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THE DIRECTOR DISTRIBUTION IN A SPINNING NEMATIC MESOPHASE SUBJECT TO A STATIS MAGNETIC FIELD

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We have determined the probability distribution function for the director in a spinning nematic mesophase subject to a static magnetic field, using electron resonance spectroscopy. For low spinning speeds the director is found to be inclined to the magnetic field as predicted by a continuum theory analysis of the system; there is however a small spread in the angle made by the director with the field. This inhomogeneity in the director alignment increases smoothly as the angular velocity of the mesophase is increased until at high speeds the director adopts an isotropic distribution in a plane containing the magnetic field. At present there are no magnetohydrodynamic theories of the nematic mesophase which account for the dispersion in the director produced by sample rotation.

1. Introduction

The behaviour of a nematic mesophase rotating in the presence of a static magnetic field has been the subject of a number of theoretical [1,2] and experimental investigations [1–5]. According to an analysis based on continuum theory the director should remain uniformly aligned although no longer parallel to the magnetic field [2]. The angle γ between the director and the field is predicted to be

$$\sin 2\gamma = \Omega/\Omega_c, \tag{1}$$

when the sample rotates with an angular velocity Ω. Here Ω_c is a critical speed above which the director should also rotate, but in practice this dynamic regime is found to be transitory [2]. It ought to be possible therefore to make the director adopt an angle close to 45° with the magnetic field provided the mesophase is spun at speeds just below the critical value. However, in several magnetic resonance experiments [2,4,5] the maximum angle which has been achieved is 35° which is considerably less than the predicted value. In closely related experiments a static nematic mesophase is subjected to a magnetic field rotating at an angular velocity Ω. The director now rotates with the same speed but lags the field by an angle, also given by eq. (1) [6–8]. In addition the sample experiences a torque which should attain its maximum value when the angular velocity is Ω_c. Experimentally the torque is a maximum at rotation speeds which do not correspond to the appropriate critical value [8–10]. These observations have prompted us to study the magnetohydrodynamic behaviour of a rotating nematic mesophase in an attempt to understand the origin of these discrepancies between theory and experiment.

2. Electron resonance theory

We have chosen to use electron resonance spectroscopy for this investigation because, as we shall see, it provides a way of determining the distribution of the director even when this is not uniformly aligned in the mesophase. With this technique the mesogen is first doped with a paramagnetic impurity or spin probe whose molecules deviate from spherical symmetry [11]. As a consequence of the resultant aniso-

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tropy in the solute–solvent interactions the spin probe is partially oriented with respect to the director. In our experiments the spin probe reorients rapidly with respect to the director, but none-the-less it may, for many purposes, be regarded as a static species with partially averaged magnetic interaction tensors [11,12]. The nematic mesophase is uniaxial and so the ordering potential has $D_{\infty h}$ symmetry which causes the magnetic tensors for this fictitious static species to possess cylindrical symmetry as well. The dominant interactions for the nitroxide spin probe used here are the electron Zeeman and nitrogen hyperfine interactions. The electron resonance spectrum contains three lines, provided the director is uniformly oriented with respect to the magnetic field. The hyperfine spacing is given by

$$\bar{a}(\gamma) = (\tilde{g}_{\parallel}^2 \tilde{A}_{\parallel}^2 \cos^2\gamma + \tilde{g}_{\perp}^2 \tilde{A}_{\perp}^2 \sin^2\gamma)^{1/2} / \bar{g}(\gamma), \qquad (2)$$

where

$$\bar{g}(\gamma) = (\tilde{g}_{\parallel}^2 \cos^2\gamma + \tilde{g}_{\perp}^2 \sin^2\gamma)^{1/2}, \qquad (3)$$

and γ is the angle between the director and the field. The component of the partially averaged hyperfine tensor parallel to the director is denoted by $\tilde{A}_{\parallel}$ and the perpendicular component is $\tilde{A}_{\perp}$. The components of the partially averaged g tensor, $\tilde{g}$ are labelled in an identical manner. Since both partially averaged tensors may be obtained from other experiments, measurements of the hyperfine spacing $\bar{a}(\gamma)$ permits the determination of the angle between the director and the magnetic field [2,11,13].

When the director is not uniformly aligned and the rate of director motion is slow on the electron resonance time scale then the observed spectrum $h(B)$ is a sum of spectra from all orientations of the director [14]. Thus

$$h(B) = \sum_m \int L[B, \tilde{B}_m(\gamma), T_2^{-1}(m)]\, p(\gamma)\, \mathrm{d}\gamma, \qquad (4)$$

where m is the nitrogen nuclear spin quantum number characterising a particular spectral line. The line shape $L[B, \tilde{B}_m(\gamma), T_2^{-1}(m)]$ is taken to be lorentzian with a width $T_2^{-1}(m)$. Each line is centred on the resonant field $\tilde{B}_m(\gamma)$ which is determined by the partially averaged magnetic tensors:

$$\tilde{B}_m(\gamma) = [h/\bar{g}(\gamma)\beta]\,[\nu - \bar{a}(\gamma)\, m], \qquad (5)$$

where h is Planck's constant, β is the electron Bohr magneton and ν is equal to the operating frequency of the spectrometer. The second order terms which normally appear in eq. (5) have been omitted because they are negligible for nitroxide spin probes. Strictly eq. (4) should also contain a term to allow for the anisotropy in the transition probability, but, because the anisotropy in $\tilde{g}$ for the spin probe is so small, it may be ignored. Finally $p(\gamma)\,\mathrm{d}\gamma$ gives the probability of finding the director between γ and $\gamma + \mathrm{d}\gamma$ with respect to the magnetic field. At present there is no transformation which would enable us to determine $p(\gamma)$ from the observed spectrum. We are therefore forced to guess various forms for the distribution function, simulate the electron resonance spectrum and select the most realistic form by comparing the simulated spectra with their experimental counterparts. To obtain good agreement between the experimental and theoretical spectra for the nitroxide spin probe used in this investigation it is necessary to allow for the inhomogeneous broadening of the spectral lines by the unresolved proton hyperfine structure. This may be accomplished simply by extending the summation in eq. (4) to all resonant fields originating from both the nitrogen and proton interactions and including the angular dependence of all the coupling constants. In practice there are many such proton interactions [15] and the computation becomes time consuming if they are all included; however we have found that, provided the peak-to-peak linewidth exceeds 1 gauss, the various protons may be replaced by five equivalent protons with a coupling constant of about 0.65 gauss but whose exact value is solvent dependent [16]. These ideas will be applied in section 4 to interpret the results of the experiments which are described briefly in the following section.

3. Experimental

Two nematogens were studied; one was Merck Phase IV which was used without further purification (T_{S-N} 16°C, T_{N-I} 75°C) [17]. The second was 4,4′-dimethoxyazoxybenzene. This was purchased from Sherman Chemicals Ltd. and was purified by recrystallisation from an acetone/ethanol mixture (T_{S-N} 119°C, T_{N-I} 136°C). The spin probe was [3-spiro-(2′-N-oxyl-3′,3′-dimethyloxazolidine)]-5αcholestane and was synthesised from 5α-cholestan-3-one [18]. The electron resonance spectra were recorded on a Varian E-3 spectrometer.

The samples of 4,4'-dimethoxyazoxybenzene were degassed prior to use in order to reduce the broadening of the spectral lines by dissolved oxygen. The possible influence of surface effects was studied by employing a variety of sample containers. These included Pyrex tubes with internal diameters of 1 mm and 3 mm, as well as two coaxial tubes with a spacing of 0.5 mm. In every case identical spectra were obtained when the sample was spun at the same speed; all measurements were made on the supercooled mesophase at 97.5°C. The samples were rotated by a stepper motor on-line to a Varian 620/i computer, and the angular velocity was calculated from the pulse generation frequency for the motor. More importantly it is possible to achieve a constant angular velocity in a variety of ways; however the appearance of the steady-state spectrum was always found to be independent of the sample's history. Each step of the motor rotates the sample through 5.4°; since this is rather large we ascertained that the behaviour of the director is not a consequence of this quantised rotation by using a dc motor operating at constant current. For identical angular velocities, the electron resonance spectra were found to be the same as those obtained with the stepper motor.

A similar sequence of experiments was performed with Merck Phase IV at a temperature of 49°C. The following sample containers were used for this nematogen, a conventional Pyrex tube with an internal diameter of 3 mm, precision ground quartz tubes with internal diameters of 1, 2.2, 3.4 and 4.1 mm,

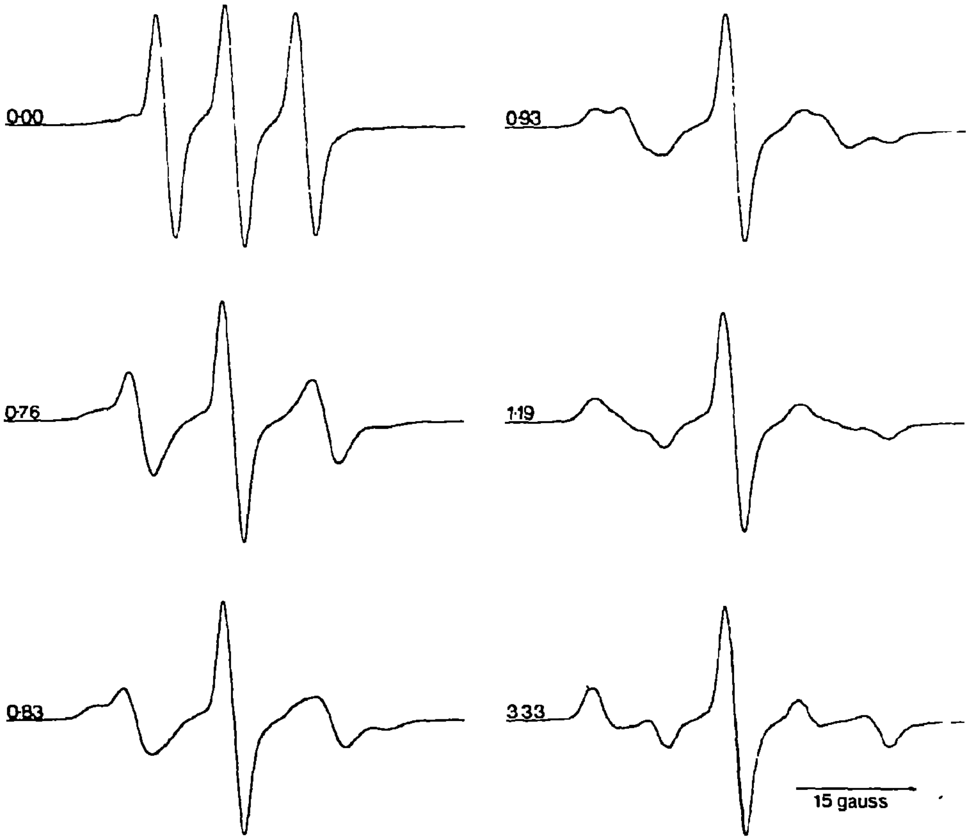

Fig. 1. The electron resonance spectra for the spin probe dissolved in the nematic mesophase of 4,4'-dimethoxyazoxybenzene measured as a function of the angular velocity; the number associated with each spectrum is the spinning speed in Hz.

and a 4 mm diameter tube made from Teflon. The spectra recorded for the same sample spinning speed were found to be independent of the container. A Pyrex tube was also coated with the surfactant hexadecyl trimethyl ammonium bromide but again the spectra were found to be identical to those obtained without the surface coating.

4. Results and analysis

The dependence of the electron resonance spectrum on the angular velocity was determined for the spin probe dissolved in the nematic phase of both liquid crystals using the techniques outlined in the previous section. For both nematogens the angular velocity was increased until no further change could be detected in the spectrum. A selection of the spectra obtained with 4,4′-dimethoxyazoxybenzene is shown in fig. 1; similar results were obtained with Merck Phase IV although the greater linewidths lead to poorer resolution. We shall therefore concentrate on the behaviour for 4,4′-dimethoxyazoxybenzene where the spectral analysis is less involved.

For angular velocities below about 0.6 Hz the spectrum contains three hyperfine lines and the spacing between them may be employed to determine the angle made by the director with the magnetic field, as in previous studies [2,4]. However at higher speeds the two outer lines are observed to broaden and become asymmetric with respect to the base line. This behaviour is symptomatic of an inhomogeneous alignment of the director. Since the behaviour of the high and low field lines is virtually identical we may conveniently restrict our attention to the low field line. Eventually this line splits into two components as we can see in fig. 1 for $\Omega = 0.76$ Hz, the additional peak occurs at a position associated with the director perpendicular to the magnetic field and so confirms the deviation from uniform alignment. As Ω is increased the intensity of this second peak also increased but at the expense of the original line; in addition another line is observed to high field and is readily discerned in the spectrum for $\Omega = 0.93$ Hz. The new peak is found to occur at the same position as the low field line in the spectrum for the static sample and so may be associated with the director aligned parallel to the magnetic field. Further increases in Ω cause the original line to decrease in intensity until in the final spectrum ($\Omega = 3.33$ Hz) it is completely replaced by the two new lines originating from the director parallel and perpendicular to the magnetic field. These spectral changes clearly demonstrate the increasing spread in the alignment of the director as the spinning speed is increased. The sequence of spectra shown in fig. 1 also indicates that this dispersion of the director increases in a continuous manner with Ω even at speeds above and below 0.74 Hz which, as we shall see, may be identified with the critical value Ω_c. Our demonstration of the spread in the alignment of the director is in accord with direct observations of non-uniformity in samples subjected to a magnetic field spinning with a speed close to Ω_c [9]. However the probability distribution function for the director was not obtained in this optical study and so we shall now attempt to determine this distribution from our electron resonance measurements.

It is appropriate to begin by indicating the reasons for our particular choice of the distribution function $p(\gamma)$. The approximately equal intensities of the parallel and perpendicular features in the limiting form of the spectrum at high angular velocities suggests that the probabilities of finding the director parallel and perpendicular to the magnetic field might also be the same. In other words the director is isotropically distributed in a plane which contains the magnetic field and in this case the normalised distribution function is

Table 1
The magnetic parameters used in the spectral simulations for the spin probe dissolved in the nematic phase of 4,4′-dimethoxyazoxybenzene at 97.5°C

$\tilde{g}_\parallel$	$\tilde{g}_\perp$	$\tilde{A}_\parallel$ (MHz)	$\tilde{A}_\perp$ (MHz)	$T_2^{-1}(1)$ (gauss)	$T_2^{-1}(0)$ (gauss)	$T_2^{-1}(-1)$ (gauss)	a_H (gauss)
2.0060	2.0056	24.5	49.5	0.92	0.75	0.95	0.62

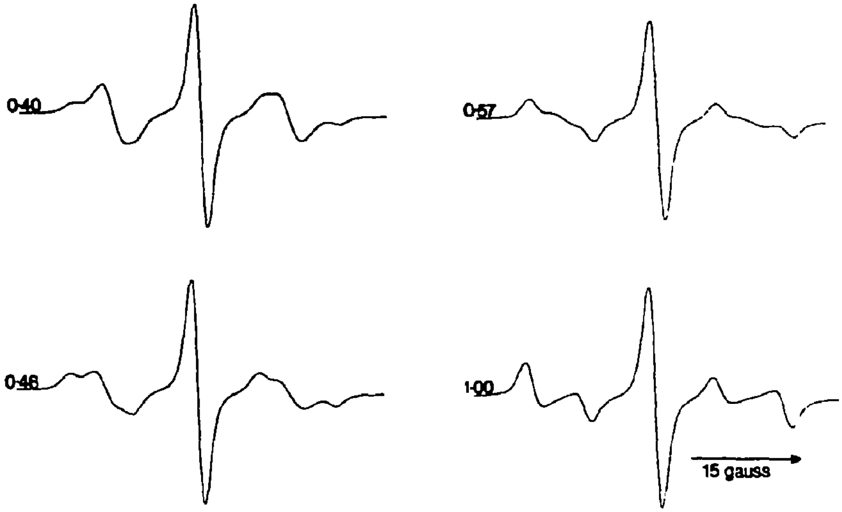

Fig. 2. Simulated spectra obtained with the elliptical distribution function given by eq. (7); each spectrum is labelled with the value of the ratio b/a.

$$p(\gamma) = 1/2\pi. \tag{6}$$

We have therefore simulated a powder spectrum using this distribution function with the parameters listed in table 1. The use of slightly different linewidths for the three nitrogen hyperfine components is justified by the observation of asymmetric line broadening in the static spectrum shown in fig. 1 [14]. The simulated spectrum is given in fig. 2, it is clearly in virtually complete agreement with experiment and so confirms previous suggestions of a two dimensional isotropic distribution [4,5]. Of course such a distribution may be achieved in a variety of ways and one possibility is for the director to be tangential to circles perpendicular to the spinning axis. Such a distribution would result from shear induced alignment and has been predicted by arguments based on the swarm theory [1]. Since the spectra vary continuously with the angular velocity then the distribution function must also change continuously between the limits of a two-dimensional isotropic distribution and a uniformly aligned director. If the notion of a circular distribution is correct then we might suppose that for intermediate rotation speeds the director is tangential to an ellipse. This distribution of the director is in qualitative agreement with experiment for as Ω is reduced the ratio, b/a of the minor to the major semi-axes should decrease together with the angle γ_0 made by the major axis with the magnetic field. The angle γ_0 corresponds to the preferred orientation of the director and for an extremely elongated ellipse might be identified with the orientation of the director itself. The exact form for this elliptical distribution function is derived in the appendix and found to be

$$p(\gamma) = \frac{\epsilon^2}{2\pi} \frac{1}{\epsilon^4 \cos^2(\gamma-\gamma_0) + \sin^2(\gamma-\gamma_0)}. \tag{7}$$

Here ϵ is the ratio b/a and ranges from zero, corresponding to an essentially uniform alignment of the director at an angle γ_0 to the magnetic field, and one for an isotropic two-dimensional distribution. The quantitative correctness of this distribution function was tested by simulating the experimental electron resonance spectra, observed for different rotation speeds, by adjusting the two parameters occurring in $p(\gamma)$. The magnetic parameters employed in the calculations were those listed in table 1; spectra were then simulated for various values of ϵ and γ_0. Fortunately γ_0 largely influences the line positions while ϵ controls their intensities, as a consequence it is straightforward to obtain an unambiguous fit to the experimental spectra. The agreement between the

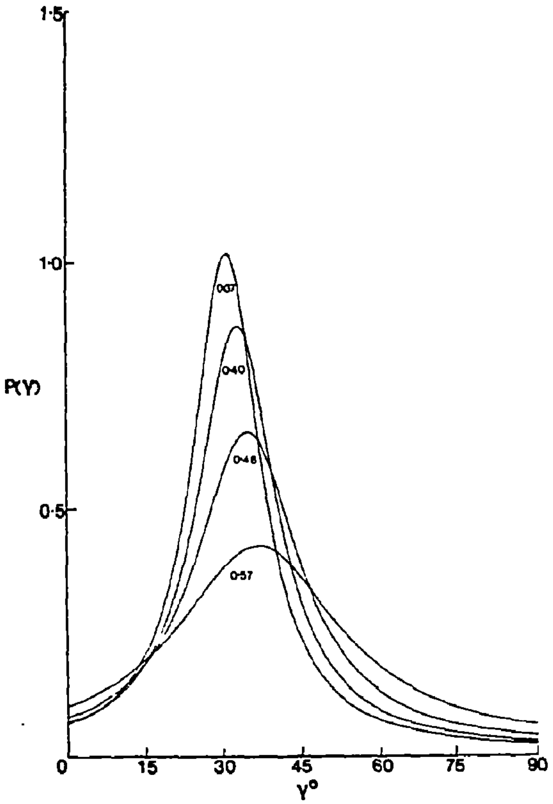

Fig. 3. The probability distribution function for the director calculated from eq. (7) for values of the parameters characteristic of 4,4'-dimethoxyazoxybenzene spinning at speeds in excess of 0.7 Hz.

theoretical and observed spectra was found to be excellent as comparison of the simulated spectra in fig. 2 with their experimental counterparts in fig. 1 shows. Spectra were also simulated for the Merck Phase IV system although here the extensive line broadening made it essential to allow for the angular dependence of the linewidths [19]; however, the simulations were again found to be in complete accord with experiment. The excellent agreement observed for both liquid crystals implies that our elliptical distribution may be a close approximation to reality.

The appearance of the probability distribution function calculated from eq. (7), with parameters obtained by fitting spectra with Ω in excess of 0.7 Hz, are shown in fig. 3; each curve is labelled with the ratio b/a. We have also attempted to fit the experimental spectra with a gaussian probability distribution of the director in two dimensions:

$$p(\gamma) = \exp[-(\gamma-\gamma_0)^2/\sigma^2] / \int_{-\pi}^{\pi} \exp[-(\gamma-\gamma_0)^2/\sigma^2]\, d\gamma, \qquad (8)$$

where σ is a measure of the spread in the director. This particular distribution certainly possesses the correct limiting forms for both high and low angular velocities although its relation to the physics of the system is not obvious. However it proved to be impossible to fit the spectra, measured for intermediate values of Ω, with this form for $p(\gamma)$. This failure strengthens our faith in the validity of the probability distribution function given by eq. (7).

Comparison of simulated spectra with a wide range of experimental spectra enabled us to determine the dependence of γ_0 and b/a on the angular velocity for the two nematogens. The values of $\sin 2\gamma_0$ obtained for 4,4'-dimethoxyazoxybenzene are plotted as a function of Ω in fig. 4; entirely comparable results were found for Merck Phase IV. If γ_0 was the angle between the director and the magnetic field, instead of the mean angle, then $\sin 2\gamma_0$ should be linear in the angular velocity. In fact fig. 4 shows that this linearity is observed for angular velocities below about

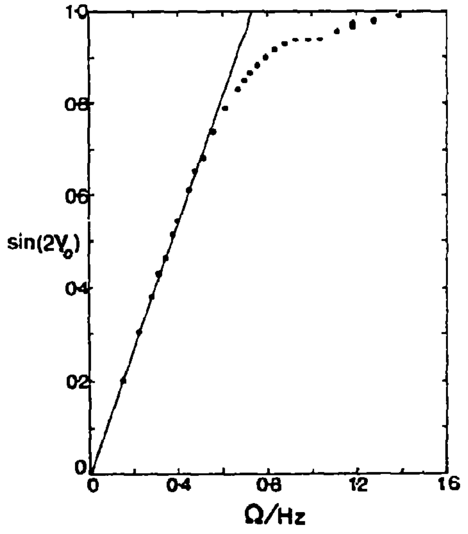

Fig. 4. A plot of $\sin 2\gamma_0$ against the angular velocity Ω for 4,4'-dimethoxyazoxybenzene at 97.5°C.

0.7 Hz but above this value there is an increasing departure from linear behaviour. Similar effects are found for the analogous experiment involving a rotating magnetic field; here the torque, which is proportional to $\sin 2\gamma$, also deviates from the predicted linear dependence on Ω [9]. According to eq. (1) the slope of the linear region of the plot should be identified with $1/\Omega_c$; although it is important to realise that while the theory assumes uniform alignment our results demonstrate a dispersion in the director. Indeed in the linear region the root mean square angle made by the director with its preferred orientation is calculated, from the measured values of b/a, to range from 0° to about 20°. This upper value would appear to be rather large, although, as fig. 3 shows, the probability distribution is broad and so its width at half height is considerably smaller, being approximately 5°. It is possible therefore that the dispersion in the director is sufficiently small for the continuum theory to hold. If this is so then we find the critical speed for 4,4'-dimethoxyazoxybenzene at 97.5°C to be 0.74 Hz and for Merck Phase IV at 49°C to be 0.28 Hz. It is of interest to note that if we define a reduced angular velocity by Ω/Ω_c then measurements of $\sin 2\gamma_0$ for both nematogens fall on a common line even when this deviates from linearity.

Unfortunately there are no measurements on Merck Phase IV with which to compare our result and there are few relevant studies of 4,4'-dimethoxyazoxybenzene. Thus Lippmann [1] has investigated spinning samples of this nematogen using nuclear magnetic resonance but there are insufficient measurements to extrapolate to the temperature employed in our work. In addition the method employed to estimate the critical angular velocity is almost certainly incorrect. All other studies involve a rotating magnetic field and so may not be directly comparable. The most relevant of these investigations is the measurement of the dependence of $\sin 2\gamma$ on Ω but this was only attempted for a temperature of 125°C [9]. The earlier measurements [20] of Ω_c were based on the observation of the angular velocity at which the torque is a maximum and so will be in error [8]. We have therefore resorted to calculating Ω_c from the expression

$$\Omega_c = -\Delta\chi B^2/2\lambda_1, \tag{9}$$

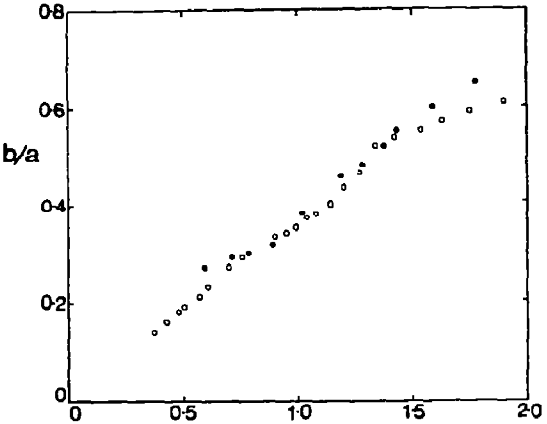

Fig. 5. A plot of the ratio b/a against the reduced angular velocity for Merck Phase IV (●) and 4,4'-dimethoxyazoxybenzene (○).

given by continuum theory [2]. Here $\Delta\chi$ is the anisotropy in the diamagnetic susceptibility, B is the magnetic field strength and λ_1 is the twist viscosity coefficient. We have obtained values for $\Delta\chi$ and λ_1 by extrapolating the results determined by Gasparoux and Prost [8] and at 97.5°C we calculate Ω_c to be 0.67 in reasonable agreement with our result.

The dispersion of the director, as measured by the ratio b/a, is plotted, in fig. 5, for both nematogens as a function of the reduced angular velocity Ω/Ω_c. The observation of a common curve for these two quite different compounds may be of some importance for it might imply that the misalignment of the director is a characteristic magnetohydrodynamic property of nematogens and is associated with those factors determining Ω_c. It is also of some importance that the director dispersion commences with sample rotation and then increases continuously until an isotropic two dimensional distribution is achieved when the angular velocity is about twice the critical value. This continuous change is in marked contrast to the discontinuous behaviour predicted by continuum theory [2]. The origin of the dispersion presents us with a major problem, although there is no lack of possible solutions. For example, when the nematic mesophase, subject to a rotating magnetic field, is pinned at a surface then inversion walls are predicted to form and migrate into the bulk mesophase [21]. Such behaviour would clearly produce a non-uniformity in the director and might be relevant in our experiments with a rotating mesophase. Alternatively the mesophase may not rotate as a rigid body and then the alignment of the director would be partly controlled by shear forces. Indeed such an idea would seem to be supported by the elliptical distribution apparently revealed by our experiments. However we must remember that the analysis of the electron resonance spectra yields only the probability distribution function for the director; it cannot provide the spatial or geometrical distribution. We must therefore conclude that although the probability distribution function for the director in a spinning nematic mesophase subject to a magnetic field is known the questions as to its geometrical form and, more importantly, its origin are still open.

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Appendix

Here we derive the probability distribution function $p(\gamma)$, given in eq. (7), for the orientation of the director when it is tangential to an ellipse whose axis makes an angle γ_0 with the magnetic field. We begin with the distribution function $P(\theta)$ for the director, where θ is the angle made by the director with respect to the major axis; a particular orientation of the director is shown in fig. 6. The probability $P(\theta)\,\mathrm{d}\theta$ of finding the director between θ and $\theta+\mathrm{d}\theta$ is equal to the probability, $f(\phi)\,\mathrm{d}\phi$, of discovering the vector radius between ϕ and $\phi+\mathrm{d}\phi$:

$$P(\theta)\,\mathrm{d}\theta = f(\phi)\,\mathrm{d}\phi. \tag{A.1}$$

However the distribution function for this radius is independent of ϕ and equal to $1/2\pi$; consequently the required distribution function is just

$$P(\theta) = \frac{1}{2\pi}\frac{\mathrm{d}\phi}{\mathrm{d}\theta}. \tag{A.2}$$

For an ellipse the angles θ and ϕ are related by

$$\tan\theta = \frac{-\epsilon^2}{\tan\phi}, \tag{A.3}$$

where ϵ is the ratio b/a of the minor to the major semi axes. The probability distribution function is then

$$P(\theta) = \frac{\epsilon^2}{2\pi(\epsilon^4\cos^2\theta + \sin^2\theta)}. \tag{A.4}$$

When the director makes an angle γ with the magnetic field the distribution function $p(\gamma)$ is obtained from eq. (A.4) simply by replacing θ with $(\gamma-\gamma_0)$; this then yields the result given in eq. (7).

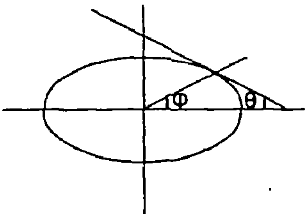

Fig. 6. The elliptical configuration for the director.

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