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Organic Reactions in Liquid-Crystalline Solvents. 9. Investigation of the Solubilization of Guest Molecules in a Smectic (Crystal-B) Liquid Crystal by Deuterium NMR, Calorimetry, Optical Microscopy, and Photoreactivity Methods[1]

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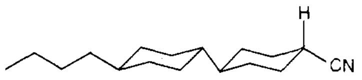
Abstract: The solubilization behavior of three aromatic ketones in the smectic (crystal-B) and nematic liquid-crystalline phases of *trans,trans*-4′-butylbicyclohexyl-4-carbonitrile (CCH-4) has been studied in detail by ^{2}H NMR spectroscopy, differential scanning calorimetry (DSC), and thermal microscopy, and complete binary phase diagrams for each ketone/CCH-4 system have been constructed. Combined with previously reported data, the results indicate that most aromatic molecules have very low solubilities (ca. 0.2–2.0 mol %) in the crystal-B phase of this mesogen. For a given solute, solubility in this phase increases with decreasing temperature. For bulk compositions above the solubility limit, the solute order parameters (from NMR) appear to decrease with decreasing temperature. This has been shown to be due to phase separation and the complex temperature-dependent behavior of the resulting smectic/nematic biphasic system. Other evidence indicates that the isotropic NMR behavior observed for many solute/CCH-4 mixtures at low temperatures is due to the formation of a smectic/isotropic biphasic system, not a plastic or cubic phase as has been proposed previously. The Norrish type II photoreactivity at 30 °C and the ^{2}H NMR behavior of γ-cyclohexylbutyrophenone-α,α-d_2 over the 30–80 °C range in CCH-4 have been investigated over a wide range of sample composition (0.6–40 mol %). The results obtained in the temperature range below the S–N transition of the pure liquid crystal can be explained within the context of a biphasic solubilization model.

The commercially available liquid crystal *trans,trans*-4′-butylbicyclohexyl-4-carbonitrile (CCH-4) and other homologues and eutectic mixtures in the CCH series have found extensive recent use as liquid-crystalline solvents in spectroscopic (including UV absorption,[3] fluorescence,[4] infrared,[5] ^{13}C NMR,[6] and ^{2}H NMR[7] spectroscopy) and photochemical studies,[8-13] because they are optically transparent at wavelengths $>$210 nm, form room-temperature nematic and smectic phases, and can be fairly easily aligned by magnetic fields. Their unusual propensity to be aligned with the liquid-crystalline director *perpendicular* to the applied magnetic field has certain advantages in NMR studies[6,7] and is the result of a negative molecular diamagnetic anisotropy[14] caused by their totally saturated hydrocarbon structures.



CCH-4

Pure CCH-4 exhibits enantiotropic nematic and bilayer crystal-B phases over the 53–80 and 28–53 °C temperature ranges, respectively, forms 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 rodlike mesogen in interdigitated bilayers, with the constituent molecules oriented with their long axes parallel to one another and perpendicular to the layer planes.[18-20] There is some degree of correlation from layer to layer, resulting in short-range three-dimensional crystalline regularity; hence the "crystal"-B designation.

While the structure of the liquid-crystalline phases of pure CCH-4 is apparently well-established,[16,17] the nature of the solubilization of guest molecules in its crystal-B phase has been subject to considerable recent discussion.[6,12,13,21,22] Studies of

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(1) Part 8: Fahie, B. J.; Mitchell, D. S.; Leigh, W. J. *Can. J. Chem.*, in press.

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(3) (a) Wedel, H.; Haase, W. *Chem. Phys. Lett.* **1978**, *55*, 96. (b) Myrvold, B. O.; Klaeboe, P. *Acta Chem. Scand.* **1985**, *A39*, 733. (c) Haase, W.; Trinquet, O.; Quotschalla, U.; Foitzik, J. K. *Mol. Cryst. Liq. Cryst.* **1987**, *148*, 15.

(4) Anderson, V. C.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6628.

(5) Jede, F.; Stratmann, A. W.; Schrader, B. *Mol. Cryst. Liq. Cryst.* **1986**, *140*, 297.

(6) (a) Fung, B. M.; Mui, D. S. L.; Bonnell, I. R.; Enwall, E. L. *J. Magn. Reson.* **1984**, *58*, 254. (b) Fung, B. M.; Gangoda, M. *J. Am. Chem. Soc.* **1985**, *107*, 3395.

(7) (a) Emsley, J. W.; Hashim, R.; Luckhurst, G. R.; Shilstone, G. N. *Liq. Cryst.* **1986**, *1*, 437. (b) Janik, B.; Samulski, E. T.; Toriumi, H. *J. Phys. Chem.* **1987**, *91*, 1842. (c) Pohl, L.; Eidenschink, R. *Anal. Chem.* **1978**, *50*, 1934. (d) Avant, A. G.; Emsley, J. W.; Ng, S.; Venables, S. M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1855. (e) Khetrapal, C. L.; Arun Kumar, B. S.; Ramanathan, K. V.; Suryaprakash, N. *J. Magn. Reson.* **1987**, *73*, 516. (f) Ambrosetti, R.; Catalano, D.; Forte, C.; Veracini, C. A. *Z. Naturforsch.* **1986**, *41A*, 431.

(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) Zimmermann, R. G.; Liu, J. H.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5264.

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

(12) Treanor, R. L.; Weiss, R. G. *J. Phys. Chem.* **1987**, *91*, 5552.

(13) (a) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413. (b) Leigh, W. J. In *Photochemistry on Solid Surfaces*; Matsuura, T., Anpo, M., Eds.; Elsevier: Amsterdam, The Netherlands, in press.

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

(15) *Licristal Liquid Crystals*; EM Chemicals: Hawthorne, NY, 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.* (*Les Ulis, Fr.*) **1979**, *40*, L-325.

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

(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, Inc.: New York, 1979. (b) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Weinheim, 1980. (c) Vertogen, G.; De Jeu, W. H. Thermotropic Liquid Crystals, Fundamentals. *Springer Ser. Chem. Phys.* **1987**; *45*.

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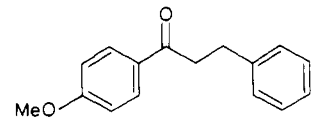
intramolecular triplet quenching in β-phenyl-4-methoxypropiophenone (**1**)[9] and remote-substituted phenolic ketones (**2**)[11] and



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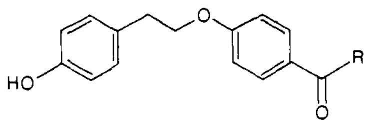

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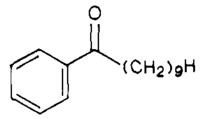

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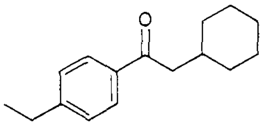

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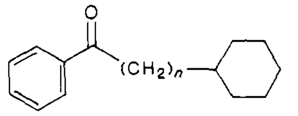

5a, $n = 3$
b, $n = 4$

of the fragmentation/cyclization ratios from the Norrish II photolysis of various substituted aromatic ketones (**3**–**5**)[10,12] (all of which depend on the conformational mobility of an excited triplet aromatic ketone or triplet 1,4-biradical)[13] in the isotropic, nematic, and crystal-B phases of CCH-4 led to the initial conclusion that solvent order in the crystal-B phase can impart very dramatic inhibitory effects on the conformational mobility of dissolved solutes.[9–12] The magnitude of the observed effect appears to depend quite critically on the structure of the solute (and its similarity to that of CCH-4) as well as the severity of the shape change that accompanies the conformational motion of interest. While the early studies of these systems more or less assumed homogeneous solvation of the probes in the crystal-B phase (based on thermal microscopic inspection of the solute/mesogen mixtures), more recent results have indicated that a much more complex situation may prevail in some or all of these cases.[6,11–13,21,22]

Fung and Gangoda first reported that mixtures containing 3–5 wt % benzene or dioxane in CCH-4 exhibit partially isotropic ^{13}C NMR behavior at temperatures below 10 °C and attributed this behavior to a solute-induced plastic or cubic phase, formed from the smectic solution, at low temperatures in this liquid crystal.[6b] Since then, Treanor and Weiss have reported similar phenomena in the deuterium NMR spectra of the α-deuterated derivatives of **3**–**5** and 4-cyclohexylacetophenone-α,α,α-d_3 (CAP) dissolved in the same liquid crystal,[12] modified their original interpretation[10] of the photochemistry of **3**–**5** in CCH-4, and emphasized the ramifications of plastic/cubic ("p") phase solubilization on the Norrish II photoreactivity of these compounds. These workers noted that the "p-phase" comprised only a small portion of the bulk (predominantly smectic) sample and described the phase as isolated pools of solute and CCH-4 (dispersed throughout the bulk smectic phase) that tumble isotropically as a unit (accounting for the NMR behavior) but are microscopically ordered (accounting for the photochemical behavior).[12] In the cases of **3**–**5** and CAP, p-phase formation occurs at somewhat higher temperatures compared to the mixtures of benzene or dioxane in CCH-4. Similar ^{1}H,[22] ^{2}H,[23] and ^{13}C NMR[22,23] results have now been obtained with mixtures of a wide variety of other solutes with this liquid crystal, and in each case, the isotropic NMR behavior observed at low temperatures has been attributed to the formation of an induced plastic phase from the smectic *solution* of the solute in CCH-4.

A second interesting feature common to all of these NMR studies is the temperature dependence of the spectral behavior in the range below the bulk N–S transition temperature and above that at which the p-phase is formed.[12,22,23] In all cases, the response of the spectrum to decreasing temperature in this range is indicative of a reduction in the orientational ordering of the solute as the temperature is lowered, and it has been proposed or implied that this reflects the behavior of the solute localized in a smectic *solution.* Fujiwara and co-workers have proposed that the behavior may result from a change in solvation site within the smectic array as the temperature is varied (from a more to a less ordered region as the temperature is lowered).[22] On the other hand, the photochemical studies that have been reported indicate that restrictions to solute conformational mobility in fact appear to *increase* with decreasing temperature over this same temperature range.[9–12] It is easy enough to rationalize this dichotomy however, because the photochemical and NMR experiments presumably probe different solute motions and could thus be affected by different aspects of smectic phase structure.[21]

Recently, we have found that **1**-α,α-d_2 exhibits NMR behavior similar in most respects to that reported previously for other solutes in the same liquid crystal but, from a detailed examination of the concentration dependence of the spectra, concluded that **1** has very low solubility in the crystal-B phase of the mesogen.[21] We have proposed that the ^{2}H NMR behavior of **1**-α,α-d_2 *and* the substantial alteration in the Arrhenius parameters for triplet decay of **1** that occurs below the S–N transition temperature of its mixture with CCH-4[9] are due to *heterogeneous* solubilization effects (phase separation); below the *bulk* S–N transition temperature, the ketone resides in both a solute-rich nematic phase (whose composition changes continuously with decreasing temperature) and a solute-depleted crystal-B phase of the almost pure (99.6–99.8 mol %) mesogen. At 35 °C, the minor, solute-rich (15–20 mol % **1**) nematic component of the two-phase system transforms into a viscous isotropic liquid or glass that is metastable and eventually crystallizes to form a stable binary smectic or solid modification of ca. 10% **1** in CCH-4. At temperatures below that of the bulk S–N transition, ^{2}H NMR spectra of **1**-α,α-d_2 are observable only for that portion of the solute localized in the mobile (nematic or isotropic) phase. The isotropic ^{2}H NMR behavior observed for **1** below 35 °C is similar to that observed for the other solutes discussed above in this liquid crystal, and which has been ascribed to the formation of a solute-induced plastic or cubic phase (the p-phase).[6b,12,22,23] On the basis of the similarities between the deuterium NMR behavior reported previously for **3**–**5**[12] and those observed by us for **1** and other solutes in CCH-4,[21] we have further suggested that the intriguing phase- and temperature-dependent photochemical behavior of **3**–**5** in this mesogen may be governed by similar solubilization phenomena as that experienced by **1** under the same conditions. Samori and co-workers have recently proposed analogous, heterogeneous solubilization effects in their studies of a thermal, bimolecular reaction in another smectic B liquid crystal.[25]

We have continued our studies of solute/CCH-4 mixtures with a view to providing a more complete indication of the range of

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[21] Fahie, B. J.; Mitchell, D. S.; Leigh, W. J. *Can. J. Chem.*, in press.

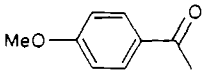
[22] Fujiwara, H.; Hirai, J.; Sasaki, Y.; Takahashi, K. *Mol. Cryst. Liq. Cryst.* **1987**, *150B*, 387.

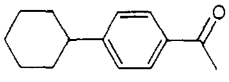
[23] While this work was in progress, we were informed of further results of ^{2}H and ^{13}C NMR studies on an additional, very extensive series of solute/CCH-4 mixtures, including CAP and PAP: Weiss, R. G., private communication.

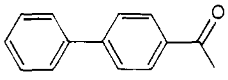
[24] For comprehensive reviews of the application of ^{2}H NMR in liquid crystals and leading references, see: (a) Nuclear Magnetic Resonance of Liquid Crystals. *NATO ASI Ser., Ser. C* **1985**, *141*. (b) Davis, J. H. *Biochim. Biophys. Acta* **1983**, *737*, 117. (c) Smith, I. C. P. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2. Chapter 1. (d) Vold, R. L.; Vold, R. R. *Isr. J. Chem.* **1983**, *23*, 315. (e) Doane, J. W. *Isr. J. Chem.* **1983**, *23*, 323. (f) Samulski, E. T. *Isr. J. Chem.* **1983**, *23*, 329. (g) Dong, R. Y. *Isr. J. Chem.* **1983**, *23*, 370. (h) Dong, R. Y. *Bull. Magn. Reson.* **1987**, *9*, 29. (i) Samulski, E. T. *Polymer* **1985**, *26*, 177. (j) Doane, J. W. In *Magnetic Resonance of Phase Transitions*; Owens, F. J., Poole, C. P., Jr., Farach, H. A., Eds.; Academic Press: New York, 1979; Chapter 4.

[25] Samori, B.; De Maria, P.; Mariani, P.; Rustichelli, F.; Zani, P. *Tetrahedron* **1987**, *43*, 1409.

solubilities of various solute molecules in the crystal-B phase as a function of structure, the morphology of the p-phase in solute/CCH-4 mixtures, and the generality of the formation of solute/CCH-4 binary solid and/or crystalline modifications and how this relates to p-phase formation, and provide discrete examples of deuterium quadrupole NMR spectra of solutes in the crystal-B phase of this mesogen. In this paper, we report the results of our investigation of the behavior of binary mixtures of three para-substituted acetophenone derivatives—4-methoxy- (MAP),


MAP


CAP


PAP

4-cyclohexyl- (CAP), and 4-phenylacetophenone (PAP)—and their α-deuterated derivatives in the liquid-crystalline phases of CCH-4 by deuterium NMR spectroscopy, differential scanning calorimetry (DSC), and thermal microscopy. The studies of MAP and CAP reported herein represent a more exhaustive investigation of the solubilization of these compounds in CCH-4 than those reported earlier by us (for MAP[21]) and by Treanor and Weiss (for CAP[12,23]). The results are correlated with binary phase diagrams constructed for each set of mixtures by DSC and thermal microscopy and suggest (among other things) that the solute-induced p-phase has a rather different morphology than that proposed by previous workers.

In addition, we have carried out an investigation of the deuterium NMR behavior of 0.6–2.3 mol % mixtures of **5a**-α,α-d_2 in CCH-4 and the Norrish II photoreactivity of this molecule in CCH-4 over a broad range of concentrations (0.6–40 mol %) at 30 °C. Our results lead to significant modification of the previously reported interpretations of solute behavior in this liquid crystal. We believe that they may further have broad general ramifications to studies of solute behavior in other highly ordered or constrained media as well.

Results and Discussion

The α-deuterated ketones employed in this study were prepared from their all-protiated analogues by exchange deuteriation in alkaline deuterium oxide/dioxane and were estimated to be ≥90% isotopically pure in the α-position by ^{1}H NMR spectroscopy.

Deuterium NMR spectra of 0.6, 2.0 or 3.0, and 8.0 mol % mixtures of MAP, CAP, and PAP (as the α-deuterated derivatives) in CCH-4 were recorded at 76.8 MHz, at various temperatures between 10 and 82 °C, using the quadrupolar echo pulse sequence.[26] Similar experiments were also carried out on a series of mixtures of **5a**-α,α-d_2/CCH-4 of varying composition between 0.6 and 2.3 mol % in ketone. Portions of these data are shown for each ketone/CCH-4 system in Figures 1, 4, 7, and 9.

The ^{2}H NMR behavior of each of the ketone/CCH-4 mixtures in the isotropic and nematic phases is unexceptional.[24] Each exhibits a single deuterium resonance in the isotropic phase at 80 °C, which splits into a quadrupolar doublet as the temperature is lowered below the range corresponding to the nematic–isotropic (N–I) transition of the mixture. The transition is fairly sharp for the 0.6 mol % mixtures and is within 1–2 °C of that for the pure liquid crystal, but is lowered and broadened in the 2–3 mol % samples. The breadth of the phase transition in these cases is reflected in the NMR spectra by the presence of both the singlet (isotropic) and doublet (nematic) patterns in relative intensities that vary monotonously as the transition is traversed. The general *appearance* of the nematic phase spectrum (i.e., a single, well-defined doublet) is in each case characteristic of a well-oriented solute experiencing restricted reorientational motions, but fast exchange of the three C–D bonds on the time scale of the experiment.[24] In these experiments the nematic phase is believed to be aligned preferentially perpendicular to the applied field direction,[7,14] because CCH-4 possesses negative diamagnetic anisotropy.[14]

For a deuterated probe molecule in a liquid crystal, the *magnitude* of $\Delta\nu_Q$ depends on the time-averaged orientation of the C–D bond(s) with respect to the applied magnetic field and thus can be related to the degree of orientational ordering associated with the probe as a whole.[24] This is commonly expressed quantitatively in terms of one or more "order parameters", which relate the time-averaged orientation of the molecule (or individual bonds in the molecule) with respect to some predefined laboratory axis system. The value of the order parameter can range from 0 (in the case of isotropic motion) to ±1 (completely uniform, fixed orientation). On a qualitative level, for a given deuterated solute in a given liquid crystal, a change in the order parameter as experimental conditions are varied results in a corresponding change in $\Delta\nu_Q$.[24]

As the temperature is lowered throughout the nematic phase, the doublet splitting increases as a result of increasing restrictions to molecular reorientation (increasing solute order parameter) as the order in the phase increases.[24] The splitting reaches a maximum at the temperature corresponding to the smectic–nematic (S–N) transition, or its onset.

At a given temperature in the nematic phase, the observed values of $\Delta\nu_Q$ for each of the three substituted-acetophenone/CCH-4 mixtures decrease in the order MAP > PAP > CAP. In the present case, the relative $\Delta\nu_Q$ values for CAP and PAP should reflect the relative magnitudes of the solute order parameters reasonably accurately, since the molecular shapes of these two solutes are virtually identical and the conformational distributions of the acetyl-d_3 group should be the same. On the other hand, the data obtained for MAP cannot be compared to those for the other two, since this compound's conformational behavior is different.[27] MAP can exist in two distinct conformational families (with syn and anti arrangements of the methoxy and acetyl substituents) that are presumably comparably populated in solution[28a] and undergoing fast exchange in the nematic phase.[28b] If the long molecular axis in the anti conformer is taken as the one that bisects the acetyl and methoxy methyl carbons, then simple calculations[24i,j] indicate that this conformer should exhibit somewhat larger quadrupolar splittings than *syn*-MAP, CAP, and PAP, since the acetyl C–D bonds are arranged at different angles with respect to the long molecular axis (and, hence, with the applied magnetic field) in this conformer than they are in *syn*-MAP or the other ketones. Fast equilibrium between syn and anti conformers would then account for the higher quadrupolar splitting observed for this derivative compared to the other two.

The spectral behavior of these mixtures below 53 °C (or more precisely, the onset of the bulk N–S transition temperature) depends on the solute and on its bulk concentration in the mixture. As a result, we discuss the deuterium NMR and other data that have been obtained for each solute/CCH-4 system in separate sections below.

The MAP/CCH-4 Binary System. The spectral pattern exhibited by the 0.6 mol % solution of MAP/CCH-4 changes dramatically below 53 °C, with the fairly sharp nematic phase doublet (ca. 4.9 kHz) being replaced by two broad doublets of considerably larger splitting (see Figure 1A). The splitting associated with the inner doublet (ca. 11.8 kHz) is more or less independent of temperature, while that of the outer one (ca. 14 kHz at 50 °C) increases markedly with decreasing temperature. This is the same spectrum that is observed as a minor component of the total spectrum for the 3.0 mol % MAP/CCH-4 sample in the 23–50 °C temperature range (Figure 1B; vide infra), and we assign it to the ketone solubilized in the crystal-B phase of the

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

[27] (a) Veracini, C. A.; Longeri, M. in ref 24a, p 123. (b) Emsley, J. W. in ref 24a, p 379.

[28] (a) Allinger, N. L.; Maul, J. J.; Hickey, M. J. *J. Org. Chem.* **1971**, *36*, 2747. (b) Emsley, J. W.; Lindon, J. C.; Street, J. M.; Hawkes, G. E. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1365.

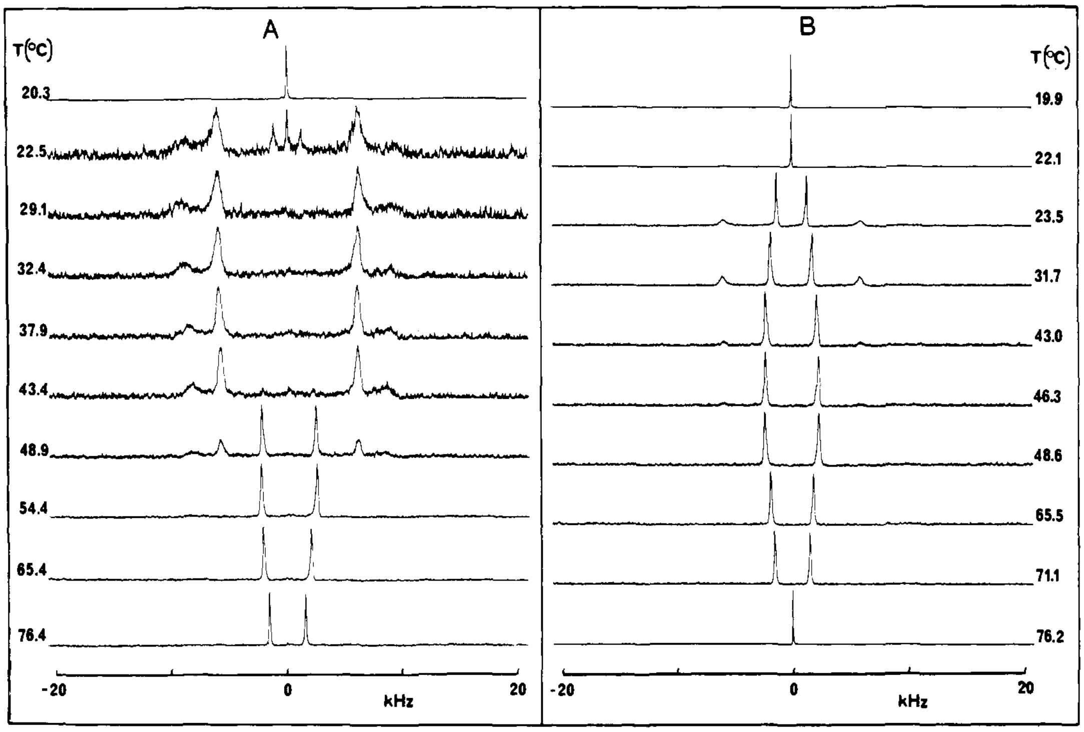

Figure 1. Deuterium NMR spectra of 0.6 (A) and 3.0 mol % (B) mixtures of MAP-d_3 in CCH-4 as a function of temperature.

mesogen. The rather broad spectral lines compared to those obtained in the nematic phase are typical of deuterium spectra in highly ordered smectic liquid crystals,[29,30] and the general appearance of the spectrum is characteristic of a uniformly oriented solute experiencing restricted reorientational motions, with the C–D bonds exchanging relatively slowly on the NMR time scale.[30] We initially assumed that this spectral pattern is due to the solute localized in a single type of environment within the highly ordered crystal-B phase.[30] However, it is also possible that the spectrum is the composite of those due to ketone in two nonexchanging environments, each characterized by a well-defined doublet splitting pattern. To try and distinguish between these two possibilities, we have determined the deuterium T_1 values associated with the two components of the spectrum at a few temperatures in the 23–53 °C range. These experiments were carried out with a standard quadrupolar echo/inversion-recovery pulse sequence. We find that the two components are characterized by *different* T_1 values (e.g., at 43 °C, 184 ± 40 and 99 ± 32 ms (errors as $\pm\sigma$) for the 11.8 and 14 kHz doublets, respectively), indicating that the spectrum is most likely the composite of those due to ketone in two nonexchanging environments.

For this mixture, the entire spectrum collapses to an isotropic singlet at 23 °C, signifying the formation of the p-phase. Figure 1A contains a spectrum recorded at 22.5 °C, which represents the midpoint of the transition to the isotropic spectrum; in addition to the presence of the two spectral patterns characteristic of MAP solubilized in the crystal-B phase and the p-phase, the spectrum shows a sharp doublet splitting of ca. 3 kHz. This additional doublet is assigned to the ketone solubilized in a *nematic* phase, and its transient presence during the phase transition is indicative of an eutectic in the MAP/CCH-4 binary phase diagram (vide infra).

In the mixtures containing ≥1 mol % MAP, the spectra in the 23–50 °C temperature range (see Figure 1B) are more complex, consisting of a prominent doublet ($\Delta\nu_Q$ = 2.6–4.8 kHz) flanked by the weaker, broader doublet of splitting (≈11.8 kHz) that was assigned to the ketone in the crystal-B phase. The inner doublet has line widths similar to those observed at higher temperatures when the bulk solution is in the nematic phase, its splitting decreases with decreasing temperature until collapsing to an isotropic-like singlet at 23 °C, and its intensity relative to that of the outer doublet decreases as the temperature is lowered.

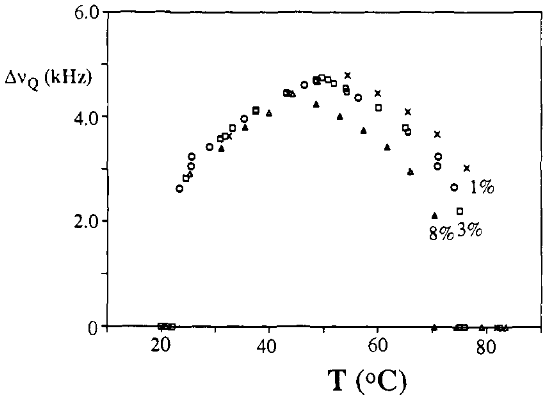

Figure 2. Composite plot of $\Delta\nu_Q$ vs temperature for 1.0 (×), 3.0 (□), and 8.0 (△) mol % mixtures of MAP and CCH-4. Only the splittings for the innermost (nematic) doublets are shown.

Figure 2 shows a composite plot of our data for the 1.0, 3.0, and 8.0 mol % MAP/CCH-4 mixtures (only the splittings for the sharp innermost doublets are plotted). As was found in our earlier study of mixtures of **1** in this mesogen,[21] the data obtained at temperatures *above* that corresponding to the apexes in the plots (the points at which the onset of the S–N transition occurs for each mixture) describe a series of parallel curves that are shifted (at a given temperature) to higher $\Delta\nu_Q$ values with decreasing solute concentration. This is the expected result for a series of homogeneous nematic phases of different bulk concentrations.[21] *Below* the apexes in the plots, the data for all three mixtures fall on the same curve. This is a very good indication that below the onset of the S–N transition in the mixtures of composition ≥1.0 mol %, the sharp inner doublet arises from ketone that is solubilized in a common phase whose composition depends only on the temperature, *not* on the bulk composition of the mixture. In the MAP/CCH-4 mixtures of ≥3.0 mol % bulk composition, the

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(29) (a) Luz, Z.; Hewitt, R. C.; Meiboom, S. *J. Chem. Phys.* **1974**, *61*, 1758. (b) Vaz, M. J.; Yaniv, Z.; Dong, R. Y.; Doane, J. W. *J. Magn. Reson.* **1985**, *62*, 461.

(30) (a) Dong, R. Y.; Schmiedel, H.; Vaz, N. A. P.; Yaniv, Z.; Neubert, M. E.; Doane, J. W. *Mol. Cryst. Liq. Cryst.* **1983**, *98*, 411. (b) Vaz, N. A.; Vaz, M. J.; Doane, J. W. *Phys. Rev. A* **1984**, *30*, 1008.

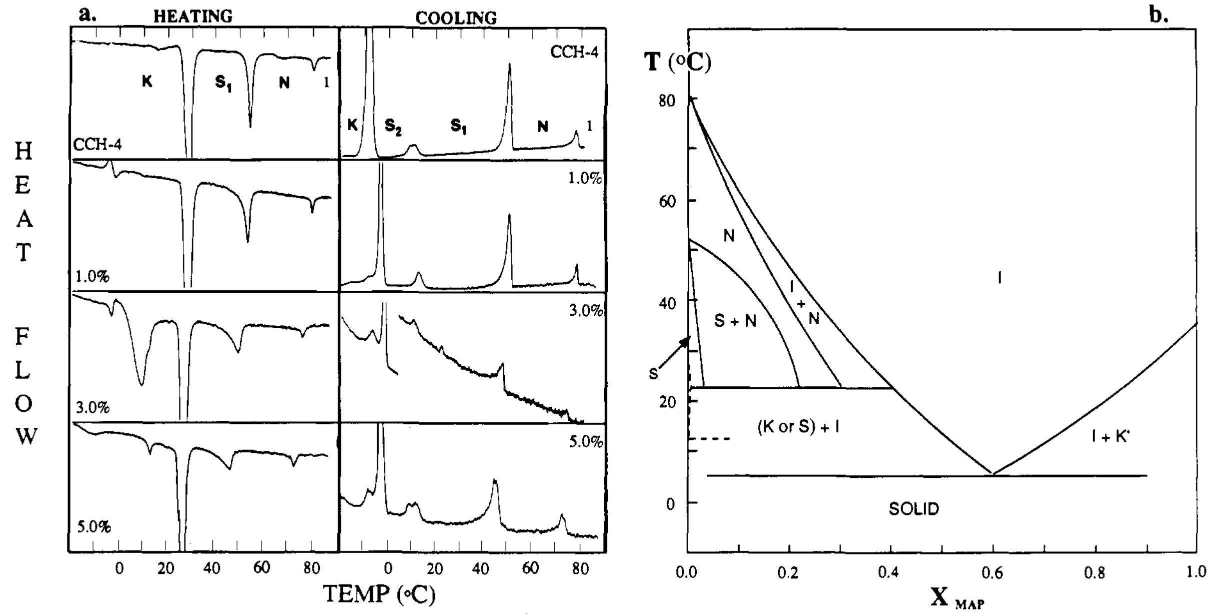


Figure 3. (a) Heating and cooling DSC thermograms for various mixtures of MAP and CCH-4 and (b) the binary phase diagram for the MAP/CCH-4 system, constructed from DSC and thermal microscopy data. Solid lines in (b) represent heating data; dashed lines show supercooled behavior. Phase identities: I, isotropic; N, nematic; S, smectic; K, solid.

spectra collapse to an isotropic singlet at 23 °C, the same temperature at which the 0.6 mol % (homogeneous crystal-B) sample does.

We assign the sharp, inner doublet splittings observed for these samples in the 23–53 °C temperature range to the ketone solubilized in a nematic phase as a result of phase separation. This nematic phase is relatively rich in solute and coexists with a crystal-B phase composed of 0.6–1.2 mol % MAP in CCH-4. The quadrupolar splitting of the doublet associated with the nematic phase component decreases with decreasing temperature because of the changing composition of the solute-rich phase as the temperature is lowered and increased amounts of the crystal-B phase are formed; as this occurs, the nematic phase becomes increasingly enriched in the nonmesomorphic solute and solute ordering decreases.[3c] A 1.0 mol % MAP/CCH-4 mixture exhibits a biphasic region from 53 to ca. 35 °C (in which signals corresponding to MAP in both nematic and crystal-B phases coexist), but shows only the crystal-B spectrum at temperatures between 35 and 23 °C. Below 23 °C, the spectrum consists only of the sharp isotropic singlet characteristic of the p-phase. Thus, from the deuterium NMR behavior of the 0.6 and 1.0 mol % MAP/CCH-4 mixtures, we estimate that the limit of solubility of MAP in the crystal-B phase varies from 0.6–0.7 mol % at the higher end of the smectic phase temperature range to 1.1–1.2 mol % at the lower end.

Additional evidence for phase separation in these mixtures is provided by DSC and thermal microscopy experiments, carried out on mixtures containing 0–50 mol % MAP (as the all-protio homologue) and CCH-4. A few representative DSC thermograms at various solute concentrations are shown in Figure 3a,b for these mixtures. For the pure liquid crystal, DSC reveals a weak (enthalpy-wise) N–I transition at 79–80 °C, a more substantial Sm (crystal B)–N transition at 53 °C (in heating, 50 °C in cooling), and a very strong K–Sm transition at 29 °C that is supercooled to −9 °C with a 2 °C/min cooling rate. As has been reported previously,[17] the DSC cooling trace reveals the presence of a second, monotropic smectic phase between 12 and −9 °C that eventually crystallizes, and the crystal-B phase exhibits partial monotropic behavior (i.e., it exists down to 12 °C in cooling runs, but is metastable with respect to solid-phase formation between 12 and 28 °C). The mixtures containing ≤3.0 mol % MAP *appeared* to form homogeneous nematic and smectic solutions by both DSC and thermal microscopy.

The DSC thermograms of the mixtures containing 0–10 mol % MAP show no consistent evidence of a new transition at 23 °C that might be assigned to p-phase formation (cf. the cooling trace for the 3 mol % mixture in Figure 3b, however). The consistent effects of increasing amounts of solute on the DSC thermograms are limited to a lowering and broadening of the N–I and Sm (crystal B)–N transition temperatures within the 0–20 mol % concentration range and complete disappearance of mesomorphic behavior in mixtures containing ≥30 mol % of the ketone.

On the other hand, thermal microscopy experiments on mixtures containing ≥3 mol % MAP provide clear verification that phase separation occurs in these samples at temperatures throughout the complete range of existence of the crystal-B phase in pure CCH-4. Furthermore, they reveal that the transition at 23 °C observed in the NMR spectra of the MAP-d_3/CCH-4 mixtures involves transformation of residual nematic phase (identified on the basis of its texture and fluidity) to a mixture of smectic phase and an optically isotropic (nonbirefringent) fluid. The transition is completely reversible and is not subject to supercooling. We identify the latter as the p-phase that is responsible for the isotropic ^{2}H and ^{13}C NMR behavior of the MAP/CCH-4 mixtures at temperatures less than 23 °C. While the p-phase is visually evident in the low-composition mixtures of MAP in CCH-4 (3.0 ≤ [MAP] ≤ 5.0), it is difficult to get an indication of the degree of fluidity of this phase by applying stress to the samples (because the bulk sample is predominantly smectic). In the >5 mol % samples however, simple tapping on the sample slide reveals that the optically isotropic phase is viscous, but clearly *mobile*.

As the concentration of ketone in the bulk mixture is increased from 1.0 to 50 mol %, the N–I and S–N transitions are progressively lowered and broadened, until in the 40% sample, the isotropic phase persists down to ca. 12 °C and slowly crystallizes at lower temperatures. These results combine to indicate that the p-phase is a viscous, isotropic *liquid* of composition 20–30 mol % MAP.

Our inability to detect the transition at 23 °C by DSC in this case is interesting, since it is clearly evident by both thermal microscopy and NMR, and the corresponding transition in mixtures of **1**/CCH-4[21] and CAP/CCH-4 (vide infra) is clearly discernible by DSC. We note, however, that the transition involves transformation of a nematic phase to *both* an isotropic phase (an exothermic process) and a smectic phase (an endothermic process). It is thus reasonable that under the right conditions such a transition might involve a net zero change in enthalpy, or at least a very small one, and this could explain our inability to detect it by DSC.

The temperature–composition binary phase diagram for the MAP/CCH-4 system, representing the various phase transition

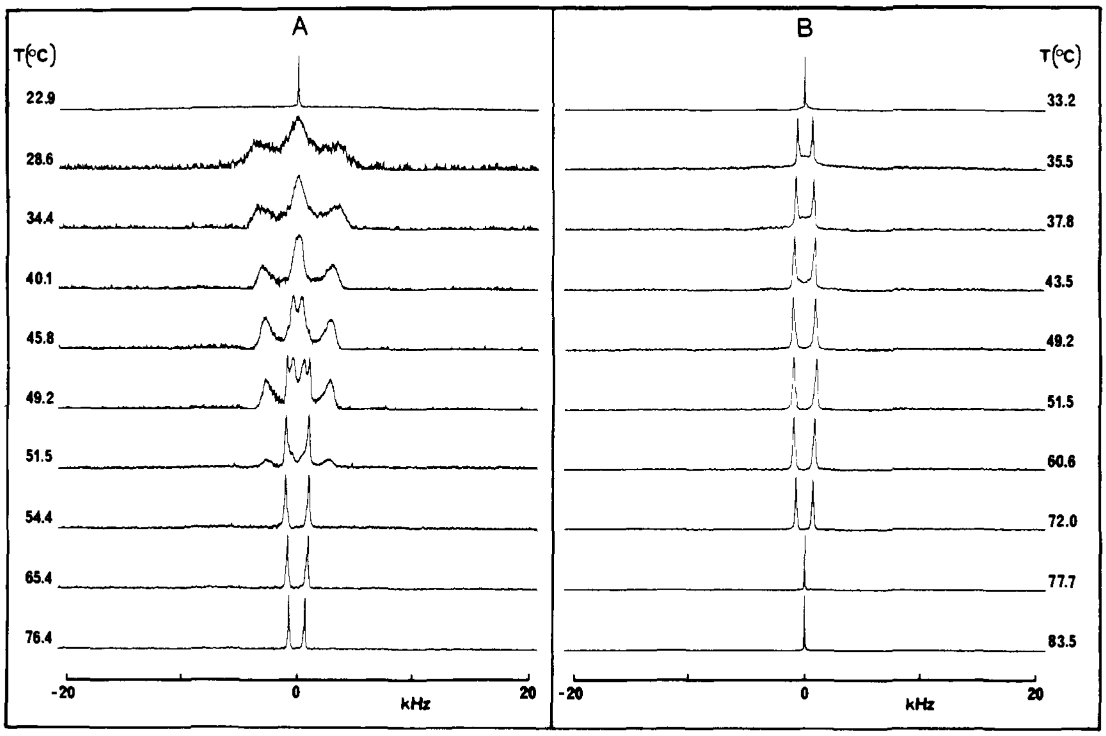


Figure 4. Deuterium NMR spectra of 0.6 (A) and 2.0 mol % (B) mixtures of CAP-d_3 in CCH-4 as a function of temperature.

temperatures obtained from thermal microscopy and DSC heating data, is shown in Figure 3b. The phase boundaries were assigned precisely on the basis of thermal microscopy cooling data, obtained with fresh solutions of ketone in the mesogen that were first homogenized in the isotropic phase at elevated temperatures and then placed on the preheated microscope hot stage. This procedure was followed in order to ensure that the samples were mixed adequately in the isotropic phase. Because of phase separation at lower temperatures, samples that are first allowed to cool suffer from inhomogeneity and sometimes behave erratically in subsequent heating and cooling cycles. The detail in Figure 3b for the composition range below 3 mol % ketone has been filled in by using the deuterium NMR data.

The diagram shows explicitly the variety of biphasic regions that exist in MAP/CCH-4 mixtures in the concentration domain above 1 mol % and indicates that the nematic phase giving rise to the doublet splittings in the NMR spectra at temperatures between 23 and 50 °C varies in composition between ca. 5 mol % at the higher temperatures and ca. 25 mol % at the lowest. Transitions detected in heating are represented by solid lines in Figure 3b. During cooling, the I $\Rightarrow$ S + I and S + I $\Rightarrow$ solid transitions are supercooled, and these are represented by dotted lines in the figure. The region marked "(K or S) + I" in the diagram actually contains additional S–S, S–K, or K–K transitions that were supercooled substantially. We have left these out of the diagram partly for clarity, but also because we are unable to discern the exact identity of these phases.

The CAP/CCH-4 Binary System. The behavior of the CAP/CCH-4 binary system is similar in many respects to that of the MAP/CCH-4 mixtures, but nonetheless exhibits a few important differences that require additional discussion. The deuterium NMR data recorded for 0.6 and 2.0 mol % CAP/CCH-4 mixtures are shown in Figure 4.

The nematic phase doublet in the spectrum of the 0.6 mol % CAP/CCH-4 mixture is replaced by two new spectral patterns as the temperature of the sample is lowered through the bulk S–N transition. Figure 4A contains spectra obtained during the phase transition (51.5 and 49.2 °C); they show the original, sharp nematic phase doublet superimposed on the new, considerably broader patterns associated with the lower temperature phase. The former (nematic doublet) disappears entirely at 46 °C. We assign the latter spectral pattern to the ketone solubilized in the crystal-B phase of CCH-4, although we are uncertain as to whether the spectrum is that of a uniformly oriented solute or a mixture of oriented (associated with the outer doublet splitting) and randomly oriented (associated with the inner, powderlike spectral pattern) material. The two spectral patterns respond differently to decreasing temperature; the inner pattern narrows markedly while the outer doublet splitting decreases in magnitude as the temperature is lowered; this could be consistent with either possibility. However, the relative intensities of the two spectral patterns do not change appreciably with the rate at which the nematic phase is cooled to form the smectic phase, and this is consistent with the spectrum being due solely to uniformly oriented solute. We note however, that such a variation in spectral appearance with sample cooling rate *is* obtained with the PAP/CCH-4 samples (vide infra), so the latter experiment should be interpreted with caution. The two possibilities could perhaps be distinguished more reliably by deuterium T_1 measurements or a careful study of the dependence of the spectrum on sample orientation with respect to the applied field, since an oriented spectrum will change with sample orientation, while a powder spectrum will not.[24]

The entire spectrum collapses to a narrow, isotropic singlet between 23 and 28 °C, signifying formation of the p-phase. It should be noted that unlike the MAP/CCH-4 system, p-phase formation in CAP/CCH-4 mixtures occurs at temperatures that vary depending on the bulk composition of the sample. This signifies a very basic difference in the phase diagram of this system in the low solute concentration region compared to that of MAP/CCH-4.

The spectrum of the 2.0 mol % CAP/CCH-4 mixture consists of a prominent, sharp doublet in the 35–50 °C temperature range, with additional, broad absorption in the spectral region between the sharp doublet components (see Figure 4B). We assign the prominent doublet splitting to the ketone solubilized in the minor, nematic component of a two-phase system consisting of solute-rich nematic phase in equilibrium with a crystal-B phase of composition that varies between 0.6 (at 46 °C; vide supra) and ca. 0.8 mol % (at 35 °C) CAP. The latter component of the mixture is the one responsible for the broad, unresolved absorption in the region between the sharp doublet components. Further evidence for this assignment has been obtained from a composite plot of $\Delta\nu_Q$ vs T for the 0.6, 2.0, and 8.0 mol % mixtures (not shown). The salient

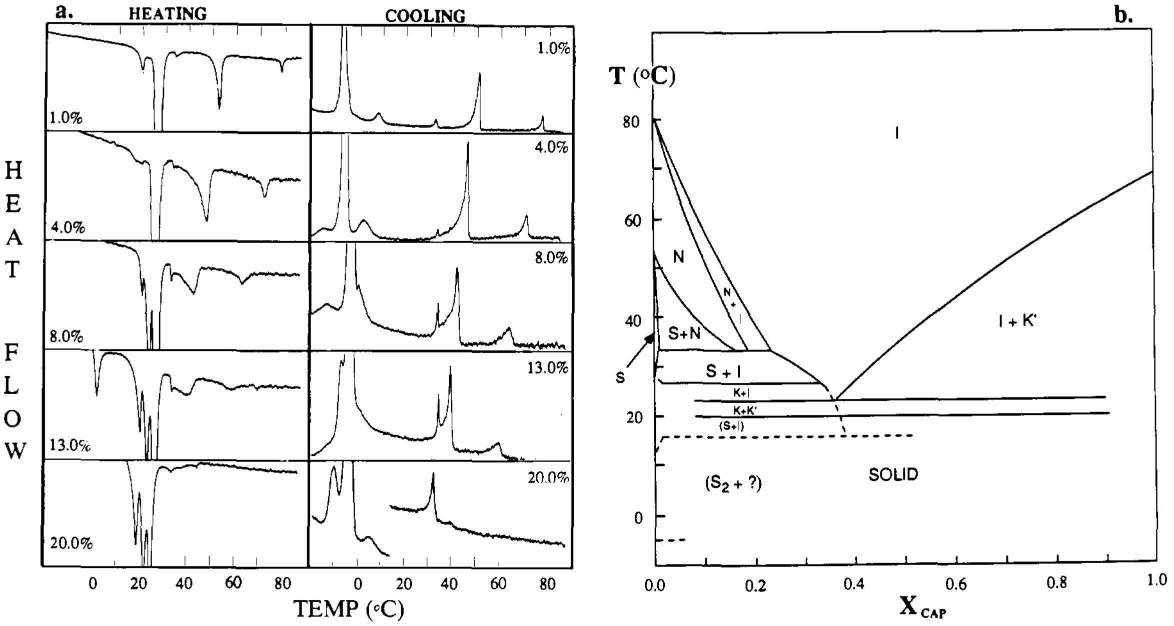


Figure 5. (a) Heating and cooling DSC thermograms for various mixtures of CAP and CCH-4 and (b) the binary phase diagram for the CAP/CCH-4 system, constructed from DSC and thermal microscopy data. Solid lines in (b) represent heating data; dashed lines show supercooled behavior. Phase identities: I, isotropic; N, nematic; S, smectic; K, solid.

features of this plot are virtually identical to those of the MAP/CCH-4 mixtures that are shown in Figure 2. Collapse of the nematic phase doublet to the isotropic singlet characteristic of the p-phase occurs at 34 °C in the 2.0 mol % mixture and at the same temperature in all mixtures of higher concentration.

Mixtures containing 0–50 mol % CAP (as the all-protio homologue) and CCH-4 were also investigated by DSC and thermal microscopy, and representative DSC thermograms recorded for various solute concentrations are shown in Figure 5a. The mixtures containing $\leq$1.0 mol % of this ketone appeared to form homogeneous solutions by both methods. The DSC thermograms of the mixture containing 1.0 mol % solute exhibit a new, weak transition at 32 °C. The intensity of this transition increases with the proportion of ketone in the sample up to 25 mol %. Furthermore, the temperature at which this transition occurs increases from 32 °C in the 1.0 mol % sample to 35 °C in the 2 mol % sample, above which it is independent of composition. In all cases, the transition temperature is the same in both heating and cooling scans.

Thermal microscopy experiments again verify that phase separation occurs in these samples at temperatures throughout the complete range of existence of the crystal-B phase, and that the new transition (at 35 °C) in the $\geq$1 mol % mixtures involves transformation of residual nematic phase to a mixture of smectic phase and an optically isotropic fluid. Again, we identify the latter phase as the p-phase that is responsible for the isotropic ^{2}H NMR behavior of the CAP/CCH-4 mixtures at temperatures less than 35 °C, and it can be seen to possess the fluidity of a viscous isotropic liquid in mixtures of composition $\geq$5 mol % CAP.

Figure 6 shows a series of photomicrographs taken of an 18 mol % CAP/CCH-4 mixture between 34.2 and 32.5 °C, before (Figure 6a), during (Figure 6b), and after (Figure 6c) the $N \Rightarrow S + I$ transition. These photographs illustrate clearly the transformation of the nematic phase to yield smectic monodomains interspersed in the isotropic phase.

As was found for the MAP/CCH-4 mixtures, the N–I and S–N transitions are progressively lowered and broadened as the concentration of ketone in the bulk mixture is increased from 1.0 to 40 mol %, until the sample remains an isotropic liquid down to ca. 12 °C for the 40 mol % mixture. Again, our results indicate that the p-phase is a viscous, isotropic *liquid* of composition 20–35 mol % in ketone.

During storage at room temperature for long periods of time (at least a few weeks), the concentrated isotropic phase formed by phase separation in the CAP/CCH-4 mixtures undergoes crystallization to yield a suspension of crystals in residual isotropic phase. The crystalline material has not been rigorously identified, but it is reasonable to assume that it is either pure (or almost pure) CAP or a binary solid modification with CCH-4. We favor the former possibility on the basis of the following experiments. Rapid cooling of the mixtures from the bulk nematic phase to a temperature below that of the N–P transition (which was found in the case of **1**/CCH-4 to yield the binary modification directly, without prior phase separation[21]) yielded samples that initially appeared to be crystalline, but that gradually (over 15–60 min) reorganized to the S + I mixture. This behavior was verified by DSC; an 8 mol % CAP/CCH-4 sample was heated to the nematic phase and immediately quenched to −20 °C (in one experiment) and 77 K (in another). The DSC heating thermograms that were then recorded were found to be identical in all respects to those obtained under "standard" conditions. We believe that the differences between the NMR spectra of freshly prepared and aged 1.8 mol % CAP/CCH-4 samples at 30 °C that have been reported previously[12] are due to crystallization of the ketone from the phase-separated isotropic phase. The NMR spectrum of the freshly prepared sample shows only the isotropic component under the conditions employed,[12] but this is presumably superimposed on a broader, much weaker spectral pattern associated with ketone solubilized in the smectic phase. After aging, considerably less ketone is left in the isotropic phase due to recrystallization, so that the reported spectrum consists of smectic and isotropic components in comparable relative intensities.

The phase-separated isotropic phase obtained in the MAP/CCH-4 mixtures behaves in similar fashion to that of CAP/CCH-4; i.e., it does not crystallize to form a stable binary modification under any conditions.

The temperature–composition binary phase diagram for the CAP/CCH-4 system, constructed from DSC and thermal microscopy cooling data, is shown in Figure 5b. The detail in the composition range below 1 mol % ketone has been filled in using the deuterium NMR data. All transitions between single-phase and biphasic regions have been verified by heating and cooling the appropriate mixtures in the polarizing microscope.

The PAP/CCH-4 Binary System. This system behaves quite differently than do the others reported in this work. First of all, it is apparent from the ^{2}H NMR spectra shown in Figure 7 that PAP/CCH-4 mixtures do not give rise to p-phase formation as the other ketone/CCH-4 mixtures do. Because this system is in

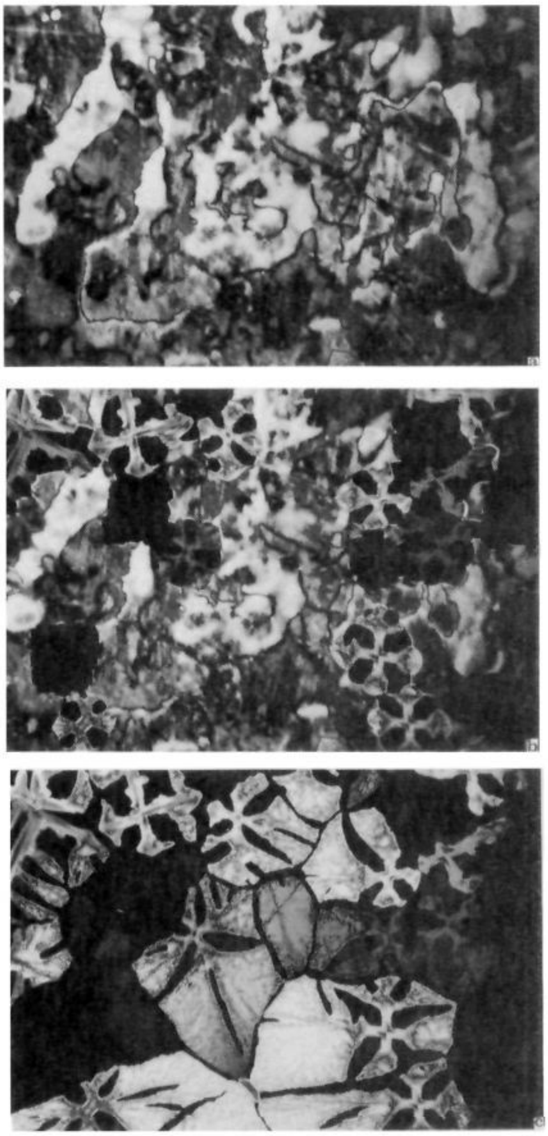


Figure 6. Photomicrographs of the 16.0 mol % CAP/CCH-4 mixture at (a) 34.2 °C (in the nematic phase), (b) 33.5 °C (during the $N \Rightarrow S + I$ transition), and (c) 32.5 °C (in the S + I phases, after the transition). The smectic phase is characterized by the distorted Maltese crosses in (b) and (c), while the isotropic phase consists of the black, optically extinct regions.

fact considerably more complex than the NMR spectra indicate, we will first present and discuss the binary phase diagram obtained from DSC and thermal microscopy data for 0–50 mol % mixtures of PAP and CCH-4.

Figure 8a shows DSC heating and cooling traces, recorded for various PAP/CCH-4 mixtures in the 0–30 mol % composition range. In the mixtures containing 2–10 mol % ketone, a new transition appears at 27–30 °C in the cooling traces and at 43 °C in the corresponding heating cycles. The relative intensity of this peak increases as the bulk concentration of ketone in the sample increases. This transition is absent in both the heating and cooling DSC traces for the mixtures containing <2 mol % PAP. Thermal microscopy indicates that this peak corresponds to interconversion between the minor, nematic component of a N + Sm two-phase system and a crystalline solid that forms as well-defined needles. The transition is evident by microscopy in cooling a 1 mol % PAP/CCH-4 sample as well, even though the sample *appears* to be homogeneously smectic at temperatures just above 27 °C. We are unable to detect the (cooling) transition in a 0.6 mol % sample by thermal microscopy. However, allowing the sample to anneal to room temperature (ca. 25 °C) for a day or two yields a sample that consists of a few fine, long needles interspersed in the mosaic platelets of the smectic liquid crystal. Upon heating, these needles transform to a nematic liquid interspersed in the smectic phase at 42–43 °C. We believe that these results indicate that PAP does form a stable crystal-B *solution* with CCH-4 (of composition 0.6–0.8 mol % ketone) between 42 and 50–53 °C. Below 42 °C, the solution is metastable and eventually separates to form a mixture of a binary solid modification (of ca. 7 mol % PAP/CCH-4; vide infra) and a crystal-B phase consisting of pure (or almost pure) CCH-4.

Cooling a 7.0 mol % sample of PAP/CCH-4 from the (homogeneous) nematic phase results in the formation of a N + Sm two-phase system at 41–42 °C by thermal microscopy. As the temperature is lowered further, progressively more smectic phase separates out until the residual nematic phase appears to crystallize at 27–28 °C. Immediate reheating of the sample results in gradual reorganization of the material and sharp, uniform melting to a nematic phase at ca. 42 °C. Allowing the sample to sit at 25 °C for a few days causes it to transform completely to fine needles. Heating this sample results in melting of most (ca. 98%) of this material at 42–43 °C to yield a nematic phase that contains a few very fine needlelike crystals. These crystals slowly dissolve as the temperature is raised over the next few degrees and are thought to consist of pure (or almost pure) PAP. Heating similarly annealed samples of higher ketone content under the microscope affords similar results, except correspondingly greater amounts of crystals persist after the main $K \rightarrow N$ transition and they require correspondingly higher temperatures to effect complete dissolution. These results combine to indicate that PAP and CCH-4 form a stable binary solid modification, consisting of ca. 6.5% ketone, that transforms to a nematic phase of the same composition at 42 °C.

Cooling runs on samples containing >10 mol % PAP afford particularly complex behavior, caused by crystallization of pure ketone from the nematic or isotropic melts.

Figure 8b shows the binary phase diagram, constructed from heating and cooling data obtained from the DSC and thermal microscopic analyses of PAP/CCH-4 mixtures in the 0–50 mol % concentration range. The binary solid modification is designated as composition A in these diagrams. Because the transitions involving crystallization of pure ketone from the isotropic and nematic phases in the samples of higher (>7 mol %) composition and the one involving $N \rightleftarrows A$ interconversion are subject to considerable supercooling, the phase diagrams constructed from heating and cooling experiments actually differ dramatically. In Figure 8b, the solid lines represent the heating phase diagram, and the dotted lines represent that obtained by cooling the mixtures. The diagram constructed from cooling data consists of both supercooled and nonsupercooled regions (below and above ca. 20 mol % ketone, respectively). The absence of supercooling effects in the mixtures above 20 mol % can be attributed to crystallization of pure PAP from the isotropic melt. The presence of crystalline ketone in the mixtures presumably provides nucleation sites to assist in formation of the smectic and binary solid phases, so that supercooling effects are minimized.

With this description of the complex phase behavior of PAP/CCH-4 mixtures, the deuterium NMR spectra shown in Figure 7 can now be more easily understood. In the case of the 0.6 mol % sample, the sharp doublet characteristic of the nematic phase is replaced by a broad central peak flanked by a broad, poorly resolved doublet as the temperature is lowered from 51 to 47 °C. This broad spectral pattern is assigned to the ketone solubilized in the crystal-B phase. The center portion of the spectrum gradually assumes the appearance of a powder pattern as the temperature is lowered further to 31.8 °C. The spectrum broadens considerably as the temperature is lowered further, and below 26 °C the spectrum takes on the appearance of a polycrystalline solid.

Again, it is not totally clear whether these spectra are due to uniformly oriented PAP or a mixture of oriented and unoriented material. However, we have observed marked differences in the relative intensities of the broad central pattern and the outer

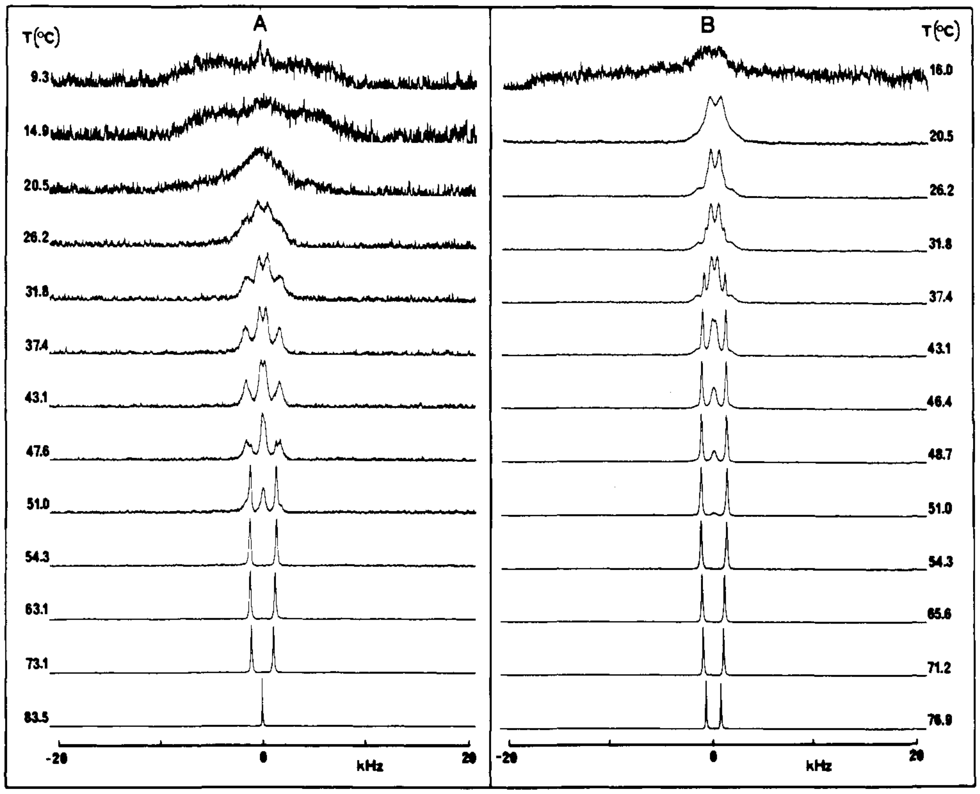


Figure 7. Deuterium NMR spectra of 0.6 (A) and 2.0 mol % (B) mixtures of PAP-d_3 in CCH-4 as a function of temperature.

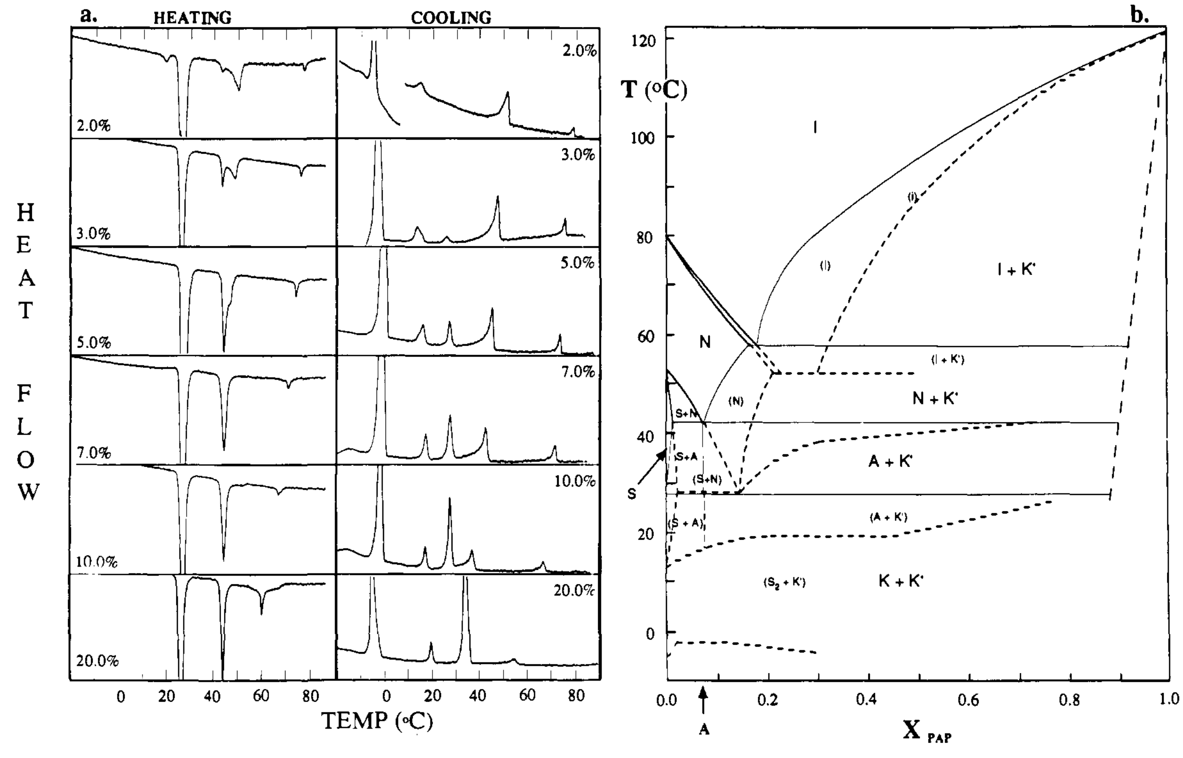


Figure 8. (a) Heating and cooling DSC thermograms for various mixtures of PAP and CCH-4 and (b) the binary phase diagram for the PAP/CCH-4 system, constructed from DSC and thermal microscopy data. The light solid lines in (b) represent transition temperatures obtained from heating data, the dashed lines represent those obtained from cooling data, and the dark solid lines represent those that are identical in heating and cooling. Phase identities: I, isotropic; N, nematic; S, smectic; K, solid.

doublet depending on the rate of cooling the sample from the nematic phase. This observation indicates that the inner spectral pattern is probably due to randomly oriented solute.

The NMR spectra of the 2.0 mol % sample (Figure 7B) indicate that the nematic phase coexists with the smectic phase throughout the 51–37 °C temperature range, as evidenced by the presence of both the sharp nematic phase doublet and the broader crystal-B spectral pattern. The latter is characterized by a much larger powder component than that obtained from the 0.6 mol % sample. The powder component in the 37 °C spectrum must be due to ketone in the crystal-B phase, because thermal microscopy indicates that the binary solid modification does not coexist with

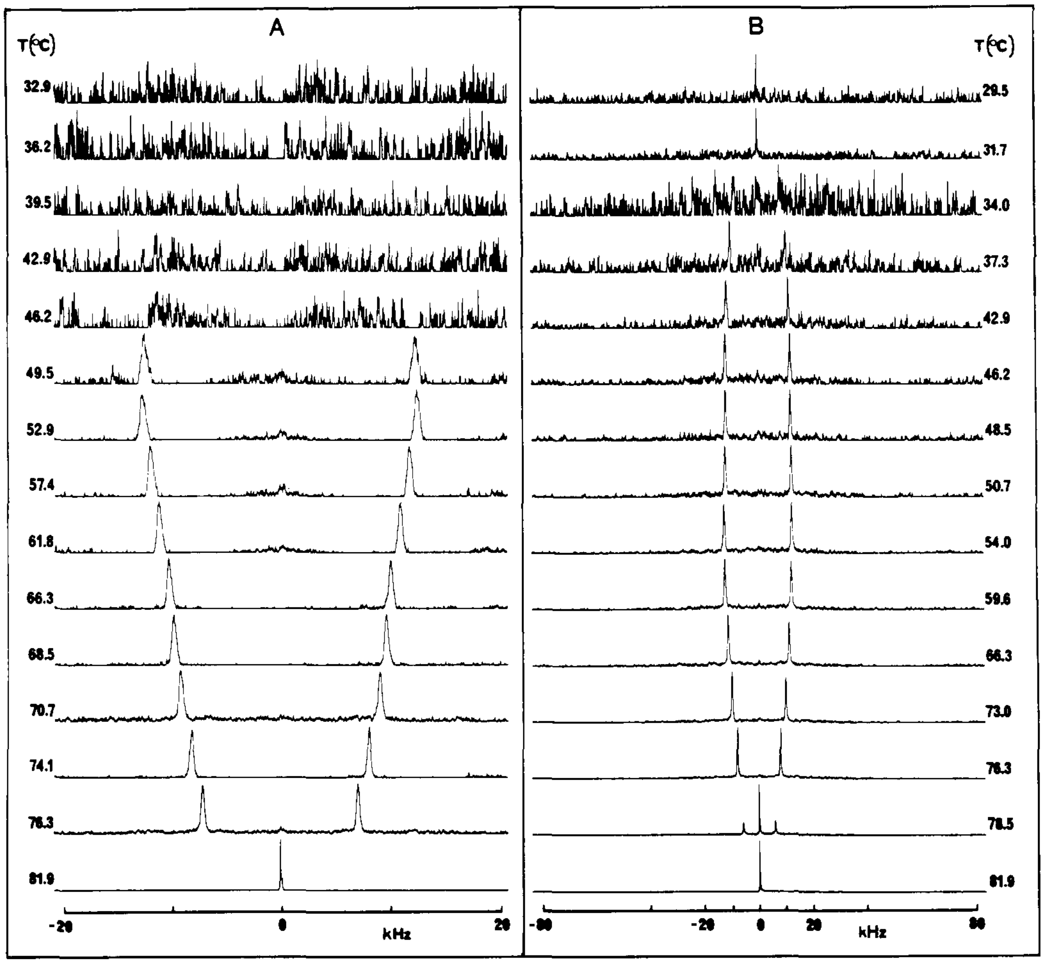


Figure 9. Deuterium NMR spectra of 1.0 (A) and 2.0 mol % (B) mixtures of **5a**-α,α-d_2 in CCH-4 as a function of temperature.

the nematic phase over an appreciable temperature range. Between 29 and 42 °C, the nematic phase component is metastable with respect to binary solid formation. The spectra recorded at 26 and 20.5 °C can be assigned to PAP present largely as the binary solid modification with CCH-4 (the broad wings of relatively low intensity are due to ketone in the crystal-B phase), and it is very similar in appearance to the powderlike pattern of the crystal-B solution. Because of this similarity, it is not clear how the 31.8 °C spectra for the 0.6 and 2.0 mol % samples should be assigned.

Deuterium NMR Spectra and Norrish II Reactivity of 5a in CCH-4. Deuterium NMR spectra were recorded at various temperatures between 29.5 and 84 °C for 0.6, 1.0, 1.5, 1.8, 2.0, and 2.3 mol % mixtures of **5a**-α,α-d_2 and CCH-4; Figure 9 shows the series of spectra obtained for the 1.0 and 2.0 mol % mixtures. The general temperature-dependent NMR behavior and the magnitude of the quadrupolar splittings observed for the 2.3 mol % **5a**/CCH-4 sample correspond quite closely to those reported earlier.[12] In all cases, the spectra in the temperature range above 50 °C show a single doublet splitting of 17–27 kHz, whose magnitude increases with decreasing temperature. As the temperature is lowered below 52 °C, the doublet splitting decreases in magnitude, the signal-to-noise ratio worsens, and all spectral features finally disappear at some temperature between 32 and 52 °C depending on the bulk ketone concentration. Throughout the series of samples, the temperature at which the spectrum disappears decreases with increasing bulk solute concentration (from ca. 50 °C in the 0.6 mol % sample to ca. 34 °C in the 2.0 mol % sample). In the 2.3 mol % sample, the doublet splitting persists at all temperatures down to 33–34 °C, below which it is replaced by an isotropic singlet due to p-phase formation. Table I lists, for each sample composition, the temperature (range) at which the doublet splitting disappears as the sample is cooled throughout the 52–32 °C temperature range.

Table I. "Spectral Transition Temperatures" from ^{2}H NMR Spectra of **5a**-α,α-d_2/CCH-4 Mixtures As a Function of Temperature and Composition[a]

[**5a**-α,α-d_2][b]	$T_{\mathrm{Sm+N \to Sm}}$[c]	$T_{\mathrm{Sm/K \to I}}$[d]	$T_{\mathrm{I \to Sm/K}}$[e]
0.6	48–50	15.4–18.7	24–26
1.0	47–49	9.8–12.0	28–29
1.5	43–46	9–12	28.5–29.0
1.8	40–43	16.5–18.0	33–36
2.0	34–37	32–34	32–34[f]
2.3	[f]	32–34[f]	32–34[f]

[a] In °C. Temperatures at which the ^{2}H NMR spectral features change; ranges correspond to the temperature interval over which spectra were recorded. The characteristic spectral patterns of this solute in the various phases are isotropic (I), singlet; nematic (N), doublet; smectic (Sm) and solid (K), unobservable. [b] Sample composition, in mol % solute. [c] Temperature at which the nematic phase doublet disappears in the ^{2}H NMR spectrum as the sample is cooled. The sample composition gives the solubility limit in the crystal-B phase at the temperautre recorded. [d] Temperature at which the isotropic singlet appears in the ^{2}H NMR spectrum as the sample is cooled. Above this temperature and below that listed in the first column, the spectrum is devoid of features. [e] Temperature at which the isotropic singlet disappears in the ^{2}H NMR spectrum as the sample is heated from 9 °C. [f] For this composition, the observed spectral change is singlet (isotropic) $\rightleftharpoons$ doublet (nematic).

We believe that the total disappearance of spectral features that occurs between 34 and 52 °C (depending on concentration) in these samples signifies complete solubilization of the ketone in the crystal-B phase. The reason for our inability to observe a spectrum for this ketone in the crystal-B phase is not clear, but we have found this to be a quite general phenomenon for α-substituted, α-deuterated acetophenone derivatives (e.g., **1**[21] and valerophenone[31]) in the crystal-B phase of this mesogen. Furthermore, we assign the doublet splitting that is observed in the spectra of the higher concentration mixtures at temperatures below 52 °C to ketone solubilized in the nematic component of a smectic–nematic biphasic system. Again, the splitting decreases in magnitude with decreasing temperature as the concentration of solute in the nematic component increases. It is important to note that this doublet accounts for only a fraction of the total amount of ketone in the sample, since the portion solubilized in the crystal-B phase is invisible to us under these conditions. The compositions of both phases change with temperature, as the solubility of the ketone in the crystal-B phase changes accordingly. Thus, the data in the first two columns of Table I can be taken to represent the variation in the limit of solubility of the ketone in the crystal-B phase as a function of temperature (e.g., the limits of solubility are ≈0.6 mol % at 50 °C, ≈1.5 mol % at 45 °C, etc.).

Continued cooling below 32–34 °C results in the eventual appearance of the isotropic singlet characteristic of p-phase formation, and the temperature at which this occurs also depends on the bulk sample composition. Spectra were recorded for each sample at various intervals as the temperature was lowered from 35 to 9 °C, and again as the temperature was raised back to 35 °C. The temperature ranges in which the characteristic isotropic singlet appears in the spectrum as the sample is cooled, and disappears again as it is reheated, are also listed for each sample composition in Table I.

From the above data, we thus estimate that the limit of solubility of **5a** in the crystal-B phase increases from ca. 0.6 mol % at 50 °C to ca. 2.0 mol % at 35 °C and then decreases again to ca. 1.5 mol % at 28–29 °C. This suggests that the binary phase diagram for the **5a**/CCH-4 system is very similar to the one for the CAP/CCH-4 system shown in Figure 5b. Indeed, the two phase diagrams should be expected to be similar, since both systems exhibit an eutectic at about 34 °C.

These data also indicate that in samples of composition ≥1.5 mol % the p-phase that is formed as the temperature is lowered below 32–34 °C involves only that portion of the solute that is in excess of the solubility limit in the crystal-B phase at a particular temperature. The remaining portion of the solute (up to ca. 1.5 mol %) is soluble in the crystal-B phase and remains solubilized in that phase until crystallization or formation of the second monotropic Sm phase occurs at 9–18 °C. Upon reheating the 1.0 and 1.5 mol % samples, the p-phase remains detectable up to 28–29 °C, which coincides with the K ⟹ Sm transition temperature of the pure liquid crystal. This implies that the limit of solubility of the ketone in the *crystalline* phase of CCH-4 is less than 1 mol %, significantly lower than that in the crystal-B phase (the behavior of the 0.6 mol % sample allows us to ascertain this limit to be 0.6 mol % at temperatures between ca. 25 and 29 °C).

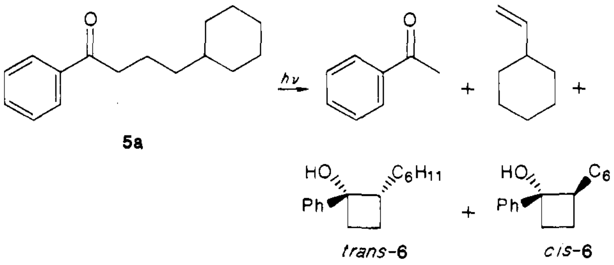
On the whole, these data support a rather different explanation for the reported phase- and temperature-dependent Norrish II photoreactivity of **5a** in CCH-4 than has been advanced previously.[10,12] It is clear that throughout most of the 28–53 °C temperature range, the solubility of **5a** in the crystal-B phase is significantly lower than the bulk composition of the sample employed in those studies (ca. 2.1 mol %[10,12]). At all temperatures in this range (except a narrow window between 34 and 36 °C), a sample of this composition is biphasic, with ketone residing in both smectic and nematic phases (between 36 and 53 °C) and smectic and p-phases (between 29 and 34 °C). The relative proportions of the two phases present and the composition of each phase all vary with temperature. For a sample of this bulk composition, the relative proportion of ketone solubilized in the crystal-B phase is ca. 30% of the total at 50 °C, increases to ca. 100% at 36 °C, and finally decreases again to 75% at 29 °C. While the observed variation in the Norrish II product yields from photolysis of this ketone in CCH-4 with temperature must at least partially reflect this complex solubilization behavior, we note that between 28 and 45 °C, the ketone is *largely* solubilized in the crystal-B phase. Thus, we believe that for this temperature range, the dramatic alterations in product ratios relative to (homogeneous) nematic and isotropic phase values that have been reported can indeed be ascribed to the influence of the smectic phase on the reaction,[32,33] as was originally proposed.[10] However, we conclude that the p-phase, whatever its true ability to influence Norrish II reactivity,[12] plays only a minor role in determining the overall product distribution under these conditions. On the basis of our results for the other three ketones reported herein, those reported previously for **1**,[21] and microscopy experiments with **5a**/CCH-4 mixtures of higher (5–20 mol %) composition, we believe that the p-phase is in fact an isotropic liquid in this case as well. A few additional experiments have been carried out to provide support for this hypothesis and demonstrate the true effects of this phase on the Norrish II reactivity of **5a**.

Table II. Norrish II Product Ratios from Photolysis of **5a** in CCH-4 and in Isotropic Solvents at 30 °C[a]

[5a][b]	F/C[c]	t/c[d]
0.58	14.2 ± 2.8	7.4 ± 3.2
0.67	11.1 ± 0.8	6.8 ± 0.8
1.01	12.0 ± 1.6	5.2 ± 1.0
1.35	9.3 ± 1.2	5.0 ± 1.0
2.36	8.21 ± 0.84	3.0 ± 0.6
4.84	6.27 ± 0.12	2.6 ± 0.2
9.51	4.78 ± 0.70	2.0 ± 0.1
39.7	4.5 ± 1.0	1.73 ± 0.12
C_6H_6[e]	1.93 ± 0.24	3.30 ± 0.18
tert-butyl alcohol[e]	3.51 ± 0.28	1.05 ± 0.01
CH_3CN[e]	3.4 ± 1.0	1.51 ± 0.04

[a] Photolyzed as the α-deuterated derivative. All solutions were deoxygenated with nitrogen in the isotropic phase. Product ratios quoted are the average of two runs, analyzed in triplicate, and errors are represented as twice the standard deviation from the mean. [b] Composition of **5a**/CCH-4 mixture in mol %. [c] Ratio of acetophenone/(*trans*- + *cis*-)**6** from photolysis. [d] Ratio of *trans*-/*cis*-**6** from photolysis. [e] Deoxygenated, 0.01 M solutions.

A series of **5a**/CCH-4 mixtures of composition ranging from 0.6 to 40 mol % in ketone were deoxygenated in the isotropic phase (at 85 °C) and irradiated (312 nm) at 30 °C to ca. 10–20% conversion. The Norrish II photoproducts, acetophenone and the isomeric cyclobutanols (*trans*- and *cis*-**6**), were identified from runs carried out in benzene, *tert*-butyl alcohol, and acetonitrile solution. The product ratios [acetophenone/cyclobutanols (F/C) and *trans*-/*cis*-cyclobutanol (t/c)] were obtained by VPC analysis and are collected in Table II for the various **5a**/solvent systems studied. We obtain F/C and t/c product ratios similar to those reported previously for this compound in benzene and *tert*-butyl alcohol.[10] However, the F/C ratio that we obtain from the 2.3 mol % mixture in CCH-4 at this temperature is a factor of 2–3 smaller than that previously reported for a 2.1 mol % mixture.[10,12] Part of the discrepancy could be due to the presence of two very minor impurities in our sample of CCH-4 that elute with retention times similar to that of *trans*- and *cis*-**6**. These would have the effect of proportionally reducing the measured F/C ratios in the



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(31) Workentin, M.; Leigh, W. J.; Jeffrey, K. R., to be published.

(32) For descriptions of the mechanistic details of the Norrish II reaction[33] in liquid crystals, see ref 10 and 13 and: (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.

(33) (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.

samples of lower concentration, and hence apparently reduce the spread in the F/C ratios throughout the composition range studied.

In both cases, the product ratios from photolysis of the **5a**/CCH-4 mixtures at 30 °C are highest for those samples in which the p-phase is *not* detectable at 30 °C by NMR and decrease consistently as the bulk sample composition is raised above that at which the phase can first be detected at this temperature (1.5 mol %). This is the expected result if the composition of the latter mixtures exceed the solubility limit of the ketone in the crystal-B phase at this temperature and the excess is solubilized in a solute-rich *isotropic* phase. Thermal microscopy experiments verified the biphasic nature of the 2.36 (with difficulty), 4.84, and 9.51 mol % samples and further indicate that the 39.7 mol % sample remains a viscous isotropic liquid to temperatures well below 30 °C.

At a given temperature in the smectic–isotropic biphasic region, the observed F/C product ratio will be a weighted sum of those due to ketone in each of the two phases present. In principle, it should be possible to quantitate this, since for a particular bulk composition the distribution of solute in the two phases is estimable from the solubility limit established by NMR, and individual phase-specific product ratios are defined by our results for the 0.6–1.35 mol % (smectic solution) and 39.7 mol % (isotropic solution) samples. However, such a treatment must also contain estimates of phase-specific and overall reaction quantum yields, which is problematic. Quantum yields for reactions in liquid crystals (as either homogeneous solutions or biphasic mixtures) are very difficult to determine reliably due to light-scattering effects.[11,12] Furthermore, the character of the sample will generally change significantly as the reaction proceeds and reactants are replaced by products in increasing quantities (the products and product/reactant mixtures will generally have different solubility properties in the smectic phase than the reactant).[34] Without additional, extremely detailed studies of the system, these problems combine to render a quantitative analysis of our data unwarranted.

Similar considerations should pertain for product ratios obtained from photolysis in the 35–52 °C temperature range, when the system is in the Sm + N biphasic region. Whatever the quantitative aspects of the system, the observed product ratio at a given temperature will be a weighted sum of those due to reaction in the two phases present. Because the solubility of the ketone in the crystal-B phase varies with temperature, the precise makeup of the sample will vary smoothly throughout this temperature range. These variations in sample morphology may or may not be reflected on the temperature dependence of the *bulk* photoreactivity of the solute, depending on the precise details of the solute/mesogen phase diagram, on what differences truly exist between reactivity in the crystal-B phase and in a solute-enriched nematic phase, and on how these differences vary with temperature and concentration. It has been reported that the Norrish II F/C ratios from photolysis of 2 mol % **5a**/CCH-4 do not vary a great deal with temperature in the 30–53 °C range,[10,12] which is probably due to the fact that throughout most of this range most (75–100%) of the ketone is in fact solubilized in the crystal-B phase. The temperature dependence reported for **5b**, on the other hand, is very different; the F/C ratios increase asymptotically as the temperature is lowered from 53 to 30 °C.[10,12] The explanation for this may be very simple; different solubility properties of this compound in the crystal-B phase compared to **5a** could result in a greater variation in solute distribution between the two phases over the full temperature range. However, a more reliable interpretation of these results can only be made within the framework of quantitative solubility data for **5b**, since as noted above, it is possible that a number of factors in addition to reactant solubility might vary significantly with temperature.

An explanation similar to that given above has recently been proposed by Samori and co-workers to account for the composition dependence of a thermal bimolecular reaction in a smectic B liquid crystal.[25] Various lines of evidence were presented to show that the solute in question had only limited solubility in the smectic B phase, and that at compositions above the solubility limit, the overall reactivity of the molecule could be described by the sum of reactivities in the two distinct phases in the biphasic system.

Summary and Conclusions

The various aromatic compounds that we have now studied as mixtures in the liquid-crystalline phases of CCH-4 have maximum solubilities of ca. 2.0 mol % or less in the crystal-B phase. In mixtures of bulk composition above this limit, our results indicate that the excess material is solubilized in a nematic or isotropic phase consisting of 5–40 mol % solute, depending on the temperature. The structural requirements that determine the solubility of a particular solute in the crystal-B phase are difficult to identify from the limited amount of data that is available, but a few rough generalizations can be pointed out. Comparison of the solubility limits of benzene (1–2 mol %),[21] MAP (0.9–1.0 mol %), and CAP (0.7–0.8 mol %) in the crystal-B phase at 30 °C suggests that solubility decreases with increasing solute size. Phenyl substitution appears to also limit solubility, as a comparison of the corresponding figures for the **1a**/CCH-4 (0.2–0.3 mol %) and **5a**/CCH-4 (0.6–2.0 mol %) systems indicates.

The dramatic differences between the oriented ^2H NMR spectra of α-deuterated aromatic ketones (and other solutes[21,22]) in the nematic and crystal-B phases of CCH-4 provide a reliable diagnostic tool with which to probe the bulk solution properties of solute/CCH-4 mixtures, and this will obviously be true for many other liquid crystals as well. In the case of aromatic ketones, certain regularities in spectral appearance and in the magnitude of the quadrupolar splitting as a function of solvent phase can be gleaned from the present data. Solubilization in the nematic phase is signaled invariably by a fairly sharp, single doublet splitting whose magnitude varies from 1–5 kHz for simple acetyl CD_3 groups to 10–27 kHz for substituted acetyl (CD_2) groups. The spectra are, in all cases, characteristic of well-oriented probes subject to restricted reorientational motion, but fast exchange of the C–D bonds within the time scale of the NMR experiment. The quadrupolar splitting, and hence the solute order parameter, increases monotonically with decreasing temperature in this phase.

The ^2H NMR spectra of solutes dissolved in the crystal-B phase are characteristic of C–D bond reorientations in the slow-motion time regime; the spectra are typically broad, more complex, and exhibit considerably larger quadrupolar splittings [2–13 kHz for acetyl groups and >50 kHz (or unobservable) for substituted acetyl groups[31]]. Depending on the cooling rate as the crystal-B sample is formed from the nematic phase in a magnetic field, a combination of oriented and powder spectra may be obtained. For the solutes we have studied, variations in temperature in this phase appear to have only a small effect (if any) on the solute order parameter.

On the basis of our results with solute/CCH-4 mixtures over broad ranges of composition, we have identified the solute-induced p-phase that is formed by many solute/CCH-4 mixtures as a highly concentrated, *viscous isotropic liquid*, not a cubic or plastic phase as previous workers have proposed.[6,12,22,23] Its origins follow quite naturally from the tenets of basic solution theory and heterogeneous phase equilibria.[35] Not surprisingly, the low-temperature features in the binary phase diagrams of solute/CCH-4 systems vary quite considerably with different solutes.

A number of compounds are now known to form stable binary solid and/or smectic modifications with CCH-4, although the precise structural requirements that dictate whether or not a given compound will form such a phase with CCH-4 are not yet clear. The modifications formed by **1a**[21] and PAP with CCH-4 consist of 7–10 mol % of the solute and exhibit a well-defined, sharp transition to a homogeneous nematic phase of the same composition. The phase may be formed by straightforward cooling of the nematic phase of the corresponding composition or by crystallization from the isotropic component of a smectic–isotropic biphasic mixture. The N–I transition of the mixture is typically

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[34] We thank a reviewer for bringing this point to our attention.

[35] Oonk, H. A. J. *Phase Theory. The Thermodynamics of Heterogenous Equilibria*; Elsevier: Amsterdam, The Netherlands, 1981.

somewhat broader however, which indicates that whatever factors are responsible for stabilization of the binary solid/smectic modification, they do not extend to the nematic phase. The formation of binary Sm-A modifications by mixtures of CCH-4 and certain aromatic amines has also been reported,[36] but these systems appear to be fundamentally different from those reported here.

Finally, it is clear that the various reported investigations of the photochemistry of solutes in the smectic phase of this mesogen require some degree of reinterpretation. It appears that, in general, they have been carried out using mixtures whose compositions are *higher* than the limit of solubility of the solute of interest in the crystal-B phase. The significant effects of "the smectic phase of CCH-4" on solute conformational mobility that have been observed are thus the result of more complex solubilization phenomena than have generally been appreciated. In each case, only a portion of the observed effect can be due to solubilization in this highly ordered phase; the rest (perhaps in some cases, the majority) is due to cosolubilization in a solute-enriched nematic or isotropic phase of temperature-dependent composition. Nevertheless, the present results do not detract in any way from the basic conclusions afforded by these studies; that solubilization in a crystal-B liquid-crystalline phase *does* impart dramatic effects on the conformational mobility and associated chemical reactivity of dissolved solutes. They do, however, indicate that in many cases only *lower limits* of the true magnitude of these effects have been identified.

Deuterium NMR spectroscopy provides a very sensitive analytical tool with which to investigate simple solution behavior in ordered media and is capable of reporting on sample homogeneity at solute concentration levels where many other methods fail. Undoubtedly, aberrations in solute behavior due to phase separation are quite general phenomena in studies of solutes in ordered or otherwise constrained media, particularly in cases where the medium is itself highly ordered.

Experimental Section

Melting points and transition temperatures (all corrected) were recorded by thermal microscopy (in transmission) on a Reichert hot-stage microscope with polarizing filters and calibrated thermometer, or a Vickers petrographic microscope fitted with an RCA CC010 color video camera (whose signal was fed into a conventional video recorder/color monitor), polarizing filters, and a homemade brass hot-stage. Hot-stage temperatures were recorded with a Cole-Parmer Type K thermocouple thermometer and calibrated with a series of melting point standards. Still photographs were recorded by using a Leitz Laborlux petrographic microscope fitted with a 10× ocular, 6.3× objective, a Leitz photoattachment, NPL flat-field lenses, the brass hot-stage and thermocouple thermometer, a 15-W tungsten lamp, Koehrler illumination, polarizing filters, and a Wratten 80A blue filter. Photographs were recorded (1.0 × 1.5 mm field) on Kodacolor VR-G CB-135 film. Samples were contained on 1 × 1.5 in. glass slides and covered with 0.75-in. glass cover slips. Liquid-crystalline, solid, and isotropic phases were identified by their textures in the polarizing microscope. During microscopy runs, the samples were moved and tapped frequently to obtain a full indication of the phase behavior of the mixture and its fluidity as the temperature was varied.

DSC experiments were carried out on a Setaram DSC111 differential scanning calorimeter, interfaced to a Hewlett-Packard HP85 microcomputer that controls the experiment and provides data storage and hard copy facilities. Samples were prepared by weighing the appropriate amounts of solute and CCH-4 into a round-bottom flask, dissolving the mixture in dichloromethane, evaporating the solvent on the rotary evaporator, and finally pumping on the mixture under vacuum (ca. 10^{-3} Torr) for ~1 h to ensure complete removal of the solvent. The mixtures were then weighed into aluminum crucibles and crimp-sealed. For each mixture, DSC thermograms were recorded between −20 and 90 °C in heating and cooling cycles, using a 2 °C/min temperature program in each case. DSC runs were usually repeated at least once to ensure reproducibility.

^{2}H 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. Temperatures were controllable to within ±0.2 °C and were calibrated with a copper–constantan thermocouple. Samples 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,[26] collecting 8K data points per scan over a 40-kHz sweep width. Depending on bulk solute concentration, 512–16000 such scans were collected (with a 0.15–0.4-s delay between scans) and averaged. The $\pi/2$ pulse width was determined by trial-and-error with a $CDCl_3$ (10%)/$CHCl_3$ solution. It was 27–30 μs for the MAP/CCH-4 spectra and 14–17.8 μs for all the others. The data were processed by using line broadening and exponential multiplication prior to obtaining the Fourier transform.

Deuterium T_1 measurements were carried out on the same spectrometer and employed a π–τ–$\pi/2$ nonselective inversion–recovery pulse sequence, followed by the quadrupolar echo. Typically, T_1 values were calculated from least-squares analysis of data from 8–12 τ-values. Errors were calculated separately by a statistical method.[37]

Gas chromatographic analyses employed a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a borosilicate megabore capillary column (30 m × 0.75 mm SPB-1; Supelco, Inc.), and a Hewlett-Packard 3396 recording integrator.

trans,trans-4′-Butylbicyclohexyl-4-carbonitrile (CCH-4; E. Merck Co.) and dichloromethane (Caledon HPLC) were used as received from the suppliers. 4-Methoxyacetophenone (MAP; Aldrich Chemical Co.) was recrystallized from ethanol [mp 35.5–36.5° (lit.[38a] mp 38–39 °C)]. 4-Phenylacetophenone (PAP; Eastman) was recrystallized twice from acetone [mp 120–121.5 °C (lit.[38a] mp 121 °C)]. 4-Cyclohexylacetophenone (CAP) was prepared by Friedel–Crafts acetylation of cyclohexylbenzene (Aldrich) with acetyl chloride and aluminum trichloride in carbon disulfide and was purified by repeated recrystallizations from ethanol/water and one treatment with decolorizing charcoal [mp 68–69.5 °C (lit.[38b] mp 68–70 °C)]. γ-Cyclohexylbutyrophenone (**5a**) was prepared by Friedel–Crafts acylation of benzene with 4-cyclohexylbutyroyl chloride [from treatment of 4-cyclohexylbutyric acid (Aldrich) with thionyl chloride followed by distillation] according to the published procedure.[10] The product was purified by vacuum distillation [bp 130–134 °C (0.2 Torr)].

The four α-deuterated ketones were prepared from their protio analogues by base-catalyzed deuterium exchange. Typically, 0.2 g of the ketone was refluxed in a mixture of sodium hydroxide (0.2 g), dioxane (40 mL), and deuterium oxide (99.8% atom D; MSD Isotopes; 3 mL) for 12–18 h. The resulting mixture was cooled to room temperature, neutralized with concentrated hydrochloric acid, and extracted a few times with ether. The extracts were washed once with water, dried over anhydrous sodium sulfate, and filtered, and the solvent was evaporated on the rotary evaporator. The deuterated ketones were recrystallized two or three times from ethanol or aqueous ethanol [**5a**-α,α-d_2 was distilled twice and recrystallized twice from aqueous ethanol: mp 35–38 °C (lit.[12] mp 39–40 °C)] and had melting points that were indistinguishable from those of their protio analogues. Their ^{1}H NMR spectra (Varian EM390; chloroform-*d*) confirmed them to be >90% deuterated in the α-position in each case.

Samples of **5a**-α,α-d_2 in CCH-4 used in photochemical 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, 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 K_2CrO_4/Na_2CO_3/Pyrex: 312 ± 10 nm) 450-W medium-pressure mercury lamp to 10–25% conversion. The tubes were then opened and the contents dissolved in methylene chloride and then analyzed by VPC. Under our conditions, the isomeric cyclobutanols elute just before **5a**, and the isomer with the longer retention time has been assumed to be the trans isomer.[10] 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.

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(36) (a) Sigaud, G.; Archard, M. F.; Hardouin, F.; Gasparoux, H. *J. Phys. Lett.* **1985**, *46*, 321. (b) Thoen, J.; Beringhs, H.; Auguste, J. M.; Sigaud, G. *Liq. Cryst.* **1987**, *2*, 853.

(37) Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistics for Experimenters*; Elsevier; Amsterdam, The Netherlands, 1981.

(38) (a) *CRC Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1985. (b) *Aldrich Catalog Handbook of Fine Chemicals*; Aldrich Chemical Co., Inc.; Milwaukee, WI, 1988.

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Electrophilic Reactions of Xanthylium Carbocations Produced by Flash Photolysis of 9-Xanthenols

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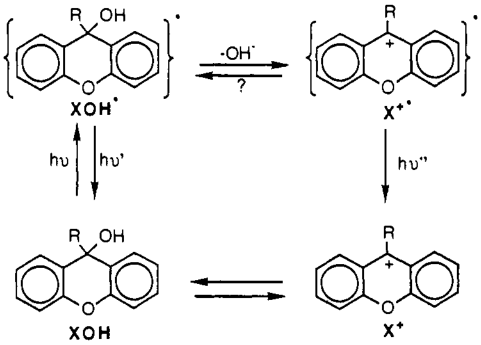
Abstract: The xanthylium ion and eight 9-aryl derivatives (*p*-MeO, *p*-Me, *m*-Me, H, *p*-F, *m*-MeO, *p*-Cl, and *p*-CF_3 phenyl) were produced in 1:4 acetonitrile/water by flash photolysis of the corresponding 9-xanthenols. The identifications of the transients as xanthylium cations were based upon their characteristic absorption spectra, as well as upon experiments with time-resolved conductivity detection. Rate constants for the reactions of these cations with solvent, with four anionic nucleophiles, and with four neutral nucleophiles (primary amines) were measured. The 9-arylxanthylium ions, which have solvent rate constants (k(solv)) at 25 °C ranging from 11 to 34 s^{-1}, follow the Ritchie equation, a plot of log k(nucleophile) versus the nucleophile N_+ parameter being linear with a slope near unity. For the more reactive parent cation, which has k(solv) at 20 °C of 2.3 × 10^4 s^{-1}, the rate constants k(nucleophile) are more poorly correlated with N_+ and the slope is less than unity. This is the second example of a reactive cation that fails to follow the Ritchie relationship. Possible explanations are that the rate constants are becoming diffusion-controlled or desolvation-controlled.

The implication that carbocations are intermediates of certain photosolvolysis and photohydration reactions[3] raises the possibility that with the use of time-resolved flash photolysis the lifetimes of the cations and their reactivities toward added nucleophiles can be directly measured under solvolytic conditions. The reactivities of very stable cations, whose reactions can be followed by conventional or stopped-flow spectroscopy, have been extensively studied,[4,5] but for less stable ions only indirect data are generally available.[6] Some triarylmethyl cations[7] and vinyl cations[8] have now been observed in flash photolysis experiments with appropriate precursors, and we have described a detailed study with the parent triphenylmethyl cation, generated from acetate and 4-cyanophenyl ether precursors.[9] Triphenylmethyl, diphenylmethyl, and even benzyl cations have been studied by pulse radiolysis,[10] but with this approach, the cations are generated in nonnucleophilic halocarbon solvents, and *not* in solvolytic media.

In this paper we report a study of xanthylium cations (X^+) generated photochemically in aqueous solution with xanthenol (XOH) precursors (eq 1). This system was suggested by the report of Wan, Yates, and Boyd that irradiation of 9-phenyl-9-xanthenol results in a weak fluorescence emission identical with that associated with the excited 9-phenylxanthylium ion.[11] This fluorescence was observed in neutral aqueous solutions where the amount of ground-state cation in equilibrium with the alcohol is extremely small. A strong fluorescence from the alcohol was also observed; the fluorescence spectrum for the cation was obtained in acid solutions where the ground-state equilibrium shifts to the cation side. Excitation of the neutral solution at 370 nm, a wavelength where the cation absorbs, produces no observable emission. The cation fluorescence at neutral pH therefore was argued to have originated from excitation of the alcohol, and a scheme (eq 1 with R = phenyl) was proposed whereby excited xanthenol undergoes heterolysis on the excited-state surface (adiabatic heterolysis) producing hydroxide ion and excited cation. Further evidence for this scheme came from photolysis in methanol, which showed a conversion of the alcohol to the methyl ether.[11]



(1)

The implication of these experiments is that photolysis produces an intermediate ground-state xanthylium ion. With the use of flash photolysis, we demonstrate that this is the case, not only for 9-phenyl but also for a series of 9-aryl derivatives and for the

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(3) (a) Cristol, S. J.; Bindel, T. H. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker, New York, 1983; Vol. 6, pp 327-415. (b) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131-137. (c) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157-182.

(4) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348-354.

(5) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239-2250.

(6) (a) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *98*, 8238-8248. (b) McClelland, R. A.; Ahmad, M. *Ibid.* **1978**, *100*, 7031-7036. (c) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *Ibid.* **1984**, *106*, 1361-1372.

(7) Ivanov, V. B.; Ivanov, V. L.; Kuzmin, M. G. *J. Org. Chem. USSR* (*Engl. Trans.*) **1972**, *8*, 626-628. (b) Ivanov, V. L.; Ivanov, V. B.; Kuzmin, M. G. *Ibid.* **1972**, *8*, 1263-1265. (c) Ivanov, V. B.; Ivanov, V. L.; Kuzmin, M. G. *Mol. Photochem.* **1974**, *6*, 125-132.

(8) (a) Schnabel, W.; Naito, I.; Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Tetrahedron* **1980**, *36*, 3229-3231. (b) Kobayashi, S.; Kitamura, T.; Taniguchi, H.; Schnabel, W. *Chem. Lett.* **1983**, 1117-1120. (c) Van Ginkel, F. I. M.; Visser, R. J.; Varma, C. A. G. O.; Lodder, G. J. *J. Photochem.* **1985**, *30*, 453-473.

(9) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023-7027.

(10) Dorfman, L. M.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352-357.

(11) Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1985**, *50*, 2881-2886.

0002-7863/89/1511-2929$01.50/0