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Dual alignment of liquid crystals under non-equilibrium conditions

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During the macroscopic reorientation of several nematic liquid crystal systems in a magnetic field, an unusual phenomenon, namely the presence of preferred macroscopic alignment at two different directions, was observed. This phenomenon is similar to the visual observation of pattern formation in liquid crystals under non-equilibrium conditions, except that our study was made at the molecular level. The technique used was C-13 NMR spectroscopy combined with rapidly decelerated sample spinning. The deceleration subjects the liquid crystal to a rapid change in the aligning torque. When the deceleration rate is slow, the alignment of the liquid crystals is predicted by their anisotropy of the magnetic susceptibility ($\Delta\chi$). When the deceleration rate is sufficiently high, the dual alignment is observed for some of the liquid crystal systems studied. In these systems, part of the liquid crystal molecules remain with the director in the initial alignment, but the rest rapidly realign to reach a surface almost perpendicular to the axis of initial alignment, similar to the 'opening' of an umbrella. The ratio of the molecules with the two kinds of preferred alignment is determined by the non-equilibrium dynamics as well as $\Delta\chi$ of the liquid crystal sample. Several liquid crystal systems were investigated: 4-*n*-pentyl-4′-cyanobiphenyl (5CB; $\Delta\chi>0$), 4′-cyanophenyl-1-*trans*-4-*n*-pentylcyclohexane (PCH5; $\Delta\chi>0$ but smaller than 5CB), and 1-(*trans*-4-*n*-pentylcyclohexyl)-4′-cyanocyclohexane (CCH5; small $\Delta\chi<0$). The dual alignment is present in 5CB and CCH5, and it is more pronounced in PCH5. We also prepared several mixtures of 5CB and 1-(*trans*-4-*n*-ethylcyclohexyl)-4′-cyanocyclohexane (CCH2; small $\Delta\chi<0$), the $\Delta\chi$ of which varies with the composition. The change in alignment became more pronounced as the magnitude of $\Delta\chi$ approached zero. An explanation for these results is suggested.

1. Introduction

Nematic liquid crystal systems undergo a change in their alignment when subjected to a new torque because the systems are forced from their equilibrium alignment. We recently studied the liquid crystal phase on the level of molecular segments [1] for the case in which the system was not driven too far from equilibrium. The relaxation mechanism was relatively straightforward and may be described in terms of liquid crystal viscosities and elastic forces. However, if the liquid crystal system is driven sufficiently far from equilibrium by the realigning torque, patterns form in the liquid crystal [2]. These patterns are changes in the alignment of the liquid crystal phase, which result from a hydrodynamic instability in, or deformation of, the equilibrium alignment of the liquid crystal. Many types exist and have attracted much attention because of their scientific and technological implications [3]. For example, in the Fréedericksz transition, when the realigning field is suddenly applied perpendicular to the direction of initial alignment, striped patterns have been visually observed which are oblique [4] or perpendicular [5] to the initial direction of the alignment. Sometimes these phenomena are attributed to non-linear static and dynamic behaviour of the liquid crystals [6], and some have been described in terms of solitons [2,4]. Because liquid crystals often produce tractable results, they may be used as models for the exploration of non-linear science [6].

In the present study, a liquid crystal system is forced from equilibrium by a very rapid deceleration of a spinning sample. In principle, this should induce pattern formation, and the C-13 NMR results are consistent with that. Because most prior observations of these phenomena have normally been made optically, we believe that our present work represents one of the first studies of pattern formation with the resolution to the level of the molecular segment, which is provided by C-13 NMR. We report the results of applying this method and a related two-dimensional C-13 experiment to the early stages of the reorientation of the nematic liquid crystals 4-*n*-pentyl-4′-cyanobiphenyl (5CB), 4-cyano-1-(*trans*-4-*n*-pentylcyclohexyl)benzene (PCH5), and 1-(*trans*-4-*n*-pentylcyclohexyl)-4′-cyanocyclohexane (CCH5), and of mixtures of 5CB and 1-(*trans*-4-*n*-ethyl-

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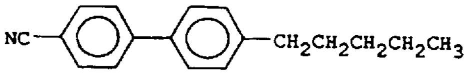
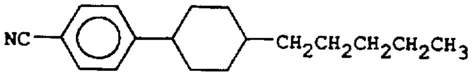
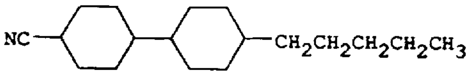
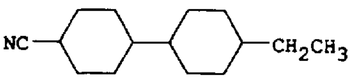
		$\Delta\chi(10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1})$
5CB		~ 13
PCH5		~ 5
CCH5		~ -5
CCH2		~ -5

cyclohexyl)-4′-cyanocyclohexane (CCH2). Different combinations of liquid crystals with phenyl and cyclohexyl rings were studied because the phenyl ring has a large positive contribution to the anisotropy of the magnetic susceptibility, $\Delta\chi$, and the cyclohexyl ring has a small negative contribution. Approximate $\Delta\chi$ values for the liquid crystals at 10 K below the nematic-to-isotropic transition temperature are listed with the structure [7]. $\Delta\chi$ values for the mixtures may be calculated, as discussed later in the text.

2. Experimental

2.1. *Spectroscopic techniques*

The study of C-13 chemical shifts during rapid deceleration of a spinning liquid crystal sample reveals the dynamical properties of liquid crystals during the reorientational process, the details of which have been described elsewhere [1]. The basis of the technique is that the C-13 NMR chemical shifts of a liquid crystal will change when a rapidly spinning (1–2 kHz) sample is quickly decelerated. To study this phenomenon, we applied a very rapid deceleration and focus on a portion of the reorientation process involving a rapid change in the magnetic and viscous torques acting on the sample. It was found that the chemical shifts are profoundly affected by the rate of deceleration, indicating that patterns have been induced in some of the liquid crystal systems.

The second technique used in this study combines rapidly decelerated sample spinning with a two dimensional C-13 NMR method known as separated local field/variable angle spinning (SLF/VAS) spectroscopy. SLF/VAS allows the carbon–proton dipolar splittings, which are related to the liquid crystal alignment and orientation order, to be resolved for each carbon [8–13].

The F-19 NMR spectra of 2,2-difluorotetrachloroethane (Aldrich Chemical) dissolved in a liquid crystal was also studied. The simple spectral pattern of this probe molecule combined with the high NMR receptivity of the F-19 nucleus provides an opportunity to gain information on the orientation which may be not be available in the C-13 NMR spectra.

All NMR spectra were measured on a Varian VXR-500S spectrometer equipped with a variable angle spinning probe manufactured by Doty Scientific, Columbia, South Carolina. The spinning angle was chosen for convenience to be ~46·0° for most experiments and was varied as specified in the results section.

The liquid crystals were obtained from EM chemicals, Hawthorne, New York. The nematic ranges of 5CB, PCH5, CCH2, and CCH5 specified by the manufacturer were 24·0–35·3°C, 30·0–55·3°C, 46·0–49·0°C, and 62·0–85·0°C, respectively. Pure CCH5 was studied because it has a large nematic range. CCH2 was selected for the mixtures to avoid overlap of aliphatic peaks of 5CB. All the mixtures of CCH2 and 5CB were nematic at room temperature.

For the liquid crystal systems which are not nematic at room temperature, the spinning air supply for the probe was heated to the selected temperature by the internal heater of the probe. The counter-current air supply used to stop the spinner was applied at room temperature. Because it was applied for no more than 150 ms, and a 15 s equilibration period was allowed between counter-current air applications, the temperature of the liquid crystal sample was not affected appreciably. This was indicated by the lack of change in the C-13 chemical shift, which is very sensitive to temperature, after the counter-current air was applied.

2.2. *The effect of rapid spinning on the alignment of a liquid crystal*

The alignment of the director of a liquid crystal spun rapidly at an angle with respect to a magnetic field has been discussed in detail elsewhere [13–15]. The key result is that for a rapidly spinning sample, the nematic director is 'tilted' by an angle, θ, relative to the magnetic field. The tilting the director of the liquid crystal scales the observed NMR properties, and the chemical shift of the liquid crystal is given by [13, 16]

$$\delta_{\text{obs}} - \delta_{\text{iso}} = \frac{\langle 3\cos^2\theta - 1\rangle}{2}(\delta_{\text{LC}} - \delta_{\text{iso}}) \qquad (1)$$

where δ_{obs} is the observed chemical shift with rapid spinning, δ_{iso} is the chemical shift in the isotropic phase, and δ_{LC} is the chemical shift of the non-spinning liquid crystal. The brackets indicate a time average quantity, which is observed on the NMR timescale. Therefore, the brackets in equation (1) may be dropped, and [17]

$$(3\cos^2\theta - 1) = \frac{1}{2}(3\cos^2\beta - 1)(3\cos^2\phi - 1) \qquad (2)$$

where β is the angle of the mechanical spinning axis relative to the magnetic field, and ϕ is the angle which the director forms with the mechanical spinning axis. For equilibrium rapid spinning, $\phi = 0°$ for liquid crystals with positive $\Delta\chi$ when $\beta < \theta_m$, the magic angle (54·74°), and $\phi = 90°$ when $\beta > \theta_m$. For liquid crystals with negative $\Delta\chi$, the situation is opposite: $\phi = 0°$ when $\beta > \theta_m$, and $\phi = 90°$ when $\beta < \theta_m$.

In SLF/VAS experiments, the splitting between the proton and a carbon nucleus, $\Delta\nu$, is given by [8]:

$$\Delta\nu = f[(3\cos^2\theta - 1)D + J]. \qquad (3)$$

In equation (3), f is a scaling factor, which is unity for broadband decoupling and equal to 0·42 when the proton–proton dipolar coupling sequence BLEW-48 [18, 19] is used, D is the dipolar coupling constant between carbon and proton, and J is the corresponding scalar coupling constant.

For 2,2-difluorotetrachloroethane dissolved in a liquid crystal, the F-19 NMR spectrum is composed of a doublet due to fluorine–fluorine coupling. The splitting is given by equation (3) where f is unity because no decoupling is necessary, and J is effectively zero because of the chemical equivalence of the fluorine nuclei. The splitting is directly related to the alignment of the liquid crystal host, and ϕ in equation (2) may be calculated from the values of the splitting, $\Delta\nu$, with and without spinning [20]:

$$\frac{\Delta\nu_{\text{spinning}}}{\Delta\nu_{\text{non-spinning}}} = \frac{(3\cos^2\theta - 1)}{2}. \qquad (4)$$

3. Results

According to equation (1), the chemical shift data can be used as criteria for judging the angle of director alignment in VAS experiments. As predicted from their values of $\Delta\chi$, it was found that 5CB and PCH5 (both with $\Delta\chi > 0$) align parallel to the mechanical spinning axis. In these cases, the liquid crystal sample is in an equilibrium state in that the magnetic and viscous torques are not changing with time (see figures 1 (*a*) and 2 (*a*), respectively). During reorientation in the rapidly decelerated sample spinning experiment, however, the sample is not in equilibrium because the decreasing spinning rate changes the aligning torque over a short period of time. The effect of this rapid change in the aligning torque varies among the liquid crystals studied.

The deceleration rate may be semi-quantitatively gauged based on the amount of time required for the rotor to stop spinning after the stopping device was activated. For example, a rotor spinning at 1800 Hz required about 94 ms to stop when a mild deceleration torque was applied [1]. Under such conditions, no unusual effects arising from the deceleration rate are observed for 5CB within the sensitivity limit of C-13 NMR, and the liquid crystal macroscopically reorients from the spinning axis toward the magnetic field. The rate of this macroscopic reorientation is described by an exponential process with a rate constant that can be determined for each molecular segment of the liquid crystal [1]. The device for stopping the spinning samples employs a counter-current air flow to supply the decelerating torque [1], so higher deceleration may be produced by increasing the air flow rate. When the deceleration rate is sufficiently high, the macroscopic reorientation of the liquid crystal molecules towards the magnetic field is preceded by an interesting dual alignment pattern. The reorientation behaviour is influenced by the physics of the deceleration process. Because the deceleration process involves a viscous fluid, the theoretical description of this deceleration becomes complicated. The deceleration process in our experiments is such that, after a time lag for the actuation of the relays controlling the counter-current air, the counter current air flow forces the spinner slightly away from its spinning axis. Then, friction between the rotor and stator decelerates the rotor. Visual observation indicated that the stator, being constructed out of sapphire, was not worn by this deceleration process. Therefore, without giving a detailed mathematical description of the deceleration process, it is sufficient for the discussion below to note that the deceleration process is repeatable in each experiment.

For 5CB at higher deceleration rates, about 25 per cent higher than in the previous study [1], the alignment is not the same as in the equilibrium system. New peaks are formed after the spinning sample has been decelerated for about 40 ms (see figure 1 (*b*)), which is a time slightly greater than the response time for the stopping device to actuate after the software command is given to stop. These new peaks are attributable to 5CB molec-

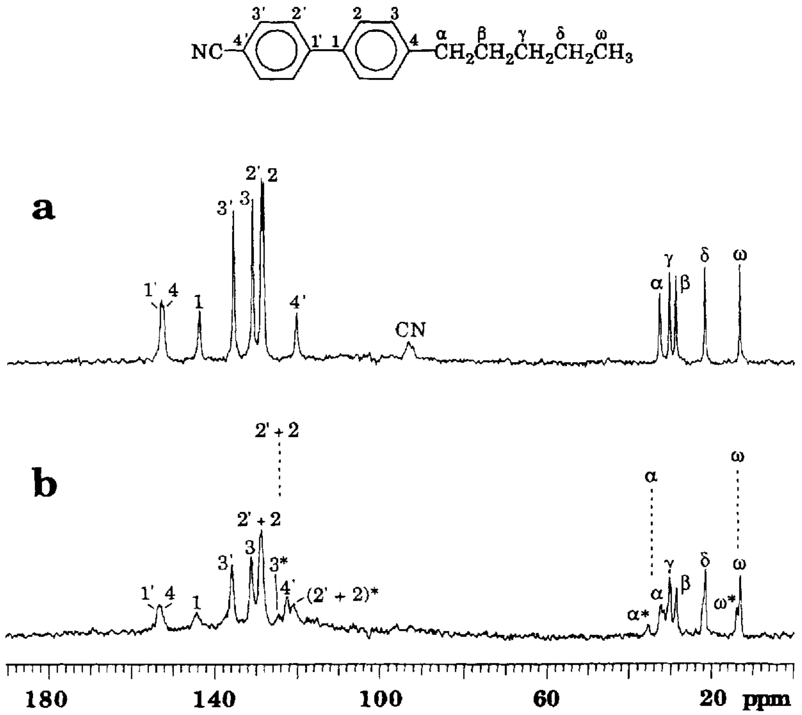


Figure 1. C-13 NMR spectra of 5CB at 125·697 MHz and a temperature of 22°C. (*a*) Sample spinning at $\beta = 46°$ at 1600 Hz. 16 scans were collected. (*b*) Sample after deceleration for 45·5 ms; 16 scans were collected. The new peaks are indicated with an *. The dashed lines indicate the positions of the isotropic peaks.

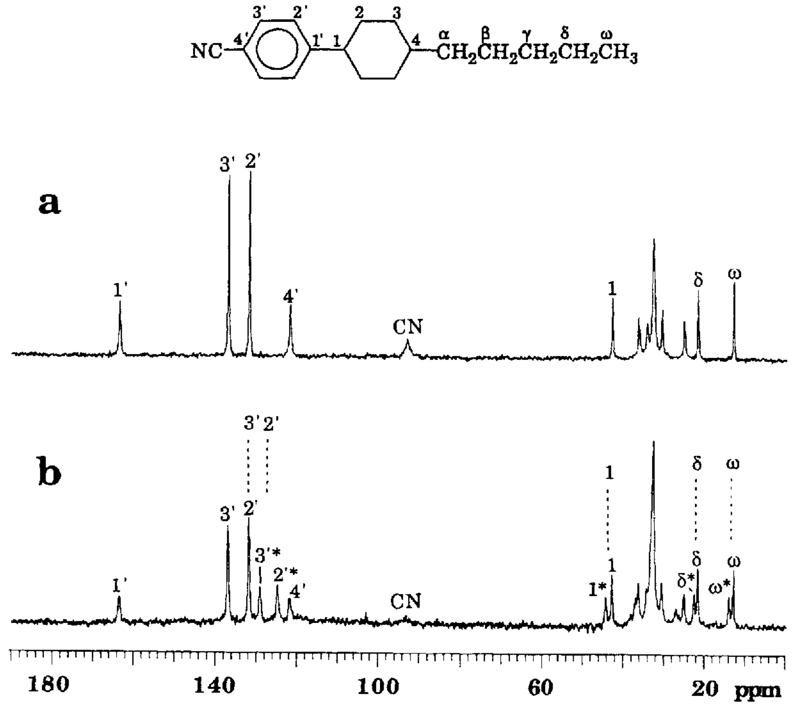


Figure 2. C-13 NMR spectra of PCH5 at 125·697 MHz and a temperature of 30°C. (*a*) Sample spinning at $\beta = 46°$ at 1600 Hz. 48 scans were collected. (*b*) Sample after deceleration for 39·5 ms; 48 scans were collected. The new peaks are indicated with an *. The dashed lines indicate the positions of the isotropic peaks.

The angles of alignment (ϕ) relative to the spinning axis calculated by equation (1) from C-13 chemical shifts of the two sets of peaks for several carbons of PCH5. Equation (1) is very sensitive to ϕ for the angles calculated here, so the differences in the tabulated values should not be regarded as very significant. The 1 and 1* peaks are broader than the other peaks and produce less accurate results; therefore, they are not included in the average. For the spinning angle $\beta=52°$, the aliphatic carbons overlap, and reliable values for ϕ could not be calculated.

Peak		3′	2′	1	δ	ϕ	Average
$\beta=46°$,	original	0°	0°	0°	0°	0°	0°
	new (*)	77°	82°	61°	75°	76°	78°
$\beta=52°$,	original	0°	0°	—	—	—	0°
	new (*)	75°	77°	—	—	—	76°

ules which align at a new angle relative to the spinning axis. Due to a distribution in the angle of alignment [21], the new peaks in 5CB are broad and not very well resolved.

For PCH5, the new set of peaks is more prominent (see figure 2(*b*)). This second set of peaks for the non-protonated carbons is very broad, and those for some of the aliphatic carbons overlap with each other, and they cannot be clearly identified. For the resolvable new peaks, the angles of alignment can be calculated according to equation (1). The results are summarized in the above table.

When 8 mol % of 2,2-difluorotetrachloroethane is dissolved in PCH5, a new set of peaks is also observed in the F-19 NMR spectrum (see figure 3) after the sample is subjected to rapid deceleration. Solutes present in this low of concentration decrease the clearing temperature of the liquid crystal but do not affect the orientational properties of their liquid crystal host [20]. For each of the sets of doublets, the two peaks of the doublets are not of equal height. However, this is also seen in the non-spinning spectrum and is likely due to frequency-dependent relaxation effects. Because the line width is related to the $(3\cos\theta^2-1)$ term of equation (2), the peaks of the 'new' doublet (see figure 3) are correspondingly broad. Additionally, the new peaks appear to be slightly asymmetrical. This may be due to frequency-dependent relaxation or a very small (<0·5°) distribution in the alignment angle. The angle of alignment of liquid crystal for the 'new' doublet was calculated using the fluorine splittings in equation (3) and (4) to be 74°, which is in good agreement with the angles calculated from the C-13 NMR spectrum of bulk PCH5 (see the table).

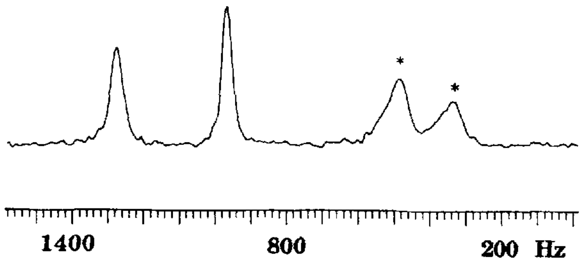


Figure 3. F-19 NMR spectrum of 8 mol % 2,2-difluorotetrachloroethane dissolved in PCH5. 64 scans were collected. The new peaks are indicated with an *. The right edge of the spectrum is arbitrarily referenced to 0 Hz. The C-13 NMR spectrum corresponding to the F-19 NMR spectrum of this decelerated sample resembles the C-13 NMR spectrum presented in figure 2(*b*).

Mixtures of 5CB and CCH2 with positive or negative $\Delta\chi$ were prepared, and several interesting results were obtained. First of all, it is useful to compare the total integrated intensity, I, of each new peak with the corresponding original peak. For this purpose, we can define a quantity, Q, as:

$$Q=\frac{I_{\text{new}}}{I_{\text{new}}+I_{\text{orig}}}\times 100 \text{ per cent} \qquad (5)$$

Thus, Q is the 'per centage of new peak formed' and can be determined from plots such as figure 4, which show the intensity of both new and original peaks as a function of time. In figure 4, the increasing percentage of new peak intensity reflects the growth of the fraction with the new direction of alignment up to about 50 ms. After that, the sum of the intensities of two sets of peaks decreases, which can be attributed to an overall broadening of the peaks as the liquid crystal reorients away from the spinning axis [1]. After 60 ms, the C-13 peaks become too broad to measure reliably, making the total integrated intensity comparable to the noise level. The time dependence of Q varies from one liquid crystal sample to another because each spinning rotor holding a sample was prepared separately and has slightly different mass and spinning characteristics. Therefore, they have different deceleration characteristics, which decreases the reliability of a relationship developed between Q and time. We can consider, however, the maximum value of Q, $Q_{\max}$, for which the differences in the deceleration characteristics are not expected to be too large. Along with the spectral noise and uncertainties in the selection of the spectral regions for the integrated intensity, these differences in the

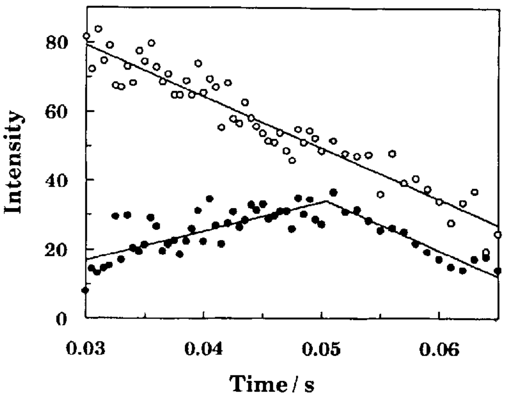


Figure 4. The total integrated intensity (arbitrary units) of the 3′ carbon (○) and 3′* carbon (●) of PCH5 as a function of time. Eight scans were collected for each point. The integration regions were held constant in each of the spectra. In order not to distort these peak height results, no nuclear Overhauser enhancement was used to enhance the C-13 NMR signal. The rate of decrease in the original peak does not appear to be equal to the rate of increase in the intensity of the new peak. This may result from the broadening of the peaks due to distribution in the angles of alignment for the director of the liquid crystals, which may cause the intensity in the integration regions to be affected. The straight lines are intended as a guide, not to imply function form. The function form may be related to the deceleration behaviour of the rotating sample as well as to the realignment of the liquid crystal: if the deceleration is not rapid enough, the dual alignment does not appear. Given the physics of the decelerating liquid crystal sample, the exact functional form is most likely complicated, if not intractable.

deceleration characteristics contribute to the error in the determination $Q_{\max}$.

The plot of $Q_{\max}$ versus mole fraction (see figure 5) has several interesting characteristics. First, for small mole fractions of CCH2 (0–0·3), the value of $Q_{\max}$ stays more or less constant at about 30 per cent. Next, $Q_{\max}$ increases with increasing CCH2 mole fraction and eventually reaches a maximum of 100 per cent, corresponding to complete disappearance of the original peak, for mole fractions in the 0·70–0·85 range. The chemical shifts in the NMR spectra revealed that the $\Delta\chi$ of the mixture changes from positive to negative between 0·75–0·80 mole fraction CCH2. The 0·90 mole fraction mixture exhibited both a nematic and smectic phase. The dual alignment was observed in the nematic phase, but was not observed in the smectic phase. For pure CCH5 ($\Delta\chi<0$), the value of $Q_{\max}$ is similar to that of pure 5CB ($\Delta\chi>0$).

Because the appearance of a new set of peaks was quite unexpected, we performed SLF/VAS experiments to ascertain that this is indeed due to a dual alignment of the liquid crystal molecules. The experiments were performed on the sample prior to deceleration and also at 39·5 ms into rapid sample deceleration. Because the two-dimensional experiment requires a time increment, the SLF/VAS spectra were acquired between 39·5 and 46·3 ms. The intensity of the peaks does change during this time period (see figure 4). The SLF/VAS experiment is an amplitude modulated two-dimensional experiment, so in addition to amplitude modulation caused by dipolar and scalar coupling, noise is introduced by the effects shown in figure 4. A line-broadening of 40 Hz applied during the two-dimensional Fourier transformation helps to improve the signal/noise ratio, but the two dimensional spectra have diminished resolution (see figure 6 (*b*), (*c*), (*e*), and (*f*)), compared to the normal SLF/VAS spectrum (see figure 6 (*a*) and (*d*)). The carbon–proton coupling patterns shown in figure 6 are due to a splitting of each protonated aromatic carbon peak into a doublet of doublets by the directly bonded proton and the proton on the neighbouring carbon [8–13]. The doublet of doublets may normally be deconvoluted to yield the individual doublet splittings. However, this is not appropriate for the decelerated spectra because the extra noise introduced into the second dimension as discussed above. Nevertheless, it is quite clear that the splittings of the new peaks in figure 6 (*c*) and (*f*), are scaled substantially, about 50 per cent, compared to those of the original peaks (figure 6 (*b*) and (*e*)). According to equation (3), this substantiates the result for the alignment angles of the molecules giving rise to the new peaks (see the table).

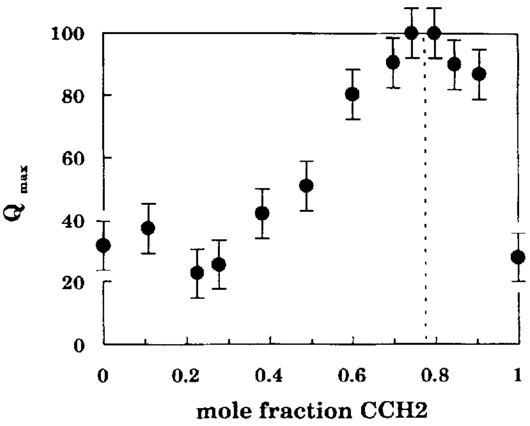


Figure 5. $Q_{\max}$ versus mole fraction CCH2. $Q_{\max}$ is defined in the text. The dashed line represents approximately the mole fraction at which $\Delta\chi=0$. Because the aromatic peaks are more broadened than the aliphatic peaks, the peak of the terminal methyl group of the 5CB aliphatic chain was used to determine $Q_{\max}$. For mole fractions greater than 0·75, the intensity of the 5CB peak was decreased, and a cyclohexyl peak was used. $Q_{\max}$ at 1·0 mole fraction was determined for CCH5. The error bars reflect the uncertainties, discussed in the text, of determining $Q_{\max}$.

The carbon–proton dipolar coupling constants, D_{ij},

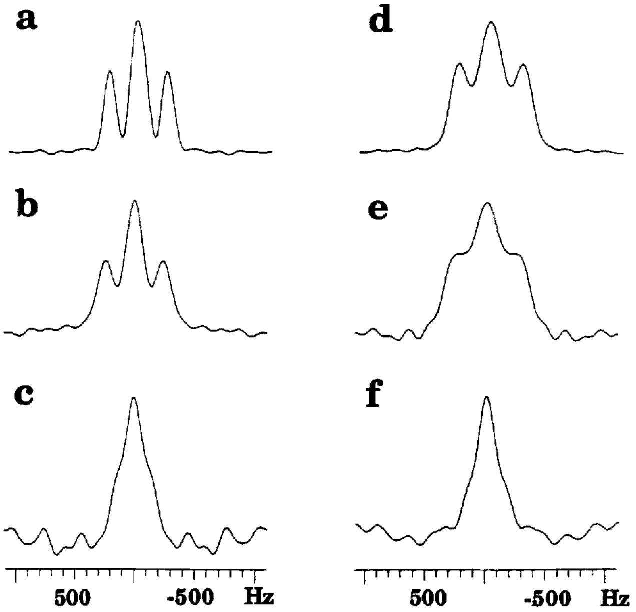


Figure 6. 2-D traces from the SLF/VAS C-13 NMR study of PCH5. 48 scans were collected for each of 16 increments. The peaks are assigned in figure 1: (*a*) trace from 3′ peak acquired without rapidly decelerated sample spinning; (*b*) trace from 3′ peak acquired with rapidly decelerated sample spinning; (*c*) trace from 3′* carbon acquired with rapidly decelerated sample spinning. (*d*)–(*f*) are analogous for the 2′ carbon.

are related to the orientation order parameter, S, by

$$D_{ij} = \frac{-\gamma_i \gamma_j h}{8\pi^2 r_{ij}^3} [(3\cos^2\theta_{ijz} - 1)S_{zz} + (S_{xx} - S_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy})] \qquad (6)$$

where γ is the magnetogyric ratio of the nuclei and i and j are the coupled nuclei, in this case H-1 and C-13. The z axis is the proper rotation axis of the segment, the y axis is normal to the segment, and the x axis is in the plane of the segment and is perpendicular to both the y and z axes. r_{ij} is the internuclear distance, and $\theta_{ij(x,y,z)}$ is the angle with r_{ij} form with the x, y, or z axis of the coordinate system. The equation refers to groups of interacting nuclei, so the order parameters describe only the orientation of the segment, not the entire liquid crystal molecule. The values of r_{ij}, which also define θ_{ij}, can be obtained from X-ray crystallography and other structural data of similar compounds. The values of r_{ij} for the liquid crystals are not expected to differ significantly from the similar compounds.

As noted above, exact values for D_{ij} need not be calculated. However, since the splittings in figure 6 for the new peaks are about half of the splitting for the original peaks, the orientational order parameter calculated from equation (6), using the value of $\phi = 78°$ (see the table), is approximately the same for both sets of peaks. Therefore, the orientational ordering of both alignments is similar.

For pure CCH5 ($\Delta\chi < 0$), no new peaks are observed when the spinning angle, β, was set at 46°. In this case, equation (2) predicts that CCH5 will be distributed in a plane perpendicular to the spinning axis. Therefore, the peaks are broader, and those due to possible pattern formation are not resolvable. On the other hand, new peaks arising from molecules with different macroscopic alignment were observed for $\beta = 65°$, in which case the director of CCH5 aligns parallel to the spinning axis, and the C-13 NMR spectrum affords higher resolution.

4. Discussion

At equilibrium, the alignment of rapidly spinning liquid crystals in a magnetic field is based on the sign of its magnetic anisotropy as discussed in §2·2. However, the alignment of a liquid crystal in a magnetic field may not solely depend on the sign of its magnetic anisotropy when the torques acting on a liquid crystal change rapidly, forcing the liquid crystal alignment away from equilibrium. Instead, the rapid change in the aligning torques in the liquid crystal can produce an alignment for the liquid crystals which is different from the equilibrium alignment, i.e. a pattern. Some patterns in other experimental geometries, studied previously by visual observation using cross polarizers, used theoretical modelling [2, 4, 5] to explain the pattern formation.

To the best of our knowledge, an exact theoretical analysis does not appear in the literature for the geometry considered in the present study. For the geometries that appear, when the realigning field is applied to liquid crystal system to make it move away from equilibrium, there are several modes through which the liquid crystal can relax back toward equilibrium after the realigning field is removed [2, 4, 5]. The simplest one, the uniform rotation mode, is responsible for the macroscopic reorientation of the liquid crystal [1] and has a growth rate assumed to be proportional to $|\Delta\chi|$ in a magnetic field. In competition with this mode are other more complicated modes which produce the patterns in the liquid crystals. The functional forms of these modes are complex and vary with geometry [2, 4, 5]. The presence of the pattern is a result of competition between the growth of the uniform rotation mode and the pattern forming modes. When the realigning torque is of sufficient magnitude, the system is driven away from equilibrium, and the pattern forming modes grow preferentially to the simple rotation mode. The presence of the pattern forming modes is generally attributed to 'back-flow' in the liquid crystal during reorientation, which reduces the rotational viscosity, γ_1, of the liquid crystal [2, 4, 5]. Because of the reduced γ_1, the liquid crystals can reorient easier by forming patterns than by the simple rotation mode. This 'back-flow' has been the predominant explanation for pattern formation in lyotropic and thermotropic liquid crystals in a large number of experimental geometries [2, 4, 5]. When the pattern formation is caused by the sudden application of a magnetic field, the growth of the pattern is related to $\Delta\chi$ [2,4,5]. Because the geometry in the present study is different, the theoretical relationships derived in previous studies are not strictly applicable [2, 4, 5]. However, it seems reasonable that a reduction in γ_1 may serve to produce the dual alignment observed here. To wit, in the geometry considered in the present study, the simple rotation mode acts over a much longer time ($\sim$100 ms) [1] than the complex modes ($\sim$30 ms) (see figure 4) which is consistent with a reduced γ_1.

In the present study, the deceleration of the spinning sample causes the alignment of the liquid crystal director to change from its initial equilibrium position of $\theta \approx \beta$ (for parallel alignment) towards the final equilibrium position of $\theta = 0^\circ$. The deceleration process is accompanied by the growth of the pattern forming modes. However, for slower deceleration the pattern may not grow rapidly enough to be observed. This may explain why 5CB shows the pattern only when the sample is decelerated very rapidly.

While undergoing a similar deceleration torque, PCH5 appears to form the pattern more easily than 5CB. This can be explained in the following way. The elastic constants are not expected to differ between 5CB and PCH5 by more than 10–15 per cent [22] and rotational viscosity by 5 per cent for the temperatures used in the current study [23]. On the other hand, $\Delta\chi$ should differ by about 50 per cent [7]. Therefore, the reduction in $\Delta\chi$ may affect the growth rate of the uniform rotation mode and favour the pattern producing mode. A similar argument may be made to explain figure 5 for liquid crystal systems having varying mole fractions of CCH2. The total anisotropy of the magnetic susceptibility of these mixtures is given by

$$\Delta\chi_{\text{mixture}} \approx P_{\text{CCH2}}\Delta\chi_{\text{CCH2}} = P_{\text{5CB}}\Delta\chi_{\text{5CB}} \qquad (7)$$

where p is the mole fraction of the components. Thus, $\Delta\chi$ of the system decreases with increasing mole fraction of CCH2 ($\Delta\chi<0$) in 5CB ($\Delta\chi>0$). When the mole fraction of CCH2 changes from 75 to 80 per cent, $\Delta\chi$ changes from positive to negative, as observed in the C-13 NMR spectra. This result is similar to previous studies which combined positive and negative $\Delta\chi$ liquid crystals to form 'magic mixtures' of very low $\Delta\chi$ [24–26]. In our study, the per centage of pattern reaches a maximum for samples with $\Delta\chi \approx 0$ (see figure 5). Other material properties are known to affect back flow in liquid crystals [2, 4, 5], but their contributions have not been explored in detail. These factors may be responsible for the lack of change in $Q_{\max}$ for the lower mole fractions of CCH2 (see figure 5), for which $\Delta\chi$ decreases with the increase of the amount of CCH2. They may also account for the approximately equal values of $Q_{\max}$ for pure 5CB and CCH5, even though the former has a much large value of $|\Delta\chi|$.

The appearance of two sets of carbon peaks, as shown in figures 1 and 2, obviously results from a re-alignment of the liquid crystal molecules under rapid deceleration, which is a non-equilibrium condition lasting for about 40 ms. This alignment pattern may be thought of being similar to the opening of an umbrella: some of the molecules form the 'umbrella handle' by staying with the director aligned parallel to the spinning axis ($\phi = 0^\circ$), but the rest re-align to reach a surface with an apex angle of $\phi \approx 78^\circ$, a flat 'umbrella top'. This situation is diagrammed in figure 7.

The actual arrangement of the molecules, of course, need not actually resemble the shape of an umbrella, and there may be a distribution of alignment angles between $\phi = 0^\circ$ and 78° (see the table). If the distribution of molecular alignment is even, i.e. the probability for each angle of alignment is the same between $\phi = 0^\circ$ and 78°, it would result in a type of 'partial' powder pattern in the NMR spectra, for which the two observed peaks for each carbon would correspond to the singularities of the partial powder pattern. Such a pattern was observed for spinning liquid crystal samples with very small $\Delta\chi$ under an equilibrium condition [27]. We note that the spectra in figures 1 and 2 do not appear to correspond to normal powder patterns. However, because of the low sensitivity of C-13 NMR, the possibil-

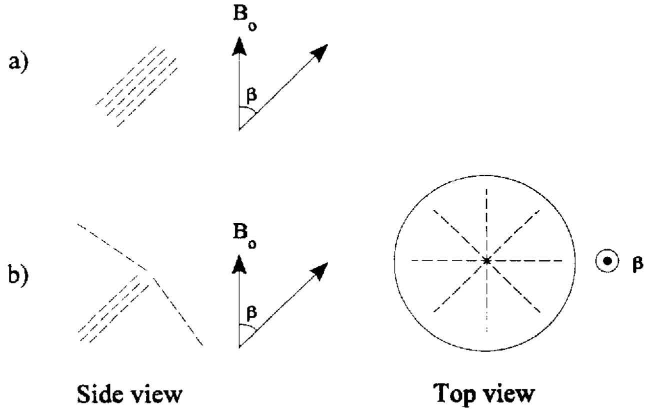


Figure 7. Schematic diagram of the alignment of liquid crystal molecules under rapid deceleration. (*a*) Before deceleration, the molecules are aligned parallel to the spinning axis. (*b*) After deceleration, the molecules may have a distribution of alignment angles, with a preference for two directions: along the original direction of the spinning axis, and on a surface almost perpendicular to that axis.

ity that the observed peaks are singularities of a partial powder pattern cannot be completely ruled out. This ambiguity was clarified by studying the F-19 NMR of a probe molecule, 2,2-difluorotetrachloroethane, dissolved in PCH5. In the F-19 spectrum, there are two distinct sets of doublets (see figure 3). Each set of doublets is due to the F–F dipolar interaction; the unequal line width of each half is likely due to differential relaxation effect, as it is also observed in a non-spinning sample at equilibrium. Thus, the absence of normal powder patterns in both the C-13 and F-19 spectra indicate that the distribution of the liquid crystal molecules in the cone in uneven, and that $\phi = 0^\circ$ and 78° are the angles of preferred alignment. This information about the preferred angles of alignment is not usually available from visual observation of patterns in liquid crystals, and it has unexplored implications in the physics of the pattern formation [2, 4, 5].

The growth of the pattern (see figure 4) represents the rapid switching of a part of the liquid crystal molecules to the 'new' preferred angle of alignment given in the table. From the present experiments, it is possible to assign an upper limit for the time it takes for this reorientation to occur. The process occurs faster than the NMR time-scale (20 ms), and at a rate sufficiently high such that the average potential theory for the alignment of rotating liquid crystals [15] does not hold. According to this theory, a rotating liquid crystal will change its alignment to minimize its potential energy, which is averaged over one cycle of rotation. In keeping with this theory, the 'new' liquid crystal alignment would not be observed unless the alignment occurs in a time shorter than one cycle of rotation. The rotation rate for the current study is about 1600 Hz, so the reorientation must occur faster than $1/1600 \approx 0{\cdot}6$ ms. Thus the umbrella 'opens' very quickly. However, it is not intuitively clear how this rapid switching occurs macroscopically, and the situation requires more extensive study and theoretical modelling in this system.

In the smectic phase, the liquid crystals are organized in layers, and the pattern would have to form in opposition to the very high rotational viscosity of the smectic phase. Therefore, the observation that dual alignment is not found in the smectic liquid crystal system is not surprising.

5. Conclusions

This study presents the technique of rapid deceleration of spinning samples to give important information about the liquid crystal during macroscopic reorientation. Using high resolution C-13 NMR, we have measured the alignment of the liquid crystal director and found that there is a preference for dual alignment of the directors in an umbrella pattern (see the table). By examining this pattern in singular and binary liquid crystal systems, we have seen that the magnitude of $\Delta\chi$ of the liquid crystal seems to have a great influence on the formation of the pattern, which appears to be the result of competing relaxation modes, attributable to reduction of the rotational viscosity by 'back-flow'. One of these relaxation modes appears to cause the liquid crystal alignment to switch from its initial alignment to its 'new' alignment in less than 0·6 msec, similar to the rapid opening of an umbrella. Because 'back-flow' involves material properties, it is important to consider rotational viscosity, elastic constants, and inertial properties of the liquid crystals as well as $\Delta\chi$.

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