

Organic Reactions in Liquid Crystalline Solvents. 10. Studies of the Ordering and Mobilities of Simple Alkanophenones in CCH-*n* Liquid Crystals by ²H NMR Spectroscopy and Norrish II Photoreactivity

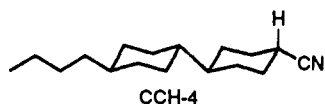
M. S. Workentin,[†] W. J. Leigh,^{*,†,1} and K. R. Jeffrey[‡]

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1, and Department of Physics, University of Guelph, Guelph, Ontario, Canada. Received October 20, 1989

Abstract: The Norrish II reactions of butyrophenone (BP), valerophenone (VP), and hexanophenone (HP) have been carried out at 30 °C as 0.6, 5.0, and 40 mol % solutions in the isotropic, smectic (crystal-B), and nematic liquid crystalline phases of *trans,trans*-4'-alkyl[1,1'-bicyclohexyl]-4-carbonitrile (CCH-*n*) liquid crystals. In each case, the distribution of fragmentation and stereoisomeric cyclobutanols from photolysis of the ketones in the nematic phase is similar to that obtained from photolysis in a model isotropic solvent. The product distribution from photolysis of 0.6 mol % BP in the crystal-B phase is also similar to that in the isotropic phase, but both the fragmentation/cyclization and *trans/cis*-cyclobutanol product ratios from photolysis of VP and HP are affected significantly by smectic liquid crystalline order. The magnitude of the effect correlates with the size of the γ -substituent and inversely with concentration. Deuterium NMR spectra of the α - and ring-deuterated analogues of the three ketones, along with those of acetophenone (AP) and propiophenone (PP), have been measured as a function of temperature and concentration in CCH-4. Homogeneous smectic solutions of α -deuterated AP, PP, and BP exhibit distinctive ²H NMR spectra with regular differences throughout the series, but VP and HP show no detectable spectral features within 100 kHz of center spectrum. These results afford a qualitative correlation of the motional behavior of the solutes in the smectic phase as a function of alkanoyl chain length, which parallels that manifested in Norrish II reactivity. The ring-deuterated derivatives of all five ketones in the smectic phase show spectra consistent with solubilization of the probe in a highly ordered, oriented environment. Order parameters for the five ketones in the nematic phase at 52 °C have been calculated from the spectra of the ring-deuterated derivatives. Solubility limits of the ketones in the crystal-B phase of CCH-4 have been determined from the concentration dependence of the spectra of the ring-deuterated derivatives.

Introduction

The potential ability of nematic and smectic liquid crystals to control or restrict the conformational mobility of dissolved solutes is of considerable current interest.^{2,3} Numerous studies have led to the general view that effects of this type can be substantial when the structure of the solute is similar to that of the mesogen and the conformational motion being probed involves fairly dramatic changes in the "shape" of the solute from its favored conformation in the mesophase.⁴⁻¹⁴ Some of the most dramatic results to date have been obtained with particularly highly ordered smectic phases, such as that of *trans,trans*-4'-butyl[1,1'-bicyclohexyl]-4-carbonitrile (CCH-4).⁹⁻¹¹ This mesogen exhibits enantiotropic nematic and



bilayer crystal-B liquid crystalline phases over the 53–80 and 28–53 °C temperature ranges, respectively, is an isotropic liquid above 80 °C, and is crystalline below 28 °C.¹⁵⁻¹⁷ The bilayer crystal-B phase is a highly ordered smectic phase type that is characterized by hexagonal close-packing of the mesogen in interdigitated bilayers, with the constituent molecules oriented with their long axes parallel to one another and perpendicular to the layer planes, and that possesses short-range crystalline regularity.¹⁸⁻²⁰ Recent ²H NMR studies from our laboratory have shown that the solubility limits of guest molecules in this smectic liquid crystal may be rather smaller than generally appreciated^{13,14} and that because of these factors many of the reported studies of solute photoreactivity in CCH-4 have afforded somewhat distorted indications of the true effects of smectic liquid crystalline solubilization on the conformational mobilities of dissolved solutes.

The Norrish II reaction of alkyl and aromatic ketones has been frequently used to probe solubilization effects in ordered media,²¹

because the product distribution from this reaction is reasonably sensitive to medium polarity and rigidity.²² The use of the reaction

(1) Natural Sciences and Engineering Research Council of Canada University Research Fellow, 1983–1993. To whom correspondence should be addressed.

(2) Leigh, W. J. In *Photochemistry on Solid Surfaces*; Matsuura, T., Anpo, M., Eds.; Elsevier: Amsterdam, 1989; Chapter 9.2.

(3) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413.

(4) (a) Anderson, V. C.; Craig, B. B.; Weiss, R. G. *J. Phys. Chem.* **1982**, *86*, 4642. (b) Anderson, V. C.; Craig, B. B.; Weiss, R. G. *Mol. Cryst. Liq. Cryst.* **1983**, *97*, 351. (c) Anderson, V. C.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6628.

(5) Nerbonne, J. M.; Weiss, R. G. *Isr. J. Chem.* **1979**, *18*, 266.

(6) (a) Poupko, R.; Luz, Z. *J. Phys. Chem.* **1981**, *75*, 1675; *Mol. Phys.* **1982**, *76*, 5662. (b) Luz, Z.; Naor, R.; Meirovitch, E. *J. Chem. Phys.* **1981**, *74*, 6624.

(7) Fung, B. M.; Sigh, R. V.; Alcock, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 7301.

(8) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7033.

(9) (a) Leigh, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6114. (b) Leigh, W. J. *Can. J. Chem.* **1986**, *64*, 1130.

(10) Leigh, W. J.; Jakobs, S. *Tetrahedron* **1987**, *43*, 1393.

(11) (a) Zimmermann, R. G.; Liu, J. H.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5264. (b) Treanor, R. L.; Weiss, R. G. *J. Phys. Chem.* **1987**, *91*, 5552.

(12) (a) Treanor, R. L.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 3137. (b) Treanor, R. L.; Weiss, R. G. *Tetrahedron* **1986**, *43*, 1371. (c) Nunez, A.; Weiss, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 6215. (d) Treanor, R. L.; Weiss, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2170.

(13) Fahie, B. J.; Mitchell, D. S.; Leigh, W. J. *Can. J. Chem.* **1989**, *67*, 148.

(14) Fahie, B. J.; Mitchell, D. S.; Workentin, M. S.; Leigh, W. J. *J. Am. Chem. Soc.* **1989**, *111*, 2916.

(15) *Licristal Liquid Crystals*; EM Chemicals: Hawthorne, N. Y., 1985.

(16) Rahimzadeh, E.; Tsang, T.; Yin, L. *Mol. Cryst. Liq. Cryst.* **1986**, *139*, 291.

(17) Mitchell, D. S.; Leigh, W. J. *Liq. Cryst.* **1989**, *4*, 39.

(18) Leadbetter, A. J.; Frost, J. C.; Mazid, M. A. *J. Phys. (Paris)* **1979**, *40*, L-325.

(19) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals—Textures and Structures*; Leonard Hill: London, 1984.

[†] McMaster University.

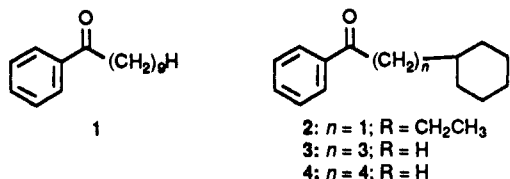
[‡] University of Guelph.

Table I. 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 (phase)	concn	BP		VP		HP	
		F/C	F/C	t/c	F/C	t/c	
CCH-4 (Sm)	0.6 mol %	8.6 ± 0.8	9.2 ± 0.4	6.30 ± 0.04	12.3 ± 1.6	6.6 ± 0.4	
	5.0 mol %	9.6 ± 0.8	7.4 ± 0.2	3.3 ± 0.1	9.1 ± 1.0	3.4 ± 1.4	
EB ^c (nem)	0.6 mol %	9.7 ± 1.1	6.1 ± 0.6	2.07 ± 0.06	6.5 ± 1.1	1.4 ± 0.2	
	5.0 mol %	8.9 ± 1.8	6.2 ± 0.4	2.2 ± 0.1	6.5 ± 1.4	2.2 ± 0.8	
CCH-4 (isot)	40 mol %	7.8 ± 0.3	6.0 ± 2.0	2.00 ± 0.04	5.6 ± 1.0	2.00 ± 0.02	
EC ^c (isot)	0.6 mol %	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	
MeCN ^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	
<i>t</i> -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 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 analyzed in triplicate by vapor-phase chromatography. The FID detector was not calibrated for differences in response factors. Errors are quoted as ±2 standard deviations from the mean. ^b Key: Sm, smectic (crystal-B); nem, nematic; isot, isotropic. ^c Solvents: EB, 2:1 CCH-2/CCH-4; EC, 6:1 CCH-2/cyclohexane; MCH, methylcyclohexane; MeCN, acetonitrile; MeOH, methanol; *t*-BuOH, *tert*-butyl alcohol.

to probe solubilization phenomena in liquid crystals has been developed largely by Weiss and co-workers.³ Their reported studies include those of α -diketones⁵ and *n*-alkanophenones⁸ in cholesteric liquid crystals and/or the smectic-B phase of *n*-butyl stearate, of *sym*- and 2-alkanones in the same liquid crystal as well as in related lyotropic liquid crystalline phases,¹² and of *n*-decanophenone (**1**) and three cyclohexylalkyl phenyl ketones (**2–4**) in

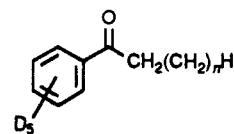
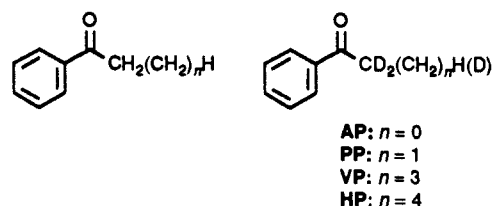


the solid, liquid crystalline, and isotropic phases of CCH-4.¹¹ Variations in Norrish II product distribution in liquid crystalline relative to isotropic solvents have been discussed in terms of the effects of the medium on the conformer distribution and kinetic behavior of the 1,4-biradical intermediate in the reaction. We have also used the Norrish II reaction in studies of this type, but as a secondary probe to monitor liquid crystalline effects on the conformational motions involved in intramolecular triplet quenching in remote-substituted phenolic ketones.¹⁰

In the course of this latter study, it was observed that the product distribution from photolysis of 4-methoxyvalerophenone (MVP) is altered significantly in the crystal-B phase of CCH-4 compared to that obtained in homologous nematic and isotropic phases.¹⁰ In fact, the magnitude of the effect on the product distribution is comparable to those reported previously for the Norrish II reactions of **1–4**,^{11a} whose product distributions should depend on substantially larger amplitude biradical conformational motions than is the case for MVP. Furthermore, our recent ²H NMR studies suggest that the results for MVP may be distorted somewhat, because the solubility limit of the ketone in the crystal-B phase is likely to be lower than the bulk concentration of the samples that were employed in these studies.^{13,14}

We have therefore initiated a study of the Norrish II reactions of a series of simple alkanophenones—butyrophenone (BP), valerophenone (VP), and hexanophenone (HP)—in liquid crystalline solvents, in order to determine the generality of our results for MVP and (perhaps) define the lower extremes of the effects

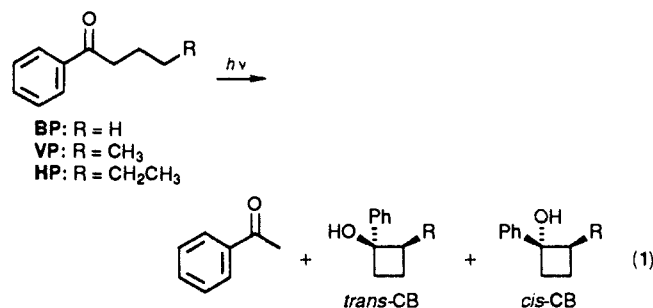
of smectic liquid crystalline phases on the conformational mobilities of dissolved solutes. In this paper, we report our results for these compounds in CCH-*n* liquid crystals. We have supplemented the Norrish II photolysis data with a study of the temperature and concentration dependence of the ²H NMR spectra of the α - and ring-deuterated analogues of the three ketones in the liquid crystalline phases of CCH-4, along with those of acetophenone (AP) and propiophenone (PP) under similar conditions. The



NMR data provide information on the ordering and mobility of these molecules in the nematic and crystal-B phases of CCH-4²³ and their dependence on solute structure. They also allow qualitative determination of the solubility limits of the ketones in the crystal-B phase.^{13,14}

Results

a. Norrish II Photolysis of BP, VP, and HP. Photolysis of BP, VP, and HP at 30 °C as 0.6 and/or 5.0 mol % mixtures in the smectic (crystal-B) phase of CCH-4, the nematic phase of a 1:2 mixture of CCH-4 and CCH-2 (EB)¹⁷ (CCH-2 is the 4'-ethyl homologue of CCH-4), and the isotropic phase of a 1:6 wt % mixture of cyclohexane and CCH-2 (EC),¹⁰ as 40 mol % (isotropic) mixtures with CCH-4; and as 0.1 M solutions in methylcyclohexane (MCH), acetonitrile (MeCN), methanol (MeOH), and *tert*-butyl alcohol (BuOH) lead to formation of acetophenone and cyclobutanol (CB) products as shown in eq 1.



(20) For comprehensive descriptions of the structure and properties of thermotropic liquid crystals, see: (a) *Liquid Crystals. The Fourth State of Matter*; Saeva, F. D., Ed.; Marcel Dekker: New York, 1979. (b) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Weinheim, 1980. (c) Vertogen, G.; De Jeu, W. H. In *Thermotropic Liquid Crystals, Fundamentals*; Schäfer, F. P., Ed.; Springer Series in Chemical Physics, 45; Springer-Verlag: Berlin, 1987.

(21) Ramamurthy, V. *Tetrahedron* **1986**, *42*, 5753.

(22) (a) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461. (b) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (c) Wagner, P. J. In *Rearrangements in the Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (d) Scaiano, J. C.; Lissi, E. A.; Encinas, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139.

(23) (a) Davis, J. H. *Biochim. Biophys. Acta* **1983**, *737*, 117. (b) Emsley, J. W. *Isr. J. Chem.* **1988**, *28*, 297.

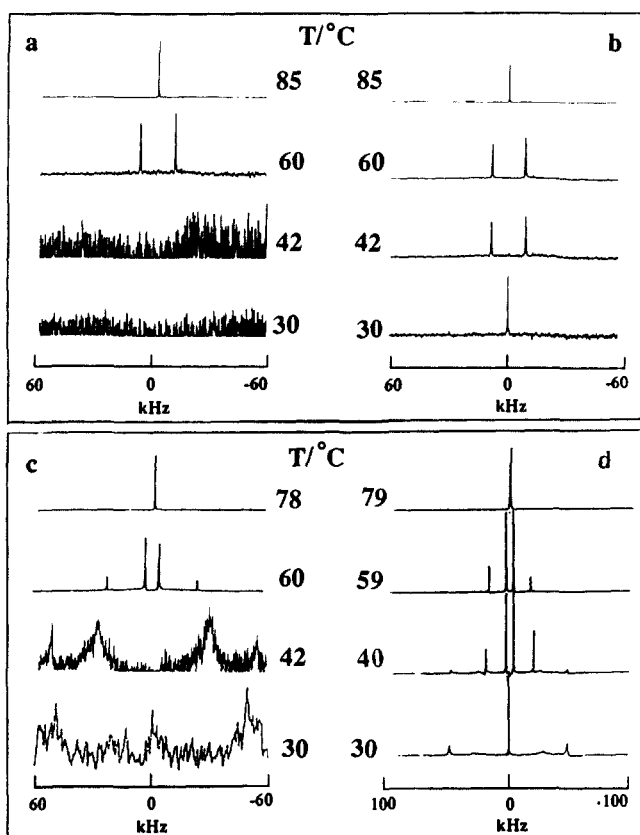


Figure 1. ^2H NMR spectra of VP- $\alpha,\alpha\text{-}d_2$ and VP- d_5 in CCH-4 as a function of temperature and concentration: (a) 1.0 mol % VP- $\alpha,\alpha\text{-}d_2$; (b) 3.0 mol % VP- $\alpha,\alpha\text{-}d_2$; (c) 1.0 mol % VP- d_5 ; (d) 5.0 mol % VP- d_5 . The spectra of the 5.0 mol % mixture and the 30 °C spectrum of the 1.0 mol % mixture were recorded at 41.3 MHz; the others were recorded at 76.8 MHz.

All samples were deoxygenated prior to photolysis by bubbling dry nitrogen through the isotropic or nematic solutions at 30 or 85 °C. Repeated gas chromatographic analyses of photolysis mixtures taken to 5–20% conversion afforded the fragmentation/cyclization (F/C; acetophenone/(total CB)) and *trans/cis*-CB (t/c) ratios collected in Table I. No other products in addition to those shown in eq 1 were observed in significant ($>\approx 2\%$) yield in any case.

b. ^2H NMR Spectroscopy. Deuterium NMR spectra of the α - and ring-deuterated analogues of BP, VP, and HP as 1.0–5.0 mol % mixtures in CCH-4 were recorded at 76.8 MHz at various temperatures throughout the 20–83 °C temperature range by use of the quadrupolar echo pulse sequence.²⁴ In each case, spectra were recorded at 3–5 °C intervals, starting at the upper end of the temperature range. This procedure ensures that spectra recorded in the bulk smectic phase are those of uniformly oriented samples, since the solvent is aligned spontaneously by the spectrometer magnetic field when in the nematic phase and the alignment persists as the temperature is lowered into the smectic phase (below 50–53 °C).^{13,14} Spectra of the 1.0 and 5.0 mol % VP- d_5 /CCH-4 samples were also recorded at 41.3 MHz under similar conditions and were similar to those obtained with the higher field spectrometer. For samples in the 20–35 °C temperature range, this spectrometer often affords spectra that are easier to phase correctly than those from the 76.8-MHz spectrometer because of its much higher bandwidth. Representative spectra from the two spectrometers are shown in Figure 1 for the VP- $\alpha,\alpha\text{-}d_2$ /CCH-4 and VP- d_5 /CCH-4 mixtures at various concentrations. Similar studies were carried out (at 76.8 MHz) for 1.0 mol % samples of AP- $\alpha,\alpha,\alpha\text{-}d_3$ and PP- $\alpha,\alpha\text{-}d_2$ and 2.6 mol

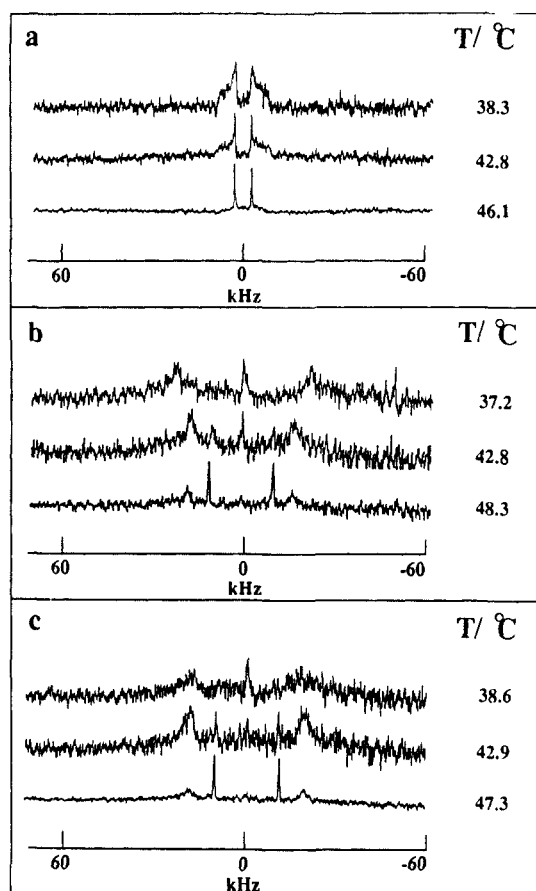


Figure 2. ^2H NMR spectra of (a) AP- $\alpha,\alpha,\alpha\text{-}d_3$ (0.67 mol %), (b) PP- $\alpha,\alpha\text{-}d_2$ (1.0 mol %), and (c) BP- $\alpha,\alpha\text{-}d_2$ (1.0 mol %) in the smectic phase of CCH-4 between 48 and 37–38 °C, recorded at 76.8 MHz.

% samples of AP- d_5 and PP- d_5 in CCH-4. The higher field spectrometer successfully resolved separate splittings for the ortho and meta deuterons in the nematic phase at $T > 50$ °C for all the ketones studied except AP.

The nematic phase spectra (55 °C) are characterized by line widths of 30–50 Hz, and the doublet splittings observed increase in magnitude with decreasing temperature throughout the 78–53 °C range. The spectra change dramatically as the temperature is lowered into the smectic phase region (ca. 25–50 °C). In those of the 1.0 mol % samples of the ring-deuterated ketones, the doublets associated with the nematic phase disappear below 47 °C and are replaced by two new doublets of 2–8 times larger splitting (see, for example, Figure 1c). This behavior presumably indicates that the solutes are, in each case, completely soluble in the smectic phase at these concentrations over the 25–47 °C temperature range. The spectra consist of a broad doublet of splitting $\Delta\nu_Q \approx 50$ kHz, due presumably to the ortho and meta deuterons, flanked by a sharper doublet of splitting $\Delta\nu_Q \approx 100$ kHz due to the para deuteron. In general, the spectral components become broader and more diffuse as the temperature is lowered in the smectic phase range. Furthermore, the line width of the inner doublet varies throughout the series, broadening with increasing alkanoyl chain length. In each case, the outer doublet is considerably sharper than the inner one.

In the case of 1.0 mol % VP- $\alpha,\alpha\text{-}d_2$, the spectra are devoid of features at temperatures below 50 °C (see Figure 1a) on either spectrometer. We interpret this as characteristic of smectic phase solubilization, since similar results have been obtained previously for other α -substituted phenylalkyl ketones at low concentrations in this liquid crystal^{13,14} and characteristic spectra are observed for the ring-deuterated ketones under these conditions for samples of similar concentration (Figure 1c). While low-concentration samples of HP- $\alpha,\alpha\text{-}d_2$ in CCH-4 behave similarly to VP- $\alpha,\alpha\text{-}d_2$, the α -deuterated derivatives of AP, PP, and BP all exhibit distinct spectral features that can be assigned as due to solubilization in

(24) (a) Davis, J. H.; Jeffrey, K. R.; Bloom, M.; Valic, M. J.; Higgs, T. P. *Chem. Phys. Lett.* 1976, 42, 390. (b) Bloom, M.; Davis, J. H.; Valic, M. J. *Can. J. Phys.* 1980, 58, 1510.

Table II. ^2H Quadrupolar Splittings from NMR Spectra of α - and Ring-Deuterated Alkanophenones in the Nematic and Crystal-B Phases of CCH-4^a

ketone	phase	$\Delta\nu_{\alpha}^b$ (kHz)	$\Delta\nu_{\rho}^c$ (kHz)	$\Delta\nu_{o/m}^c$ (kHz)
AP	nem	5.47	-32.11	-11.09
	sm	11	-70.5	-43.0
PP	nem	19.95	-43.00	-6.83
	sm	29	-93.5	-51.2
BP	nem	20.37	-40.03	-7.64
	sm	32	-94.7	-53.4
VP	nem	22.10	-43.27	-6.67
	sm ^d	e	-98.7	-54.0
HP	nem	22.52	-42.74	-6.81
	sm ^d	e	-98.3	-52.2

^aData recorded at 76.8 MHz from 1.0 and 2.6 mol % solutions of the α - and ring-deuterated ketones, respectively. Errors in $\Delta\nu_i$ are ca. 10 Hz for the nematic phase. For the smectic phase, they are ca. 1 kHz for $\Delta\nu_{\alpha}$, ca. 0.5 kHz for $\Delta\nu_{o/m}$, and ca. 0.2 kHz for $\Delta\nu_{\rho}$. Key: nem = nematic; sm = crystal-B. ^bNematic phase spectra recorded at 50 °C, smectic phase spectra at 43 °C. The signs are not known. ^cNematic phase spectra recorded at 52 °C, smectic phase spectra at 33 °C. ^dRecorded at 36 °C (VP) or 38 °C (HP). ^eUnobservable.

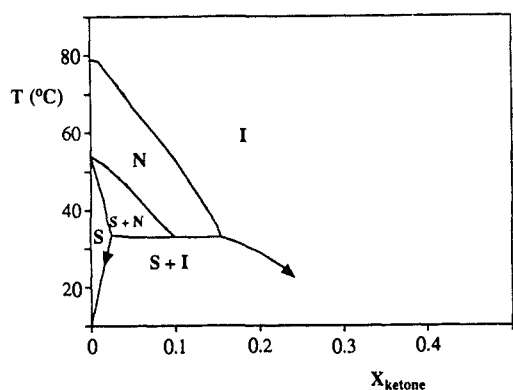


Figure 3. Generalized temperature-composition binary-phase diagram for ketone/CCH-4 mixtures. The portion of the diagram below $X_{\text{ketone}} = 0.05$ has been constructed from ^2H NMR data for VP- α,α - d_2 and VP- d_5 in CCH-4. Key: I, isotropic; N, nematic; S, smectic (crystal B).

the smectic phase at temperatures below ca. 50 °C. Representative examples of smectic phase spectra for these three ketones are shown in Figure 2. The spectra of PP and BP consist of diffuse doublets of ca. 1.5 times larger splitting than those observed for the nematic phase. In both cases, the doublets grow more diffuse and difficult to resolve as the temperature is lowered below ca. 36 °C. The spectrum of AP- α,α,α - d_3 resembles a powder pattern and is observable without difficulty throughout the complete smectic-phase temperature range.

Table II lists the quadrupolar splittings found for the five α -deuterated ketones at 50 °C (nematic phase) and 43 °C (smectic phase), obtained from the 76.8-MHz spectra of 1.0 mol % solutions in CCH-4. The table also includes quadrupolar splittings for the ring-deuterated analogues at 51–52 °C (nematic phase) and at 33–38 °C (smectic phase), where the splittings are at their maximum values, from the 76.8-MHz spectra of 2.6 mol % mixtures.

For both the ring- and α -deuterated ketones, the spectra of higher concentration mixtures show behavior typical of biphasic solubilization at temperatures below ca. 50 °C. These results, typified in Figure 1 parts b and d, can be discussed more clearly with the aid of the partially generalized binary-phase diagram for VP/CCH-4 shown in Figure 3. For the composition range below 5 mol % ketone, the phase diagram has been constructed from the ^2H NMR data, while the region above 5 mol % has been generalized from the phase diagrams of other ketone/CCH-4 mixtures that we have studied.^{13,14}

In the 2.5 mol % samples, the nematic phase spectrum persists at temperatures as low as 40 °C, indicating biphasic solubilization (Sm + N) over the 40–52 °C temperature range and homogeneous solubilization in the smectic phase at temperatures below 40 °C.

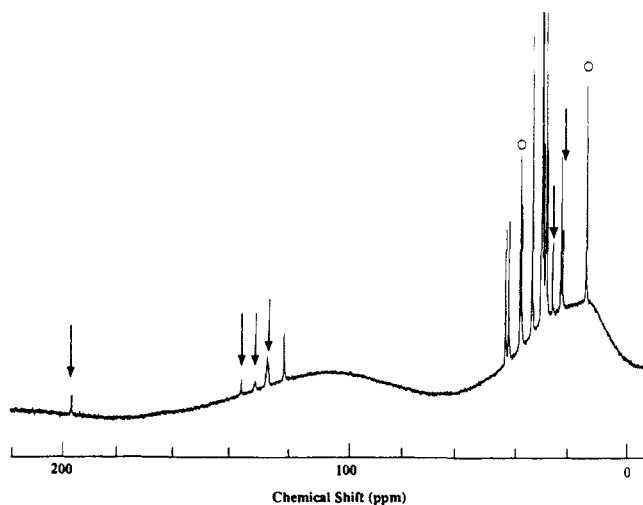


Figure 4. ^{13}C NMR spectrum of a 5.0 mol % sample of VP- d_5 in CCH-4 at 30 °C, recorded at 125.7 MHz. The peaks designated by arrows (\downarrow) are due to VP- d_5 , while the remaining ones are due to CCH-4. Two other ketone signals, designated by circles (\circ), overlap with solvent signals.

Table III. Solubility Limits of Alkanophenones in the Crystal-B Phase of CCH-4 at 30 and 45 °C^a

ketone	solubility limit	
	30 °C	45 °C
AP	1–1.5 ^b	<0.6 ^b
PP	1.5–2 ^b	≈0.8 ^b
BP	2.3	≈0.8
VP	2.6	1.0
HP	2.2	1.3

^aEstimated by ^2H NMR spectroscopy (see text). Errors are roughly 10%. ^bEstimate is based on behavior of 1.0 and 2.6 mol % samples only.

The ^2H NMR spectra of samples of higher (≥ 3 mol %) bulk composition show these to be biphasic throughout the entire 28–53 °C temperature range. For each solute studied, the samples are mixtures of smectic (major component) and nematic (minor component) phases between ca. 33 and 52 °C. At temperatures below 32–34 °C, the nematic phase doublet is replaced by a sharp singlet that we assign to ketone solubilized in an isotropic phase. Evidence that this mobile component consists of an isotropic solution of ketone in CCH-4, in equilibrium with the bulk smectic phase, can be obtained from the ^{13}C NMR spectrum of the mixture, an example of which is shown in Figure 4 for a 5 mol % sample of VP- d_5 in CCH-4 at 30 °C. The spectrum consists of sharp lines due to the ketone and CCH-4 in the isotropic component, superimposed on a broad featureless absorption due to the smectic phase. A similar spectrum has been reported previously for a benzene/CCH-4 mixture,²⁵ although it was incorrectly attributed to a solute-induced plastic or cubic phase.^{13,14} By analogy to the other systems that we have studied, the concentration of ketone in the mobile component of these mixtures is likely to be in the 5–40 mol % range and is highest at the lower temperature extreme.¹⁴

Solubility limits for each ketone at various temperatures in the crystal-B phase between 28 and 52 °C can be estimated by determining, for a particular sample composition, the temperature below which the nematic phase component is absent from the spectrum and repeating the experiment for a series of samples of different composition (in these cases, between 0.6 and 3.0 mol %).^{13,14} Solubilities in the smectic phase at 30 and 45 °C, determined from the concentration and temperature dependence of the 76.8-MHz spectra of each of the ring-deuterated ketones, are reported in Table III. Those for BP, VP, and HP have been determined most accurately, while those for AP and PP have been estimated from spectra recorded only for mixtures of 1.0 and 2.6

mol %. The 30 °C spectra for the 2.6 mol % mixtures of the latter two ketones consist of both nematic and smectic phase components. The solubility limits in the smectic phase at this temperature have been estimated from the relative intensities of the signals due to the two phase types in these spectra. A similar procedure was used to estimate the solubility limits at 45 °C for these compounds, from the spectra of the 1.0 mol % mixtures. The solubilities of VP in the smectic phase as determined from the spectral behavior of VP- α,α - d_2 /CCH-4 mixtures match those obtained using the ring-deuterated derivative.

The solubilities of the five ketones appear to increase precipitously with chain length, leveling off to roughly equivalent values for BP, VP, and HP (2.2–2.6 mol % at 30 °C). Interestingly, the solubility limit of 3 in smectic CCH-4 is also within this range at 30 °C.¹⁴

Discussion

The data in Table I show the Norrish II product distributions obtained from photolysis of the three alkanophenones in homogeneous solutions of four basic types: (i) nonviscous isotropic (nonpolar, polar aprotic, and polar protic), (ii) viscous isotropic (at low (EC) and high (40 mol % in CCH-4) ketone concentration), (iii) nematic liquid crystalline (EB), and (iv) smectic liquid crystalline (0.6 mol % in CCH-4). Our results in the nonviscous isotropic solvents agree quite closely with previously published ones.²⁶ As well, the table contains data for photolysis of the ketones in a heterogeneous mixture of isotropic and smectic solutions (5.0 mol % in CCH-4). Due to the solubilities of the ketones in the smectic phase at this temperature, the solutes in these samples will be roughly equally proportioned between a smectic solution of concentration given by the solubility limit (the bulk of the sample) and relatively small amounts of a highly concentrated (20–40 mol %) isotropic liquid.

The photolyses in the two viscous isotropic phases (EC, a 6:1 mixture of CCH-2 and cyclohexane, and the 40 mol % ketone/CCH-4 solutions) yield similar product distributions. When these results are compared with those obtained in the nonviscous isotropic solvents, it is observed that the product ratios are closest to those obtained in the protic solvents. This overall similarity to hydrogen-bonding solvents may be the result of a combination of weak solvent polarity and high viscosity in EC and the 40 mol % mixtures. High solvent viscosity is known to have little effect on the lifetimes of Norrish II biradicals,²⁷ but there appear to be very few data available on viscosity effects on product distributions, at least in the case of alkanophenones.⁸ Wagner and co-workers have reported that Norrish II quantum yields and F/C ratios from alkanophenones generally increase with increasing ketone concentration and suggested that this is due to specific biradical solvation by ground-state ketone, probably via hydrogen bonding, which ultimately affects biradical reactivity in ways similar to alcohol solvents.²⁸ It is reasonable that these effects might be magnified with increasing viscosity.

Photolysis of the three ketones in the nematic solvent (EB) affords product ratios comparable to those of the viscous isotropic solvents in each case. The extremely small or negligible effects of nematic solvents on reactions involving conformational motions in the rate-determining step are quite general,^{2,3} and the present results are analogous to those found for other reported Norrish II reactions in nematic or cholesteric liquid crystalline solvents.^{5,8,10,11}

The results in the crystal-B solutions are more dramatic. While the F/C product ratio from photolysis of BP is more or less identical with the (nematic) EB and (isotropic) EC results, both and F/C and t/c ratios from photolysis of VP and HP increase dramatically in the crystal-B phase, particularly in the 0.6 mol % samples. Furthermore, the degree to which the F/C ratios are

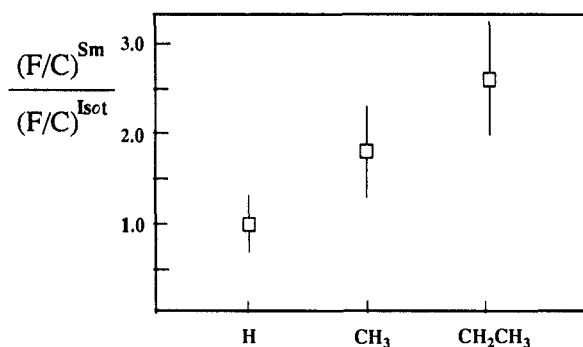
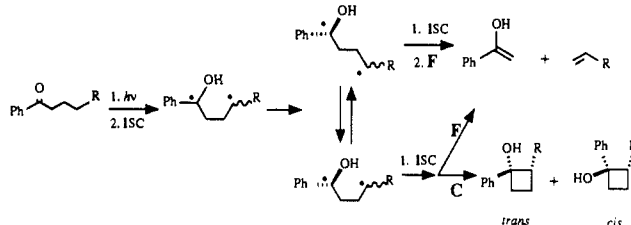


Figure 5. Plot illustrating the variation with alkanoyl chain length in the F/C ratios from photolysis of BP, VP, and HP as 0.6 mol % solutions in the crystal-B phase of CCH-4 at 30 °C, relative to the ratios obtained in isotropic CCH-2/cyclohexane (EC) under similar conditions.

Scheme I. Triplet Norrish Type II Reaction



affected increases with the size of the substituent on the γ -carbon; this is illustrated graphically in Figure 5, which plots, as a function of γ -substituent, the ratio of the F/C values from photolysis of the 0.6 mol % CCH-4 (Sm) and EC (Isot) solutions. The t/c cyclobutanol ratios, though sensitive to smectic solvent order, do not appear to follow a systematic trend with γ -substituent size.

For both VP and HP, the F/C and t/c ratios observed for the 5.0 mol % mixtures are intermediate between the values observed for the 0.6 and 40 mol % samples, due to the biphasic nature of the 5.0 mol % mixtures. The measured product ratios are a weighted average, reflecting reaction of the ketone in the two environments (smectic solution + isotropic solution) in which it is solubilized.^{13,14}

The various factors that control the product distribution obtained in the triplet Norrish II reaction are reasonably well understood.^{12,22} In liquid crystals and other constrained media, the main controlling factors are thought to relate to the effects of medium ordering on the conformational distribution of the (triplet) 1,4-biradical intermediate prior to intersystem crossing and the effects of medium constraints on the reactivity of the various singlet 1,4-biradical conformers after intersystem crossing occurs. These factors are depicted in Scheme I. While transoid biradicals can yield only fragmentation products, cisoid biradicals can yield fragmentation and cyclization products in addition to starting material by hydrogen back-transfer.²⁹ A recent study by Caldwell et al. suggests that cyclization may dominate over fragmentation in cisoid biradicals.³⁰ However, other results suggest that this is not general and that the proportion of fragmentation and cyclization products obtained from cisoid species depends on subtle conformational factors.³¹

Weiss and co-workers have reported numerous studies of the Norrish II reactions of alkanones and alkanophenones in liquid crystalline solvents.^{5,8,11,12} In all cases where an effect on product distribution is observed, the trend is toward an increase in fragmentation over cyclization products compared to the situation in isotropic solvents, and this is generally accompanied by an increase in the yield of *trans*- relative to *cis*-cyclobutanols. The increased fragmentation product yield has been explained as being due to alterations in both the biradical conformational distribution (in

(26) (a) Wagner, P. J.; Kelso, P. A.; Kempainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506. (b) Wagner, P. J.; Kempainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

(27) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

(28) Wagner, P. J.; Kochevar, I. E.; Kempainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.

(29) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

(30) Caldwell, R. A.; Dhawan, S. N.; Majima, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 6454.

(31) Johnston, L. J.; Scaiano, J. C.; Sheppard, J. W.; Bays, J. P. *Chem. Phys. Lett.* **1986**, *124*, 493.

favor of transoid conformers, which can only undergo fragmentation) and the reactivity of cisoid singlet biradicals in favor of the least sterically demanding pathways in terms of interactions of the reacting solute with the ordered solvent matrix (i.e., fragmentation over cyclization; *trans*- over *cis*-cyclobutanol formation).^{8,12} However, it has also been suggested that, depending on the degree of molecular contortion involved in C_β-C_γ bond rotation, interconversion between triplet biradical conformers in the smectic phase may be slower than intersystem crossing, in which case a higher proportion of the total reactivity must ensue from cisoid biradical conformers that undergo fragmentation in preference to cyclization.^{11a}

Furthermore, the magnitude of the observed effects on Norrish II product ratios in liquid crystalline solvents has been shown to correlate with structural similarities between the reactive solute and the mesogen. For example, the largest effects on Norrish II F/C and t/c product ratios from photolysis of 2- and *sym*-alkanones in the smectic-B phase of *n*-butyl stearate are observed for C₁₉-C₂₁ ketones, i.e., those solutes whose molecular lengths are most similar to that of the mesogen and hence might fit most unobtrusively into the liquid crystalline matrix.¹² The magnitude of the effect falls off as the ketone is either shortened or lengthened from this optimum chain length. A study of the Norrish II reaction of a series of *n*-alkanophenones in the same liquid crystal revealed analogous effects only with the longer chain (C₁₇-C₂₁) members of the series.⁸

Of special pertinence to the present work are the studies of the Norrish II reactions of 1-4 as a function of temperature in the crystal-B, nematic, and isotropic phases of CCH-4.^{11,14} Significant increases in the F/C and t/c product ratios were observed for 1, 3, and 4 upon photolysis in the smectic phase relative to the isotropic and nematic phase values.³² The largest effects were observed with 3 and 4, and this was rationalized as being due to the particular compatibility with the solvent matrix that is afforded by the cyclohexyl substituent and the rather large shape changes that are involved in the conformational motions that interconvert the triplet 1,4-biradical conformers prior to intersystem crossing.¹¹ As we have pointed out previously,¹⁴ the published product ratios for 1-4 were obtained under biphasic conditions and thus do not present a uniformly significant indication of the effects of the crystal-B phase on the Norrish II reactivity of these compounds. From the solubility limits of 3¹⁴ and AP-HP, however, we estimate that at 30 °C the product ratios reported by Weiss and co-workers¹¹ for 1 (and with less certainty, 4) are only 10-30% lower than the "true" values that would be obtained at lower solute concentrations. Because solubility in the crystal-B phase decreases with increasing temperature, the deviation from "true" smectic phase behavior will increase as the temperature is increased in the 30-50 °C range, and proportionately larger amounts of the ketone(s) are solubilized in a nematic solution that coexists with the smectic phase.

The present study indicates that in the crystal-B phase of CCH-4 large γ -substituents are in fact *not* a prerequisite for the realization of dramatic effects of smectic solvent order on Norrish II photoreactivity, since the observed enhancements in the F/C and t/c product ratios for VP and HP in smectic CCH-4 are of magnitude similar to those reported previously for 3³³ and 4.¹¹ It is interesting to compare the ca. 2.6-fold difference in the F/C ratio from photolysis of HP in the smectic and isotropic phases at 30 °C to the analogous numbers reported previously for 1

[(F/C)_{sm}/(F/C)_{isot} ≈ 1.5¹¹] and 3 [(F/C)_{sm}/(F/C)_{isot} = 3³³]. The similarity in the (F/C)_{sm}/(F/C)_{isot} values for HP, 1, and 3 (allowing for the estimated 10-30% distortion in the values for 1) suggests that drastic increases in the length or steric bulk of substituents at the γ -carbon result in surprisingly little (or even deleterious) effects on *this* liquid crystal's ability to impede conformational mobility and reactivity of the 1,4-biradical.

In the case of 4-methoxyvalerophenone (MVP), we previously reported that the F/C ratio obtained from photolysis of a 1 mol % sample in CCH-4 at 30 °C is ca. 2 times higher than that obtained from a solution of similar concentration in EC.¹⁰ Since 4-methoxy-substituted ketones appear to be 2-3 times less soluble in the crystal-B phase than their unsubstituted counterparts,¹⁴ the "true" (F/C)_{sm}/(F/C)_{isot} value for this compound is probably somewhat higher than that actually reported, but qualitatively similar to that for VP.

We believe that, considered together, these results underline the idea that *two* opposing, interdependent factors contribute to the observed effects of solubilization in a highly ordered smectic phase on the conformational mobility of a solute: the amplitude of the conformational motion *and* the packing of the solute in the liquid crystalline matrix.^{2,3} Substituents chosen so as to maximize the shape changes that accompany conformational motions may also have the effect of loosening or disrupting the solvent matrix in the solute's vicinity. The end result may be the same or even smaller than the effect on analogous motions in solutes with smaller substituents that allow for tighter (though perhaps much different) packing of the solute in the solvent matrix. In the crystal-B phase of CCH-4, minor variations in solute structure such as those in the present series of ketones may result in only small differences in the nature of the probes' solvation shell in the smectic phase (i.e., solute packing), but large effects on the sensitivity of the matrix to conformational motions.

The relation between solute conformational mobility and structure in the crystal-B phase that is suggested by the Norrish II data for BP, VP, and HP is also manifested in the ²H NMR spectra of the series of α -deuterated ketones (AP-HP) in the crystal-B phase. The spectra of α -deuterated AP, PP, and BP exhibit a marked increase in line width with decreasing temperature and increasing chain length throughout the series. This behavior is a qualitative indication of decreasing C-D reorientation rates as these parameters are varied. We believe that these reorientations are slowed to such an extent in VP- α,α -d₂ and HP- α,α -d₂ in the smectic phase that spectra are no longer observable. Such will be the case when the C-D bond reorientational rates are of magnitude similar to the quadrupolar splitting (ca. 180 kHz).³⁴ In fact, none of the α -deuterated phenylalkyl ketones that we have studied^{13,14} (except AP-BP) afford observable spectra in the crystal-B phase of CCH-4. Since spectral features would be expected to "reappear" as C-D bond reorientational rates are slowed even further from the 180-kHz range,³⁴ it appears that this is another indication of the leveling off that occurs in phenylalkyl ketone mobility as the α -substituents are increased in size or length. As discussed above, similar (though less accurately defined) behavior is observed in the Norrish II product ratios from BP-HP and 1, 3, and 4. Both these indicators of alkyl chain mobility suggest a distinct difference between the behavior of short (AP, PP, BP) and longer or bulkier chain (VP, HP, 1, 3, 4) ketones in the crystal-B phase. Strictly speaking though, the Norrish II F/C ratios report on rather specific conformational motions occurring within the 10-150-ns time scale, while the ²H NMR spectra reflect C _{α} -D bond reorientations that may result from both conformational and bulk molecular motions occurring over a much longer (ca. 10- μ s) time scale.

The spectra for the ring-deuterated ketones allow qualitative statements concerning reorientational motions that specifically involve the phenyl ring of the solutes in the crystal-B phase. The observed splittings for the ortho/meta and para deuterons on the ring suggest that 3-fold or higher symmetry reorientations of the phenyl ring about the long axis of the solute molecule(s) do *not*

(32) The reported behavior of 2 appears to be rather unique. At 30 °C, where the solubility of 2 in the crystal-B phase will be highest, the F/C ratio is evidently *lower* than that obtained in the isotropic phase at higher temperatures.¹¹ Interconversion of the cisoid and transoid biradicals derived from this compound requires a 180° flip of the cyclohexyl ring. If ring flipping is slowed dramatically in the crystal-B phase (as our ²H NMR results indicate, at least for the aryl rings in AP-HP), then a decrease in F/C might be expected for 2 since the initially formed (cisoid) biradical would be essentially "frozen" in that geometry.

(33) From the reported product ratios¹¹ at 30 °C (sm) and 80 °C (isot), this ratio is 6 ± 3. From our own data for this compound as 0.6 mol % (sm) and 40 mol % (isot) mixtures with CCH-4 at 30 °C,¹⁴ we obtain a ratio of 3 ± 1 (errors in both cases are ±2 σ).

(34) Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* 1981, 42, 381.

take place in the smectic phase within a time scale of ca. 10^{-5} s. This can be inferred from a comparison of the observed ring deuteron splittings with the maximum expected values, calculated with a simple model for solute motions in liquid crystals. In the case where the solute *does* reorient about the long molecular axis with 3-fold or higher symmetry, the maximum splittings will be obtained when the molecular axis is perfectly and rigidly aligned along the smectic phase director.²³ For this model, the quadrupolar splittings for the various ring deuterons are given by eq 2,^{35a} where

$$\Delta\nu_i^{\max} = \frac{3}{2} \frac{e^2qQ}{h} \frac{3 \cos^2 \theta - 1}{2} \frac{3 \cos^2 \beta - 1}{2} \quad (2)$$

e^2qQ/h is the quadrupolar coupling constant (ca. 185 kHz for aromatic deuterons^{35b}), θ is the angle subtended by the solute molecular axis and the applied field, and β is the angle subtended by the C–D bond and the molecular axis. Because CCH-4 has negative diamagnetic anisotropy,³⁶ the long molecular axis of the solute is aligned perpendicular to the applied field (i.e., $\theta = 90^\circ$). The maximum splittings predicted by this model are 138 kHz for the para deuterons ($\beta = 0^\circ$) and 17.3 kHz for the ortho/meta deuterons ($\beta = 60^\circ$). Any motion of the para axis of the solute with respect to the director would reduce both splittings. While the observed splittings in the smectic phase for the para position are less than 138 kHz, those for the ortho/meta positions are much greater than 17.3 kHz. These observations are strong evidence that rapid (on the time scale of 10^{-5} s) reorientation of the phenyl ring about a 3-fold or higher symmetry axis does not take place in this highly ordered liquid crystalline phase.

Because of the rigid ring structure of the ketones used in these experiments, 2-fold reorientation may be possible or, more likely, the motion may be restricted to small angle libration. More information about the dynamics of the CCH-4 molecules in the crystal-B phase is needed before a clearer picture of the motion of the solute molecules in this time scale will be possible. Nevertheless, the conclusion that the phenyl rings are subject to only small-angle librations in the crystal-B phase indicates that the motions of the C_α deuteria that are probed in their spectra are due primarily to conformational changes and not molecular reorientations.

In the nematic phase, the Norrish II data indicate that on the 10–150-ns time scale the effects on solute conformational mobility are indistinguishable from those of a viscous isotropic liquid, and there is no variation with ketone structure. There is, however, a structural effect on the *average ordering* of the solutes, as revealed by the quadrupolar splittings in the ²H NMR spectra of the α - and ring-deuterated derivatives. On a qualitative level, the variation in the magnitude of $\Delta\nu_Q$ within a series of homologous solutes will be proportional to variations in the degree of ordering of the solutes within the series. At a single temperature and concentration in nematic CCH-4, the present series of ketones exhibit an irregular increase in $\Delta\nu_\alpha$ with alkyl chain length. The effect levels off at higher chain lengths, to a maximum $\Delta\nu_\alpha$ of ca. 23 kHz (in the present cases). This leveling off for the higher ketones is borne out by the ²H NMR data reported for 1–4 in the same liquid crystal,^{11b} these compounds (2–3 mol %) all show maximum splittings of ca. 24 kHz in the nematic phase. The data indicate a leveling off of the ordering of the alkyl chains in these ketones, which is ca. 95% complete at remarkably short (C₅–C₆) chain lengths.

The same trend is also exhibited by the para and ortho/meta splittings in the spectra of the ring-deuterated ketones, except the initial variation in the splittings with chain length is much more dramatic than that observed for the α -deuterated analogues. The trend is consistent with an increasing effectiveness of the alkanoyl group in “anchoring” the phenyl ring as the alkanoyl chain is lengthened, which again levels off at moderately short (C₅–C₆)

Table IV. Order Parameters from ²H NMR Spectra of Ring-Deuterated Alkanophenones in the Nematic Phase of CCH-4 at 52 °C^a

	AP	PP	BP	VP	HP
S_{zz}	-0.116	-0.155	-0.144	-0.156	-0.154
$S_{xx} - S_{yy}$	-0.142	-0.113	-0.117	-0.111	-0.112

^a Calculated from eq 4. Errors are estimated to be ca. 3%.

chain lengths. Interestingly, the increases in the splittings throughout the series are not monotonic, but exhibit a saw-tooth correlation reminiscent of an odd–even effect. Correlations of this type are common in liquid crystal chemistry.²⁰

The ²H NMR data for the ring-deuterated ketones are capable of affording a more quantitative indication of how solute ordering in the nematic phase varies with solute structure. The quadrupolar splitting data obtained for these derivatives can be used to derive local order parameters for the phenyl ring in each case, following the treatment of Emsley and co-workers for polydeuterated ethyl- and *n*-propylbenzene in nematic liquid crystalline solvents.³⁷

In general, the ²H NMR frequencies observed for deuterated solutes in liquid crystals can be written in terms of a symmetric, traceless matrix that describes the average molecular ordering of the solute in the liquid crystal.²³ The elements of this tensor are given by eq 3, where p and q are the axes of the molecule-fixed

$$S_{pq} = \frac{1}{2}(3 \cos \theta_p \cos \theta_q - \delta_{pq}) \quad (3)$$

Cartesian coordinate system ($p, q = x, y, z$), θ_p and θ_q are angles between the molecular axes and the applied magnetic field, and the constant $\delta_{pq} = 1$ ($p = q$) or 0 ($p \neq q$).^{23b} The angular brackets indicate that the order parameters are an ensemble average. Since the phenyl ring forms a rigid segment in the molecule, the observed resonance frequencies for the ring deuterons can be used to determine the order parameter tensor for the ring.³⁷ If rotations about the phenyl–carbonyl carbon bond are subject to a potential of at least C_{2v} symmetry, then the order parameter tensor is diagonal in the coordinate system, originating in the phenyl ring, in which the long molecular axis defines the z -axis and the y -axis is perpendicular to the phenyl ring. The resulting expression for the observed quadrupolar splittings ($\Delta\nu_i$) is shown in eq 4, where

$$\Delta\nu_i = \frac{3}{2}q_{zz}^i \{ S_{zz} [(3 \cos^2 \beta - 1)/2 + (\eta/2) \sin^2 \beta \cos(2\alpha)] + (S_{xx} - S_{yy}) [\frac{1}{2} \sin^2 \beta \cos(2\alpha) + (\eta/2) (1 - \cos^2 \beta) \sin(2\alpha) \cos(2\gamma) - \cos \beta \sin(2\alpha) \sin(2\gamma)] \} \quad (4)$$

the Eulerian angles, α , β , and γ describe the transformation from the principal axis system of the electric field gradient at the i th site (x_i, y_i, z_i) to the frame of reference fixed in the phenyl ring.^{23b} For deuterons in hydrocarbons the C–D bond direction is chosen as the z_i -axis in the principal axis system, so that q_{zz}^i is the largest component of the electric field gradient tensor. The asymmetry parameter $\eta = (q_{xx} - q_{yy})/q_{zz}$ is defined to be positive and is assumed to be identical in both the nematic and smectic phases. By use of $q_{zz}^i = 185 \pm 5$ kHz^{35b} and $\eta_i = 0.03 \pm 0.03$ ³⁸ and undistorted benzene bond angles (C–C–D = 120°), the two resolved splittings for the para ($\Delta\nu_p$) and ortho/meta deuterons ($\Delta\nu_o \approx \Delta\nu_m$) are sufficient to determine S_{zz} and $(S_{xx} - S_{yy})$, the principal elements of the local order matrix for the phenyl ring. Since the alkanophenones will tend to align with the long (z -) axis oriented parallel to the nematic director, which will in turn be aligned orthogonal to the magnetic field direction, the signs of S_{zz} and each of the quadrupolar splittings are expected to be negative.³⁶ The values of S_{zz} and $(S_{xx} - S_{yy})$ calculated according to eq 4 are collected in Table IV.

It is possible to calculate each of the order parameters individually from the data in Table IV, by use of the additional condition that $S_{xx} + S_{yy} + S_{zz} = 0$,²³ although the S_{xx} and S_{yy} values so calculated are somewhat less accurate than the differences ($S_{xx} - S_{yy}$) and hence have not been included in the table.

(35) (a) Charvolin, J.; Hendriks, Y. In *Nuclear Magnetic Resonance of Liquid Crystals*; Emsley, J. W., Ed.; NATO ASI Series C; Reidel: Dordrecht, 1985; Vol. 141, p 449. (b) Veracini, C. A. *Ibid.* p 114.

(36) Pohl, L.; Eidenschink, R.; Krause, J.; Weber, G. *Phys. Lett.* **1978**, *65A*, 169.

(37) Avant, A. G.; Emsley, J. W.; Ng, S.; Venables, S. M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1855.

(38) Emsley, J. W.; Longeri, M. *Mol. Phys.* **1981**, *42*, 315.

In principle, these numbers can vary between -0.5 and $+1.0$, with values near 0 indicating random ordering and values at the extremes indicating perfectly uniform ordering with respect to the magnetic field direction.^{23b} For the series PP through HP, $S_{xx} \approx +0.02$ and $S_{yy} \approx +0.13$ in the nematic phase.

The calculated order parameters demonstrate that the long molecular (z -) axis of the alkanophenone is the most highly ordered of the three in the nematic phase, while the x -axis is the least ordered. Ordering about the z -axis varies only slightly for PP-HP. In the nematic phase, the fact that $S_{yy} > S_{xx}$ indicates that the alkanophenones tend to align with a slight preference for the plane of the phenyl ring being perpendicular to the applied field direction (i.e., with the y -axis parallel to the field).

For the smectic phase, an analysis of the quadrupolar splittings in terms of order parameters, similar to that carried out for the nematic phase, leads to inadmissible values. Order parameters relative to the mesophase director were calculated, but regardless of the sign chosen for the observed quadrupolar splitting, negative values greater than -0.5 were obtained. This is a further indication that phenyl-ring reorientations are slowed to such an extent in the highly ordered crystal-B phase that the ordering (or even the observed quadrupolar splittings) cannot be described by the same model as that used for conventional liquid crystals.

Summary and Conclusions

The combination of ^2H NMR and photoreactivity studies offers a qualitative picture of the molecular and conformational mobility of solutes in liquid crystals, at several different sites in the molecule, and over widely different time scales. The deuterium quadrupolar splittings and spectral line widths are sensitive to C-D bond reorientations (which can be due to molecular reorientations or conformational motions) in the 10–100- μs range while Norrish II product ratios are affected by more specific conformational motions in the 10–150-ns time scale. It is dangerous to compare the spectroscopic and photoreactivity data directly since they are clearly subject to different molecular and/or conformational motions, yet several generalizations can be made from the present data.

In the nematic phase, the rate of molecular reorientation is rapid on the time scale of the quadrupolar interaction (ca. 10 μs) since the observed NMR lines are very narrow. However, the observed quadrupolar splittings indicate that the motions of the solutes are not isotropic. The Norrish II reactivity of VP and HP indicate that the nematic phase has no effect on conformational motions or equilibria involving the alkanoyl chains in the 10–150-ns time scale above that expected on the basis of simple microviscosity factors.

In the crystal-B phase there are an increase in the ordering and a slowing of the molecular reorientation rates compared to the nematic phase. The NMR data indicate that, in phenylalkyl ketones with α -substituents larger than ethyl, the phenyl rings and the α -carbons are effectively immobilized within the 10–150-ns time scale. The slowing of α -CD motions grows rapidly for small α -substituents such as methyl (i.e., PP) and ethyl (i.e., BP) and then levels off for longer or bulkier chain ketones. The Norrish II data indicate that in VP, HP, and longer chain ketones the mobility at sites further along the alkanoyl chain is restricted. Again, the effect grows rapidly in the shorter chain ketones and then appears to level off or even decrease for longer chain or higher substituted derivatives. Presumably, these effects are due to an inverse dependence between solute-packing effects and the amplitude of biradical conformational motions, both of which are functions of the structure of the solute and its relationship to that of the mesogen.

Further work, aimed at defining the generality of these observations to other smectic liquid crystals, is in progress.

Experimental Section

^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.³⁹ Temperatures were controllable

to within ± 0.2 °C 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 of the spectrum. Spectra were recorded on stationary samples with the quadrupolar echo pulse sequence,²⁴ collecting 16K data points per scan over a 100–170-kHz (typically 150-kHz) sweep width. Depending on bulk solute concentration, 96–16000 such scans were collected (with a 0.2–0.4-s delay between scans) and averaged. The $\pi/2$ pulse width was determined to be 14.5–16 μs by trial and error with a CDCl_3 (10%)/ CHCl_3 solution. The data were processed by use of 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 kHz; 500 kHz at lower temperatures) sweep width and with a 1-s delay between scans. The $\pi/2$ pulse width is 3 μs on this spectrometer.

^{13}C NMR spectra 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).

Gas chromatographic analyses employed a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396 recording integrator, and a fused-silica megabore capillary column (10 m \times 0.53 mm HP-FFAP; Hewlett-Packard, Inc.). Semipreparative GC separations employed a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector and a 10% FFAP on 80/100 Supelcoport (10 ft \times 1/4 in.) stainless steel column.

The liquid crystals CCH-4 and CCH-2 were used as received from E. Merck Co. Dichloromethane, methanol, acetonitrile (all Caledon HPLC-grade), cyclohexane (Baker Phrotex), and *tert*-butyl alcohol (BDH Reagent) were used as received from the suppliers. Acetophenone, propiophenone, butyrophenone, and valerophenone (all 99+%) were used as received from Aldrich Chemical Co. *n*-Hexanophenone was prepared by Friedel-Crafts acylation of benzene with *n*-hexanoyl chloride and aluminum chloride and had bp = 75 °C (0.75 mm) [lit.⁴⁰ = 265 °C (760 mm)]. The α -deuterated ketones were prepared from their protio analogues by base-catalyzed deuterium exchange and were shown to be >90% α -deuterated by ^1H NMR (Varian EM390; CDCl_3). The ring-deuterated analogues were prepared by Friedel-Crafts acylation of benzene- d_6 (MSD Isotopes) with the appropriate acid chloride and aluminum chloride. All were purified by repeated vacuum distillation after workup.

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-o.d. 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 with a filtered (aqueous $\text{K}_2\text{Cr}_2\text{O}_7/\text{Na}_2\text{CO}_3/\text{Pyrex}$; 312 ± 10 nm) 450-W medium-pressure mercury lamp to 5–20% conversion. The tubes were opened and the contents were dissolved in methylene chloride and then analyzed by vapor-phase chromatography. Under our conditions, the isomeric cyclobutanols elute just after the starting material, and the *trans* isomer has the shorter retention time. This was shown explicitly by vpc isolation of the cyclobutanols from semipreparative scale photolyses of the three ketones in deoxygenated methanol (to >90% conversion) and identification of the two isomers on the basis of their infrared, mass, and ^1H NMR spectra.^{26a} 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 1.1 and that of the *cis* isomer occurs at δ 0.5 (CDCl_3).

The fragmentation/cyclization and *trans/cis*-cyclobutanol ratios reported in Table I are the average of 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.

Acknowledgment. We thank Dr. D. Hughes and Mr. B. Sayer (McMaster University) for technical assistance. We are also grateful to E. Merck (Darmstadt) for generous supplies of CCH-4 and CCH-2 and the Natural Sciences and Engineering Research Council of Canada for financial support.

(39) Montgomery, C. R.; Bunce, N. J.; Jeffery, K. R. *J. Phys. Chem.* **1988**, *92*, 3635.

(40) *Aldrich Catalog Handbook of Fine Chemicals*. Aldrich Chemical: Milwaukee, WI, 1989.