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The twist elastic constant and anchoring energy of the nematic liquid crystal 4-*n*-octyl-4′-cyanobiphenyl

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The twist elastic constant of the nematic liquid crystal 4-*n*-octyl-4′-cyanobiphenyl (8CB) and the azimuthal anchoring energy at the SiO–nematic interface have been measured by using the torsion pendulum technique. The twist elastic constant of 8CB is found to be systematically larger than that measured by the Freedericksz transition technique. The azimuthal anchoring energy is found to decrease rapidly as the nematic–isotropic transition temperature is approached. This behaviour is analogous to that already reported by us for the nematogen 5CB and can be interpreted by extending the Berreman model of the anchoring energy at a grooved interface.

1. Introduction

The elastic constants of nematogens are usually measured by the Freedericksz transition method [1, 2]. However for the twist elastic constant K_{22}, the optical measurements of the threshold field are of low accuracy [2]. As a consequence of this, new experimental methods to measure K_{22} have been recently proposed [3–5]. The experimental technique of [5], in particular, is based on a direct measurement of the elastic torque exerted from a twisted nematic sample on a glass plate. This technique enables both the twist elastic constant and the azimuthal anchoring energy to be measured.

In recent papers [5, 6] this novel method was used to measure the twist elastic constant K_{22} of the nematogen 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and the azimuthal anchoring energy at the SiO–nematic interface. K_{22} was found to be systematically larger than that obtained by Madhusudana and Pratibha [2]. Furthermore the azimuthal anchoring energy was found to decrease rapidly as the nematic–isotropic transition was approached. This almost critical behaviour was interpreted by generalizing the Berreman model [7] in such a way as to account for the presence of a reduced surface order at the SiO–nematic interface [8–11].

In this paper we report new experimental results for the nematogen 4-*n*-octyl-4′-cyanobiphenyl (8CB) which exhibits a low temperature smectic A phase. Both the twist elastic constant and the azimuthal anchoring energy at the SiO–nematic interface were measured for the complete nematic phase. As for 5CB, the anchoring energy is found to decrease rapidly as the nematic–isotropic transition is approached. The experimental results agree satisfactorily with the theoretical model proposed in [6] and this allows us to estimate the surface order parameter at the SiO–nematic

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interface. As observed for 5CB, we find K_{22} is systematically larger than that reported in [2].

2. Experiment

2.1. *The experimental method*

The experimental method has been already described in [5], and so here we only recall the main features of this method. A thin horizontal glass plate is dipped in a large volume (~ 3–$4\,cm^3$) of the nematic and is suspended at the centre by a thin quartz wire (torsion pendulum). Both surfaces of the glass plate were treated by oblique evaporation of SiO in such a way as to induce a uniform orientation of the director $\mathbf{n}$ along the x axis in the horizontal xy plane. The temperature of the nematic sample was stabilized to within $\pm 10\,mK$. A uniform magnetic field $\mathbf{H}$ ranging from 50 G to 8800 G can be applied (in the horizontal xy plane) along a direction which makes an angle α with the easy axis (x axis). Under these conditions the director near the glass plate is not uniformly aligned but twists continuously on going from the surface into the bulk. The excess elastic free energy associated with the twist of the director can be relaxed in two different ways.

(*a*) The glass plate tends to rotate in such a way as to orient the easy axis along the magnetic field; then the glass plate is subject to a mechanical torque τ_m. At equilibrium this torque is balanced by the restoring torque $(-K\Delta\alpha)$ due to the quartz wire of the torsion pendulum.

(*b*) The glass plate remains fixed whilst the director at the surface tends to rotate toward the direction of the magnetic field. In consequence the director at the surface is subject to an orienting torque τ_o (For a simple twist we can easily show that $\tau_o = \tau_m = \tau$.) At equilibrium τ_o is balanced by the anchoring torque $\left(-\frac{\partial W(\phi_0)}{\partial \phi_0}\right)$ which tends to maintain the director parallel to the easy axis.

At equilibrium the equations

$$K\Delta\alpha = \sqrt{(K_{22}\chi_\alpha)}HS\cos(\alpha + \phi_0) \tag{1}$$

and

$$\frac{\partial W(\phi_0)}{\partial \phi_0} = \sqrt{(K_{22}\chi_\alpha)}H\cos(\alpha + \phi_0) \tag{2}$$

must be satisfied [5]. Equation (1) and (2) establish the balance of the torques on the glass plate and on the director at the surface, respectively. K is the torsion coefficient of the quartz wire, $\Delta\alpha$ is the angular displacement of the glass plate from the equilibrium position, K_{22} is the twist elastic constant, χ_α is the anisotropy of the diamagnetic susceptibility, H is the magnetic field intensity, S is the total area of the glass plate, α is the angle between the easy axis and the magnetic field, ϕ_0 is the angle between the director at the surface and the easy axis and $W(\phi_0)$ is the azimuthal anchoring energy.

If the magnetic field is low enough, the director at the surface remains almost parallel to the easy axis ($\phi_0 \sim 0$), and thus the surface torque $(-K\Delta\alpha)$ is proportional to the magnetic field (see equation (1)). In this regime ($\phi_0 = 0$) we obtain from equation (1)

$$K_{22} = \left[\frac{K\Delta\alpha}{HS\cos\alpha}\right]^2 \frac{1}{\chi_\alpha}, \tag{3}$$

where K, $\Delta\alpha$, H, α, S are measured in the experiment and χ_a is obtained from the literature.

If the magnetic field is strong enough (or the anchoring energy low enough) the director angle ϕ_0 becomes significantly different from zero and increases as the magnetic field is increased. This means that, for large magnetic fields, the dependence of the surface torque on the magnetic field becomes more and more non-linear because of the magnetic field dependence of $\phi_0(H)$ in the cosine function of the right hand side of equation (1). From equation (1) we obtain therefore

$$\phi_0 = -\alpha + \arccos\left(\frac{K\Delta\alpha}{\sqrt{(K_{22}\chi_a)}HS}\right), \tag{4}$$

which allows us to measure ϕ_0 at different magnetic fields. Note that the experimental anchoring torque $\frac{\partial W(\phi_0)}{\partial\phi_0}$ which corresponds to the measured value of ϕ_0 can be obtained via equations (1) and (2): this gives

$$\frac{\partial W(\phi_0)}{\partial\phi_0} = \frac{\tau_m}{S},$$

where τ_m is the mechanical torque ($+K\Delta\alpha$) on the torsion pendulum. Therefore the measurement of τ_m enables a direct determination of the anchoring torque. Finally $W(\phi_0)$ versus ϕ_0 is obtained, in principle, by numerical integration of the experimental value of $\frac{\partial W(\phi_0)}{\partial\phi_0}$. In our experiment, however, the experimental data are always consistent (within the experimental error) with the simple assumption

$$W(\phi_0) = W_a \sin^2\phi_0, \tag{5}$$

where W_a is the azimuthal anchoring energy coefficient. By substituting equation (5) into equations (2) and (1) we obtain

$$W_a = \frac{\sqrt{(K_{22}\chi_a)}\, H\cos(\alpha + \phi_0)}{\sin 2\phi_0}. \tag{6}$$

Then W_a can be obtained by substituting the experimental values of K_{22}, $\phi_0(H)$, α and H into the right-hand side of equation (6). More details on the experimental apparatus, the calibration procedure and the error sources are given in [6].

2.2. *Experimental results*

The nematogen studied in our experiment was 4-*n*-octyl-4′-cyano-biphenyl produced by B.D.H. Chemicals Ltd and has a high purity; the nematic–isotropic transition temperature of our sample was 40·6 ± 0·1°C.

Figure 1 shows the mechanical torque for unit surface area versus the magnetic field H for selected temperatures. The surface torque is almost proportional to the magnetic field for temperatures 1–2°C lower then the transition temperature (T_{NI}), whilst large deviations from the linearity occur when the temperature approaches T_{NI}. As shown in §2.1, this clearly indicates that W_a decreases largely as the temperature approaches T_{NI}. This behaviour is analogous to that which we have already reported for 5CB [7].

The twist elastic constant K_{22} can be obtained from the experimental surface torques according to the procedure discussed in §2.1 by substituting in to equation (3) the measured values of K, $\Delta\alpha$, H, α and χ_a. To the best of our knowledge the only value

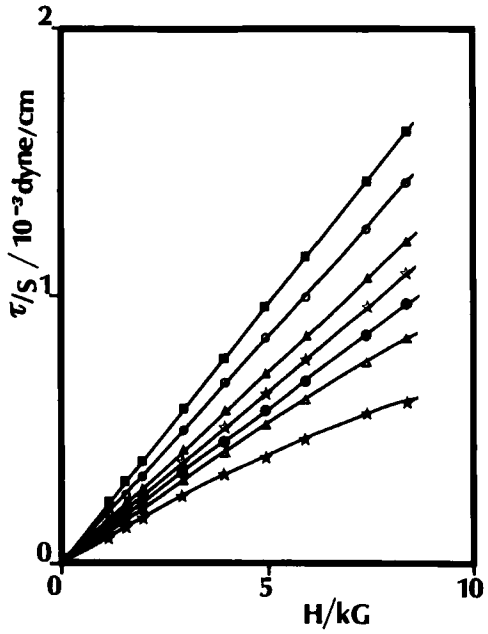

Figure 1. Torque per unit surface area versus the magnetic field at selected temperatures. Different symbols correspond to the following values of the temperature: (■), $T_{NI} - T = 6{\cdot}24$ K; (○), $T_{NI} - T = 4{\cdot}26$ K; (▲), $T_{NI} - T = 2{\cdot}75$ K; (☆), $T_{NI} - T = 1{\cdot}16$ K; (●), $T_{NI} - T = 0{\cdot}56$ K; (△), $T_{NI} - T = 0{\cdot}28$ K; (★), $T_{NI} - T = 0{\cdot}007$ K. The full line corresponds to the best fit of the experimental results to equations (1) and (2) where $\frac{\partial W(\phi_0)}{\partial \phi_0} = W_a \sin(2\phi_0)$ and W_a and K_{22} are free parameters.

of χ_α for 8CB is reported in [12]. However, as noticed by Madhusudana and Pratibha [2], the results of [12] are about 8 per cent larger than those which are predicted by the Pascal rule and they do not exhibit a temperature dependence in complete agreement with the experimental measurements of the scalar order parameter Q. Furthermore the χ_α values of 5CB given in [12] are also 8 per cent larger than those given in [13], which, in contrast, agree (to within 2 per cent) with the Pascal rule and with the temperature dependence of the scalar order parameter. Therefore Madhusudana and Pratibha [2] retain the χ_α-values given by the Pascal rule as being more accurate and use them to calculate K_{22} from their Freedericksz transition measurements. Here we follow the same approach as [2] to calculate K_{22} from our experimental results. Note, however, that the choice of the χ_α values of [12] would reduce the values of the twist elastic constant measured in the present experiment by about 8 per cent.

The full points in figure 2 represent the experimental values of the twist elastic constant of 8CB versus the temperature as deduced by torque measurements. The open symbols (circles and triangles) in figure 2 correspond to the K_{22} elastic constant of [2]. The estimated uncertainty of the K_{22} measurements is approximately 10 per cent (for a detailed discussion of the errors see [5]). Note that our results are systematically larger than those of [2]. The same kind of discrepancy was already found by us [5] and by other authors [3, 4] for the nematogen 5CB. This suggests that some systematic error was present in the experiment of [2]. However we do not believe that the discrepancy of our results from those reported in [2] could be attributed to a deficiency of the Freedericksz transition method. As a matter of fact we note that Schad and

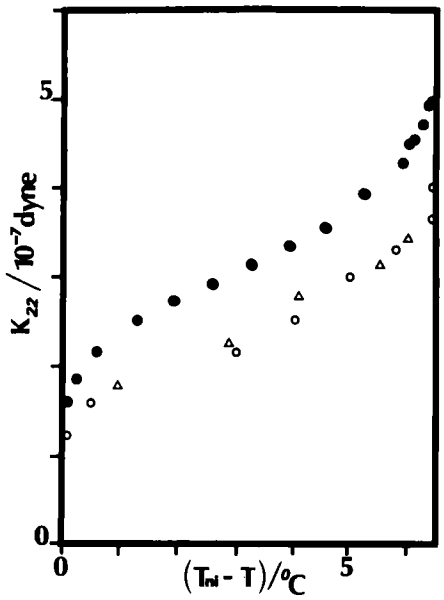

Figure 2. Twist elastic constant of 8CB versus temperature as deduced from the experimental values of the torques per unit surface area by using the χ_a-diamagnetic anisotropy given in [2]. The solid circles correspond to our experimental results whilst the open symbols (circles and triangles) correspond to the experimental results of [2]. Note the large increase of K_{22} near the nematic–smectic A transition ($T_{NI} - T = 6{\cdot}5^{\circ}$C). The estimated accuracy of the K_{22} measurements is about 10 per cent.

Osman [20] measured the twist elastic constant of 7CB by using the same experimental method of [2] and obtained values of K_{22} systematically larger by 20 per cent than those reported there.

As shown in §2.1, the experimental results of figure 1 allow us to obtain the azimuthal anchoring coefficient W_a (see equation (6)) at different temperatures. Figure 3 shows the temperature dependence of W_a near the transition temperature. Solid squares correspond to our experimental results whilst the full line corresponds to the prediction of the theoretical model of [6] which is based on the Berreman theory of the anchoring at a grooved interace [7]. According to this model the azimuthal anchoring energy coefficient is given by

$$W_a = \frac{2\pi^3 A^2}{\lambda^3} \bar{K}, \tag{7}$$

where A and λ are the amplitude and the wavelength of grooves at the SiO–nematic interface, respectively, whilst $\bar{K}$ is an average elastic constant in a thin layer of thickness $h \sim \lambda/2\pi$ ($h \sim 50$ Å for the SiO surface [15]) near the surface. Note that the elastic constants of nematics are known to be approximately proportional to the square of the order parameter Q, i.e. $\bar{K} = \beta Q^2$. Therefore $\bar{K}$ scales as the square of the order parameter Q_s close to the surface. For the SiO–nematic interface of some nematics, there is strong circumstantial evidence that $Q_s \sim 0$ near the transition. The surface order parameter Q_s can be obtained by using the phenomenological model of Sluckin and Poniewierski [14]. After some straightforward calculations we obtain (see [6])

$$W_a = \frac{2\pi^3 A^2}{\lambda^3} \beta Q_s^2 = [a + b(T_{NI} - T)^{1/2}]^2, \tag{8}$$

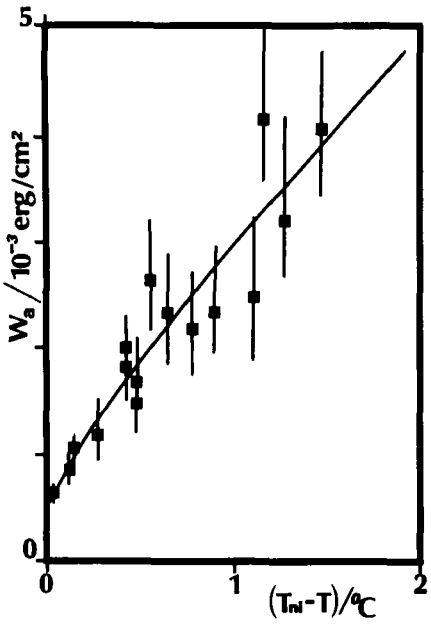

Figure 3. Azimuthal anchoring coefficient W_a versus temperature, as deduced by substituting into equations (4) and (6) the experimental values for K, $\Delta\alpha$, K_{22}, α, S and H and the χ_a values used in [2]. The full line corresponds to the best fit of the experimental data to the theoretical expression $W_a = [a + b(T_{NI} - T)^{1/2}]^2$. The values of the phenomenological coefficients a and b are $1{\cdot}5 \times 10^{-2}$erg$^{1/2}$/cm and $3{\cdot}9 \times 10^{-2}$erg$^{1/2}$/cm K$^{1/2}$, respectively.

where a and b are phenomenological parameters related to the surface free energy at the SiO–nematic interface and β is the proportionality coefficient between the elastic constant and Q^2.

According to equation (8), if $a \ll b$, the anchoring coefficient decreases greatly as T_{NI} is approached and reaches a small but non-vanishing value ($W_a = a^2$) at $T = T_{NI}$. The full line in figure 3 corresponds to the best fit relative to equation (8) of the experimental results. The corresponding values of a and b are $a = 1{\cdot}5 \times 10^{-2}erg^{1/2}$/cm and $b = 3{\cdot}9 \times 10^{-2}erg^{1/2}$/cm K$^{1/2}$. Note that these values are of the same order of those already found for 5CB ($a = 1{\cdot}5 \times 10^{-2}erg^{1/2}$/cm and $b = 3{\cdot}7 \times 10^{-2}erg^{1/2}$/cm K$^{1/2}$). Therefore we infer that the physical mechanisms in both cases are the same. Typical values of A and λ at the interface SiO–8CB are $A = 100$ Å [15] and $\lambda = 300$ Å [15], whilst $\beta = 8{\cdot}5 \times 10^{-7}$dyne [2]. Therefore the azimuthal anchoring energy can be written as (see equation (8))

$$W_a = 1{\cdot}95\, Q_s^2 \text{erg/cm}^2. \tag{9}$$

The experimental value of the anchoring energy at T_{NI} can be substituted in equation (9) to obtain the surface order parameter Q_s of approximately 0·01. This value is very close to that already measured by us for 5CB (Q_s(5CB) ~ 0·008). Unfortunately to the best of our knowledge there are no measurements of Q_s for 8CB. Very accurate optical measurements of Q_s for 5CB have been performed by Yokoyama *et al.* [11] which found $Q_s = 0{\cdot}01$ when the transition temperature was approached from the isotropic phase. More recently [16] the same authors of [11] also estimated the value of the order parameter at the SiO–nematic interface when the transition temperature was approached from the anisotropic phase by using a Landau–de Gennes

model. They found $Q_s \sim 0{\cdot}04$ which is significantly larger than the value estimated here. However we note that the discrepancy between our results and those of [16] is not surprising. In fact our evaluation of Q_s is highly approximate since it is based on the Berreman expression for the azimuthal anchoring energy which holds exactly only for a sinusoidal profile and for $A/\lambda \ll 1$. Furthermore the azimuthal anchoring energy W_a of equation (7) depends largely on the actual values of the A and λ parameters which are known only approximately.

A decrease of the anchoring energy near T_{NI} analogous to that shown in figure 3 has been reported already for the polar anchoring coefficient at the free surface of 4-methoxy-benzylidene-*n*-butyl-aniline (MBBA) [16], at a surfactant-treated interface [17] and at the SiO–nematic interface [18]. However, we point out that the proposed physical mechanism (see also [6, 7]) is peculiar to the azimuthal anchoring and, in our opinion, the similarity of our results with those of [16] to [18] is only accidental. This is particularly evident for the free surface of MBBA [16] where the reduction of the anchoring energy is strictly related to the presence of an orientational transition. This conclusion is also supported by the theoretical analysis given in [19].

The reason for the large error bars of figure 3 when the temperature is far from the transition can be easily understood. In fact, for high anchoring energy coefficients, the available magnetic field (< 9 kG) is not enough to modify appreciably the surface director azimuthal angle ϕ_0. As a consequence of this, the surface torque is an almost linear function of the applied magnetic field (see equation (1)). Under these conditions is difficult to detect deviations from the linearity and to measure the director angle ϕ_0 (see equation (4)). Therefore the measurements of higher anchoring energy coefficients are affected by larger errors. Note, however, that this drawback is not peculiar to our experimental method but is common to all experimental methods so far proposed where magnetic or electric fields are used. Much more accurate experimental measurements could be performed if higher magnetic fields were available (this is just the main improvement proposed in [17]).

3. Concluding remarks

In this paper the novel method of the torsion pendulum has been used to measure the twist elastic constant K_{22} of the nematogen 8CB and the anchoring energy at the obliquely evaporated SiO surface. Our experimental results confirm the main results of previous experimental studied of 5CB. In particular, the twist elastic constant of 8CB is found to be larger than that measured by the Freedericksz transition technique [2], whilst the azimuthal anchoring coefficient is found to decrease rapidly as the nematic–isotropic transition is approached. This result confirms that the Berreman model of the azimuthal anchoring energy at a grooved interface must be modified in order to account for the presence of a reduced surface order near the transition temperature.

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