited by a probe can also provide some information on the relative amount of order and the resulting restricted mobility experienced by the probe molecule in the smectic phase.

The triplet decay rate measured for homogeneous smectic solutions of **1** ranges from a factor of 1.7 times slower in CCH-502 to *ca.* 3 times slower in CCH-4 and OS-nm liquid crystals, compared to the corresponding nematic and isotropic phase values. The Arrhenius behaviour of **1** in each of the mesogens is again quite general, with a substantial decrease in the rate of triplet decay occurring at the Sm→N phase transition temperature of each solute/mesogen mixture. The magnitude of the change in lifetime that occurs at the Sm→N transition are a function of the relative amount of order associated with the smectic phases. The Cr_B phases of the CCH-4 and the OS-nm mesogens have a

greater effect on the conformational mobility of 1 than the Sm_B phase of CCH-502, which has been found to be only as effective as the viscous nematic phase of EB. The generality of the results in the CCH-n and OS-nm liquid crystals suggests that the forces responsible for increasing the triplet lifetime of the probe are similar in this class of smectic phases.

The differences between the triplet lifetimes of 1 in the smectic and nematic/isotropic phases of each mesogen are the result of barely perceptible differences in the activation parameters for triplet decay. The small changes in Arrhenius parameters between phase types for a particular mesogen indicate that either (i) there is loose packing of the solute with little restriction to large amplitude conformational motions, (ii) the probe experiences relatively minor restrictions to the rate-determining conformational motions required for quenching, due to the probe being tightly packed in the smectic phase in a conformation close to that required for quenching, or (iii) the smectic phase controls the conformational distribution of the probe in favour of a non-quenching geometry, with the quenching process remaining the rate-determining step.

The Arrhenius behaviour of homogeneous smectic phase solutions of 1 is dramatically different than that obtained from heterogeneous mixtures- as illustrated by the photochemical results obtained for samples of 1 in CCH-n and OS-nm liquid crystals at concentrations above and below the solubility limits. These experiments provide dramatic illustrations of the importance of determining the solubilisation behaviour of a probe molecule to protect against misinterpretation of the true effects an ordered phase may have on the chemistry of an incorporated solute.

The present work provides evidence that a number of other studies involving probe molecules in the smectic phases of liquid crystalline solvents may require reevaluation. For example, Stumpe and coworkers have recently investigated the

photodimerisation reaction of ethyl-4-methoxycinnamate (Scheme 3.1) in a number of

different smectic and nematic mesophases (including CCH-2 and CCH-4), comparing the

efficiency of the reaction in relation to isotropic phases.[141] They observed that for low

Scheme 3.1 Photodimerisation reaction of Ethyl-4-methoxy cinnamate.

Bz= 4-methoxyphenyl
R= ethyl

concentrations of solute (0.02M ≈ 0.5 mol %), the relative quantum yield for dimerisation

increases by a factor of 5- 30 times in a number of smectic phases, in comparison with

viscous isotropic solutions. In addition, the quantum yields tend to increase with

temperature in the smectic phases. They rationalised that the increased efficiency was due

to (i) the smectic phases exerting an ordering effect on the solute's critical orientation

required for reaction, and to (ii) anisotropic diffusion of the solute in the smectic phase,

which increases in rate at higher temperatures. In contrast to the smectic phase of CCH-2,

where the photoefficiency was 18 times that observed in the isotropic phase, no

photodimerisation was detectable for similar concentrations of solute in the smectic phase

of CCH-4. Stumpe and coworkers suggested that the difference between the enhancement

in the smectic phase of CCH-2, and the inhibition in the same phase of CCH-4, was due to

the different smectic phase structures of the two mesogens or due to CCH-4 forming a

plastic crystal[25] with the solute. Based on the relative solubility limits determined for 1 in

these two smectic phases, and on what we have learned about the phase behaviour of solutes in these smectic phases in general, we believe that the observed effects are more likely due to differences in the solubility limits in the various phases. The increased efficiency observed in some of the smectic phases is most likely due to phase separation of the solute into a highly concentrated solute-enriched nematic or isotropic phase, similar to what is observed for 1 and other solutes we have studied in this mesogen. The increased *effective* concentration of the solute in this phase separated region could be responsible for the increased efficiency. In addition, the temperature dependence observed in the quantum yield in the smectic phase is consistent with the phase separation explanation, since the heterogeneous mixture changes as a function of temperature. The absence of a reaction in CCH-4 may be the result of the probe being soluble in the smectic phase at the concentration used, thereby decreasing the rate by dramatically slowing diffusion of the reactants in the ordered phase.

Samori and coworkers have reported a number of studies on the quaternisation rearrangement of two alkyl *para*-(dimethylamino)benzenesulfonate esters, MSE and ASE, to their corresponding zwitterion (Scheme 3.2), in several nematic and smectic liquid crystalline solvents.[33,34,142,143] When both esters are dissolved in the smectic phases at low concentrations, the quaternisation reaction proceeds readily. Interestingly, the same rearrangement does not take place at any detectable rate in the nematic phases of the same solvents nor in isotropic solvents. Their results have proven to be one of the most interesting examples of the use of the order associated with the liquid crystalline solvents to catalyse a bimolecular reaction. These workers went on to investigate the kinetics of the quaternisation of ASE in the smectic phase of OS-35 as a function of temperature and solute concentration. The Arrhenius plot of a 0.3 mol % mixture of ASE in OS-35 shows

Scheme 3.2. Quaternisation rearrangement of alkyl *para*-(dimethylamino)-
benzenesulfonate esters.

$$CH_3\text{-}N\text{-}C_6H_4\text{-}SO_3R \xrightarrow{\Delta} (CH_3)_2\overset{+}{N}\text{-}C_6H_4\text{-}SO_3^-$$

MSE: R = CH$_3$
ASE: R = CH$_2$CH=CH$_2$

an unusual strong upward curvature above 40°C. They also showed that the rate constant for reaction at 40°C is depressed when the solute concentration was increased beyond the threshold value of 0.3 mol %. In addition they observed that the threshold concentration decreased with increasing temperature. The results were initially described as being due to reaction occurring from two independent sites in the smectic phase lattice, each with a distinct contribution to the overall rate. The strange Arrhenius behaviour was suggested to be due to the relative populations of the solutes in the two sites being temperature dependent. Given the low solubility limits we have determined for 1,[131] and other solutes,[90,91,105] in the smectic phases of OS-53 and OS-35 the complex concentration and temperature dependence observed in this system are more likely due to phase separation phenomena. Indeed, in an unpublished report[144] Samori and coworkers have found ^{2}H NMR evidence, similar to what we have observed and attributed to biphasic solubilisation, for ASE-d$_2$ in OS-35 at the concentrations used in their kinetic studies. A proper investigation of the kinetics of this catalysis reaction in OS-35 requires proper determination of the solubility limit of ASE in this mesogen (the solubility limit is below 0.3 mol %).

CHAPTER 4

SUBSTITUENT EFFECTS ON THE PHOTOCHEMISTRY OF ALKOXY-β-ARYL-PROPIOPHENONES IN CCH-n AND CCH-nOm LIQUID CRYSTALS

4.1   Introduction

This chapter describes the results of nanosecond laser flash photolysis studies of the photochemical behaviour of a series of benzoyl and β-aryl substituted derivatives of β-phenylpropiophenone (4-alkoxy-β-arylpropiophenones 2-7) in the mesophases of CCH-nOm and CCH-n liquid crystals. The goals of this study include investigating the effects that solute size and structure might have on (i) the solubility properties, and (ii) the rate of β-phenyl quenching in the smectic phases of these mesogens. Early photochemical studies (reviewed in Chapter 1) employing a number of substituted derivatives of 1 at high concentrations (1 mol %) in CCH-4 and CCH-2 showed that, with the exception of 1, β-phenyl ketones exhibited phase independent Arrhenius behaviour.[85] However, based on our ^{2}H NMR and photochemical studies with 1, the behaviour exhibited by the substituted derivatives of 1 in the earlier study can now be attributed to the samples being heterogeneous in nature at the concentrations employed. In these cases the solutes were predominantly solubilised in a nematic or isotropic phase-separated region coexisting with the bulk smectic phase (vide supra). It was therefore of interest to determine the solubility
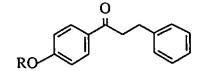
1: R = H
2: R = methyl
3: R = ispropyl
4: R = n-hexyl
5: R = cyclohexyl

1: R = methyl
6: R = ethyl
7: R = propyl

limits for **2-7** in CCH-4, using the techniques we have developed. Once these were obtained, it might then be possible to investigate the effect of changes in solute length and rigidity on the conformational motions leading to β-phenyl quenching in homogeneous smectic phase solutions. Preliminary ^{2}H NMR experiments indicated that the solubility limits of the larger probes in smectic CCH-4 are too low to allow a practical investigation of their photochemistry in this mesogen.[145] However, the solubility limits of **2-7** were found to be high enough in the smectic phase of CCH-502 to make further photochemical studies practical.

In the previous chapter, smectic phase order was shown to have dramatic effects on the triplet lifetimes and the Arrhenius behaviour of **1**. Based on the results, the nature of the observed effects in the various smectic phases were proposed to be the result of (a) a solvation effect on the *rate-determining conformational motions* leading to quenching, or (b) a result of an *alteration of the conformational distribution* of the solute in a step prior to the actual rate-determining quenching process. In order to distinguish between these possibilities it is necessary to employ analogues of **1** in which the rate of β-phenyl quenching is enhanced once the required geometry is achieved. It has recently

been reported that methyl substituents on the β-aryl ring shorten the triplet lifetime of β-aryl ketones.[146] This has been proposed to be due to the electron-donating ability of these substituents lowering the oxidation potential of the β-aryl ring. The decreased oxidation potential of the β-aryl ring facilitates the charge-transfer process involved in the quenching mechanism. It was hoped that the results of photochemical studies with 2-5 in smectic CCH-4 and smectic CCH-502 would help to delineate between the two possible mechanisms proposed for the observed effects on the photochemistry of 1 in the same mesogens. The results presented below allow us to discriminate between these two possibilities and has given a fairly complete understanding of the effect that smectic phases have on the conformational mobility of this probe.

4.2   Results

4.2.1   Preparation of Compounds

The ketones used in this study were prepared using modifications of the procedure used in the preparation of 1 and are described in Chapter 6. The α-deuterated ketones (2-7-αd$_2$) were synthesized by base catalysed deuterium exchange from the parent ketones in the same manner as was described for 1 in Chapter 3. Methoxy-d$_3$ analogues, 4-Od$_3$ and 5-Od$_3$, the ethoxy-d$_5$ analog of 6 (6-Od$_5$) were synthesised from the phenolic ketones with iodomethane-d$_3$ or iodoethane-d$_5$ by a Williamson etherification procedure (see Chapter 6 for details).

2-7 -αd₂

4, 5-Od₃

6-Od₅

4.2.2 ²H NMR Spectroscopy: Determination of Solubility Limits of 2-7 in Smectic CCH-4 and CCH-502

Deuterium NMR spectra were recorded for each solute in CCH-4 and CCH-502 using procedures we have developed and have outlined in the previous chapters. Solubility limits were determined by adjusting the concentration of the solute in the mesogen until monophasic spectra were obtained throughout the majority of the smectic phases.

CCH-4: Compound 2-αd₂ was found to be soluble in the smectic phase of CCH-4 at a concentration of 0.25 mol % over a similar temperature range as for 1, and 6-αd₂ was determined to be soluble over the same temperature range at a slightly lower concentration of 0.2 mol %. Ketones 2 and 6 exhibited quadrupolar doublets in the nematic phase with maximum splittings of 25.2 and 26.6 kHz, respectively. These doublets disappear on lowering the temperature into the smectic phase region, leaving

spectra devoid of any features below 46°C. Based on our studies with $1-\alpha d_2$ and other

α-deuterated probes, this behaviour was taken to be indicative of homogeneous

solubilisation in the smectic phase. In the case of 6, experiments were repeated with

$6-Od_5$. In the nematic phase at 55°C $6-Od_5$ exhibits two quadrupolar doublets of splitting

7.4 and 19.5 kHz with a relative intensity of 2:1. These signals can be assigned to the CD_3

and CD_2 portions, respectively. On lowering the temperature into the smectic phase

region, these signals are replaced by two new doublets with splittings of 6.6 and 10 kHz.

The signals are much broader than the nematic phase signals and converge into a single

broad doublet at low temperatures. This latter experiment confirmed the solubility limit

determined using the α-deuterated analog.

Compound $7-\alpha d_2$ was determined to be less soluble in smectic CCH-4 than 2

or 6, with the concentration of 7 having to be lowered to 0.1 mol % in order to be

homogeneously solubilised over a similar temperature range as 1, 2, and 6. Mixtures of

0.2 mol % samples of 3-, 4- and $5-\alpha d_2$, on the other hand, were found to exhibit spectra

similar to that observed for 1 mol % samples of $1-\alpha d_2$ and were thus concluded to be

biphasic throughout the entire smectic phase temperature region. Based on the behaviour

of the 0.2 mol % samples, the solubility limits for 3-5 are estimated to be well below 0.1

mol %.

CCH-502: Similar ^2H NMR experiments were carried out for 0.5 mol %

mixtures of $2-7-\alpha d_2$ in the liquid crystalline phases of CCH-502. All ketones exhibit

distinct signals for the α-deuterons in the smectic phase that can be assigned to the ketone

solubilised in the higher ordered environment. The signals observed had larger

quadrupolar splittings than the nematic phase doublet and were similar in linewidth to

those described for $1-\alpha d_2$ in the same mesogen (see Figure 3.5). At a single temperature,

the quadrupolar splittings increase in magnitude in the nematic and smectic phases with increasing substituent size and rigidity. The maximum splittings observed for the α-deuterons for 1-7 in the two phase types are summarised in Table 4.1. In the cases of 3, 4, and 5 the signals in the smectic phase overlap to some extent with the signals due to the deuterated impurities in the mesogen itself (see Chapter 3). However, quadrupolar splittings could be determined based on the intensities of the spectral absorptions. As a control experiment, ^2H NMR spectra were also recorded for 4, 5, and 6 using the alkoxy-deuterated derivatives. Deuterium NMR spectra for 5-Od$_3$ and 6-Od$_5$ as 0.5 mol % mixtures in CCH-502 are shown in Figure 4.1. Nematic phase doublets for each non-equivalent deuteron were replaced by new sets of doublets of larger splitting in the smectic phase. The maximum splittings observed for these probes are also included in Table 4.1. Identical solubility limits were obtained using the alkoxy-deuterated ketones as using the α-deuterated derivatives. The NMR results indicate that like 1, 0.5 mol % mixtures of 2-7 in CCH-502 are homogeneously solubilised in the smectic phase between 48°C and < 20°C.

In an effort to further investigate the effect of substituents on the solubility behaviour of these probes, deuterium NMR experiments were also performed on β-phenyl-propiophenone-αd$_2$ (8-αd$_2$) and β-phenylbutyrophenone-αd$_2$ (9-αd$_2$) in CCH-4 and CCH-502. Compound 8 was found to be soluble in the smectic phase of each mesogen at the same concentrations as those determined for 1. In CCH-4, 8 exhibits spectral features virtually identical to 1. In CCH-502 however, the nematic phase doublet had a larger splitting (13.5 kHz) than the doublet due to the ketone solubilised in the smectic phase (7.5 kHz). This was also the case for 9 in the same mesogen and it may indicate that these probes are solvated differently in the smectic phase of CCH-502 than are the alkoxy

8-αd₂ structure and 9-αd₂; R = H, 10-αd₂; R = OCH₃ structures

8-αd$_2$

9-αd$_2$; R = H

10-αd$_2$; R = OCH$_3$

substituted probes. Interestingly, in the nematic phases of CCH-4 and CCH-502, **9**

exhibits two sets of doublets, of equal intensity, separated by *ca.* 1.5 kHz. In the nematic

phase of CCH-4 the doublets have splittings of 15.6 and 17.2 kHz and in CCH-502 the

quadrupolar splittings are 8.8 and 10.3 kHz. The origin of the two quadrupolar doublets is

the result of either some motional inequivalence of the two deuterons brought about by the

fact that the carbon is diastereotopic (due to the neighbouring chiral centre), or the result

of the probes being solvated in two distinct sites. Similar observations have been reported

for deuterated phosphatidylglycerol derivatives in lipid bilayers.[147,148] The quadrupolar

PPG-d$_2$

R-PPG-d

^{2}H NMR spectrum of the phosphatiglycerol **PPG-d$_2$** exhibits two quadrupolar doublets of

equal intensity when incorporated in a lipid bilayer. Only a single doublet is observed for

the stereospecifically monodeuterated derivative *R*-PPG-d under the same conditions.

This latter result provides unambiguous proof that the two quadrupolar splittings observed

in PPG-d$_2$ must be the result of the inequivalence of the two deuterons and not the result

of an equilibrium between two sites (or conformational structures). It may be likely that a

similar explanation may also apply in our cases. Only the synthesis of stereospecifically

deuterated compounds will aid in confirming this. Our results for **9** (and **10**, *vide infra*) are very interesting and definitely warrant further ^{2}H NMR studies to determine the nature of the effect observed in the liquid crystalline solvents. However, such studies are not essential for the current discussion.

Ketone **9** was determined to be insoluble throughout the smectic phase temperature region of CCH-4 when present at a concentration of 0.2 mol %. In a 0.5 mol % mixture of **9** in CCH-502, the nematic phase doublets were replaced by a new doublet of smaller splitting (5.6 kHz) upon lowering the temperature into the smectic phase region. This doublet resolved into a set of doublets (Δv_Q= 13.7, 5.2 kHz) as the temperature was decreased further. For *para*-methoxy-β-phenylbutyrophenone-αd_2 (**10**-αd_2), the ^{2}H NMR behaviour in CCH-502 is similar in most respects to that of **9**, except the splittings in the smectic phase of CCH-502 are larger than in the nematic phase, as is observed for all alkoxy substituted probes. These last two results provide further evidence that the C-^{2}H bonds of **9** are oriented quite differently in the smectic phase of CCH-502 (and CCH-4) than are the alkoxy deuterated probes.
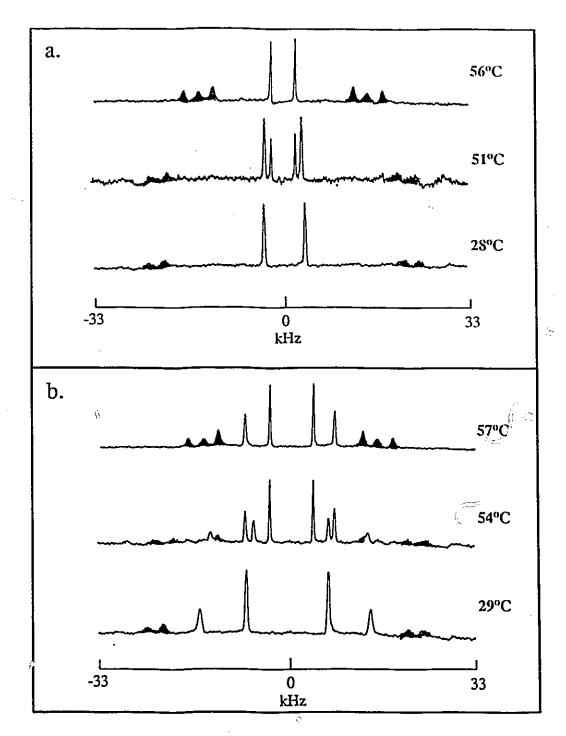
Figure 4.1. Deuterium NMR spectra of (a) 0.5 mol % 5-Od$_3$ in CCH-502 and (b) 0.5 mol % 6-Od$_5$ in CCH-502 in the nematic, biphasic, and smectic temperature regions.

Table 4.1. Quadrupolar splittings from ^{2}H NMR spectra of α- and alkoxy deuterated ketones 1-7 in the nematic and smectic phases of CCH-502.[a]

Ketone	Phase	α-d$_2$	Od$_3$ (OCD$_2$CD$_3$)	
1[b]	N[c]	17.3	3.5	
	Sm[d]	27.1	5.2	
2	N[c]	18.7	e	
	Sm[d]	37.9	e	
3	N[c]	17.9	e	
	Sm[d]	40.8	e	
4	N[c]	19.8	4.0	
	Sm[d]	42.5	5.6	
5	N[c]	20.7	4.4	
	Sm[d]	45.8	6.9	
6	N[c]	18.1	7.4	15.3
	Sm[d]	36.9	13.7	28.8
7	N[c]	18.0	-	
	Sm[d]	41.4	-	

a. Recorded at 76.8 Mhz, using the quadrupolar echo pulse sequence. Errors in splittings are ca.±0.1 kHz.

b. Data taken from Table 3.1.

c. N= nematic; spectra were recorded at Sm-N transition temperature.

d. Sm= smectic; spectra were recorded at 35°C.

e. Not recorded.

4.2.3   Determination of Triplet Lifetimes and

Arrhenius Parameters for 2-7 by NLFP

Nanosecond laser flash photolysis experiments were performed in a similar

manner to those previously described (Chapter 3). The triplet-triplet absorption spectra

for all six ketones (2-7) in the mesogenic solvents were virtually identical to that shown

for 1 in CCH-4 in Figure 3.7. The transient absorption spectrum of 4 as a 0.5 mol %

solution in CCH-301 is shown in Figure 4.2. Triplet lifetimes were measured for 0.5 mol

% mixtures of 2-7 in CCH-502 and CCH-301 as a function of temperature by monitoring

the decay of the triplet-triplet absorption. For all cases in CCH-502 and CCH-301, the

decay traces follow clean first order kinetics with only a small amount of residual

absorption in some cases. A typical decay trace, obtained for a 0.5 mol % mixture of 4 in

smectic CCH-502 at 32°C is shown in Figure 4.3. Least squares fitting of the data to a

first order kinetic expression gave correlation coefficients of 0.99 or better. A plot of the

residuals obtained from such an analysis of the data is also included in the Figure 4.3.

Similar experiments were also performed for 0.2 mol % mixtures of 2, 3, 5

and 6 in CCH-4, for a 0.1 mol % mixture of 7 in CCH-4, and for 1.0 mol % mixtures for 2,

6, and 7 in EB and CCH-4. Decay traces in the smectic phase of CCH-4 were similar in

nature (*i.e.* multiexponential) to that described for 1 in the same phase. The data was

analysed to a single exponential and gave correlation coefficients of 0.99 in almost every

case.

Arrhenius plots for triplet decay of 2 (0.2 mol %), 6 (0.2 %), and 7 (0.1 mol%)

in CCH-4 showed similar discontinuities at the N·→Sm transition to that observed for 1

(see Figure 3.10). The Arrhenius plot constructed from the data for a 0.2 mol % 6/CCH-4

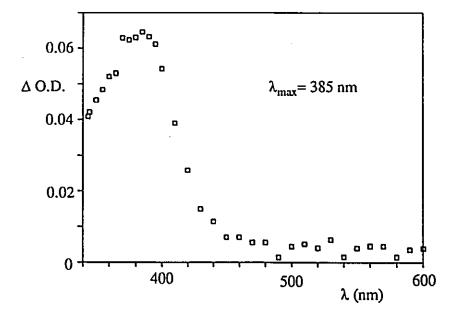$\lambda_{max} = 385$ nm

Figure 4.2. Triplet-triplet absorption spectrum of a 0.5 mol % mixture of 4 in CCH-301. The spectrum was recorded between 15-30 ns after 337 nm laser pulse excitation.
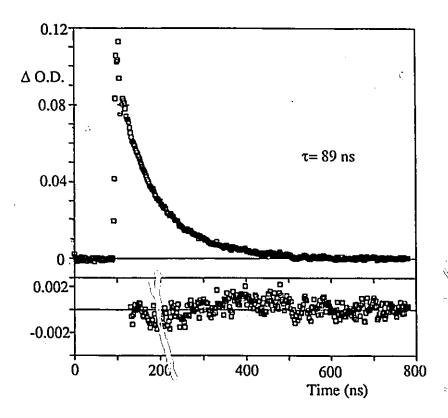
Figure 4.3. Transient decay trace of 0.5 mol % 4 in CCH-502, recorded at 385 nm following 337 nm excitation at 32°C. A plot of the residuals of a single exponential kinetic analysis is also shown.

mixture is shown in Figure 4.4. The (upper) nematic phase line contains points from a 1 mol % sample. Activation parameters and triplet lifetimes of the ketones in the smectic and nematic phases of CCH-4 (where measurable) and the nematic/isotropic phase of EB for ketones 2, 6, and 7 are summarised in Table 4.2. The low solubilities of 3 and 5 in CCH-4 precluded the study of the Arrhenius behaviour of homogeneous smectic phase solutions of these ketones. However, the lifetimes of these ketones at 30°C, measured using 0.2 mol % samples in CCH-4, are included in Table 4.2.

The Arrhenius plots for 0.5 mol % 6 in CCH-502 and CCH-301 are very similar to that for 1 in the same solvents except the gap between the nematic and smectic phase lines is somewhat narrower in the former. In contrast, the Arrhenius plot for a 0.5 mol % solution of 7 in CCH-502 shows no break in the plot at the N→Sm transition, and is almost superimposable on the line defined by the 0.5 mol % solution of 7 in CCH-301 (see Figure 4.5). The triplet lifetimes of 6 and 7 were slightly longer than that of 1 in the isotropic phase of CCH-301 at the same temperature. The same differences are observed in deareated solutions of 1, 6, and 7 in acetonitrile, for which the lifetimes at 23°C are 52, 64, and 69 ns, respectively.

Figure 4.6 shows Arrhenius plots for compounds 4 and 5 as 0.5 mol % solutions in the smectic phase of CCH-502 and in the isotropic phase of CCH-301 over similar temperature ranges. Data in the nematic and isotropic phases of CCH-502 could not be obtained because the extremely short triplet lifetimes at these temperatures do not allow the decay traces to be resolved from the laser pulse profile. Arrhenius plots for 2 and 3 were qualitatively very similar to those for 4 and 5 and are not shown.

Triplet lifetimes of 2-5 in deareated acetonitrile and cyclohexane solutions were determined to be in the 9-12 ns range. In tetrahydrofuran the lifetimes are extended
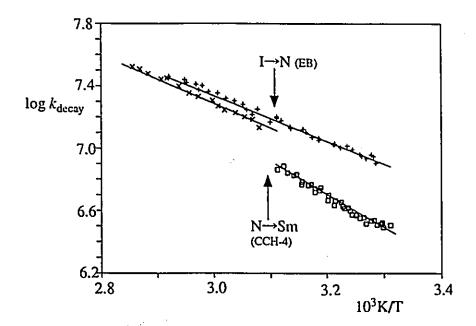
Figure 4.4. Arrhenius plots for the triplet decay of 6 in CCH-n liquid crystals. Key: □, 0.2 mol % in smectic CCH-4; x, 1.0 mol % in nematic CCH-4; +, 1.0 mol % in nematic and isotropic phases of EB.

Table 4.2. Activation parameters and triplet lifetimes at 30°C for solutions of
ketones 1-7 in CCH-n mesogens.[a]

Ketone	Solvent (phase)	E_a (kcal/mol)	log A (s^{-1})	$\Delta S^{\neq}$ (calmol^{-1}K^{-1})	τ_T^{30C} (ns)	k_N/k_{Sm}
1	CCH-4 (Sm)[b]	8.8 ± 0.4	12.8 ± 0.2	-2.1 ± 0.1	346	3.1
	EB (N/I)[c]	7.0 ± 0.4	12.0 ± 0.3	-5.8 ± 3.9	112	
2	CCH-4 (Sm)[b]	6.2 ± 0.7	11.4 ± 0.5	-8.3 ± 0.5	111	2.8
	EB (N/I)[c]	4.6 ± 1.4	10.7 ± 1.0	-11.6 ± 3.9	40	
6	CCH-4 (Sm)[b]	8.7 ± 0.6	12.8 ± 0.4	-1.8 ± 0.1	301	
	CCH-4 (N)[c]	7.8 ± 0.3	12.4 ± 0.2	-4.0 ± 0.1	169	2.4
	EB (N/I)[c]	6.9 ± 0.4	11.8 ± 0.3	-6.6 ± 0.2	124	
7	CCH-4 (Sm)[d]	8.0 ± 0.8	12.4 ± 0.5	-4.0 ± 0.2	259	
	CCH-4 (N)[c]	6.3 ± 0.5	11.4 ± 0.3	-8.6 ± 0.3	126	2.2
	EB (N/I)[c]	7.3 ± 0.3	12.1 ± 0.2	-5.2 ± 0.1	120	
3	CCH-4 (Sm/I)[e]	f	f	f	189[g]	
5	CCH-4 (Sm/I)[e]	f	f	f	170[g]	

a. Errors in Arrhenius parameters are quaoted as ±2σ. Errors in lifetimes are ca. 10%.
   Key: Sm = smectic; N = nematic; I = isotropic. Data for 1 from Table 3.3.
b. Sample composition = 0.2-0.25 mol %. c. Sample composition = 1.0 mol %. d. Sample composition = 0.1 mol %.
e. Sample composition = 0.2 mol %. Sample is heterogeneous at this concentration.
f. Could not measure as homogeneous smectic solution.
g. Lifetime is average of smectic phase and isotropic phase components.
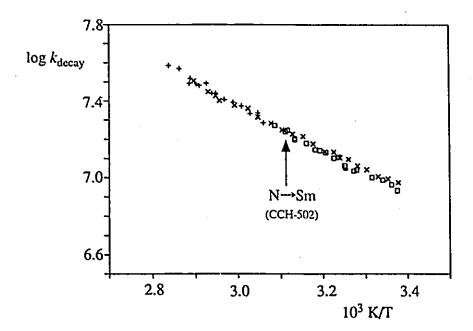
Figure 4.5. Composite Arrhenius plot for 0.5 mol % samples of 7 in ☐, smectic CCH-502; +, nematic/isotropic CCH-502; x, isotropic CCH-301.
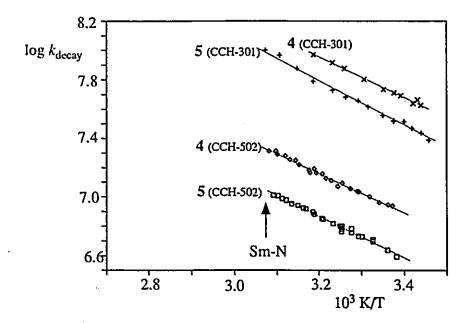
Figure 4.6. Arrhenius plots for the triplet decay of **4** and **5**, as 0.5 mol % solutions in the smectic phase of CCH-502 and the isotropic phase of CCH-301.
Key: □, **5** in CCH-502; +, **5** in CCH-301; ◊, **4** in CCH-502; x, **4** in CCH-301.

somewhat to 14-16 ns. The effect of THF on the triplet lifetimes of 2-5 is similar in magnitude to that observed for 1 in the same solvent. Triplet lifetimes measured for each ketone at 23°C in the smectic phase of CCH-502, the isotropic phase of CCH-301, and in acetonitrile are summarised in Table 4.3. Also included in this table are the ratios of the rate constants for triplet decay in the smectic phase of CCH-502 and the isotropic phase of CCH-301 at this temperature. Table 4.4 summarises the Arrhenius and Eyring activation parameters for triplet decay of 2-7 in the smectic phase of CCH-502, along with the differences between the smectic and the isotropic phase values, obtained in CCH-301. The values for 1 in the same phases are also included for comparison.

Experiments were also performed with 8 as a 0.2 mol % solution in CCH-4 and as a 0.5 mol % solution in CCH-502. In these cases the 308 nm pulses of the laser were used and attempts were made to detect the triplet at 320 nm. The triplet of 8 is known to absorb below 330 nm.[74,76] In neither case was there evidence of a transient of longer lifetime than the pulse width of the laser (15 ns).

Table 4.3.. Triplet lifetimes for 1-7 in homogeneous solutions of CCH-502, CCH-301 and acetonitrile at 23°C.[a]

Ketone	Lifetimes at 23°C (ns)			k_I/k_{Sm}[b]
	CCH-502 (Sm)	CCH-301 (Isotropic)	CH_3CN	
1	122	74	52	1.7
2	66	20	9	3.3
3	119	24	12	5.0
4	115	21	10	5.5
5	255	30	12	8.5
6	130	97	64	1.3
7	117	106	69	1.1

a. Errors in lifetimes are approximately 10-15%. Sm= smectic
b. Ratio of rate constants for triplet decay in CCH-301:CCH-502 at 23°C.

Table 4.4. Arrhenius and Eyring parameters for triplet decay of ketones 1-7 in the smectic phase of CCH-502 and differences between smectic and isotropic activation parameters.[a]

Ketone	E_a (kcalmol^{-1})	$\Delta S^{\neq}$ (e.u.)	log A (s^{-1})	ΔE_a (kcalmol^{-1})[b]	$\Delta(\Delta S^{\neq})$ (e.u.)[c]
1[d]	5.3 ± 0.3	-11.6 ± 0.3	10.8 ± 0.2	0.8 ± 0.5	1.1 ± 0.5
2	5.5 ± 0.5	-9.1 ± 0.3	11.2 ± 0.3	-0.5 ± 0.9	-3.8 ± 0.5
3	6.1 ± 0.4	-8.3 ± 0.3	11.4 ± 0.2	-0.8 ± 0.9	-7.9 ± 0.5
4	6.2 ± 0.3	-8.0 ± 0.2	11.5 ± 0.2	0.0 ± 0.7	-4.1 ± 0.3
5	6.5 ± 0.3	-8.5 ± 0.1	11.4 ± 0.2	0.1 ± 0.8	-4.4 ± 0.2
6	5.3 ± 0.4	-11.4 ± 0.4	10.8 ± 0.3	-0.1 ± 0.6	-1.3 ± 0.6
7	5.2 ± 0.3	-11.1 ± 0.3	10.8 ± 0.2	0.2 ± 0.5	-2.0 ± 0.5

a. Errors in Arrhenius parameters are quoted as ± 2σ.

b. Difference in activation energy in smectic phase to that in isotropic phase over similar temperature range.

c. Difference in reaction entropy in smectic phase to that in isotropic phase over similar temperature range.

d. Data from table 3.3.

4.3   Discussion

4.3.1   Substituent Effects on the Solubility Limits
of 2-7 in Smectic CCH-4 and CCH-502

Interestingly, the solubilities of ketones 2-7 in the smectic phase of CCH-502 are the same as that determined for 1 in the same phase, indicating that they are roughly *independent* of substituent. This is in stark contrast to the solubility behaviour of these solutes in CCH-4, where we have found that the ability of the mesogen to solubilise the probe molecules varies dramatically with quite subtle changes in the size (length) of the probe. For example, while the solubility limits of 1 and 2 in CCH-4 were found to be 0.25 mol %, that of 6 was slightly lower and 7 was found to have a solubility limit of *ca*. 0.1 mol% over a similar temperature range. The solubilities of 3, 4, and 5 were determined to be much lower than 0.1 mol % and the actual values could not be conveniently determined by our ^{2}H NMR method. These results are another indication that the degree of order present in the smectic phase of CCH-502 is lower than that present in the Cr_B phase of CCH-4.

Other indications of the lesser degree of order in smectic CCH-502 were obtained from the ^{2}H NMR behaviour of 1 in this phase, compared to those in the other mesogens. Many of the spectral features outlined for 1 in the previous chapter which support the above statement are also observed for 2-7. These features include the fact that smectic phase spectra are readily observable for all α-deuterated ketones, unlike that in CCH-4, indicating that the solutes are subject to faster reorientation rates than in CCH-4. Furthermore, the linewidths of the alkoxy-deuterated derivatives (and α-deuterated

derivatives) are narrower than are observed in CCH-4, again suggesting faster C-^{2}H reorientation rates and a lower degree of order. Evidently, the less ordered matrix of CCH-502 enables the smectic phase to incorporate the larger probes more easily and without as great a disruption to the surrounding environment.

The solubilities of 1-7 in smectic CCH-4 are substantially lower than the solubilities of the phenyl alkyl ketones used in the Norrish II study described in Chapter 2. In order to investigate whether the lower solubilities can be attributed to the alkoxy substituent or to the phenyl substituent on the β-carbon, ^{2}H NMR spectra of 8- and 9-αd$_2$ were recorded. Since the solubility of 8 in CCH-4 is similar to that of 1 and that of 9 is lower, it appears that the substitution on the alkanoyl chain affects the solvation properties of aromatic ketones more than alkoxy substitution on the benzoyl ring. The results from 7 (and 6) indicate that the length of the alkoxy substituent also plays a slight role in the solubility in the smectic phase of CCH-4.

4.3.2 Average Ordering of 1-7 as a Function of Substituent

While the solubility limits in CCH-502 are essentially independent of probe structure, the quadrupolar splitting observed in the ^{2}H NMR spectra vary as a function of substituent. As discussed earlier, the magnitude of the quadrupolar splittings for a series of similar solutes, measured at identical concentration and temperature, provide qualitative information on the relative ordering in the mesophase. For each of the ketones 1-7 in CCH-502, the deuterium quadrupolar splitting is larger in the smectic phase than it

is in the nematic phase. This is consistent with a greater degree of orientational ordering in the smectic phase. Furthermore, it is observed that the quadrupolar splitting for the α- and methoxy deuterated analogues <u>increase</u> in magnitude as the size of the probe is increased in both the nematic and smectic phases. This correlation with solute length suggests that the solutes are being solubilised in a preferred elongated form. There is a similar effect on the magnitude of the splitting for the same ketones in the nematic phase of CCH-4; unfortunately, no data is available for the α-deuterated ketones in the smectic phase. Ketones 8 and 9 both have smaller splittings in the smectic phase of CCH-502 than in the nematic phase. This observation suggests that the orientation of these solutes is different in the smectic phase than it is for the alkoxy deuterated ketones. Even though the exact nature of the cause of this behaviour is not known based on our studies, it appears as if the non-alkoxy substituted derivatives are solubilised differently than the alkoxy derivatives. Solubility factors are, therefore not only determined by the size of a probe in relation to the mesogen, but also by the functional groups attached to a solute.

The orientational ordering of the solutes in the nematic phase which is indicated by the ^{2}H NMR results does not manifest itself in the observed triplet lifetimes. For compounds 6 and 7, where the triplet decay rates are large enough to be measurable in the nematic phase of CCH-502, the rates of decay are essentially the same as in the isotropic phase of CCH-301. Similarly, no break in the Arrhenius plot for triplet decay occurs for 2, 6, or 7 at the N→I transition temperature in EB. The absence of an effect of nematic phase ordering on conformation-dependent reactivity in phenyl ketone photochemistry has been a general observation in the majority of the studies reported in this thesis. The increased orientational order experienced by the ketones on lowering the temperature into the smectic phase of each mesogen is, on the other hand, accompanied by

a dramatic slowing of the triplet decay rates (with the exception of 6 and 7 in CCH-502). No direct correlation can be made between the substituent effect on the ^2H quadrupolar splittings and that on the triplet decay rates in smectic CCH-502. The quadrupolar splittings are a function of molecular motions of different types and which occur over different timescales than those probed in the photochemical studies. However, both techniques illustrate the substantial amount of ordering which the probes are subject to in the smectic phases.

4.3.3   The Mechanism of Triplet Decay of 1-7

Before the nature of the observed effect on the rate of triplet decay in the smectic phases can be addressed, it is prudent to recall the important mechanistic features that are known about the β-phenyl quenching process of these probe solutes in solution.

The mechanism for β-phenyl quenching is believed to involve charge transfer interactions between the β-phenyl ring and the n-π* triplet state of the carbonyl.[76] Therefore, the rate of β-phenyl quenching is fastest when the lowest excited triplet state of the carbonyl is of n-π* configuration, and when the ionisation potential of the β-phenyl ring is lowered by electron-donating substituents in order to facilitate the charge transfer quenching interaction. As discussed earlier, β-phenylpropiophenone (8) and related molecules, in which there is no alkoxy substituent on the benzoyl ring, have lowest n-π* triplet states, and the triplet lifetime of these ketones have been found to be exceedingly short in isotropic solvents (<1 ns).[75,76] These ketones have also been found to be insensitive to substituent effects on the β-phenyl ring,[76] consistent with conformational motions comprising the rate determining step for triplet decay.

The *para*-alkoxy β-phenyl ketones, such as 1-7, have lowest π-π* triplet states and as a result have substantially longer triplet lifetimes than the unsubstituted analogues. This reflects the necessity for thermal population of the upper n-π* state (which is 2-3 kcal/mol higher in energy than the π-π* triplet state[76]) in order for quenching to occur. In these cases, the rate determining step for triplet decay changes from conformational dynamics to the β-phenyl quenching process, which includes population of the upper excited state prior to quenching. With β-phenyl quenching being the rate-determining step, the triplet lifetimes of the alkoxy-derivatives would be expected to be more sensitive to substituent effects on the β-phenyl ring than the unsubstituted ones. This has been shown explicitly in this study with ketones 2-5 in several non-viscous solvents, where the triplet lifetimes are 4-5 times shorter than that of 1 at the same temperature. Although the lifetimes of the alkyl-substituted derivatives of 1 are lowered substantially, β-phenyl quenching is still thought to be rate determining in the isotropic solvents, since the rate constant for conformational interconversions is on the order of *ca.* 1×10^9 s^{-1} (based on the lifetime of β-phenylpropiophenone (8) at the same temperature)[76]- at least ten times faster than the rate of triplet decay in 2-5. The lifetimes measured for 2-5 in acetonitrile and cyclohexane are all similar, and range from 9-12 ns (see Table 4.3). This similarity is expected, since the oxidation potential of the β-aryl moiety should not vary dramatically throughout this series of substituents. For a derivative with a methyl substituent in the *meta*-position of the β-aryl ring, the triplet lifetime in acetonitrile is 29 ns[146] (three times longer than that of 2) and is a reflection of the higher oxidation potential of the *meta*-substituted β-aryl ring compared to the *para*-substituted analog.

The longer triplet lifetimes of the *para*-alkoxy substituted β-aryl ketones makes them more amenable for nanosecond laser flash studies. However, the fact that

conformational motions are not the rate determining step in isotropic solvents (even for 2-5) makes estimation of the role of the liquid crystalline medium on the intramolecular quenching process more complicated, because it is difficult to determine what the rate determining step is in the more ordered phases. β-Phenyl quenching can be thought of as a two step process involving (i) a fast pre-equilibrium between the conformer required for quenching and all other non-quenching conformers, and (ii) the β-phenyl quenching process, which involves thermal population of the n-π* state (see Figure 4.7). If the orientational ordering of the liquid crystalline solvent impedes the conformational interconversions, increasing the barrier to such an extent that conformational dynamics become rate determining, then the rate constant for triplet decay will be a direct reflection of the extent to which the ordered solvent impedes this process. If conformational motions are not rate determining, then the observed rate of triplet decay can be expressed as in Equation 4.1 (when $k_\beta \ll k_{con}$-1), where k_d^0 is the rate of carbonyl triplet decay by processes other than β-phenyl quenching, k_{con} and k_{con}-1 are the rate constants reflecting the equilibrium between quenching and non-quenching conformers, and k_β is the rate constant for intramolecular triplet quenching.

4.3.4   Role of Solvent Ordering on the Triplet Decay Rate
of the Alkoxy Substituted Derivatives 1, 6, and 7.

The triplet lifetimes of the ethoxy (6) and the propoxy (7) derivatives of 1 are apparently less effected by the smectic phase environments of CCH-4 and CCH-502 than is 1 (see Tables 4.2 and 4.3). In smectic CCH-502, there is essentially no variation in the triplet lifetimes as the alkoxy substituent is changed in length from methyl to propyl, in
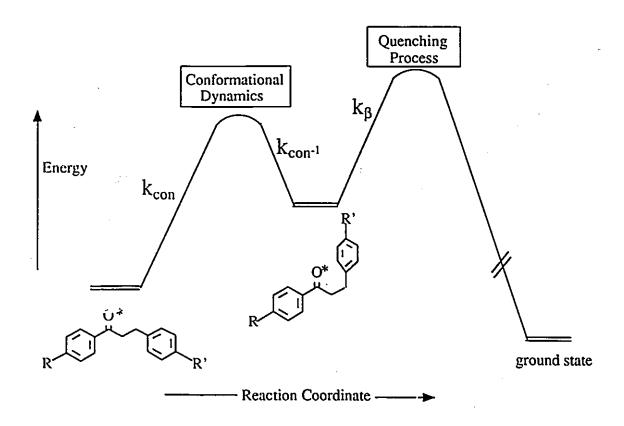
Figure 4.7. Reaction coordinate diagram illustrating the key steps involved in the intramolecular β-phenyl quenching process in solution. Energy differences are only for illustration and are not absolute.

$$k_{decay} = k_d^0 + (k_{con}/k_{con\text{-}1})\ k_\beta = k_d0 + K^{con}\ k_\beta \qquad \text{[Eq. 4.1]}$$

spite of the fact that the lifetimes in non-viscous isotropic and isotropic CCH-301 solvents increase regularly throughout the series. The latter effect may be due to a small substituent effect on the energy gap between the π-π^* and the n-π^* triplet states. As the electron donating ability of the alkoxy substituent increases the more it will stabilise the π-π^* state and destabilise the n-π^* state, thereby increasing the energy gap.[61] The fact that the lifetimes of 1, 6, and 7 are virtually identical in the smectic phase of CCH-502 suggests that the effect of the ordered medium on the conformational mobility of the solute in fact decreases as the length of the alkoxy substituent increases. The ^{2}H NMR results for 6 and 7-αd$_2$ suggest that these two solutes are better oriented in the smectic phase of CCH-502 than 1. The apparent anomaly is undoubtedly the result of the different timescales which the two techniques probe. The decrease in the ability of the smectic phase to impede solute conformational mobility as the length of the alkoxy chain increases is more apparent in smectic CCH-4, where the ordered environment has a greater effect on the mobility of these solutes in the smectic phase. Even though there is a dramatic slowing of the rate of triplet quenching for 6 and 7 in the smectic phase of CCH-4 compared to the nematic phase, the magnitude of the difference between the two phase types decreases as the length of the alkoxy substituent is increased. Since the β-phenyl portion of these solutes are identical, the observed effects in CCH-502 and CCH-4 could be due to an increased disruption of the local solvent order around the solutes with increasing alkoxy chain length.

4.3.5   Effect of Smectic Phase Ordering on the Triplet Decay of the β-Aryl Substituted Derivatives 2-5

The results for 2-5 in aprotic isotropic solvents are mirrored in the isotropic phase of CCH-301, where the lifetimes are substantially shorter than those observed for 1, 6 and 7 in the same solvent. However, the lifetimes of 2-5 (as are those of 6 and 7) are extended by a factor of two compared to those observed in acetonitrile. Since these solvents are not expected to exert an appreciable effect on the π-π^* - n-π^* energy gap, the decrease in the quenching rate constants are a measure of the degree to which the conformational motions involved in achieving the quenching geometry are slowed. This is most likely to be the result of solvent viscosity affecting the equilibrium between the quenching and non-quenching conformers prior to rate determining β-phenyl quenching, rather than a change in the rate determining step. If conformational motions became rate determining, a larger variation in the observed lifetimes in CCH-301 might be expected as the size and bulkiness of the β-aryl substituent are increased. As discussed in Chapter 3 the longer triplet lifetimes of 2-7 in the more viscous isotropic solvents are due to a combination of solvent polarity and viscosity effects.

In the smectic phase of CCH-502, the triplet decay rates of 2-5 are slowed substantially compared to those in isotropic CCH-301. The effect is quite dramatic compared to the observed effects for 1, 6, and 7 in the same phase, as is illustrated by the lifetime and k_I/k_{Sm} values given in Table 4.3. These data clearly demonstrate the effectiveness with which the smectic phase impedes intramolecular triplet quenching in these solutes. The magnitude of the effect correlates with the size and structure of the substituent: H (1) < methyl (2) < isopropyl (3) < n-hexyl (4) < cyclohexyl (5).

The effect is particularly large for 5, where the lifetime is extended by 8.5 times in the smectic phase compared to the model isotropic solvent. The effect falls off somewhat for 4 and 3 is the smallest for 2. These observations are consistent with the notion that the β-aryl substituents act in such a way as to anchor the β-phenyl ring, slowing down the conformational motions required to obtain the quenching geometry or altering K^{con} in favour of non-quenching conformers. While the n-hexyl derivative (4) has the longest chain length, its lifetime is not extended to as great a degree as the cyclohexyl derivative (5). Perhaps the latter has the best combination of added length and rigidity to maximize the effect of the liquid crystalline matrix on β-phenyl quenching. In addition, the structure of the cyclohexyl substituent may facilitate solubilisation of the probe in the bicyclohexyl derivatised liquid crystal. The smectic phase of CCH-502 is found to have a similar effect on the triplet lifetime of 4 as it does on the shorter yet more rigid 3. In 4 the longer, more flexible chain may act in a way to disrupt the solvent order more than the rigid groups, considering the conformational motions available to the flexible chain compared to the more rigid substituents. Alternatively, the lengthening of the triplet lifetimes as the β-phenyl substituent is altered may be the result of the β-aryl moiety having a different preferred orientation in the smectic phase compared to the unsubstituted analogues. In the former cases, the overall effect of the smectic phase would essentially be the same (*i.e.* slowing the conformation motions required to achieve the quenching geometry), but the magnitude and type of conformational change required may be much different.

The trend in the rate of triplet decay observed for 1-7 in the smectic phase of CCH-502 also appears to be present in the smectic phase of CCH-4 although it is not well defined. The lifetimes of 3 and 5 at 30°C in CCH-4 are greater than that measured for 1,

consistent with our conclusions for CCH-502. However, the true magnitude of the effect
is not known for 3 and 5, since the lifetimes are measured under conditions where the
solutes are not homogeneously solubilised in smectic phase solutions. The fact that the
lifetime for 5 is less than that of 3 is presumably a result of the relative proportion of the
smectic phase component being lower for 5 than for 3 due to differences in the solubilities.
However the increase in length and rigidity in the β-aryl ring seems to have similar effects
on the magnitude of the change in lifetimes in the two smectic phases.

What is the Rate-Determining Step in the Smectic Phases?

The magnitude of the effect for 2 in smectic CCH-4 and smectic CCH-502 is
particularly interesting. The lifetime of 2 in the smectic phases of both mesogens is
roughly three times greater than that observed in the corresponding viscous isotropic or
nematic phases (Tables 4.2 and 4.3). However, in either of the two smectic phases the
decay rate of 2 is at least two times faster than 1 in the same phase. Since these two
derivatives are the least different in terms of size and shape, they may be expected to
experience only minor differences in the nature of their solubilisation within the smectic
phase matrices. Therefore, the lifetime data indicates that in the smectic phase of both
mesogens, *trans-gauche* interconversions involved in the conformational dynamics step,
outlined in Equation 4.1, are <u>not</u> **the rate determining step** for β-aryl quenching in either
1 or 2. If conformational motions were rate determining in these phases, one would
expect the lifetime of 2 to be the same or perhaps even greater than that measured for 1
under the same conditions. By similar arguments, the lifetimes of 8 and 1 might also be
expected to be the same in the smectic phases, if conformational motions were rate

determining for **1**; the triplet lifetime of **8** is at least ten times shorter than that of **1**. However, ^{2}H NMR experiments indicate that there are fundamental differences in the solubilisation of **1** and **8** in the smectic phases, so conclusions based on their relative triplet state behaviour should be viewed with caution.

The results do show that conformational control is an important factor in the rate of decay of the ketone triplets in the smectic phase. However, the effect of the smectic phase on the triplet lifetime of **1-7** is due to an <u>alteration of the equilibrium constant</u> for population of the quenching and non-quenching conformers *prior* to rate determining β-aryl quenching. The increased triplet lifetimes are due to the smectic phase lattices favouring the structurally more compatible, non-quenching conformers. We interpret the variation in k_I/k_{Sm} that occurs throughout the series **1-7** as due almost entirely to substituent effects on the equilibrium constant, k_{con}/k_{con}-1, for formation of the conformer required for triplet deactivation. By our interpretation $k_I/k_{Sm} = K^{con(I)}/K^{con(Sm)}$ if k_β^{Sm} equals k_β^I. As we have already mentioned, increasing the length of the alkoxy-substituents disrupts the environment around the solute, increasing K^{con}. β-Aryl substituents act in such a way so as to anchor the β-phenyl ring thereby decreasing K^{con}. It is interesting that the small change in solute size in going from **1** to **2** has as substantial an effect on K^{con} as it does. As the substituent becomes larger and more rigid, the greater the observed effect on the triplet lifetime. It is conceivable that if the β-aryl ring becomes increasingly immobilised with other substituents the rate determining step may change to that involving conformational motions. We do not believe this to be the case for the solutes studied here.

In CCH-4, the magnitude of the effect of the smectic phase on the lifetimes of **1** and **2** (given by k_N/k_{Sm}) are essentially the same. This suggests that the factors

responsible for the extended lifetimes are the same for both solutes. This is consistent with the highly ordered smectic phase of CCH-4 having a similar effect on the equilibrium constant between the conformer populations for both 1 and 2. Compounds 1 and 2 are therefore believed to be solubilised similarly in the Cr_B phase, with similar restrictions to motion.

4.3.6   Discussion of Observed Activation Parameters

The activation parameters for triplet decay of 6 and 7 in the smectic phase of CCH-4 are very similar to those measured for 1 in the same phase. The activation energies for 2-7 in CCH-502 are all lower than those obtained in CCH-4, and the entropies are all higher, a further reflection of the lesser degree of order associated with the smectic phase of CCH-502. The activation parameters for 6 and 7 in CCH-502 do not vary significantly from those for 1, or from those measured for 1, 6, and 7 in CCH-301 or acetonitrile solution. This is not unexpected, considering the relatively small differences between the rates of decay of these three solutes in CCH-502 and the isotropic phases. For ketones 2-5 in the smectic phase of CCH-502, the activation energies (E_a) increase regularly throughout the series and are higher than those of ketones unsubstituted on the β-phenyl ring. This is consistent with the increased bulkiness of these substituents impeding the mobility of the β-aryl ring. However, the increases in activation parameters in the smectic phases are paralleled in isotropic CCH-301 and thus approximately phase independent.

Based on our interpretation of the manner in which the smectic phase alters the triplet lifetimes of these probes, the observed Arrhenius behaviour of 1 and 2-7 in the

various smectic phases can be explained. Fairly small changes in the ΔG^{con} value for the conformational equilibrium (of a kcal/mol or less) can easily account for the observed variations in the triplet lifetimes of 1-7 and rather small variations in the Arrhenius parameters in the smectic phases. These changes are presumably due to a combination of enthalpic and entropic factors.

Analysis of the differences between the activation parameters in smectic CCH-502 and isotropic CCH-301 for the probe ketones is rather intriguing. The indication from the data is that the main factor in increasing the lifetime of 1-7 in the smectic phases is entropic in nature. For 2-7 in smectic CCH-502 the $\Delta S^{\neq}$ values are more negative than in isotropic CCH-301. The slightly negative $\Delta(\Delta S)^{\neq}$'s are quite unusual. In general, reactions in liquid crystals are characterised by more positive entropy factors compared to isotropic solvents (*vide supra*).[41c,45b,52c,54] This is the result of the increased disorder to the liquid crystalline matrix that must be induced for the well ordered probes to achieve a disruptive transition state. The overall reaction entropy ($\Delta S^{\neq}$) determined from the triplet decay rate data can be approximated as the sum of the entropy terms (ΔS^{con} + ΔS^{β}) from the two steps in the quenching process defined in Figure 4.7. The process defined by k_{β} will have a negative contribution to $\Delta S^{\neq}$, and ΔS^{con} will have a positive contribution to $\Delta S^{\neq}$ (*vide supra*). If we assume that in the liquid crystalline phases the quenching process (k_{β}) is phase independent (*i.e.* $\Delta(\Delta S)^{\beta} = 0$) then any variations in $\Delta S^{\neq}$ between the two phase types must arise from differences in ΔS^{con} . If the $\Delta(\Delta S)^{\neq}$ values in our system are real, then it may suggest that as we add substituents to the β-phenyl ring that increase its size and rigidity the solvent matrix prefers the more ordered elongated quenching conformer to a greater extent than for the unsubstituted analog. This interpretation is purely tentative however, considering the narrow temperature range over

which the activation parameters were obtained and considering the differences in the $\Delta S^{\neq}$ terms are only on the order of 1-8 calmol^{-1}K^{-1}.

4.4   Summary   •

The solubilities of β-aryl-4-alkoxypropiophenones in the smectic B phase of CCH-502 have been found to be relatively independent of the size of the alkoxy or aryl substituent. In contrast, the Cr_B phase of CCH-4 is more sensitive to the size of the solute, with the solubilities decreasing as the length of the probe increased. This result is a reflection of the higher degree of order associated with the Cr_B phase in comparison to a Sm_B mesophase.

As was observed for 1 in the smectic phases of CCH-n, OS-nm, and CCH-nOm mesogens, the solubilisation of 2-7 in CCH-502 and CCH-4 results in enhanced triplet lifetimes in the smectic phases compared to model nematic or isotropic phases. The magnitude of the enhancement has been determined to be a function of substituent, with the largest effects being observed for derivatives with large, rigid substituents on the β-aryl ring. Lengthening the alkoxy portion of the probe was found to have a deleterious effect on the restrictions to mobility of the solute in the smectic phases. For 2-7, as homogeneous smectic phase solutions, little variation in the activation parameters for triplet decay between the smectic and nematic/isotropic phase types was observed. The similarities between the results with these solutes with those obtained for 1, described in Chapter 3, lead us to conclude that the nature of the effect that the orientational ordering of the smectic phases has on the conformational mobility are the same for all solutes investigated.

We have proposed that, as in the case in isotropic phases, the rate determining step for intramolecular triplet deactivation of *para*-alkoxy β-arylpropiophenones in the smectic phases is the β-phenyl quenching process, and not conformational dynamics. The increased lifetimes observed in the more highly ordered phases have been attributed to these phases altering the equilibrium between quenching and non-quenching conformers in favour of the non-quenching conformers. The latter is suggested to be the preferred geometry for solubilisation in the smectic phase matrices.

CHAPTER 5

Contributions of Our Studies

The majority of the studies involving solutes in liquid crystalline solvents have been aimed at defining their potential at altering the chemical reactivity of dissolved solutes. If these microenvironments are to emerge as important media to synthetic and mechanistic chemists, more specific information on the nature of solute/solvent interactions is required. To this end, the present work was aimed at investigating the solubilisation and photochemical behaviour of two probe systems in a series of similar smectic mesogens. Many of the important contributions this work has provided to those involved in liquid crystalline research have been summarised at the end of each chapter. This chapter summarises in more general terms the conclusions that can be drawn from our work with regards to solute/liquid crystal interactions. The knowledge gained in this study will have important ramifications to all researchers who employ liquid crystals as reaction solvents.

One important consequence of this thesis is the development of the use of deuterium NMR as a technique for the identification of phase separation in solute/liquid crystal mixtures and for the construction of the binary phase diagrams of these mixtures. The NMR method allows such analyses in cases where the more widely-used techniques (D.S.C., thermal microscopy) fail. We have explored the solubility properties of several labelled phenyl ketones in the smectic phases of various liquid crystalline compounds and shown that in many cases even extremely low concentrations of solutes can grossly

perturb the phase behaviour of such media. Through careful analysis of the results from the ^{2}H NMR studies we have accumulated a knowledge base of spectral characteristics that have enabled us to establish an experimental regimen for the determination of the homogeneity of solute/mesophase solutions. While the technique has been developed using a limited number of deuterated probes in a single mesogen (CCH-4) the extension to the OS-nm and CCH-nOm families of mesogens has illustrated that the interesting solubility properties observed for solutes in CCH-4 are the *rule* rather than the *exception*.

Results of the variable concentration studies of the photochemistry of solutes in the smectic mesogens, which have been performed in conjunction with the deuterium NMR work, have illustrated the extent to which ignorance of basic solubility behaviour can lead to **misinterpretation** and **underestimation** of the magnitude of the effects of liquid crystals on chemical reactivity. A few examples have been discussed to illustrate the far reaching implications which our investigations have on a number of recent studies of this type. Undoubtedly, the technique developed here, using phenyl ketones, can be extended to any solute provided the probe can be deuterated conveniently. In fact, we believe that deuterium NMR techniques analogous to those established here may become invaluable in defining homogeneity in other microenvironments.

Deuterium NMR studies of selectively labelled probes also provides qualitative information on the mobility of the solutes in the smectic phases. The degree of order experienced by the probe is a function of the rigidity of the phase type as well as the size and structure of the solute in relation to those of the mesogen. Unfortunately, only qualitative comparisons can be made between these types of NMR studies and the photochemistry of the probe solutes since the two techniques investigate the effects of liquid crystalline order on quite different motions over different timescales. Quantitative

information on solute dynamics can be obtained from relaxation time measurements, but again, the motions and timescales over which they occur may be different than those probed in the photochemical reactions.

Intramolecular ketone photochemistry has been shown to be a useful probe for the investigation of the properties of highly ordered mesogenic phases with respect to their effects on the conformational mobility of dissolved solutes. The Norrish II reaction of simple alkanophenones is limited in its ability to provide details of liquid crystalline effects on solute conformational mobility. However, results reported in this thesis do indicate, contrary to previous belief, that reactions which involve even very minor changes in shape are *potentially* alterable by smectic liquid crystalline order. The results may indicate that substituents chosen so as to maximise the shape changes that accompany a particular reaction may in fact have a detrimental effect on the ability of the smectic matrix to effectively pack the solute. Thus, smaller probes may be more effectively immobilised in the more highly ordered phases, resulting in surprisingly large effects on reactivity.

Intramolecular triplet quenching in β-arylpropiophenones is a much more informative probe of conformational mobility in liquid crystals since rate constants for conformation-dependent processes can be measured directly. By comparison to data in model solvents a measure of the magnitude of the effect which smectic phases have on the kinetics and energetics of this reaction has been obtained. The results for the parent ketone in the three families of mesogens indicate that the ability of smectic phases to affect the conformational mobility of this probe is quite general. Differences in the magnitude of the effect vary as a function of the degree of order inherent in the smectic phase. This study represents the first to provide such detailed comparisons of the effects

of different smectic phases on solute reactivity.

Unfortunately, the complexities added by the π-π^* nature of the lowest triplet excited state of *para*-methoxy-β-phenyl ketones hinder the interpretation of the photochemistry of these probes in ordered media. On the basis of substituent effect studies, it has been determined that the role of the smectic phases in extending the triplet lifetimes of these probes lies in their ability to alter the equilibrium distribution of quenching and non-quenching conformers in favour of the latter. The effectiveness with which smectic phases do this increases as the size of the substituent on the β-ring increased. Further studies should involve derivatives of the n-π^* analogs where conformational motions are thought to comprise the rate determining step for triplet decay. Such studies, if feasible, might provide a better indication of the extent to which the energetics of the molecular contortions involved in the quenching process can be effected by the ordered environment.

The effect of nematic phases on the conformational mobility of the photochemical probes was found to be quite small and is most likely the result of microviscosity effects. Not surprisingly, smectic phases exhibit the more dramatic results. The more highly ordered Cr_B class of smectic liquid crystals (exhibited by CCH-4 and OS-nm) provide substantial restrictions even to both small and medium-amplitude conformational motions. Unfortunately, the solubility limits of solutes in these phases are generally low, limiting the usefulness of these mesogens in further studies of this type. The less ordered Sm_B phases (*e.g.* CCH-502) exhibit higher solvating power, but exert weaker control on solute reactivity. Nevertheless, they are probably the most generally useful as reaction solvents and should be the focus of future studies.

Considering the continuing growth in the area of liquid crystal technology,

research involving solute/mesogen mixtures will remain a discipline of key importance. If the highly ordered phases of liquid crystals are to be utilised to affect the chemical reactivity of dissolved solutes in a predictable way, much more needs to be learned about the subtle ways these materials solubilise and restrict the motions of dissolved solutes. This thesis has established the groundwork that will aid in the success and development of future studies aimed at utilising liquid crystals as reaction media for organic reactions.

CHAPTER 6

EXPERIMENTAL

6.1   General

^{1}H NMR spectra were recorded on Varian EM390 (90MHz) or Bruker AC200
(200 MHz) spectrometers in deuteriochloroform solution, and are reported in parts per
million downfield from tetramethylsilane. ^{13}C NMR spectra were recorded on a Bruker
AC200 (50.3 MHz) spectrometer and are reported downfield from tetramethylsilane.
Ultraviolet absorption spectra were recorded on a Hewlett-Packard HP8451 UV
spectrometer or a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 Data
Station. Mass spectra and exact masses were recorded on a VG Analytical ZABE mass
spectrometer; the latter employed a mass of 12.000000 for carbon. Infrared spectra were
recorded on a Perkin-Elmer 283 spectrometer or a Biorad FTS-40 FTIR spectrometer and
are reported in wavenumbers (cm^{-1}) calibrated using the 1601.8 cm^{-1} polystyrene
absorption. Melting points and transition temperatures were determined on a hot stage
microscope with a Cole-Parmer Model 8110-10 Type K thermocouple or a Mettler FP82
hot stage controlled by a Mettler FP80 Central Processor, mounted on an Olympus BH-2
polarizing microscope and are not corrected.

Gas chromatographic analyses employed a Hewlett-Packard 5890 gas
chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396
recording integrator, and one of the following fused silica megabore capillary columns: a)

10m × 0.53mm HP-FFAP; Hewlett-Packard, Inc., b) 30m x 0.53mm DB-1;

Chromatographic Specialties, c) 10m x 0.53mm HP-17; Hewlett-Packard, Inc.

Semi-preparative gc separations employed a Hewlett-Packard 5750B gas chromatograph

equipped with a thermal conductivity detector and a 10% FFAP on 80/100 Supelcoport

(10ft × 1/4in.) stainless steel column.

Semi-empirical dihedral angle calculations were carried out on a PCMODEL4

(Serena Software) generated model of 1 using the general purpose molecular orbital

computational package AMPAC (AM1).[140] Energies were obtained by fixing the dihedral

angle and minimising the rest of the structure. Dihedral angles were incremented by 10°

with the minimisation starting from the minimised structure of the previous dihedral angle.

All energies are for the ground state molecule.

6.2   NMR in Liquid Crystalline Solvents

Carbon 13 NMR Spectroscopy: ^{13}C NMR spectra in CCH-4 as solvent were

recorded at 30°C on the Bruker AM500 spectrometer (125.7 MHz), and are the average of

200,000 scans (0.3 s delay between scans).

Deuterium NMR Spectroscopy:

^2H NMR experiments were carried out at 76.78 MHz on a Bruker AM500

NMR spectrometer equipped with an Aspect 3000 computer, a Bruker BVT-100 Variable

Temperature Unit, and a 10 mm VSP broadband probe, or at 41.3 MHz on a home-built

NMR spectrometer that has been described in detail previously.[97] Temperatures were

controllable to within ±0.2°, and were calibrated (76.78 MHz) or determined (41.3 MHz)

with a copper-constantan thermocouple. In the 41.3 MHz spectrometer, the thermocouple is attached to a copper can surrounding the sample. Samples for the 76.78 MHz spectrometer were prepared in 5 mm NMR tubes by adding the appropriate amounts of solute and liquid crystal and heating to the isotropic phase to ensure complete sample mixing. The sample and probe were allowed to equilibrate at each temperature for 5-20 min. prior to recording the spectrum. Spectra were recorded on stationary samples using the quadrupolar echo pulse sequence,[93,94] collecting 16K data points per scan over a 100-170 kHz (typically 150) sweep width. Depending on bulk solute concentration and temperature, 96-16000 such scans were collected (with a 0.2-0.4 sec. delay between scans) and averaged. The $\pi/2$ pulse width was determined by trial-and-error prior to each set of experiments using a $CDCl_3(10\%)/CHCl_3$ solution. The data were processed using 80-100 Hz line-broadening and exponential multiplication prior to obtaining the Fourier transform.

Samples for the 41.3 MHz spectrometer were prepared similarly and sealed in 9 mm Pyrex tubes. Spectra were recorded as above, collecting 2K data points per scan (4K total) over a 200-500 kHz (typically 200; 500 at lower temperatures) sweep width, and with a 1 sec delay between scans. The $\pi/2$ pulse width is 3 μs on this spectrometer.

6.3   Nanosecond Laser Flash Photolysis Experiments

Nanosecond laser flash photolysis experiments employed the pulses from a Lumonics TE-861M excimer laser filled with $Xe/HCl/H_2/He$ (308 nm, 15 ns, *ca. 40 mJ*) or N_2/He (337 nm, 6 ns, ca. *4 mJ*) mixtures. The detection system, which is computer controlled, has been described recently.[133] The sample compartment was surrounded by

an insulated quartz sleeve, through which heated nitrogen was passed in order to heat the sample. Sample temperatures were measured using a copper-constantan thermocouple or a Cole-Parmer Type K digital thermocouple thermometer and are accurate to $\pm 0.1^{\circ}C$. The · samples were allowed to equilibrate at each temperature for at least 20 minutes prior to recording the decay trace.

Sample Preparation: Samples in liquid crystals were contained in 3 x 7 mm or 0.7 x 7 mm cells constructed from rectangular Suprasil quartz or Pyrex tubing, respectively (Vitro Dynamics). Except for the low concentration samples in CCH-2, they were prepared by weighing out the appropriate amount of solute and liquid crystal and heating to the isotropic phase to ensure complete sample mixing. Samples of composition < 0.1 mol% were prepared by adding an aliquot of a standard solution of 1 in dichloromethane to the appropriate amount of liquid crystal. The mixture was dissolved completely in dichloromethane and the solvent was removed on a rotary evaporator and then pumped under high vacuum (ca. 10^{-4} Torr) for several hours. Samples of 1 at 1 mol% or greater were contained in cells with a pathlength of 0.7 mm, while all others were contained in 3 mm path length cells. In all cases the samples were degassed with at least five freeze-pump-thaw cycles and sealed on a vacuum line. Samples in CCH-4 and OS-nm were annealed for several days at $38^{\circ}C$, which produced homeotropically aligned samples.

Samples in solution were placed in 7 x 7mm quartz cells, sealed with a septum, and purged with dry nitrogen prior to use.

6.4   Commercial Solvents and Reagents Used

Dichloromethane (Caledon; HPLC grade), methanol (Baker; HPLC grade),
cyclohexane (Baker; Photrex), *tert*-butyl alcohol (BDH; reagent), tetrahydrofuran (Baker;
HPLC grade), diethyl ether (Fischer; dry reagent), ethyl acetate (Caledon; HPLC grade),
dioxane (Caledon; reagent), ethanol (absolute and 95%), and pentane (Baker Photrex)
were all used as received from the suppliers. Benzene (Caledon and BDH; reagent) was
purified by extraction with concentrated sulfuric acid followed by distillation. Carbon
disulphide was distilled from P_2O_5. Acetonitrile (Caledon; HPLC grade) was dried over
calcium hydride and distilled under nitrogen. Acetone (BDH; reagent) was dried over
anhydrous potassium carbonate and distilled.

Acetophenone, propiophenone, butyrophenone, valerophenone (all 99+ %),
4-methoxyacetophenone, 4-hydroxyacetophenone, Raney Nickel, benzaldehyde,
para-isopropyl benzaldehyde, *para*-hexyl benzaldehyde, iodomethane-d_3,
bromobenzene-d_5, iodopropane, iodoethane-d_5, iodoethane, N-formylmorpholine,
hydrocinnamic acid, and anisole were used as received from Aldrich Chemical Co..
Benzene-d_6 (MSD Isotopes), D_2O (MSD Isotopes), *para*-methylbenzaldehyde (Matheson),
butyric acid (Matheson), valeric acid, thionyl chloride, aluminum trichloride (Fischer),
iodomethane (BDH), acetyl chloride, n-hexanoyl chloride (MCB), propanoyl chloride,
phenol (BDH) were all used as received from the suppliers.

CCH-4, CCH-3, CCH-2, OS-35, OS-53, CCH-502, CCH-301, and CCH-303,
from E. Merck Co. (Darmstadt, Germany) were used as received. For some experiments
CCH-2 and CCH-4 were recrystallised from pentane (Photrex).

6.5   Norrish Type II Study in CCH-n

6.5.1   Preparation of Compounds

n-Hexanophenone was prepared by Friedel-Crafts acylation of benzene with

n-hexanoyl chloride and aluminum chloride, and had b.p. = 75°C (0.75 mm) (lit. = 265°C

(760 mm)[149]). The α-deuterated ketones (AP-d_3 and PP-HP-αd_2) were prepared from

their protio-analogues by base-catalysed deuterium exchange and were shown to be >90%

α-deuterated by ^{1}H NMR (Varian EM390; CDCl$_3$). The ring-deuterated analogues

(AP-HP-d_5) were prepared by Friedel-Crafts acylation of benzene-d_6 (MSD Isotopes)

with the appropriate acid chloride and aluminum chloride.[150] In some cases the acid

chloride had to be prepared from the carboxylic acid using thionyl chloride.[150] All

ketones were purified by repeated vacuum distillation after workup. All deuterated

ketones were >99 % pure by vpc analysis and were identified by NMR and mass

spectroscopy by comparison to their parent compound.

6.5.2   Irradiation Procedures and Product Analysis

Solutions of ketone of 0.1 M concentration in the standard isotopic solvents

were prepared and placed in 5 mm OD quartz tubes and purged with nitrogen. Samples

were irradiated in a Rayonet reactor with 313 nm mercury lamps or in a "merry-go round

apparatus" with a filtered (aqueous K$_2$CrO$_4$ / Na$_2$CO$_3$ / Pyrex: 312 ± 10 nm) 450 W

medium pressure mercury lamp, contained in a water cooled, quartz immersion well. Samples were taken to 5-20% conversion and analysed by vpc.

Samples of the ketones in CCH-4, EB, or EC for photolysis experiments were prepared by weighing the appropriate amount of ketone and mesogen (*ca.* 150 mg total) into a 5 mm OD quartz tube that was then sealed with a rubber septum. The samples were heated to the isotropic phase and deoxygenated with dry nitrogen for 5-10 min., and then further sealed with Parafilm. The samples were irradiated in a thermostated water bath (30°C), using the "merry-go round" set-up described above, to 5-20 % conversion. The tubes were opened, the contents were dissolved in methylene chloride, and then analysed by vpc. In some control experiments samples were taken to higher conversion to see how product ratios varied as a function of percentage conversion.

Primary identification of products was done by vpc analysis of the ketones in the standard isotropic solvents. Besides starting material, the only other components in the mixture were assigned to acetophenone (verified by co-injection of an authentic sample) and the cyclobutanols. In the cases where there are isomeric cyclobutanols the signal with the larger area was taken as the *trans* isomer since the reported *t/c* ratio is always greater than one in the solvents used.[58-61] For CHBP vpc analysis employed column (b) and under the conditions the cyclobutanols eluted just before the starting material and the *trans* isomer had the longer retention time. Analysis of the mixtures of BP, VP, and HP employed column (a) and under the conditions used, the cyclobutanols eluted after the parent ketone with the *trans* isomer having the shorter retention time.

Identification of the cyclobutanols from photolysis of BP, VP, and HP were explicitly identified by vpc isolation of the products from semi-preparative scale photolysis of the ketones in deoxygenated methanol to > 90 % conversion. The

identification of the two isomers was done on the basis of their IR (OH stretches at 3400-3600 cm^{-1}), mass spectra (characteristic M-18, M-28 and m/e 120 peaks of 1-phenylcyclobutanols), and ^{1}H NMR.[61] The isomeric cyclobutanols from **VP** were identified on the basis of the chemical shift of the doublet due to the methyl group. That of the *trans* isomer occurs at δ 1.18 and that of the *cis* is upfield at δ 0.6 (CDCl$_3$), due to the methyl being held in the shielding region of the neighbouring phenyl ring. The isomeric cyclobutanols for **HP** were identified in a similar manner based on the chemical shift of triplet of the methyl group (of the ethyl substituent) which is also effected by the shielding region of the phenyl group.

The fragmentation/cyclisation and *trans/cis*-cyclobutanol ratios reported in Tables 2.4 and 2.5 are the average of at least two runs with analyses carried out in triplicate. The flame ionization detector was not calibrated for differences in response to the various products and starting material.

6.6   Alkoxy-β-Aryl-Propiophenones

6.6.1   Preparation of Compounds

The β-phenyl ketones **1-5** were either available from a previous studies or were prepared by condensing equimolar amounts of 4-methoxyacetophenone with the appropriate alkyl-benzaldehyde and NaOH in ethanol/H$_2$O and refluxing,[151] followed by hydrogenation of the resulting chalcone derivative over Raney Nickel in nitrogen purged ethyl acetate. Condensing 4-hydroxy-acetophenone with benzaldehyde, in a similar manner (2 equivalents of base),[152] and hydrogenating the resulting chalcone over Raney

nickel in 10 % sodium hydroxide, yielded 4-hydroxy-3-phenylpropiophenone. The β-phenyl ketone 4-hydroxy-3-phenylpropiophenone was used in the preparation of **6** and **7** by alkylation with iodoethane or iodopropane and potassium carbonate in refluxing acetone.[153] The compounds 4-hydroxy-(4'-cyclohexyl)-3-phenylpropiophenone, 4-hydroxy-(4'-n-hexyl)-3-phenylpropiophenone were prepared in earlier studies.[85]

β-Phenyl propiophenone (**8**) was prepared in a similar fashion to **1** using acetophenone and benzaldehyde to yield chalcone and then hydrogenating with Raney Nickel as described above. β-Phenylbutyrophenone (**9**) was prepared in an analogous manner to **1** except acetophenone was self-condensed using $AlCl_3$[154a] to yield dypnone, which was then hydrogenated. Compound **10** (4-methoxy-β-phenylbutyrophenone) was prepared from 3-phenyl-butanyl chloride (prepared from the corresponding carboxylic acid) and anisole using a Friedel-Crafts reaction procedure.[146]

Physical and spectral data for the ketones used in this study are listed below:

4-Methoxy-3-phenylpropiophenone (**1**) was recrystallised twice from ethanol/H_2O, m.p. 95-97°C (ref. 96-97[85]); Spectral data agreed with those reported. ^{1}H NMR (CDCl$_3$) δ (ppm): 3.0-3.1 (m, 2H), 3.20-3.30 (m, 2H), 3.86 (s, 3H), 6.92 (d, 2H), 7.16-7.34 (m, 5H), 7.94 (d, 2H); ^{13}C NMR (CDCl$_3$) δ: 30.3, 40.1, 55.4, 113.7, 126.0, 128.4, 128.5, 129.9, 130.3, 141.4, 163.4, 197.8. Exact mass calculated for $C_{16}H_{16}O_2$, 240.1150; found 240.1155.

4-Methoxy-(4'-methyl)-3-phenylpropiophenone (**2**) was recrystallised twice from ethanol and water, m.p.=63.5-65°C (ref. 64-66°C[146]). ^{1}H NMR and ^{13}C NMR data agreed with those recently described.[146] Exact mass: calc. for $C_{17}H_{18}O_2$, 254.1307; found, 254.1297.

4-Methoxy-(4'-isopropyl)-3-phenylpropiophenone (**3**) was recrystallised twice

from ethanol and water, m.p.43.5-45°C. ^{1}H NMR spectrum δ (ppm): 1.23 (d, 6H), 2.87 (sept., 1H), 3.0 (m, 2H), 3.2 (m, 2H), 3.85 (s, 3H), 6.9 (d, 2H), 7.2 (d,d, 4H), 7.9 (, 2H). ^{13}C (CDCl$_3$): δ 24.0, 29.9, 33.7, 40.2, 55.4, 113.7, 126.5, 128.3, 129.0, 130.3, 138.7, 146.6, 163.4, 197.9. IR (CCl$_4$) 3009 (w), 2952(s) 2840 (w), 1683 (s), 1604 (m), 1460 (w), 1361 (w), 1309 (w), 1171 (s), 1036 (m); Exact mass calc. for C$_{19}$H$_{22}$O$_2$, 282.1620; found, 282.1624.

4-Methoxy-(4'-n-hexyl)-3-phenylpropiophenone (4), m.p. 56-57°C, *4-methoxy-(4'-cyclohexyl)-3-phenylpropiophenone* (5), m.p. 89-90°C, and *4-propoxy-3-phenylpropiophenone* (7), m.p. 43.5-45°C were prepared in previous studies.[85]

4-Ethoxy-3-phenylpropiophenone (6) was recrystallised from ethanol and water, m.p. 41.7-43°C. ^{1}H NMR (CDCl$_3$) δ ppm: 1.42 (t, 3H), 3.02 (m, 2H), 3.2 (m, 2H), 4.07 (q, 2H), 6.88 (d, 2H), 7.24 (m, 5H), 7.91 (d, 2H). Exact mass calculated for C$_{17}$H$_{18}$O$_2$ 254.1302; found, 254.1307.

3-Phenyl-propiophnone (8) was recrystallised form methanol, m.p. 69-70°C (ref. 72-73°C[155]). ^{1}H NMR (CDCl$_3$) δ ppm: 3.07 (t, 2H), 3.31 (t, 2H), 7.20- 7.30 (m, 5H), 7.42-7.56 (m, 3H), 7.95 (d, 2H). Mass spectroscopy agreed with those previously reported.[155]

3-Phenylbutyrophenone (9) was recrystallised from methanol 3 times, m.p. 69.5-71°C (lit. 70-72°C).[154] ^{1}H NMR (CDCl$_3$) δ ppm: 1.32 (d, 3H), 3.10-3.27 (m, 2H), 3.44-3.52 (m. 1H), 7.16-7.28 (m, 5H), 7.33-7.58 (m, 3H), 7.90-7.94 (d, 2H). Mass spectroscopy and IR (KBr) agreed with those previously reported.[154b]

4-Methoxy- 3-phenylbutyrophenone (10), was recrystallised from ethanol/H$_2$O, m.p. 86-87°C (ref. 86.5-87°C[146]). ^{1}H NMR and mass spectroscopy agreed with those recently described for 10.[146]

6.6.2   Preparation of Deuterated Compounds

The α-deuterated analogs (1-9-αd₂) were prepared from their protio analogs using NaOH and D_2O in refluxing dioxane. The ketones were then recrystallised and identified by ¹H NMR, mass spectroscopy and melting points, in comparison with the parent compounds. In all cases deuterium incorporation was greater than 90% in the α-position.

The methoxy deuterated compounds (1, 4, and 5-Od₃) and the ethoxy deuterated compound (6-Od₅) were prepared from the corresponding 4-hydroxy--3-arylpropiophenone and iodomethane-d₃ or iodoethane-d₅ with K_2CO_3 in refluxing acetone.

Physical and spectral data for the alkoxy deuterated compounds are listed below:

4-(Methoxy-d₃)-3-phenylpropiophenone (1-Od₃) was recrystallised form ethanol/H₂O, m.p. 93.8-95°C. ¹H NMR was as described for 1 except the singlet at 3.86 was absent. ²H NMR (ref. $CDCl_3$) δ ppm: 3.86. IR (KBr): 3064 (w), 3026 (w), 2953 (w), 2932 (w), 2231 (w), 2077 (w), 1670 (s), 1602 (s), 1574 (m), 1506 (m), 1492 (m), 1309 (m), 1270 (s), 1211 (m), 1180 (m), 1104 (s). Mass spectra *m/z* (%): 243 (28, M⁺), 139 (10), 138 (100), 92 (10), 78 (10). Mass calc. for $C_{16}H_{13}O_2D_3$, 243.1339; found 243.1346.

4-(Methoxy-d₃)-(4'-hexyl)-3-phenylpropiophenone (4-Od₃) was recrystallised from ethanol/H₂O, m.p. 54-55°C. ¹H NMR ($CDCl_3$) δ ppm: 0.86 (t, 3H), 1.27 (m, 6H), 1.55 (m, 2H), 2.55 (t, 2H), 3.0 (m, 2H), 3.21 (m, 2H), 6.9 (d, 2H), 7.05 (dd, 4H), 7.92 (d, 2H). ²H NMR (ref. $CDCl_3$): δ 3.86. IR (KBr): 3020 (w), 2955 (m), 2922 (s), 2853 (m),

2223 (w), 2072 (w), 1668 (s), 1602 (s), 1576 (m), 1514 (m), 1270 (s), 1105 (s). Mass calc. for $C_{22}H_{25}O_2D_3$ 327.2278; found, 327.2272.

4-(Methoxy-d_3)-(4'-cyclohexyl)-3-phenylpropiophenone (5-Od_3) was recrystallised from ethanol/H$_2$O, m.p. 90-91°C. ^{1}H.NMR (CDCl$_3$) δ ppm: 1.32 (m, 5H), 1.81 (br m, 5H), 2.45 (m, 1H), 3.0 (m, 2H), 3.22 (m, 2H), 6.9 (d, 2H), 7.1 (dd, 4H), 7.92 (d, 2H). ^{2}H NMR (ref. CDCl$_3$): δ 3.85. IR (KBr): 3052 (w), 3023 (w), 2922 (s), 2849 (s), 2219 (m), 2067 (m), 1679 (s), 1606 (s), 1576 (m), 1507 (m), 1423 (m), 1364 (m), 1270 (s), 1104 (s). Mass calc. for $C_{22}H_{23}O_2D_3$, 325.2121; found 325.2130.

4-(Ethoxy-d_5)-3-phenylpropiophenone was recrystallised from ethanol/H$_2$O, m.p. 42-43°C. ^{1}H NMR (CDCl$_3$) δ ppm: 3.08 (m, 2H), 3.27 (m, 2H), 6.92 (d, 2H), 7.29 (s, 5H), 7.96 (d, 2H). ^{2}H NMR (ref. CDCl$_3$): δ 1.47, 4.16. ^{13}C (CDCl$_3$): δ 13.9 (t), 30.3, 40.0, 62.9 (q), 114.1, 126.0, 128.4, 128.5, 129.7, 130.3, 141.5, 162.9, 197.7. IR (KBr): 3065 (w), 3208 (w), 2933 (w), 2236 (m), 2216 (m), 1667 (s), 1602 (s), 1575 (s), 1506 (m), 1408 (m), 1363 (m), 1297 (m), 1264 (s), 1176 (s), 1106 (s). Mass calc. for $C_{17}H_{13}O_2D_5$, 259.1620; found, 259.1611.

4-Methoxy-3-(phenyl-d_5)propiophenone (1-d_5) was prepared by condensing 4-methoxyacetophenone with benzaldehyde-d_5 in a manner similar to as described for **1** above. Benzaldehyde-d_5 was prepared by adding an equimolar amount of N-formylmorpholine in ether to the Grignard reagent prepared from bromobenzene-d_5 at 0°C and stirring for 30 mins.[126] The reaction was than quenched to pH = 2 by 3N HCl and extracted in a normal manner. Work-up yielded a yellow oil which was then purified by distillation. ^{1}H NMR of the purified oil indicated a sharp singlet at 10 ppm. The aldehyde was used immediately to guard against oxidation. Compound 1-βd_5 had the following physical and spectral characteristics: m.p. 95-97°C; ^{1}H NMR: δ (ppm) = 3.04

(m,2H), 3.24 (m, 2H), 3.85 (s, 3H), 6.90 (d, 2H), 7.92 (d, 2H). ^{2}H NMR (ref. CDCl$_3$): δ 7.4. IR (KBr): 3011 (w), 2974 (w), 2913 (w), 2842 (w), 2274 (w), 1670 (s), 1602 (s), 1576 (m), 1507 (m), 1422 (m), 1364 (m), 1260 (s), 1178 (s), 1028 (m). Exact mass: calc. for C$_{16}$H$_{11}$O$_2$D$_5$, 245.1464; Found, 245.1465.

4-Methoxy-3-phenylpropiophenone-d (1-Acd) was prepared from partially phenyl-deuterated anisole and 3-phenyl-propanyl chloride (synthesised from hydrocinnamic acid) by the Friedel-Crafts reaction using AlCl$_3$ in CS$_2$. Anisole was deuterated by the high temperature dilute acid method of Werstiuk and Kadai.[156] Approximately three deuteria were incorporated into each anisole by this method, however the *para* -deuteria is subsequently lost in the preparation of 1-Acd. 1-Acd was recrystallised from ethanol and water and had a m.p. 95-97°C. ^{1}H and ^{13}C NMR were similar to that obtained for 1. Incorporation of deuteria was determined to be approximately equal on the two positions on the ring. Mass spectroscopy indicated that deuterium incorporation in the final product was approximately 1.8 deuteria per molecule.

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