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Rotation in a magnetic field of nematic liquid crystalline samples with a negative anisotropy of their magnetic susceptibility

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The behaviour of the mesophase directors when a sample with a negative anisotropy $\Delta\chi$ in the magnetic susceptibility is rotated at a speed ω in a magnetic field B_0 about an axis inclined at an angle β is investigated by deuterium NMR spectroscopy. There are combinations of β and ω which lead to the directors aligning along the spinning axis (stable region), and other combinations where the directors are either unaffected by the rotation, or have a time-dependent distribution (unstable region). These two regions are separated by a line (the q line) whose position depends on β and $\omega_c = \Delta\chi B_0^2/2\mu_0\gamma_1$, where γ_1 is a twist viscosity coefficient. Experiments on 4-*n*-propyl-4′-cyanobicyclohexane (CCH3) are used to demonstrate how the q line, and hence ω_c may be determined. Combining this result with a measurement of the anisotropy in the magnetic susceptibility, $\Delta\chi$, yields a value for γ_1.

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1. Introduction

The directors of nematic liquid crystals can be uniformly aligned by application of a magnetic field, B_0. Materials with a positive anisotropy $\Delta\chi$ of their magnetic susceptibility have their directors **n** aligned parallel to B_0, whilst when $\Delta\chi$ is negative the **n** are aligned in a plane orthogonal to the field. The effect of rotating a nematic liquid crystalline sample in a field depends on the sign of $\Delta\chi$, the angle β between the rotation axis R and B_0, and the rotation speed ω. There are combinations of these variables which result in the directors adopting a single orientation α with B_0, and others which result in a time-dependent distribution of the directors with respect to B_0. The two regimes are separated by what Courtieu *et al.* [1] term the q line, which is shown in figure 1.

For $\Delta\chi$ positive, the q line is determined by

$$\cos^2\beta = 1/3 - 6/[27(q^2 - 1)] \qquad (1)$$

for $70{\cdot}5° > \beta > 54{\cdot}7°$, with

$$q = [1 - 3/(\omega/2\omega_c)^2]^{1/2} \qquad (2)$$

and

$$\omega_c = |\Delta\chi B_0^2/2\mu_0\gamma_1| \qquad (1)$$

where γ_1 is the twist viscosity coefficient and $\mu_0 = 4\pi \times 10^{-7}$ is the magnetic constant.

For $90° > \beta > 70{\cdot}5°$ the relation between β and q is given by

$$\cos^2\beta = (1+q)(1-2q)/[9(1-q)] \qquad (4)$$

For $\Delta\chi$ negative, q is the solution of equation (1) for $70{\cdot}5 > \beta > 54{\cdot}7°$, and for $90° > \beta > 70{\cdot}5°$ q is given by

$$\cos^2\beta = (1-q)(1+2q)/[9(1+q)] \qquad (5)$$

The critical speed ω_c has been obtained for $\Delta\chi$ positive materials by experiments in which the sample is rotated with $\beta = 90°$, and the director orientation followed by either ESR [2,3] or NMR [4,5] spectroscopy. Thus, Emsley *et al.* [5] used deuterium NMR to follow the effect of rotating a sample of 4-*n*-octyl-d$_{17}$-4′-cyanobiphenyl (8CB) in the field of the NMR spectrometer. The spectrum of the methyl deuterons is a doublet from the quadrupole-electric field gradient interaction, which has a splitting $\Delta\nu(0°)$ when the sample is stationary. Rotating with $\beta = 90°$ and $\omega < \omega_c$ produces a reduction in the splitting and a broadening of the lines. At $\omega = \omega_c$ the spectrum is that from a uniform distribution of the directors in the plane perpendicular to R. As ω increases, the powder pattern breaks up into a series of sidebands spaced at ω, which corresponds to the regime marked as unstable in figure 1 (*a*). The experiment yields the critical speed, and γ_1 if $\Delta\chi$ is known. A stationary sample with $\Delta\chi$ negative has the directors uniformly distributed in the plane perpendicular to B_0. The deuterium NMR spectrum of such a sample shows a doublet splitting for each deuteriated site, with a separation, $\Delta\nu(90°) = -\frac{1}{2}\Delta\nu(0°)$. Rotating the sample with $\beta = 90°$ aligns all the directors along R for all values of ω, but this has no effect on the NMR spectrum, and so cannot be used to obtain ω_c.

Figure 1 (*b*) indicates that to obtain ω_c for a material with $\Delta\chi$ negative it is necessary to rotate with β between $54{\cdot}7°$ and $90°$, and to locate the q line. We will demonstrate

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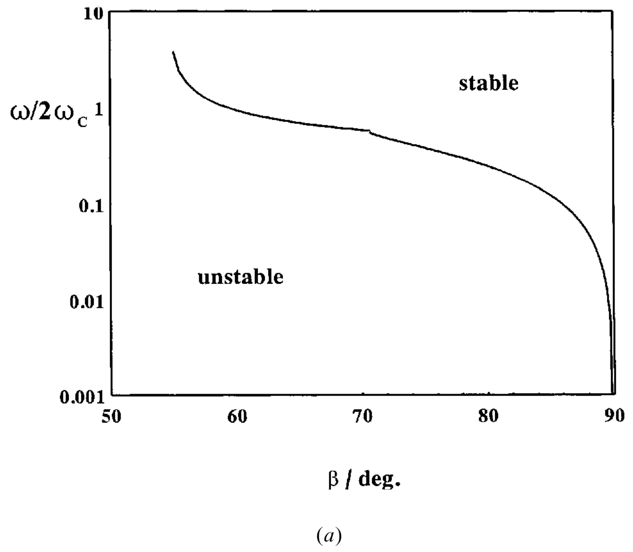

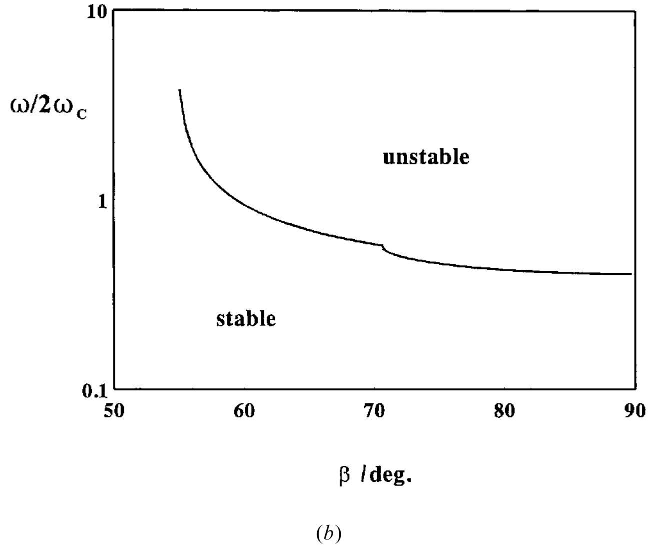

Figure 1. The q line separating the regions where the director aligns with the spinning axis, which is at an angle β with the magnetic field, from the region where the directors have a time-dependent orientational distribution for liquid crystals for which (*a*) $\Delta\chi<0$ and (*b*) $\Delta\chi>0$. The sample is rotating with a speed ω relative to ω_c, which is the critical speed when β is 90°. Note that the vertical axis is $\omega/2\omega_c$ so as to give the same scale as that used by Courtieu *et al.* [1], whilst adopting the more usual definition of ω_c [2–5].

this experiment for the liquid crystal CCH3 (4-*n*-propyl-4′-cyanobicyclohexane or more precisely, *trans*-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexylcarbonitrile), whose structure is shown in figure 2. The director orientations are monitored by deuterium NMR, and the sample contains deuterium in one of the rings, as shown in figure 2.

The rotation experiment yields $\Delta\chi/\gamma_1$, and $\Delta\chi$ may also be measured by an NMR experiment, thus yielding γ_1. The method used here to obtain $\Delta\chi$ is that of Bernheim and Krugh [6] in which the proton NMR signal is recorded of a reference sample contained in the outer annulus of a coaxial, cylindrical tube. The liquid crystalline sample is placed in the inner tube.

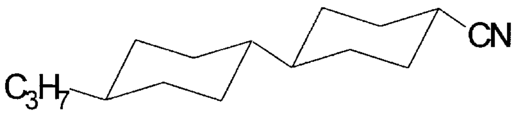

Figure 2. The structure of the liquid crystal CCH3.

2. Experimental

The preparation of the deuteriated sample has been described previously [7]: it has six deuterons in the cyano substituted ring distributed randomly between six axial and four equatorial positions. It was contained in a glass bottle which just fits inside a rotor of type BL-7 which is used with a Bruker MAS probe modified to spin at angles between 40° and 90°. The bottle was sealed by gluing a circular glass disk on to the open end, as shown in figure 3. The rotor is designed to spin fast, and the rotation speed is normally controlled by a Bruker MAS remote control pneumatic unit, which has the capability to lock the speed to a pre-set value. Slow speeds were achieved by using a teflon plug in the top of the rotor instead of a fluted rotor cap, using the pneumatic unit in manual mode, setting the drive pressure to zero, and changing only the bearing pressure to set the speed. The angle the rotation axis makes with B_0 is set with a micrometer, calibrated by measuring the deuterium spectra of a sample of deuteriated benzene dissolved in a nematic liquid crystalline solvent. A solvent with $\Delta\chi$ positive was used for $\beta<54{\cdot}7°$, and a $\Delta\chi$ negative solvent was used for $90°>\beta>54{\cdot}7°$. The angle can also be determined from the spectrum given by the CCH3-d$_6$ sample when the rotation speed is above the q line. The deuterium spectra were recorded on a Bruker MSL spectrometer at 30·7 MHz. All the

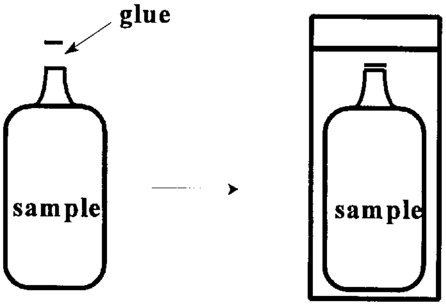

Figure 3. Sample bottle used in the VAS experiments.

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spectra were recorded at 72°C, which is 8°C below the transition temperature to the isotropic phase.

The experiments to determine $\Delta\chi$ cannot be done on a spectrometer in which the B_0 field is vertical, as in the MSL 200, and so a Jeol FX90Q which does have the required horizontal field was used. The coaxial sample tube was purchased from Wilmad Glass Company (type 516-CC-5). The reference liquid used was *p*-xylene, which was chosen because it has a large liquid range, and the signal from the aromatic protons is not obscured by the peaks from the liquid crystalline sample when this is in the isotropic phase.

3. Results and discussion

3.1. *Determination of the critical speed*

Figure 4 shows a deuterium spectrum taken on a stationary sample of CCH3-d$_6$, and figure 5 contains spectra taken with rotation of the sample with $\beta=56{\cdot}5°$. At speeds below 153 Hz, the spectra have splittings essentially identical to those of the stationary sample, but with broader lines. The line broadening may be a consequence of worse temperature control at low spin-

Table 1. Critical speed ω_c obtained for different angles β between the rotation axis and the magnetic field.

β/deg	ω_c/Hz
$55{\cdot}3 \pm 0{\cdot}3$	51 ± 12
$56{\cdot}5 \pm 0{\cdot}3$	48 ± 3
$59{\cdot}5 \pm 0{\cdot}2$	51 ± 3
$64{\cdot}8 \pm 0{\cdot}2$	55 ± 4
$70{\cdot}0 \pm 0{\cdot}2$	55 ± 5
$75{\cdot}1 \pm 0{\cdot}2$	53 ± 4

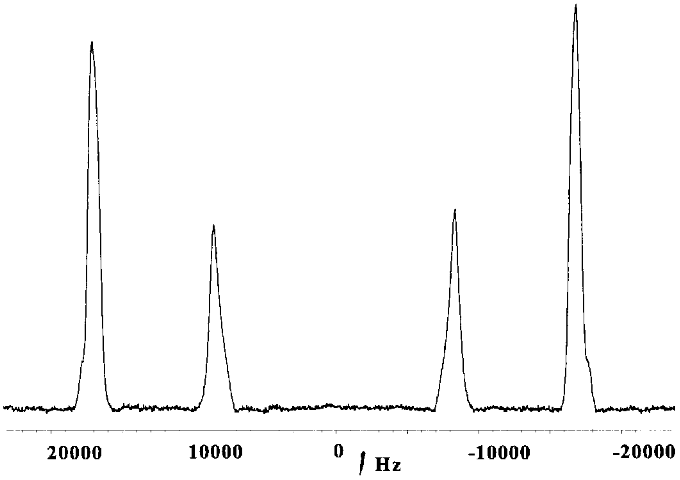

Figure 4. 30·7 MHz deuterium NMR spectrum of a stationary sample of CCH3-d$_6$ in the nematic phase at 345 K.

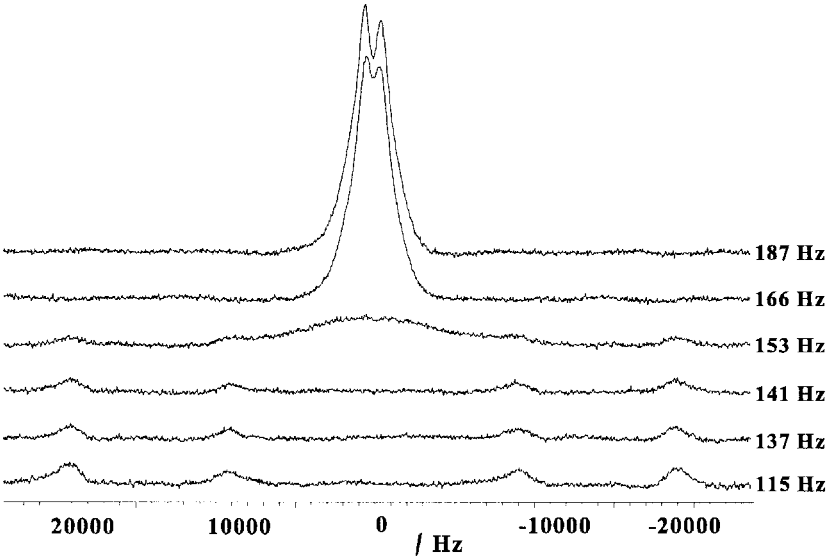

Figure 5. 30·7 MHz deuterium spectra at 345 K of a sample of CCH3-d$_6$ rotating about an axis inclined at 56·5° to B_0, and at a range of rotation speeds.

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ning speeds, or a small spread in the director orientation. The directors remain in the plane perpendicular to B_0 and do not adopt a distribution in the plane perpendicular to the spinning axis, as suggested by Courtieu *et al.* [1]. Above 153 Hz, the splittings collapse to a value of $\Delta\nu(0°)(3\cos^2\beta - 1)/2$, which shows that the directors are now all aligned along, or close to, the spinning axis, i.e. the q line has been crossed. The experiment was repeated with values of β of 55·3°, 56·5°, 59·5°, 64·8, 70°, 75·1°, and values of ω_c obtained which are shown in the table. Averaging these values gives ω_c as 52 ± 3 Hz.

3.2. *Measurement of the anisotropy in the magnetic susceptibility*

Figure 6 shows a proton spectrum from the *p*-xylene contained in the outer annulus of the coaxial tubes taken when the CCH3 in the inner tube is in the nematic phase. The magnetic field for a static sample with a negative $\Delta\chi$ aligns the directors of the liquid crystalline sample in the plane perpendicular to B_0. For this geometry the peak separation, δ (Hz), is related to $\Delta\chi$ by

$$\Delta\chi = (3/4\pi)(r_1/r_2)^2(\delta_{\mathrm{iso}} - \delta_{\mathrm{nem}})/\nu_0 . \qquad (6)$$

The ratio (r_1/r_2) for the radii of the Wilmad tubes is $1{\cdot}92 \pm 0{\cdot}01$, and the proton resonance frequency ν_0 is 90 MHz. Spectra were taken over the temperature range 62° to 90°, and this enabled a value of $\Delta\chi = -2{\cdot}3 \pm 0{\cdot}5 \times 10^{-8}$ to be obtained for the same temperature, 72°C, used in the rotation experiments. Combining the values of ω_c and $\Delta\chi$ yields a value for γ_1 of $0{\cdot}61 \pm 0{\cdot}17 \times 10^{-3}$ Pa s.

4. Conclusion

The main conclusion is that the results from the rotation experiments are consistent with the theory described by Courtieu *et al.* [1] and the expressions they derive for the line separating stable and unstable solutions to the equation of motion of a nematic sample, with a negative anisotropy in the magnetic susceptibility, rotating at an angle β to the magnetic field.

The NMR rotation experiment described here enabled the critical speed to be obtained with a precision of about ±10%. The precision is determined mainly by the accuracy with which the q line can be located. This was done by adjusting the spinning speed and noting the value at which the spectrum changed from being that characteristic of alignment of the directors orthogonal to the magnetic field, to one corresponding to alignment of the directors along the spinning axis. In the present experiments, which used a probe designed for spinning at a known, controlled speed in excess of about 500 Hz, it was difficult to proceed stepwise through the region close to the q line, since this is in the region of about 150 Hz. In principle, however, the speed could be set more precisely and the experiment is capable of greater accuracy.

The rotation experiment determines the quantity $\Delta\chi B_0^2/2\mu_0\gamma_1$, and combining this with a measurement of $\Delta\chi$ has enabled a value for γ_1 to be obtained. The precision on measuring $\Delta\chi$ by the NMR method used here is not high, particularly for a material with a negative value since this reduces the observed splittings Δ_{nem} by a factor of a half relative to the case of $\Delta\chi$ positive. In addition, the magnitude of $\Delta\chi$ for CCH3 is small, and so the overall precision is low (±20%). The value of $\Delta\chi$ obtained for CCH3 of $-2{\cdot}3 \pm 0{\cdot}5 \times 10^{-8}$ compares well with that of $-2{\cdot}8 \times 10^{-8}$ measured by Schad *et al.* [8] for CCH7 at the same reduced temperature.

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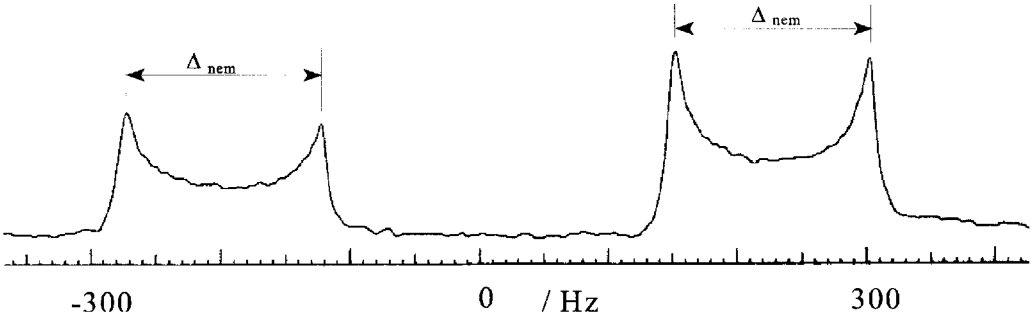

Figure 6. 90 MHz NMR spectrum of the protons in a sample of *p*-xylene contained in the outer annulus of a coaxial cylindrical tube which has the inner tube filled with CCH3. The temperature of 352 K corresponds to CCH3 being in the nematic phase.

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