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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Bayle, J. P. , Khandar-shahabad, A. , Courtieu, J. and Kan, S. K.(1986) 'Orientalional Behaviour of the Nematic Director upon Macroscopic Rotation at the Magic Angle', *Liquid Crystals*, 1: 4, 371 – 377

To link to this Article: DOI: 10.1080/02678298608086669

URL: <http://dx.doi.org/10.1080/02678298608086669>

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Orientalional behaviour of the nematic director upon macroscopic rotation at the magic angle

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(Received 14 April 1986; accepted 3 May 1986)

The ^{19}F N.M.R. spectrum of 1,2,2,2-tetrachloro-1,1-difluoroethane has been studied in the nematic liquid crystal ZLI 1167 (Merck) upon rotation at the magic angle. The director of the liquid crystal is oriented perpendicular to the spinning axis when the angle between the rotation axis and the magnetic field is less than the magic angle and parallel when this angle is more than the magic angle. It is shown that exactly at the magic angle the spectrum corresponds to a frequency modulated powder pattern. This powder pattern leads to an understanding of the orientational behaviour of the director when a nematic is spun at the magic angle.

1. Introduction

In magic angle N.M.R. experiments on solids high resolution is achieved only for high speed rotation. By reducing the spinning speed, typically when the spinning frequency is less than the chemical shift anisotropy, the isotropic line in the N.M.R. spectrum is flanked on both sides by sidebands spaced at the spinning frequency. The intensities of the spinning sidebands are related to the chemical shift parameters as described by Herzfeld and Berger [1].

The effect of rotation upon nematic liquid crystals with negative diamagnetic anisotropy, $\Delta\chi$, is quite different [2]. If the spinning speed is faster than the director reorientation rate, typically 10 Hz for a 1.5 T magnetic field, the nematic director reaches a state where it is distributed in the plane perpendicular to the spinning axis when the angle β between the rotation axis and the magnetic field is smaller than the magic angle, and it lies parallel to the rotation axis when β is larger than the magic angle.

In the present study, we have tried to discover what happens to the director when the rotation angle passes through the magic angle. For this purpose, we have used a sample of 1,2,2,2-tetrachloro-1,1-difluoroethane dissolved in the Merck mixture ZLI 1167. The ^{19}F N.M.R. spectrum at the magic angle for slow spinning speeds did not consist either of a degenerate doublet as expected if the director was parallel to the rotation axis nor of a degenerate doublet modulated by the rotation as expected if the director was distributed in the plane perpendicular to the spinning axis. A set of unsymmetrical sidebands appeared which described a powder pattern as in classical solid-state experiments. This powder pattern leads to an understanding of the director behaviour when spinning at the magic angle.

2. Experimental

For the experiment, commercial 1,2,2,2-tetrachloro-1,1-difluoroethane was dissolved in the nematic Merck mixture ZLI 1167 ($\Delta\chi < 0$). The ^{19}F N.M.R. spectra were recorded on a WP 60 Bruker spectrometer modified to receive a ^{19}F signal. The field was locked on an external D_2O signal. The magic angle device has been described elsewhere [3]. It allows the rotation of liquids and variable temperature experiments. The liquids were contained in an N.M.R. tube of 15 mm length and 5 mm diameter. This tube was inserted in a 10 mm cylindrical rotor which permits the rotation speed to be adjusted between 20 and 2000 Hz. A goniometer is mounted at one end of the spinner holder which gives an accuracy of $\pm 0.2^\circ$. The temperature of the sample can be adjusted within an accuracy of $\pm 1^\circ\text{C}$ by controlling the temperature of the gas for the spinner.

3. Results and discussion

Figure 1 shows the ^{19}F N.M.R. spectrum of 1,2,2,2-tetrachloro-1,1-difluoroethane for four different rotation speeds recorded at the magic angle together with the static spectrum. In (a) it can be seen that the sidebands spaced at ω_r intervals are not symmetric with respect to the isotropic line. If the director was perpendicular to the spinning axis, as for $0^\circ < \beta < \theta_m$, symmetrical sidebands spaced at $2 * \omega_r$ for each line of the A_2 spin system should appear and if the director was parallel to the spinning axis, as for $\theta_m < \beta < 90^\circ$, a degenerate doublet without modulation sidebands would be expected [2]. This set of sidebands indicates that the director does not lie in these two directions. The envelope of the spectrum resembles the powder pattern observed in solids experiments when the spinning speed is less than the chemical shift anisotropy. This modulated powder pattern indicates that the director is distributed over the sample. In order to confirm this observation and to determine the distribution we have performed theoretical calculations on the spinning sideband intensities and on the envelope of the powder pattern applied to the A_2 spin system. In the following calculations it has been assumed that in all domains the ordering matrix of the dissolved molecule expressed in the local director frame is the same as that measured for the static sample.

3.1. Sideband intensity calculation

The orientational dependence of the ^{19}F doublet transition frequencies is given [4] as a function of the angle α between the local director and the magnetic field by

$$\text{and} \quad \left. \begin{aligned} & \left(-\frac{2}{3}\Delta\sigma\nu_0 - \frac{3}{2}D_0 \right) S_{ZZ}^D \left(\frac{3\cos^2\alpha - 1}{2} \right) \\ & \left(-\frac{2}{3}\Delta\sigma\nu_0 + \frac{3}{2}D_0 \right) S_{ZZ}^D \left(\frac{3\cos^2\alpha - 1}{2} \right), \end{aligned} \right\} \quad (1)$$

where $\Delta\sigma$ is the fluorine shielding anisotropy, ν_0 the Larmor frequency of the nucleus, S_{ZZ} is the order parameter of the F-F axis and D_0 is the dipolar coupling constant between the two fluorine nuclei. In the following we use C and D defined as

$$C = -\frac{2}{3}\Delta\sigma\nu_0 S_{ZZ}^D$$

and

$$D = \frac{3}{2}D_0 S_{ZZ}^D$$

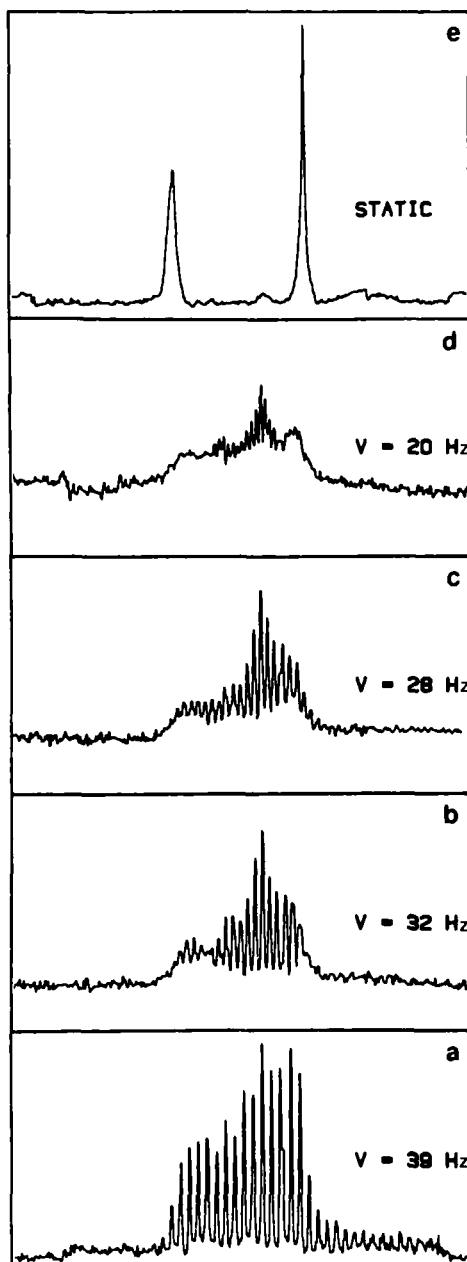


Figure 1. The ^{19}F N.M.R. experimental spectra of 1,2,2,2-tetrachloro-1,1-difluoroethane for various rotation speeds in the nematic liquid crystal ZLI 1167. The spectra (a), (b), (c) and (d) correspond to speed rotations of 39 Hz, 32 Hz, 28 Hz and 20 Hz respectively and (e) is the static spectrum obtained one second after stopping the rotation. Both lines do not have the same intensity showing that the director is not yet totally in the plane perpendicular to the magnetic field. Each spectrum is the sum of 32 scans. In (b), (c) and (d) the bands far from the isotropic line are broadened due to the unsteadiness of rotation at slow speeds. The envelope of the sidebands describes a powder pattern.

It should be noted that C and D are the experimental shielding anisotropy and dipolar coupling constant respectively that we measured on the static sample and have used in numerical calculations.

When the sample is spun, the angle α (the angles are defined in figure 3) between the director and the magnetic field is modulated by the rotation. We have shown, using a classical approach for the calculation of the sidebands intensities, that the relative intensity of the N th sideband is [6]

$$I \propto (F)^2, \quad (2)$$

where

$$F = \frac{1}{2\pi} \int_{-\pi}^{+\pi} \exp[i(-N\theta + \bar{B} \sin \theta + \bar{C} \sin 2\theta)] d\theta, \quad (3)$$

with

$$\bar{B} = \frac{3(C \pm D)}{4\omega_r} \sin 2\beta \sin 2\delta$$

and

$$\bar{C} = \frac{3(C \pm D)}{8\omega_r} \sin^2 \beta \sin^2 \delta.$$

If the director is distributed over the sample, the relative intensity becomes

$$I \propto \int_0^{\pi/2} |F|^2 P(\delta) \sin \delta d\delta, \quad (4)$$

where $P(\delta)$ is the distribution function of the director. Note that \bar{C} is an odd function of δ and \bar{B} an even one, so for the N th and $-N$ th sidebands the symmetry is lost in the numerical integration of equation (4) and the spectrum must appear unsymmetrical.

For the numerical calculation of the spectra of the A_2 spin system, D was chosen as 565 Hz and C as -228 Hz from the static spectrum. The intensity was scaled by setting the height of the central lines equal in the experimental and the calculated spectra. A better sideband separation is observed near the isotropic line for spectra (b) and (c) because of the stability of the rotation speed which is ± 2 Hz. In fact the bands far from the isotropic line have their natural linewidth increased by an increment of $\pm N\Delta\omega_r$. In order to take account of the fluctuations in the rotation speed and its effect on the sideband linewidth, the latter was increased in the calculated spectra using a width gradient from the isotropic line to fit the experimental line broadening.

Since the theory expressed in [2] indicates that at the magic angle the resultant orientating torque vanishes, it seems reasonable to try first an isotropic distribution of the director over the sample. The agreement between the calculated and the experimental spectra is fairly good. It shows that the distribution of the director at the magic angle is quite homogeneous over all the sample. Small differences in line intensities may arise from experimental difficulties in adjusting the magic angle and in monitoring the variation of the temperature over the sample. As can be seen from figure 2 (a), the most important difference arises in the intensity of the isotropic line which is weaker than in the experimental spectrum (cf. figure 1 (a)). This is consistent with the existence of some domains where the director is still perpendicular or parallel

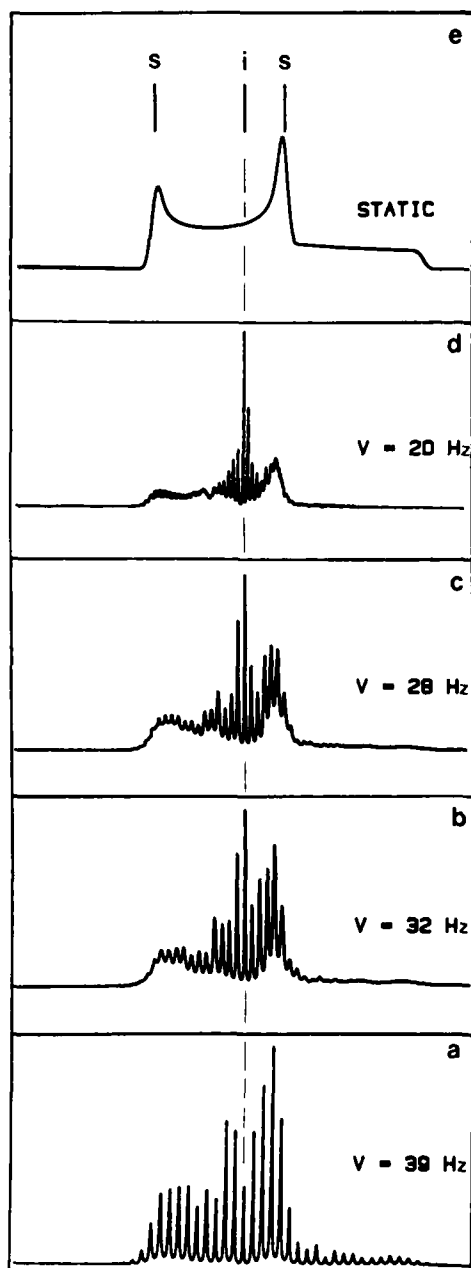


Figure 2. Calculated spectra for the same speeds as in figure 1, with the assumption that the director of the nematic is randomly distributed. Details of the numerical calculations are given in [6]. In (a) the intensity of the isotropic line is less important than in the experimental spectrum, indicating that some domains in the nematic crystal are not randomly distributed. In (b), (c) and (d) a linewidth gradient was used in order to fit the experimental broadening. In (e) the powder pattern for a randomly distributed director is shown, this pattern cannot be observed experimentally because when the sample rotation is stopped the nematic director aligns itself perpendicular to the magnetic field (cf. figure 1 (e)). The position of the static lines are indicated by (s) and the isotropic line by (i).

to the axis of rotation. In such cases, as the reduction factor $R \equiv (3 \cos^2 \beta - 1)/2$ is zero there is a contribution from these domains to the central line relative to the sidebands.

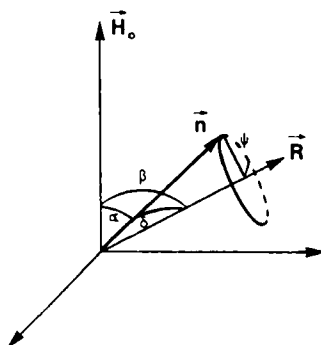


Figure 3. Relative position of the director in the laboratory frame and the definition of the angles used in the text.

3.2. Powder pattern calculation for a static distribution of the director

In order to show that the envelope of the spinning sidebands describes an isotropic powder pattern, we have calculated the lineshape function for a random alignment involving a doublet using a standard procedure [5] with

$$g(\nu) = \{1/\sqrt{3}(C \pm D)\} \{1/[1 + 2\nu/(C \pm D)]^{1/2}\}. \quad (5)$$

The positive sign in the parentheses in the denominator occurs when ν takes a value such that $(C - D) < \nu < (-C - D)/2$, the other sign occurs when $(D - C)/2 < \nu < D + C$, and so the sign combination of positive and negative obtains when $(-C - D)/2 < \nu < (-C + D)/2$. In general, this pattern has two singularities. If the chemical shift anisotropy is low, as for protons, this pattern is symmetrical. However for fluorine this is not true, and this explains why the pattern is unsymmetrical (cf. figure 2(e)). This pattern cannot be observed experimentally because if the sample rotation is stopped, the director will align perpendicular to the magnetic field as can be seen in figure 1(e). None the less experimental spectra seem to present three singularities, actually the middle one is an artefact corresponding to the isotropic line, since this is not sensitive to the fluctuations in the speed of rotation.

Note the shoulder on the right of the pattern which arises from the line where the contributions from D and C have the same sign. This shoulder leads to the small modulation sidebands on the right-hand side of the spectra for the rotating sample.

In the static sample the director is perpendicular to the magnetic field, the static lines are positioned at $(-C - D)/2$ and $(-C + D)/2$ from the isotropic line and therefore at the same place as the two singularities. This is observed in the static spectrum (cf. figure 2(e)).

4. Conclusion

The ^{19}F N.M.R. spectra of 1,2,2,2-tetrachloro-1,1-difluoroethane in the Merck nematic liquid crystal ZLI 1167 obtained at the magic angle for slow rotation speeds (20–40 Hz) are shown to describe a powder pattern as in classical N.M.R. experiments

on solids. Calculations of the powder pattern envelope and of the rotation sideband intensities indicate that the director is homogeneously distributed over the sample at this peculiar position of the rotation axis.

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