Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

An investigation of solute-liquid crystal interaction in hydrogen bonded complexes of palmitic acid and *p*-octyloxybenzoic acid

E. J. Delikatny[a]; E. E. Burnell[a]
[a] Department of Chemistry, University of British Columbia, Vancouver, Canada

To cite this Article Delikatny, E. J. and Burnell, E. E.(1990) 'An investigation of solute-liquid crystal interaction in hydrogen bonded complexes of palmitic acid and *p*-octyloxybenzoic acid', Liquid Crystals, 7: 6, 797 — 813
To link to this Article: DOI: 10.1080/02678299008033841
URL: http://dx.doi.org/10.1080/02678299008033841

LIQUID CRYSTALS, 1990, VOL. 7, NO. 6, 797–813

An investigation of solute–liquid crystal interaction in hydrogen bonded complexes of palmitic acid and *p*-octyloxybenzoic acid

by E. J. DELIKATNY and E. E. BURNELL
Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, V6T 1Y6 Canada

(*Received 12 April 1989; accepted 30 November 1989*)

The orientational order of a liquid crystalline phase which has a specific solute–liquid crystal interaction was investigated using nuclear magnetic resonance. Three isotopically substituted species of palmitic acid (palmitic acid-d_{31}, 1-^{13}C-2,2-H_2-palmitic acid-d_{29} and 2,2,3,3-H_4-palmitic acid-d_{27}) were dissolved in the liquid crystal *p*-octyloxybenzoic acid (*p*-OOBA) and the proton, deuteron and carbon 13 NMR spectra recorded as a function of temperature. ^{1}H–^{1}H dipolar couplings were observed using a spin echo pulse sequence which removes heteronuclear dipolar couplings to the chain deuterons. In the case of the carbon 13 labelled compound, ^{1}H–^{13}C dipolar couplings could be observed by applying an additional refocusing pulse to the ^{13}C spins. The dipolar and quadrupolar couplings were used to calculate the complete orientational order matrix of the alpha methylene segment of palmitic acid in *p*-OOBA. The liquid crystal was shown to largely determine the orientational order of the head group and this was attributed to intermolecular hydrogen bonding. The dipolar and quadrupolar couplings for the rest of the chain were interpreted in terms of a mean field equilibrium statistical model, based on the Samulski Inertial Frame Model. Hydrogen bonding was shown to be of greater importance in the orientational ordering of the solutes in the liquid crystal than are electrostatic interactions in the ordering of the amphiphile in the potassium palmitate/water system.

1. Introduction

Nematic liquid crystals, which align spontaneously in the presence of an external magnetic field, are often used as solvents for small molecules. The solutes experience a partial orientation due to the presence of the liquid crystal. The effects of this orientation can be studied with the use of nuclear magnetic resonance (NMR). The dipolar hamiltonian, normally averaged to zero by rapid molecular motion in the isotropic liquid state, becomes the dominant interaction in the spin hamiltonian. The NMR spectrum now depends solely on the time averaged distance between resonant nuclei, and on the order matrix, S, which describes the average orientational order of the solute. For solutes containing nuclei with $I \geqslant 1$, a quadrupolar splitting, which depends on the interaction of the nuclear quadrupole moment and the average electric field gradient experienced by the nuclei, may be observed.

The mechanism of solute orientational order is still not completely understood. The primary mechanism of orientational order has been suggested to be related to various molecular properties such as the solute moment of inertia [1, 2], dispersion forces [3], the solute polarizability [4, 5], and the size and shape of the solute [6–9]. Of course, the orientational order depends on the nature of the liquid crystal as well. One contribution to solute orientation is the interaction between the solute molecular quadrupole moment and the average external electric field gradient of the liquid crystal [8, 10, 11]. Specific intermolecular interactions may also be important: aromatic π-association, hydrogen bonding etc. The present study describes a system in which hydrogen bonding between solute and liquid crystal is a dominant mechanism of solute orientation. The solutes are isotopically substituted near the H-bonding site so the multinuclear NMR spectra can be used for a description of the orientational order due to this specific intermolecular interaction.

Several isotopically substituted palmitic acids (palmitic acid-d_{31}, 1-^{13}C-2,2-H_2-palmitic acid-d_{29}, and 2,2,3,3-H_4-palmitic acid-d_{27}) were dissolved in the liquid crystal *p*-octyloxybenzoic acid (*p*-OOBA) at a constant concentration of 11 mole per cent. *p*-OOBA forms a liquid crystalline phase by virtue of its ability to form dimers via intermolecular hydrogen bonding [12]. The dimers then have the approximate molecular shape characteristic of many thermotropic liquid crystals, the 'rigid' aromatic core attached to floppy alkyl chains. This ability to dimerize leads to an interesting side effect: the liquid crystal can form hydrogen bonds with appropriate solutes, for example other carboxylic acids. The first C–C bond of the solute then lies approximately parallel to the para axis of the benzoic acid moiety of the solvent, approximately along the long axis of the liquid crystal, which leads to a large molecular solute orientation [13, 14]. Large orientation results in large dipolar splittings and hence more easily resolvable spectra. The main disadvantage to using *p*-OOBA as a nematic solvent is its high nematic temperature range (108–147°C) [15] which is often lowered by the presence of solutes, but which still leads to some experimental difficulties in the form of line broadening due to temperature gradients across the sample.

The experimental information is treated in two related fashions. Dipolar and quadrupolar splittings obtained from a rigid segment of the molecule are treated rigorously, solving for an order matrix as a function of temperature and measuring the rotation of the principal orientation axis of the head group of the molecule by diagonalization of this order matrix. Extra information obtained from non rigid parts of the molecule (i.e. adjacent methylene segments) are by necessity subjected to a molecular modeling procedure to calculate a set of dipolar and quadrupolar couplings. The analysis closely parallels a similar study performed in our laboratory on the lamellar phase of the potassium salts of these compounds in water [16, 17]. These two papers can be treated as a companion to the present work and the entire set comprises a complementary body of information on the same molecule in two different liquid crystalline phases, lyotropic and thermotropic. The liquid crystal used in this study is chosen to have a solute–liquid crystal electrostatic interaction similar to the electrostatic interaction present between the lyotropic liquid crystal and water.

The underlying NMR theory is relatively simple and straight forward and for details of this and on the calculations performed in the present work the reader is referred to [16, 17] and references therein.

2. Materials and methods

Synthesis of the three species of palmitic acids follows standard methods (references [18], [19], and [20–23] for the -d_{31}, -d_{29}, and -d_{27} compounds respectively) and has been described elsewhere [16, 17]. The labile acid proton of the liquid crystal was replaced by exchange with D_2O. 3·0 g of 4-(octyloxy)-benzoic acid (*p*-octyloxy benzoic acid, *p*-OOBA), purchased from Frinton Laboratories, Vineland, N.J., was dissolved in

100 ml hexane and 2 ml D_2O with heating. The mixture was refluxed for 1 hour, the flask was cooled below the boiling point, the D_2O was drawn from the bottom with a Pasteur pipette and replaced with fresh D_2O. This process was repeated. Upon cooling the *p*-OOBA crystallizes. *p*-OOBA was recrystallized from hexane and dried *in vacuo*. The yield was 2·5 g (84 per cent). The absence of the carboxyl proton was confirmed by ^{1}H NMR and mass spec.

Liquid crystal samples were prepared by weighing 11 mole % of the appropriate solute into the liquid crystal (*p*-OOBA-d_1) in a 8 mm (o.d.) by 2 cm tube attached to a ground glass joint by a narrow constriction. Samples were then degassed using a freeze–pump–thaw procedure and flame sealed under 0·5 atm nitrogen gas. Before each experiment, the mixtures were twice heated to a temperature above the nematic–isotropic phase transition and mixed thoroughly in order to ensure sample homogeneity.

The NMR methods have been described elsewhere [16, 17] so only a brief outline of the experimental procedure will be given here. Deuteron NMR experiments were performed on a Bruker BKR 322 s pulsed NMR spectrometer equipped with a 4·7 T Oxford Instruments superconducting magnet which gives a deuteron resonance frequency of 30·7 MHz. The quadrupolar echo pulse sequence (90_x–τ–90_y–τ–echo) [24] was used and the pulses were cycled through a 4-pulse phase cycling sequence: xy, $-xy$, $x-y$, $-x-y$ with the resulting echoes being alternately added to and subtracted from memory. Good quality spectra could be collected with less than 9000 scans. Both the real and the imaginary signal were kept and a quadrature Fourier transform was performed from the peak of the echo and a zero order phase correction of usually less than 10° was applied to phase the spectrum.

Proton NMR experiments were performed on a Bruker CXP-200 solid state NMR spectrometer equipped with a 4·7 T Oxford Instruments wide bore superconducting magnet and a solid state (solenoidal coil) probe. The 90° pulse length ranged from 3–5 μs. A proton spin echo, essentially a variant of 2D J spectroscopy [25–32], was necessary to remove heteronuclear dipolar couplings to the chain deuterons which obscured the proton–proton and proton–carbon 13 dipolar couplings. Chemical shifts are also removed by this sequence. A 90° pulse was followed after a time τ by a 180° refocusing pulse to produce a spin echo at a time 2τ. One point was collected at the peak of the echo, the delay time τ was incremented and the pulse sequence was repeated 1 K times to produce a 1 K data set. Spectra were processed by baseline correction, zero filling to 4 K and quadrature Fourier transformation. In order to observe proton–carbon 13 dipolar couplings in the proton spin echo spectra, a 180° pulse was applied simultaneously to the carbon spins [29, 33–35]. The proton homo- and heteronuclear experiments were analysed using a modified version of the computer program LEQUOR [36, 37].

Carbon 13 NMR experiments were executed on the CXP-200 NMR spectrometer using a ^{13}C cross polarization probe. The ^{13}C pulse length ranged from 3 to 5 μs and pulses were cycled through a 4 phase cycling scheme.

3. Results and discussion

The quadrupolar echo deuteron NMR spectra of the three isotopically substituted acids (11 mole per cent) in the liquid crystal *p*-OOBA were recorded as a function of temperature. A typical spectrum of the perdeuterated acid is presented in figure 1. The variation of quadrupolar splittings as a function of temperature and chain position

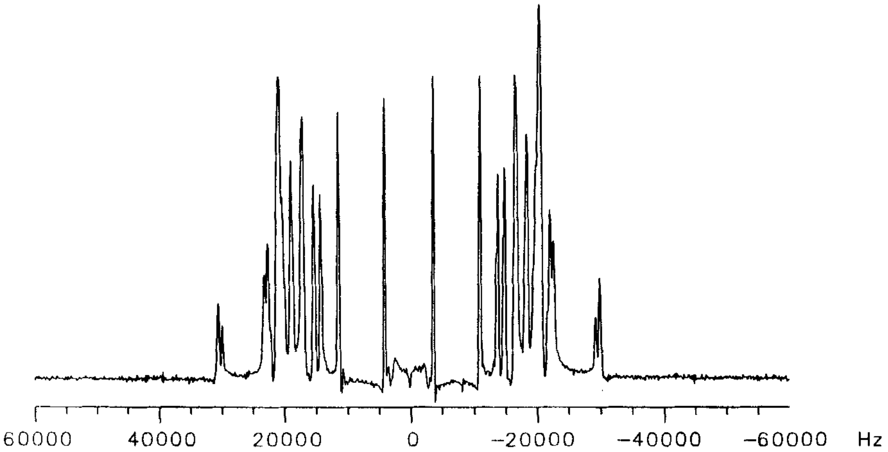

Figure 1. ^{2}H NMR spectrum of 11 mole % perdeuterated palmitic acid in *p*-OOBA. Experimental: temperature = 100°C, 90° pulse length = 5 μs, τ = 96 μs, relaxation delay = 0·5 s. Spectrum recorded on the BKR 322-s at 30·7 MHz. The assignment of these peaks is detailed in figure 2.

are shown in figure 2. The spectra are symmetric and consist of a number of relatively sharp doublets corresponding to the quadrupolar splittings of CD_2 groups along the methylene chain. The difference in quadrupolar splittings reflect the difference in orientational order down the chain. Near the head group where angular fluctuations are restricted due to electrostatic interactions with the liquid crystal, the quadrupolar splittings are large. Further down the chain, the quadrupolar splittings decrease as angular excursions from the all trans configuration increase. The methyl group, which experiences additional motional averaging due to rapid rotation about the local C_{3v} axis, has the smallest quadrupolar splitting. The assignment of the peaks to the positions on the chain is also shown in figure 2. These assignments were based on integration of the deuteron spectra and on the assumption that the quadrupolar splitting decreases monotonically towards the methyl end of the molecule. This is not necessarily the case in liquid crystals [38]. For example in the liquid crystal 5CB (5-cyanobiphenyl) the quadrupolar splitting at the 3 position in the alkyl chain is greater than the quadrupolar splitting at the 2 position [39, 40]. In the case of carboxylic acids oriented in thermotropic liquid crystals, the 2-position has a characteristically large quadrupolar splitting relative to the rest of the molecule [41]. This is also true in lamellar lyotropic phases of the potassium salt [16]. The alpha quadrupolar splitting of potassium soaps dissolved in lyotropic nematic liquid crystal phases also shows this behaviour whereas the corresponding fatty acids in the same system do not [42–45]. In the present study the deuteron splitting of the 2 position is unambiguously assigned by comparison with the deuteron spectra of the corresponding protonated acid.

Close examination of the deuteron NMR peaks at the 2 and 3 positions reveals fine structure which is assumed to arise from intramethylene deuteron–deuteron dipolar coupling. The width of the dipolar coupled multiplet should be reduced from that for proton–proton dipolar coupling by a ratio of ~21 [46]. This fine structure has been observed before [47] and has been used to describe orientation (S_{DD}) in decanol/sodium decanoate/water multilayers. The lines are considerably broadened by intermethylene deuteron–deuteron dipolar interactions.

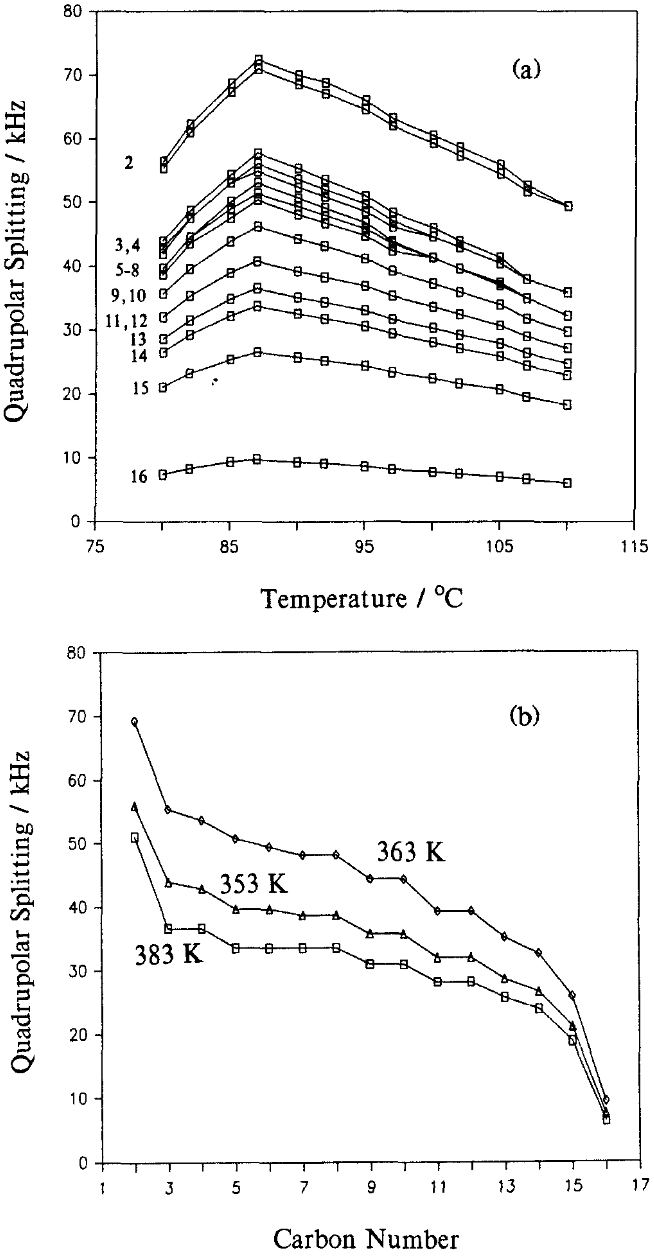

Figure 2. (*a*) Temperature dependence of the ^{2}H NMR quadrupolar splittings in 11 mole % palmitic acid-d_{31} in *p*-OOBA. The assignment of the deuteron peaks is shown on the left side of the figure. Assignment is based on integration and assuming that the quadrupolar interaction is progressively averaged towards the methyl end of the alkyl chain. (*b*) ^{2}H NMR quadrupolar splitting profile of 11 mole % palmitic acid-d_{31} in *p*-OOBA as a function of chain position. The splitting for the methyl group (16) is reduced due to extra motional averaging. The splitting for the 2 position is increased as a result of H-bonding to the liquid crystal. At higher temperatures, separate peaks for the deuterons on the 3–4 carbons and on the 5–8 carbons are not resolvable. The error in the measurement is within the size of the points.

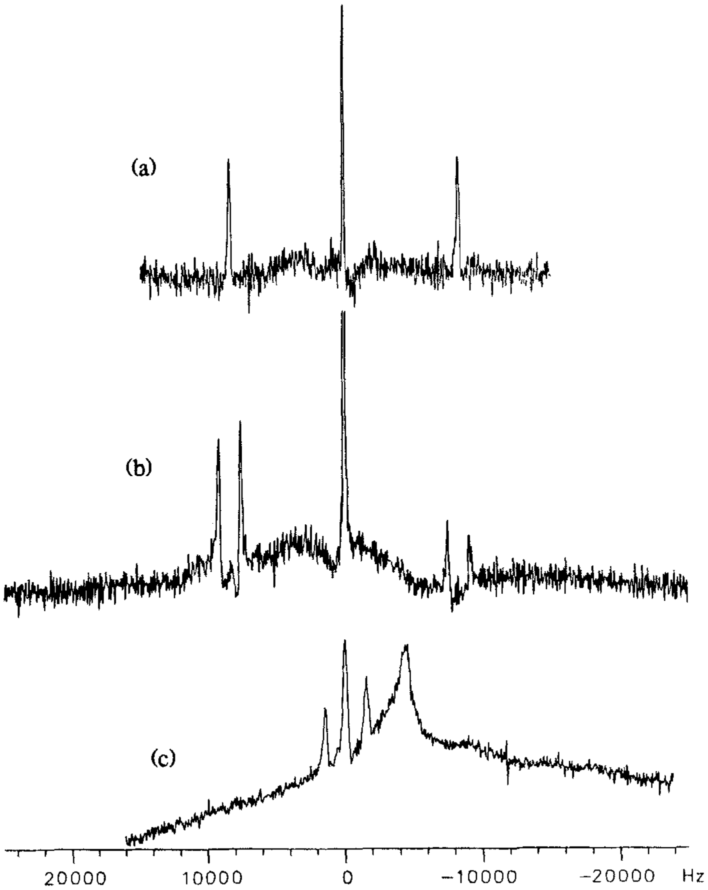

Figure 3. NMR spectra of 11 mole % 1-^{13}C-2,2-H$_2$-palmitic acid-d_{29} in p-OOBA. (a) ^{1}H spin echo spectrum without ^{13}C refocusing pulse: temperature = 110°C, 90° pulse length = 3·0 μs, τ = 5 μs, 180° pulse length = 6·5 μs, relaxation delay = 0·5 s, 8 acquisitions. (b) ^{1}H spin echo spectrum with ^{13}C refocusing pulse: parameters as above. The central peak is an artifact due to H$_1$ inhomogeneities. The large splitting in both spectra is the ^{1}H–^{1}H dipolar coupling. The small splitting in (b) is the ^{1}H–^{13}C dipolar coupling. (c) ^{13}C single pulse NMR spectrum: temperature = 110°C, 90° pulse length = 3·0 μs, relaxation delay = 1·0 s, size = 2 K, 2500 acquisitions. The triplet shows the carbon proton dipolar coupling. The large broad peak is residual carbon signal from the teflon in the probe.

The proton spin echo spectra of 11 mole % ^{13}C-2,2-H$_2$-palmitic acid dissolved in p-OOBA, without and with a ^{13}C refocusing pulse, are displayed in figure 3. Proton single pulse spectra were obscured by the heteronuclear dipolar couplings to the deuterons on the chains and the single pulse spectrum consisted of a broad background triplet characteristic of the liquid crystal. With the heteronuclear couplings removed, the proton single pulse spectrum appears as a triplet, the central peak arising from the inhomogeneous refocusing pulse and the two outer peaks from the alpha protons with a dipolar splitting of $3D_{\mathrm{HH}}$. The second refocusing pulse at the ^{13}C Larmor frequency allows observation of the ^{13}C–^{1}H heteronuclear dipolar couplings, the smaller couplings in figure 3 (b), which have a spacing of $(2D_{\mathrm{CH}} + J_{\mathrm{CH}})$. ^{13}C–^{1}H dipolar couplings were also measured from the ^{13}C single pulse spectrum and a representative spectrum is shown in figure 3 (c). In this oriented sample, the resonances

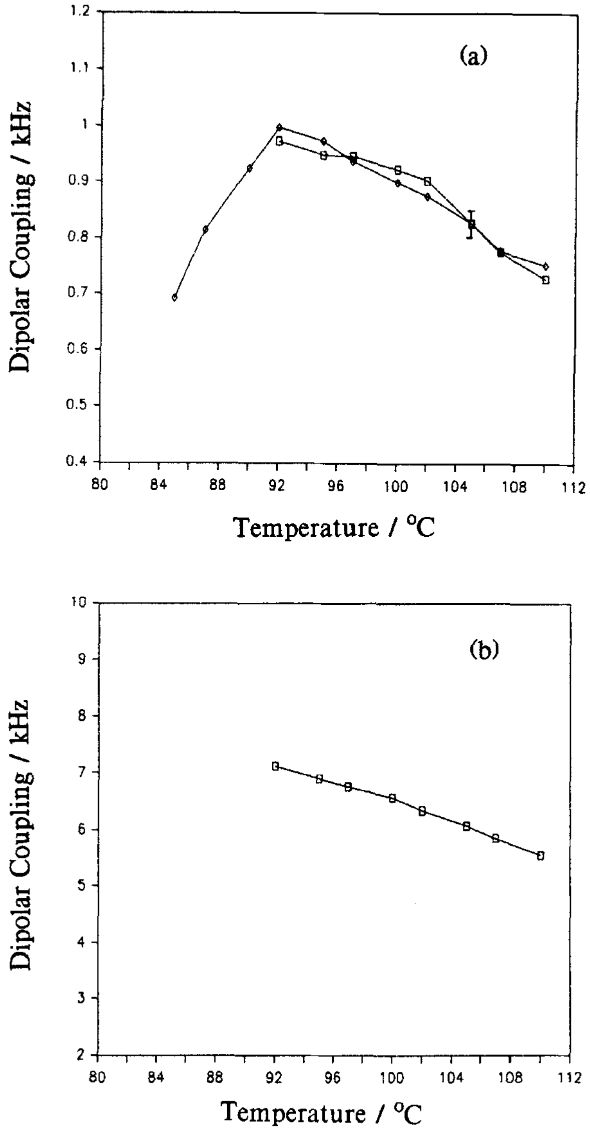

Figure 4. Temperature dependence of the dipolar couplings of 11 mole % 1-^{13}C-2,2-H_2-palmitic acid-d_{29} in *p*-OOBA. (*a*) ^{13}C–^{1}H dipolar couplings measured from the ^{13}C single pulse spectrum, ◇, and the ^{1}H spin echo spectrum, □. Dipolar couplings were resolvable in the ^{13}C spectrum 7° lower than in the ^{1}H spectrum. Each line is the average of two measurements. (*b*) ^{1}H–^{1}H dipolar couplings measured from the ^{1}H NMR spin echo spectrum. The couplings are the average of four measurements. The error in the measurement is within the size of the points.

appear as single peaks (as opposed to the chemical shift anisotropy pattern observed in the palmitate/water system [16]) and the triplet intensity pattern of 1 : 2 : 1 is easily seen. The peak separation is also $(2D_{CH} + J_{CH})$. The large background signal upon which the triplet sits arises from carbons in the teflon coil support in the probe. The linewidth of the triplet is broadened by long range ^{13}C–^{2}H dipolar couplings. The temperature dependence of the dipolar couplings is shown in figure 4. Both the ^{1}H–^{1}H and the ^{1}H–^{13}C couplings rise steadily with decreasing temperature until 92°C.

Below this temperature, the ^{13}C–^{1}H couplings measured from the ^{13}C single pulse spectra drop off rapidly until 84°C when the system undergoes a phase transition into the solid phase. Below 92°C the quality of the ^{1}H spin echo spectra degenerates rapidly. It is estimated that the ^{1}H–^{1}H dipolar coupling at 90° is 5543 Hz (not shown in figure 4(*b*)) but below this temperature no measurements of dipolar couplings could be made in the spin echo spectra of the ^{13}C labelled compound. *p*-OOBA has a nematic–smectic C phase transition at 108°C. This transition, which would be lowered by the presence of the solute, could explain the drop in and/or disappearance of the dipolar couplings (figure 4) and the quadrupolar splittings (figure 2 (*a*)) at lower temperatures. A fall in dipolar couplings upon entry to a smectic C phase has been observed before in CH_2Cl_2 dissolved in *p*-OOBA at 2·1 mole per cent [48]. The presence of CH_2Cl_2 lowers the nematic–smectic C phase transition to 98°C and the smectic C–solid phase transition to 76°C. Below 76°C no couplings were observed in that study. Orientational order is more difficult to describe in smectic C phases due to the biaxiality of the phase and no attempt will be made.

The nematic phase of *p*-OOBA aligns with its director parallel to the magnetic field. The order parameters of the alpha methylene group of the solute can be directly calculated from the dipolar and quadrupolar couplings as is described in reference [16]. Since the orientation of the palmitic acid molecule at the head group is expected to be along the long axis of the liquid crystal, the order parameters S_{HH} and S_{CD} should be negative in sign whereas S_{CH} should be positive. This would give the dipolar couplings D_{HH} and D_{CH} signs of positive and negative respectively.

To calculate an order matrix for the alpha methylene group, a molecule fixed axis system must be chosen: x as the H–H internuclear vector, y the bisector of the HCH plane, and z mutually perpendicular and in the direction of the carboxyl group. Using this axis system, S_{HH} is S_{xx}, and S_{yy} can be calculated from S_{HH} and S_{CD} [16, 49]. The off diagonal element, S_{yz}, is calculated from S_{CH} and from the diagonal elements by a coordinate transformation [16]. S_{zz} is easily calculated as the order matrix is traceless by definition. All other elements in the order matrix are zero as the average effective plane of symmetry in the α-CH_2 segment determines the number of independent elements in the order matrix as 3. The complete order matrix for all temperatures at which all dipolar couplings are measurable is shown in figure 5. Several trends are evident: S_{zz}, representative of the ordering of the methylene group along approximately the nematic director of the phase, is large and increases steadily with decreasing temperature. In addition, the absolute values of S_{xx}, S_{yy}, and S_{yz} increase through the same temperature range. The values of S_{xx} and S_{yy} differ by approximately 0·2 throughout the entire temperature range. The order matrix is diagonalized and the results are presented in figures 5(*b*) and (*c*). The angle of rotation in the yz plane necessary to diagonalize the order matrix is shown in figure 6. The average angle of rotation at high temperatures (110°C) is 26·1°—on average the first C–C bond is only 7·6° away from coincidence with the principal orientation axis direction. This angle decreases with decreasing temperature. The onset of a smectic C phase is accompanied by a tilt in the director of the phase and the decrease in rotation angle could represent the onset of the tilt. Note that the measurement of proton–proton dipolar couplings was difficult below 92°C and that the ^{2}H and ^{1}H couplings peak at different temperatures; thus not much weight should be attributed to the point at 90°C. The value of S_{33}, the major principal diagonal element of the order matrix, ranges from approximately 0·5 to 0·65. This is a huge order parameter for a solute and represents the ordering imparted onto the alpha methylene segment by electrostatic H-bonding to

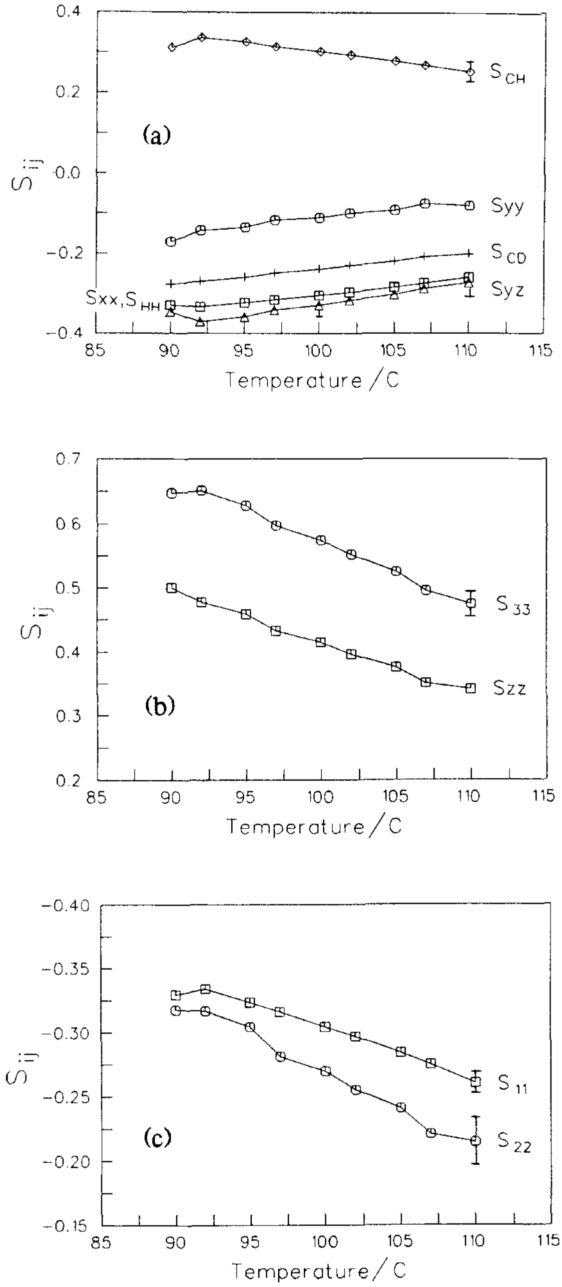

Figure 5. Temperature dependence of the order parameters for the α-methylene segment of 11 mole % 1-^{13}C-2,2-H$_2$-palmitic acid-d_{29} in *p*-OOBA. (*a*) S_{xx}, □, and S_{CD} are measured from the ^{1}H and ^{2}H spectra respectively. S_{CH} can be measured from both the ^{1}H and the ^{13}C spectra. (*b*) S_{zz} and S_{33} (diagonalized) for the α-methylene segment of 1-^{13}C-2,2-H$_2$-palmitic acid-d_{29}. Presented on the same figure to conserve space. (*c*) Temperature dependence of the diagonalized order parameter matrix for the α-methylene segment of ^{13}C labelled palmitic acid-d_{29} in *p*-OOBA. Notice that the ordinate is inverted relative to (*a*). Note also S_{11} (diagonalized) = S_{xx}.

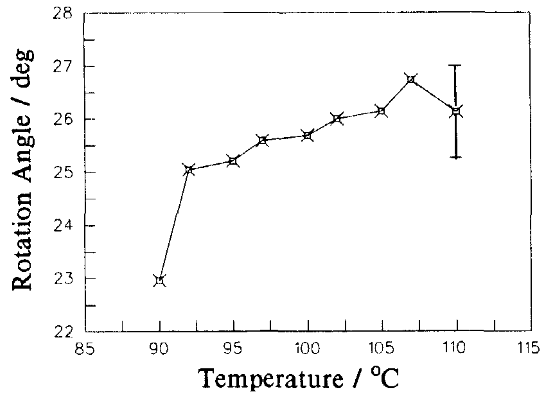

Figure 6. Rotation angle needed to diagonalize the order matrix of the α-methylene segment of the 11 mole % ^{13}C labelled palmitic acid-d_{29} in *p*-OOBA. This angle is in the *yz* plane and is the angle between the alpha methylene fixed *z* axis and the principal orientation of 3 axis.

the liquid crystal. The values of S_{33} are similar to measured order parameters for liquid crystals [27, 50, 51]. The fact that S_{33} exceeds 0·5 determines the sign of S_{33} (and therefore S_{zz}) to be positive. This lends credence to the assignment of the signs of the order parameters in this and in previous publication [16]. The absolute values of S_{11} and S_{22} both increase with decreasing temperature, and at low temperatures become almost equal.

The proton spin echo spectra of 11 mole % 2,2,3,3-H_4-palmitic acid-d_{27} (αβ palmitic acid) in *p*-OOBA is shown in figure 7 (*a*). The simulated spectrum displayed in figure 7 (*b*) is calculated for a refocusing pulse of 156°. The proton dipolar couplings calculated

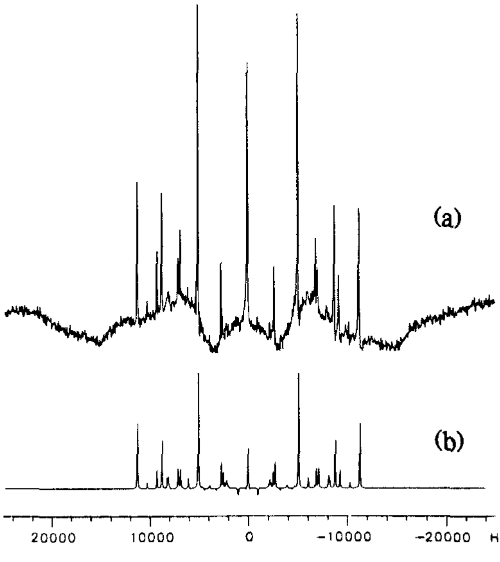

Figure 7. ^{1}H spin echo NMR spectra of 11 mole % 2,2,3,3-H_4-palmitic acid-d_{27} in *p*-OOBA. (*a*) Experimental: temperature = 110°C, 90° pulse length = 2·5 μs, τ = 5 μs, 180° pulse length = 5·1 μs, relaxation delay = 0·5 s, 8 acquisitions. (*b*) Calculated: D_{22} = 5788 Hz, D_{23} = 1312 Hz, D'_{23} = 938 Hz, D_{33} = 3430 Hz, 156° refocusing pulse, lorentzian linewidth = 30 Hz.

from a least squares fit to the spectra using a modified version [25, 29, 30] of LEQUOR [36, 37] are presented in figure 8 as a function of temperature. The dipolar couplings rise steadily from 110° to 92°C. At 90°C (not shown), the proton spectrum appears to be a superposition of two spectra corresponding to a two phase region between nematic and smectic C. At 87°C, only a single spectrum is observed and the dipolar couplings are reduced relative to 92°C. At 85°C, a two component spectrum is again observed and below this temperature no spin echo spectra could be obtained due to a phase transition to a low temperature phase. The values of the alpha proton dipolar couplings for the two isotopes, the 1-^{13}C-2,2-H_2 and the 2,2,3,3-H_4, differ by less than ~200 Hz (<4 per cent difference). The ratio of alpha/beta dipolar couplings is 1·7 whereas the same ratio obtained from the deuteron spectra is 1·4. The value of the alpha coupling is quite high (5788 Hz), but of the same order of magnitude as that of acetic acid (5555 Hz) and propionic acid (5619 Hz) in the same liquid crystal at the same concentration and temperature [52]. This would indicate that the ordering of the solute, at least near the central aromatic region of the liquid crystal, is not vastly different regardless of the length of the solute chain. The flexibility and the lack of symmetry in the palmitic acid molecule preclude a rigorous analysis of the data from the alpha beta labelled compound. Instead, all the NMR information is treated simultaneously and a molecular modelling procedure is employed.

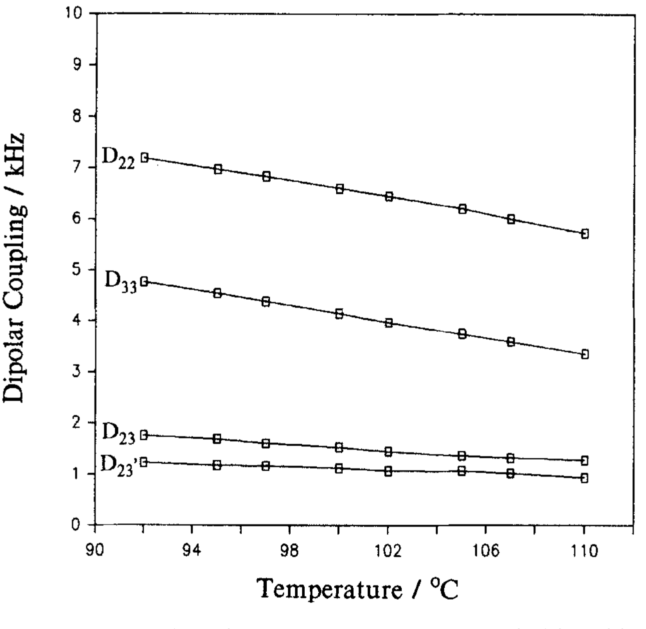

Figure 8. ^{1}H–^{1}H dipolar couplings for 11 mole% 2,2,3,3-H_4 palmitic acid-d_{27} in p-OOBA. Calculated from experimental splittings using the computer program LEQUOR.

In an analysis similar to one described previously in a study on the related soaps [17], the entire palmitic acid/p-OOBA complex is treated using a modified inertial frame (IF) model [2, 53–55]. The molecule is parsimoniously truncated after 7 (or 9) carbons with a mass of 64 amu (attached to the end carbon in the position that a third deuteron would occupy) to represent the rest of the chain. A number of conformations are generated based on a 3-fold rotation potential about each CH_2–CH_2 bond

[56]. The external forces acting on the solute are crudely assumed to be characterized by a mean field cylinder representing a steric interaction with the liquid crystal and a head group interaction which simulates the electrostatic interaction of the solute–liquid crystal complex. The coordinates of the liquid crystal are not explicitly calculated, rather the liquid crystal is replaced by a mass of 500 amu on a rod (coincident with the first C–C direction) of variable length. This is equivalent to r_{HG} in reference [17]. The change in the length of this rod imposes a direction on the head group of the molecule by altering the moment of inertia of a particular conformation. A conformer order matrix is calculated from the principal moments of inertia, and a set of dipolar and quadrupolar couplings is calculated from this order matrix and from the orientation of the relevant nuclei relative to an external director. The couplings are first scaled by a conformer probability obtained from the Boltzmann factor, and then to one experimental coupling, the α-CD_2 deuteron quadrupolar coupling. The calculation is performed iteratively, varying the cylinder radius and the head group interaction length until a best fit is found.

The fitting procedure used in this paper only accounts for the effects of intermolecular forces on the asymmetry in the order matrix and on the conformational averaging of the solute. The overall magnitude of the interactions are accounted for simply by scaling each spectrum to the alpha methylene deuteron coupling. To a first approximation this scaling accounts for the change with temperature of the liquid crystal order, and the parameters of the model relate to details of the intermolecular forces between liquid crystal and solute.

The experimental and calculated dipolar and quadrupolar couplings as a function of temperature are shown in figure 9. The calculation is for 50 conformers which represents rotations about 5 methylene segments. This fit is good at all temperatures for the dipolar couplings but rather poor for quadrupolar couplings below the 4 position. The poor fit results from the simplistic truncation of the molecule after seven carbons. Deuteron couplings past the 4th carbon were given no weight in the calculation of couplings or of the RMS error. A calculation including rotations about 7 methylene segments (288 conformers) was made for two temperatures. In this case, deuteron couplings past the 6th carbon were given no weight in the calculation of couplings or of the RMS error. The result is compared with the 50 conformer fit and with experiment in figure 10. The fit at the 5 and 6 positions is markedly improved, but falls off from there. The corresponding dipolar couplings are shown as the diamonds in figure 9. Calculation of more than 288 conformers becomes prohibitively expensive and not necessarily useful for a description of head group ordering.

The variation in the two adjustable parameters is presented in figure 11. The cylinder radius, characteristic of the mean field steric forces exerted by the liquid crystal, increases constantly with temperature reflecting the increased angular librations expected of the molecule. The head group interaction length, a measure of the electrostatic interaction between solute–liquid crystal, also increases with increasing temperature implying that hydrogen bonding becomes more important at higher temperature. Intuitively this does not make much sense. However, it must be remembered that the change in this parameter actually reflects the relative orientation of the head group as a function of temperature. In other words, at higher temperatures the orientation of the first C–C bond is closer to the director of the phase but as temperature is decreased the orientation tilts away from the director. This is also evident in the calculated rotation angle of the order matrix shown in figure 6. The onset of a smectic C phase, which is the phase below the nematic in *p*-OOBA, is

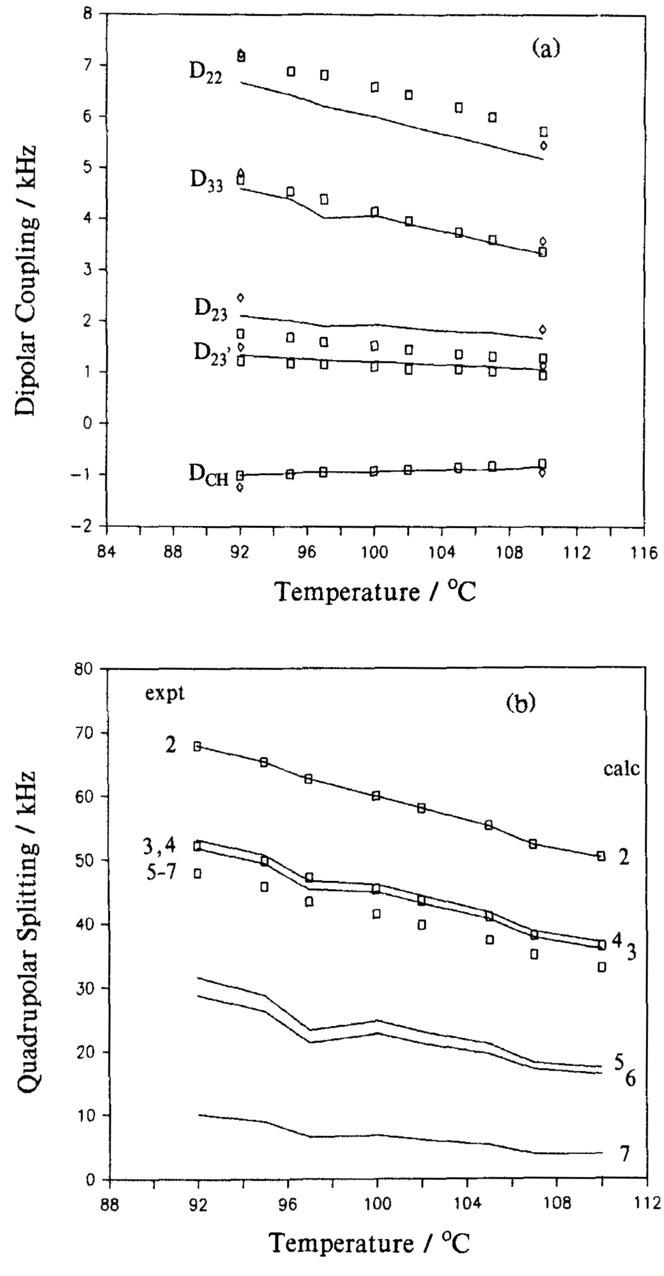

Figure 9. The IF model: calculated, —, and experimental, □, dipolar couplings and quadrupolar splittings. (*a*) Dipolar couplings (◇, calculation for rotation about 7 methylene segments, 288 conformers). (*b*) Quadrupolar splittings. Experimental numbers are taken from perdeuterated palmitic acid.

accompanied by a tilt in the director of the phase (i.e. the phase becomes biaxial). These results demonstrate that the molecules may prepare for the transition to the smectic C phase by small changes in orientation as the phase transition is approached.

The cylinder radius, r_{cyl}, is almost identical to that calculated for the same molecule in a lamellar lyotropic phase [17]. In the lyotropic phase, r_{cyl} ranges from

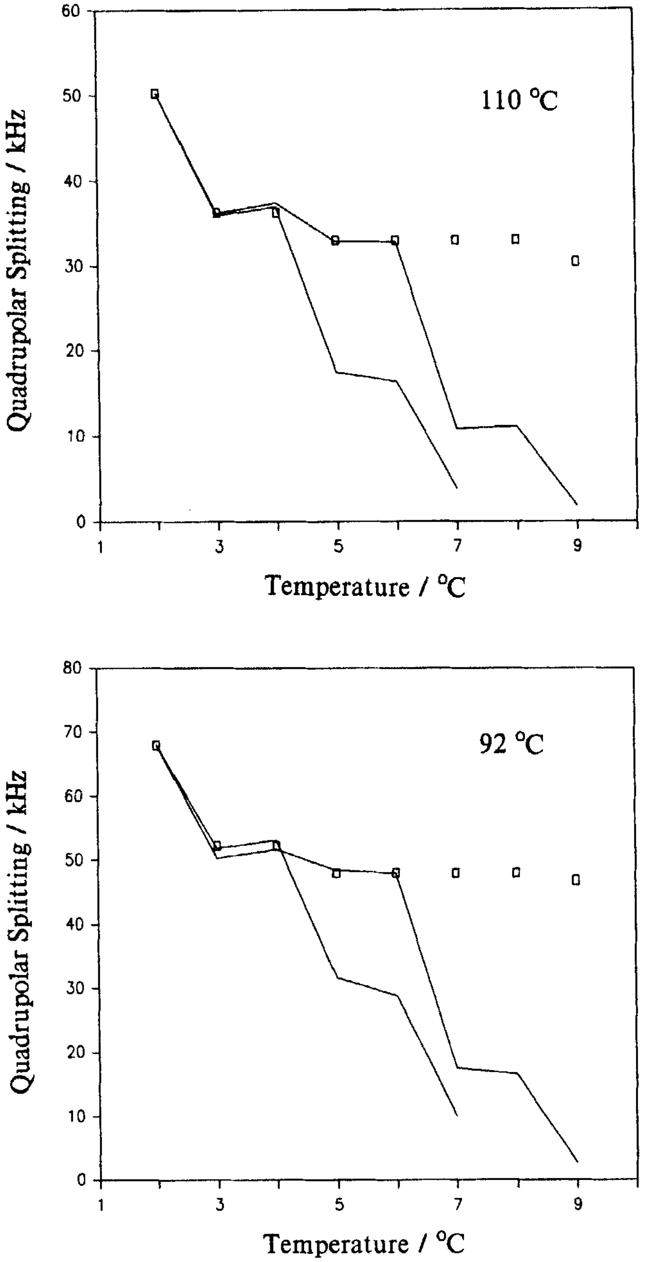

Figure 10. The IF model: quadrupolar splitting profiles: □, experimental, —, calculated. The results of the regular and extended chain (in brackets) calculation at 110°C and 92°C. The values for the adjustable parameters are r_{cyl} = 5·98 (6·27) Å, and r_{HG} = 9·16 (13·48) Å at 110°C with an RMS error of 291 (379) Hz. At 92°C, r_{cyl} = 5·79 (6·17) Å, and r_{HG} = 5·82 (10·96) Å with an RMS error of 289 (521) Hz.

5·85 Å to 5·94 Å, in the thermotropic phase from 5·79 Å to 5·98 Å. On the other hand the head group interaction length which ranges from 2·71 Å to 3·55 Å in the soap has leaped to a range of 5·82 Å to 9·97 Å in the liquid crystal. Obviously, the orientation of the head group is much more influenced by hydrogen bonding to a large, rigid,

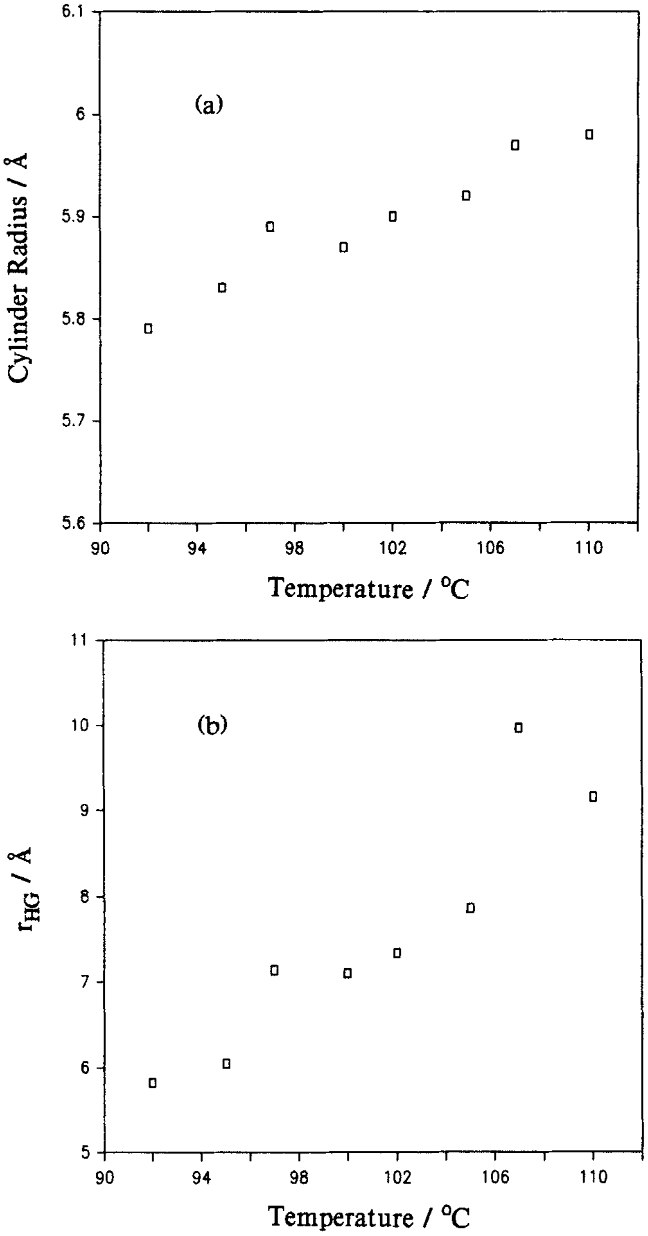

Figure 11. The IF model: variation in adjustable parameters with temperature. (*a*) Cylinder radius (r_{cyl}). (*b*) Head group interaction length (r_{HG}).

ordered liquid crystal than it is by hydrogen bonding to relatively disordered water molecules in the lamellar phase. This is confirmed by both the large alpha dipolar splitting and the long calculated r_{HG}. The similar cylinder radius implies that the steric constraints placed on a long chain fatty acid are similar in a uniaxial nematic mean field and in a lamellar liquid-crystalline phase.

An interesting point for future experiments is that it is not absolutely necessary to use a liquid crystal with which the fatty acids can form intermolecular hydrogen bonds. A recent publication [41] demonstrates that long chain fatty acids in liquid crystals dimerize and given order parameters of similar magnitude to those observed here.

4. Conclusions

In this paper we have investigated the orientational order of molecules which form lyotropic lamellar phases by dissolving them in nematic liquid crystals. The NMR spectra are simplified because the nematic phase orients spontaneously in the magnetic field and the spectra do not show the powder patterns of randomly dispersed lyotropics. The liquid crystal was chosen so that the forces experienced by both nematic solute and lyotropic amphiphile are similar; while the information available is not identical between the two phases, it is certainly complementary. The NMR spectra were simplified by isotopic substitution and by choice of pulse sequence and the complete order matrix for parts of the large molecule, palmitic acid, were determined. With the help of a statistical model to simulate the experimental couplings, this work provides a convenient bridge between the two types of liquid crystalline phases, and provides insight into the intermolecular forces involved in orientational ordering.

Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada and The Petroleum Research Fund, administered by the ACS, for support of this research. E.J.D. thanks the Natural Sciences and Engineering Research Council of Canada for the award of a Graduate Scholarship.

References

[1] Anderson, J. M., 1971, *J. magn. Reson.*, **4**, 231.
[2] Samulski, E. T., 1980, *Ferroelectrics*, **30**, 83.
[3] Saupe, A., 1966, *Molec. Cryst.*, **1**, 527.
[4] Toriumi, H., and Samulski, E. T., 1983, *Molec. Crystals liq. Crystals*, **101**, 163.
[5] Janik, B., Samulski, E. T., and Toriumi, H., 1987, *J. phys. Chem.*, **91**, 1842.
[6] Robertson, J. C., Yim, C. T., and Gilson, D. F. R., 1971, *Can. J. Chem.*, **49**, 2345.
[7] van der Est, A. J., Kok, M. Y., and Burnell, E. E., 1987, *Molec. Phys.*, **60**, 397.
[8] Burnell, E. E., van der Est, A. J., Patey, G. N., de Lange, C. A., and Snijders, J. G., 1987, *Bull. magn. Reson.*, **9**, 4.
[9] Kok, M. Y., van der Est, A. J., and Burnell, E. E., 1988, *Liq. Crystals*, **3**, 485.
[10] Patey, G. N., Burnell, E. E., Snijders, J. G., and de Lange, C. A., 1983, *Chem. Phys. Lett.*, **99**, 271.
[11] Barker, P. B., van der Est, A. J., Burnell, E. E., Patey, G. N., de Lange, C. A., and Snijders, J. G., 1984, *Chem. Phys. Lett.*, **107**, 426.
[12] Takenak, S., and Labes, M. M., 1983, *Molec. Crystals liq. Crystals*, **90**, 365.
[13] de Lange, C. A., 1974, *Chem. Phys. Lett.*, **28**, 526.
[14] Dunn, M. B., 1968, *Molec. Phys.*, **15**, 433.
[15] Miljković, L., Thompson, T., Pintar, M. M., Blinc, R., and Zupančič, I., 1976, *Chem. Phys. Lett.*, **38**, 15.
[16] Delikatny, E. J., and Burnell, E. E., 1989, *Molec. Phys.*, **67**, 757.
[17] Delikatny, E. J., and Burnell, E. E., 1989, *Molec. Phys.*, **67**, 775.
[18] Hsiao, C. Y. Y., Ottaway, C. A., and Wetlaufer, D. B., 1974, *Lipids*, **9**, 913.
[19] Atkinson, J. G., Csakvary, J. J., Herbert, J. G., and Stuart, R. S., 1968, *J. Am. chem. Soc.*, **90**, 498.
[20] Tulloch, A. P., 1977, *Lipids*, **12**, 92.
[21] Tulloch, A. P., 1979, *Chem. Phys. Lipids*, **24**, 391.
[22] Crossland, R. K., and Servis, K. L., 1970, *J. org. Chem.*, **35**, 3195.
[23] Spener, F., and Mangold, H. K., 1973, *Chem. Phys. Lipids*, **11**, 215.

[24] DAVIS, J. H., JEFFREY, K. R., BLOOM, M., VALIC, M. I., and HIGGS, T. P., 1976, *Chem. Phys. Lett.*, **42**, 390.

[25] TURNER, D. L., 1982, *J. magn. Reson.*, **46**, 213.

[26] EMSLEY, J. W., and TURNER, D. L., 1981, *J. chem. Soc., Faraday Trans. II*, **77**, 1493.

[27] AVENT, A. G., EMSLEY, J. W., and TURNER, D. L., 1983, *J. magn. Reson.*, **52**, 57.

[28] AVENT, A. G., EMSLEY, J. W., and LUCKHURST, G. R., 1983, *Molec. Phys.*, **49**, 737.

[29] KUMAR, A., 1978, *J. magn. Reson.*, **30**, 227.

[30] KUMAR, A., 1980, *J. magn. Reson.*, **40**, 413.

[31] KUMAR, A., and KHETRAPAL, C. L., 1978, *J. magn. Reson.*, **30**, 137.

[32] KHETRAPAL, C. L., KUMAR, A., KUNWAR, A. C., MATHIAS, P. C., and RAMANATHAN, K. V., 1980, *J. magn. Reson.*, **37**, 349.

[33] GRIFFIN, R. G., BODENHAUSEN, G., HABERKORN, R. A., HUANG, T. H., MUNOWITZ, M., OSREDKAR, R., RUBEN, D. J., STARK, R. E., and VAN WILLIGEN, H., 1981, *Phil. Trans. R. Soc.* A, **299**, 547.

[34] MÜLLER, L., KUMAR, A., and ERNST, R. R., 1977, *J. magn. Reson.*, **25**, 383.

[35] NIEDERMEYER, R., and TURNER, D. L., 1981, *Molec. Phys.*, **43**, 13.

[36] DIEHL, P., KELLERHALS, H., and NIEDERBERGER, W., 1971, *J. magn. Reson.*, **4**, 352.

[37] DIEHL, P., KELLERHALS, H., and LUSTIG, E., 1972, *NMR Basic Principles and Progress*, Vol. 6, edited by P. Diehl, E. Fluck and R. Kosfeld (Springer-Verlag).

[38] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1981, *Molec. Phys.*, **44**, 565.

[39] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1982, *Proc. R. Soc.* A, **381**, 117.

[40] WEAVER, A., VAN DER EST, A. J., RENDELL, J. C. T., HOATSON, G. L., BATES, G. S., and BURNELL, E. E., 1987, *Liquid Crystals*, **2**, 633. HOATSON, G. L., BAILEY, A. L., VAN DER EST, A. J., BATES, G. S., and BURNELL, E. E., 1988, *Liq. Crystals*, **3**, 683.

[41] SAMULSKI, E. T., 1987, in *Physics of Complex and Supermolecular Fluids*. Edited by S. A. Safran and N. A. Clark (John Wiley and Sons), p. 157.

[42] FORREST, B. J., and REEVES, L. W., 1979, *Chem. Phys. Lipids*, **24**, 183.

[43] FORREST, B. J., FUJIWARA, F. Y., and REEVES, L. W., 1980, *J. phys. Chem.*, **84**, 662.

[44] FORREST, B. J., and REEVES, L. W., 1981, *Chem. Rev.*, **81**, 1.

[45] CHEN, D. M., FUJIWARA, F. Y., and REEVES, L. W., 1977, *Can. J. Chem.*, **55**, 2404.

[46] BURNELL, E. E., DE LANGE, C. A., and SNIJDERS, J. G., 1982, *Phys. Rev.* A, **25**, 2339.

[47] DIEHL, P., and NIEDERBERGER, W., 1974, *J. magn. Reson.*, **15**, 391.

[48] LUZ, Z., and MEIBOOM, S., 1973, *J. chem. Phys.*, **59**, 275.

[49] HIGGS, T. P., and MACKAY, A. L., 1977, *Chem. Phys. Lipids*, **20**, 105.

[50] DOANE, J. W., 1979, *Magnetic Resonance of Phase Transitions*, Chap. 4, edited by Frank J. Owens, Charles P. Poole, Jr. and Horacio A. Farach (Academic Press).

[51] LUCKHURST, G. R., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, Chap. 3, edited by J. W. Emsley (D. Reidel Publishing Co.).

[52] DELIKATNY, E. J., HELDMAN, M. A., and BURNELL, E. E. (in preparation).

[53] SAMULSKI, E. T., and DONG, R. Y., 1982, *J. chem. Phys.*, **77**, 5090.

[54] SAMULSKI, E. T., and TORIUMI, H., 1983, *J. chem. Phys.*, **79**, 5194.

[55] SAMULSKI, E. T., 1983, *Isr. J. Chem.*, **23**, 329.

[56] FLORY, P. J., 1969, *Statistical Mechanics of Chain Molecules* (Wiley Interscience).