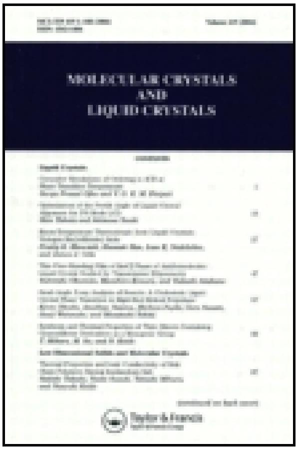

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Electric Field Induced Birefringence in Nematic Liquid Crystal Films: Evidence for Wall Quenching of Director Fluctuations

D. A. Dunmur [a] , T. F. Waterworth [a] & P. Palffy-Muhoray [b]

[a] Department of Chemistry, The University, SheffieldU, U.K.

[b] Department of Physics, University of British Columbia, Vancouver, B. C., Canada

Version of record first published: 17 Oct 2011.

To cite this article: D. A. Dunmur , T. F. Waterworth & P. Palffy-Muhoray (1985): Electric Field Induced Birefringence in Nematic Liquid Crystal Films: Evidence for Wall Quenching of Director Fluctuations, Molecular Crystals and Liquid Crystals, 124:1, 73-88

To link to this article: http://dx.doi.org/10.1080/00268948508079466

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 73–88
0026-8941/85/1244-073/$20.00/0

Electric Field Induced Birefringence in Nematic Liquid Crystal Films: Evidence for Wall Quenching of Director Fluctuations

D. A. DUNMUR and T. F. WATERWORTH
Department of Chemistry, The University, Sheffield, U.K.

and

P. PALFFY-MUHORAY
Department of Physics, University of British Columbia, Vancouver, B.C., Canada

(*Received October 15, 1984*)

The effect of an electric field on the measured order parameter of a liquid crystal is considered. It is pointed out that an external field may influence the apparent degree of order by changing the microscopic order parameter, and by quenching director fluctuations. In nematic liquid crystals the latter dominates, but for smectic phases the effects of field-induced molecular order may be observable.

Measurements are reported of the electric field-induced birefringence in nematic 44′-n-pentylcyanobiphenyl (5CB) and the nematic and smectic phases of 44′-n-octylcyanobiphenyl (8CB). The modular dependence of induced order on electric field strength predicted for nematics is experimentally confirmed by Fourier analysis of the electro-optic response. At low field strengths, and in the smectic phase, the induced order varies as the square of the field strength, and the dependence on cell thickness is not as predicted by continuum theory. By introducing two scaling parameters into the theory it is possible to fit quantitatively the experimental results for the nematic phase, and it is suggested that these parameters may describe the effect of the cell walls on the fluctuation mode spectrum in the liquid crystal. The birefringence induced in the smectic phase by an electric field is measured to be 100 times smaller than in the nematic phase, and this can be explained in terms of field-induced microscopic order.

1. INTRODUCTION

The characteristic anisotropic properties of liquid crystals arise from short range molecular interactions which are coupled over many molecular diameters to give macroscopic anisotropy in such properties as magnetic susceptibility, electric permittivity and refractive indices. Thus the magnitude of the measured anisotropy depends both on the local molecular order and the extent to which this propagates over long distances. Traditionally the local order is measured by the Maier-Saupe order parameter (S), while the long range order is described in terms of the director. A uniformly aligned liquid crystal is one in which the average director orientation does not vary through the sample.

The Maier-Saupe order parameter is an average over the thermally excited rotational states of a mesogenic molecule interacting with its environment. Similarly the director orientation will be subject to thermally excited fluctuations which are opposed by the torsional elastic forces in the liquid crystal. Both the short range molecular disorder and long range director disorder will influence the macroscopic anisotropy in the physical properties of liquid crystals. A continuum theory of nematic liquid crystals based on the concept of director fluctuations was proposed by Faber,[1] but as yet no attempt has been made to produce a theory which unites the molecular and continuum approaches. The effect of director fluctuations on various physical properties such as light scattering, NMR and ESR has been discussed in a recent publication.[2]

A convenient probe of order in liquid crystals is through measurements of refractive indices, and changes in both microscopic and macroscopic order will be accompanied by corresponding changes in the refractive indices. External electric and magnetic fields quench microscopic and long range fluctuations, and this leads to an increase in the optical anisotropy. The purpose of this paper is to report some preliminary measurements of electric field-induced birefringence in nematic liquid crystals; our results suggest that the existing theory of fluctuation damping by external fields is incomplete.

In a liquid crystal in which the director is not uniformly aligned, the molecular order parameter measured with respect to laboratory fixed axes will vary with position according to:

$$S^{(\mathrm{lab})}_{\alpha\beta} = \tfrac{1}{2}S(\mathbf{r})[3n_\alpha(\mathbf{r})n_\beta(\mathbf{r}) - \delta_{\alpha\beta}] \qquad (1)$$

$n_\alpha(\mathbf{r})$ is the director at point $\mathbf{r}$ in the fluid, and $S(\mathbf{r})$ is the value of the microscopic order parameter defined with respect to the local director orientation as:

$$S(\mathbf{r}) = \langle P_2(i_\alpha n_\alpha(\mathbf{r}))\rangle_{V(\mathbf{r})} \qquad (2)$$

The average in Eq. (2) is over a volume $V(\mathbf{r})$ centered on the point $\mathbf{r}$ but extending over a distance that is small compared with the fluctuations in $n_\alpha(\mathbf{r})$. A unit vector $\mathbf{i}$ defines the long axis of a cylindrical molecule at the position $\mathbf{r}$.

The measured anisotropy of a macroscopic property that depends on $S_{\alpha\beta}$ will be an average over the sample of $S_{\alpha\beta}{}^{(\mathrm{lab})}$, and assuming that the macroscopic symmetry is uniaxial, we may write:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle = \langle \tfrac{1}{2}S(\mathbf{r})[3n_z^2(\mathbf{r}) - 1]\rangle \tag{3}$$

The decoupling of averages over molecular orientation and director fluctuations is discussed by Faber[1] and Warner;[2] making this approximation Eq. (3) becomes:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle = \tfrac{1}{2}S_0\langle[3n_z^2(\mathbf{r}) - 1]\rangle \tag{4}$$

where S_0 is the average local order parameter defined with respect to $\mathbf{n}$. The spatial variation of the director components may be expressed in terms of their Fourier components as:

$$n_z(\mathbf{q}) = \int n_z(\mathbf{r}) \exp i\mathbf{q}\cdot\mathbf{r}\, d\mathbf{r} \tag{5}$$

and the average in Eq. (4) becomes:[3,4]

$$\langle S_{zz}^{(\mathrm{lab})}\rangle = S_0\left\{1 - \frac{3kT}{16\pi^3}\int \sum_{j=1,2}(K_j q_\perp^2 + K_3 q_\parallel^2)^{-1}\, d\mathbf{q}\right\} \tag{6}$$

$q_\parallel$ and $q_\perp$ are components of the wave-vector of the fluctuation mode parallel and perpendicular to the optic axis, while K_1, K_2 and K_3 are the splay, twist and bend elastic constants. The integral in Eq. (6) may be evaluated, and provided that S_0 is known, the measured order parameter can be determined. Faber assumed that $S_0 = 1$, and identified the sole source of disorder in liquid crystals as being director fluctuations. However, it should be pointed out that S_0 is in reality a function of q, since for very small q, $S_0(q \to 0) = \langle S_{zz}^{(\mathrm{lab})}\rangle$, while for large q, $S_0(q \to q_{\max}) = 1$. The latter corresponds to a director fluctuation of the same wavelength as an intermolecular distance, and so the average in Eq. (2) only extends over a single molecule.

In this paper we are concerned with the effect of an external electric field on the order parameter as measured using a birefringence method. From Eq. (3) the field may influence the measured order parameter through $S(\mathbf{r})$ and through its effect on the instantaneous director orientation $n_\alpha(\mathbf{r})$. Ignoring for the moment the former effect, then the measured order parameter given by Eq. (6) will increase if the field quenches the elastic fluctuations of the director. Including an appropriate electric field (E) term in Eq. (6) gives:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle_E = S_0\left\{1 - \frac{3kT}{16\,\pi^3}\int \sum_{j=1,2}(K_j q_\perp^2 + K_3 q_\parallel^2 + \Delta\chi E^2)^{-1}\,d\mathbf{q}\right\} \tag{7}$$

where $\Delta\chi = \epsilon_0\Delta\epsilon$ is the anisotropy of the electric susceptibility. For a qualitative discussion of the effect it is sufficient to introduce the one constant approximation, i.e. to assume that the three principal elastic constants are equal to each other, and Eq. (7) becomes:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle_E = S_0\left\{1 - \frac{3kT}{2\,\pi^2}\int(Kq^2 + \Delta\chi E^2)^{-1}q^2\,dq\right\} \tag{8}$$

Evaluating the integral in Eq. (8) gives:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle_E = S_0\left\{1 - \frac{3kT}{2\pi^2 K}[q_{\mathrm{max}} - q_{\mathrm{min}} - \xi^{-1}(\tan^{-1}\xi q_{\mathrm{max}} - \tan^{-1}\xi q_{\mathrm{min}})]\right\} \tag{9}$$

where $\xi = (K/\Delta\chi E^2)^{1/2}$ is a field dependent coherence length, while q_{max} and q_{min} are the limits of the integral in Eq. (8). The longest wave length fluctuation mode that can be sustained in sample of thickness D has a wave-vector $q_{\mathrm{min}} = 2\pi/D$, and the short wavelength cut off $q_{\mathrm{max}} = 2\pi/l$ must be related to an average intermolecular distance l. The evaluation of this distance is crucial to the correct interpretation of any measurements of nematic order.

If $q_{\mathrm{max}} >> \xi^{-1}$ and $q_{\mathrm{min}} \simeq 0$, then the result in Eq. (9) becomes:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle_E = S_0\left[1 - \frac{3kT}{\pi l K} + \frac{3kT}{4\pi\,K}\left(\frac{\Delta\chi}{K}\right)^{1/2}|E|\right] \tag{10}$$

In the absence of director fluctuations, the order induced by an external field can be calculated[5-7] using the Maier-Saupe or Landau-de Gennes theories. This is the nematic phase analogue of the Kerr effect in isotropic fluids, and neglecting the effects of biaxiality and internal fields, the order induced by an electric field parallel to the director is:

$$S = S_0 + \frac{\Delta\kappa E^2}{3kT}\left(\frac{1}{5} + \frac{2S_0}{7}\right) + \cdots \tag{11}$$

where $\Delta\kappa$ is the microscopic susceptibility anisotropy. To combine the effects described by Eqs. (10) and (11) one would have to allow for the fact that the instantaneous director would not be along the field direction: this immediately introduces biaxiality into the problem and considerably complicates its analysis. An order of magnitude calculation of the field terms in Eqs. (10) and (11) indicates that for $E \sim 10^6$ Vm^{-1} the effect of the field on the measured order parameter through fluctuation quenching is a thousand times greater than the field-induced microscopic order. In the smectic phase of liquid crystals the effect of the field on the local order may be dominant, but for nematics we may concentrate on the order induced by director fluctuation quenching described by Eq. (7).

The high field limit of Eq. (8) predicts that the induced order is a modular function of the field strength, and experiments by Poggi and Filippini[8] using magnetic fields have confirmed a linear relationship between magnetic field-induced birefringence and magnetic field strength for the nematic phases of two materials. In this paper we report measurements of the electric field-induced birefringence in 44'n-pentylcyanobiphenyl (5CB) and 44'n-octylcyanobiphenyl (8CB). There are some important differences between our experiments and those previously reported[4,8] for magnetic fields. We adopt a different cell configuration, and have examined the effect of varying the cell thickness on the induced birefringence. Using a modulation technique we have been able to confirm the modular (rather than linear) dependence of birefringence on field strength, and the sensitivity of our experiment has enabled us to obtain measurements in the smectic phase of 8CB.

2. EXPERIMENTAL AND RESULTS

Our experimental arrangement is illustrated in Figure 1. Samples of homeotropically aligned liquid crystals were subjected to an ac electric field (ω = 1000 Hz), the field direction being parallel to the average orientation of the director. The effect of the field on the order pa-

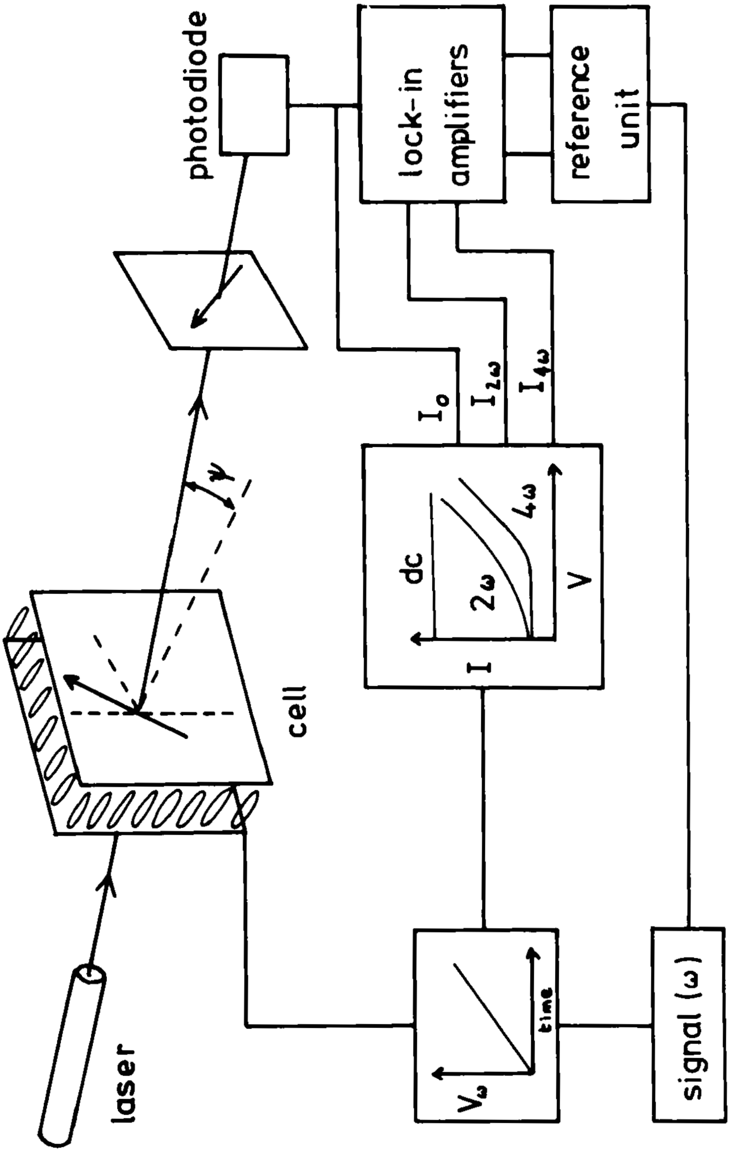

FIGURE 1 Schematic plan of experiment

rameter was determined by measuring the change in birefringence of the sample. A beam of plane-polarised light passed through the sample, at a small angle to the field direction, and the intensity of the light transmitted by an analyser crossed with respect to the incident polarisation was detected. Components of the transmitted intensity modulated at frequencies of 0, 2ω and 4ω were separately measured. The dc component of intensity was almost independent of applied field strength, and provided a measure of the zero-field birefringence of the sample.

The optical phase difference ϕ between vertically and horizontally polarised light passing through a homeotropically aligned cell inclined to the beam is given by:[9,10]

$$\phi = \frac{2\pi n_o D}{\lambda}\left\{\left(1 - \frac{\sin^2\psi}{n_e^2}\right)^{1/2} - \left(1 - \frac{\sin^2\psi}{n_o^2}\right)^{1/2}\right\} \qquad (12)$$

where D is the cell thickness, n_e and n_o are the extraordinary and ordinary refractive indices of the liquid crystal and ψ is the angle of incidence. In the presence of an electric field the refractive indices become functions of the field through the field dependence of the order parameter. For the optical configuration shown in Figure 1, and for small changes in n_e and n_o the normalised intensity (I/I_0) transmitted by the analyser crossed with respect to the incident polarisation direction is:

$$I/I_0 = \frac{1}{2}[1 - \cos\phi_0 + \phi_E \sin\phi_0 + 0(\phi_E^2)] \qquad (13)$$

ϕ_0 is the zero-field phase difference, and ϕ_E is the field-induced optical phase difference. In order to detect ϕ_E, voltages up to 100V were applied to cells of different thicknesses in the range 12–100 μm.

Figure 2 shows the transmitted intensity plotted against voltage for 8CB (2a—nematic at 35.1°C, 2b—smectic at 24.7°C): the induced birefringence was detected at modulation frequencies of 2ω and 4ω. For a squared dependence of order parameter and hence birefringence on field strength we expect that the transmitted intensity will be modulated at 2ω but if the induced birefringence is proportional to $|E|$, the situation is more complicated. The Fourier components of $|E|$ for sine-wave excitation are:

$$|E_0 \sin \omega t| = \frac{2E_0}{\pi}\left(1 - \frac{2}{3}\cos 2\,\omega t - \frac{2}{15}\cos 4\,\omega t + \cdots\right) \qquad (14)$$

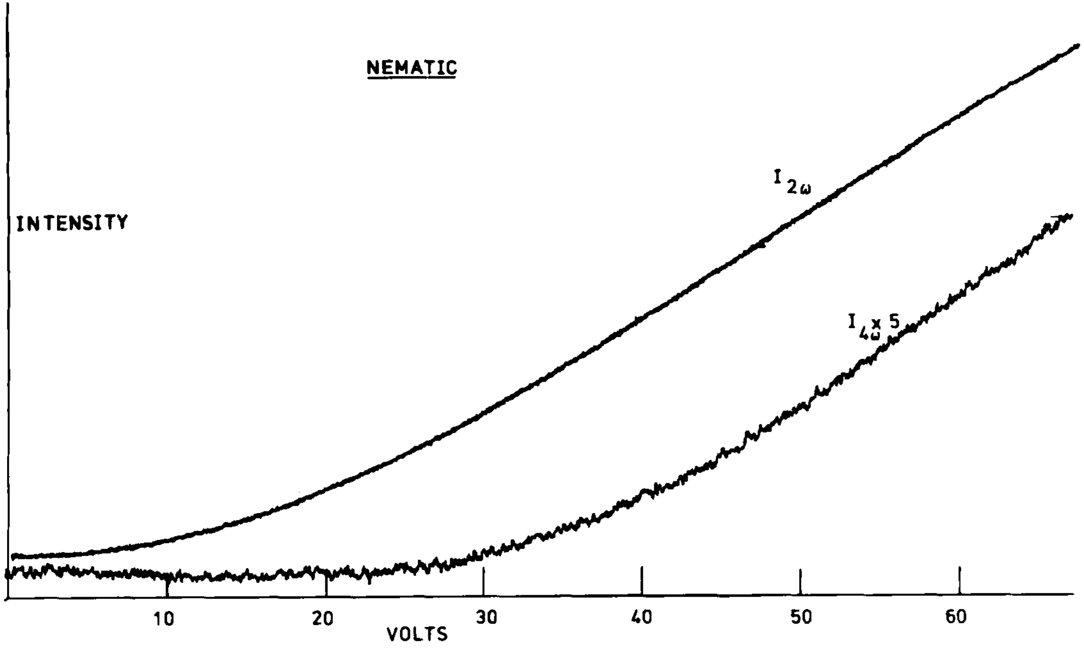

FIGURE 2 (a) Field dependent intensity (Eq. 13) in arbitrary units plotted against applied voltage for a 20 μm cell of 8CB-nematic phase at 35.1°C.

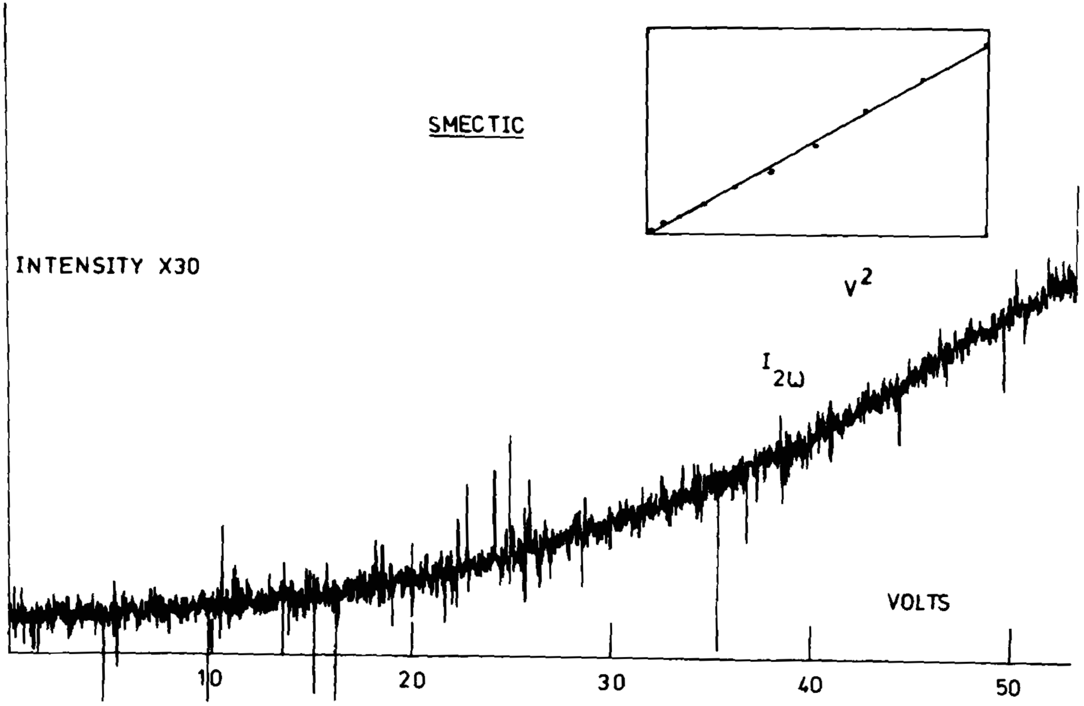

FIGURE 2 (b) Field dependent intensity (Eq. 13) in arbitrary units plotted against applied voltage for a 20 μm cell of 8CB- smectic phase at 24.7°C.

and so the transmitted intensity will contain components modulated at even harmonics of the excitation frequency. The results in Figure 2 show that the induced birefringence is proportional to E^2 at low field strengths where only a 2ω component is detected. At higher field strengths the birefringence becomes linearly dependent on applied voltage and a 4ω component in the intensity is readily detectable. In the linear region of the graphs in Figure 2a the relative intensity of the 2ω component is five times that of the 4ω component providing confirmation (see Eq. (14)) of the modular response of the liquid crystal to the applied electric field.

The effect of varying the cell thickness on the measurements is illustrated in Figure 3, where we have plotted the electric field-induced birefringence $\delta\Delta n(E)$ in nematic 5CB as a function of field strength for three different cell thicknesses. The quantity $\delta\Delta n(E)$ is obtained by rearranging Eqs. (12) and (13) to give $\Delta n = (n_e - n_o)$ as a function of ϕ_0 and ϕ_E. Since the measured ϕ_E depends sensitively on the angle of incidence ψ we have carried out experiments for different values of ψ in the range 5–20°. Results so obtained for $\delta\Delta n(E)$ are in reasonable agreement for different angles: ϕ_E depends strongly on the cell configuration, but the induced birefringence $\delta\Delta n(E)$ is a material quantity.

From the results in Figure 3 we observe that as the sample thickness decreases, the squared response of the liquid crystal to electric fields extends to higher field strengths. Furthermore the slope of the linear (modular) part of the plot of $\delta\Delta n(E)$ against field strength is not independent of cell thickness, as would be predicted by Eq. (10).

In Figure 4 we plot the field-induced birefringence in the smectic phase of 8CB. There is only a quadratic response to the applied electric field, and the effect is about one hundred times smaller than in the nematic phase. Both the twist-bend ($q_\perp$) and splay-bend ($q_\parallel$) director fluctuations are totally quenched in the smectic phase, and so the integral in Eq. (8) is zero. However field-induced changes of the microscopic order parameter can occur in the smectic phase, and are expected to be proportional to the square of the field strength.

3. DISCUSSION

The measurement of magnetic field-induced birefringence in 7CB and 8CB reported by Poggi and Filippini[8] showed a linear dependence on magnetic field strength, and their results were interpreted[4] in terms of field-quenching of director fluctuations. These measurements were carried out on relatively thick cells (200 μm), and for such sample

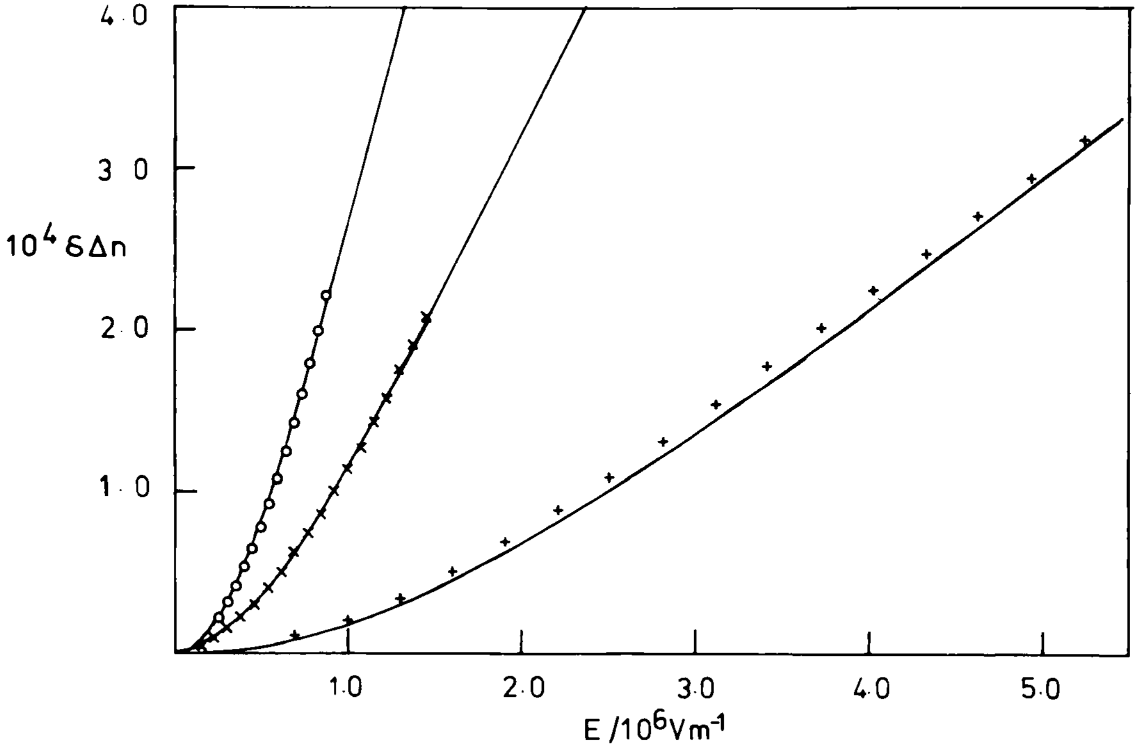

FIGURE 3 Electric field-induced birefringence as a function of field strength for different cell thicknesses of 5CB; O – 111 μm; x – 55 μm; + – 15 μm; (temperature = 28°C).

thicknesses we would expect the field response of the birefringence to be modular. However our results show that in thinner cells and at low temperatures the electric field-induced birefringence does not obey the modular field strength dependence predicted by simple fluctuation damping theory. Malraison, Poggi and Guyon[4] have suggested that improper surface alignment can result in anomalous results at low field strengths. We have carried out our experiments on cells rotated through $\pm\psi^\circ$ about the light propagation direction, and there is no asymmetry in the results, which indicates that our assumption of perfect homeotropic alignment is valid. Furthermore the detection of 2ω and 4ω components in the modulated intensity unequivocally distinguishes between a modular and squared response of the birefringence to applied field.

The simple theory of director fluctuations assumes that the elastic constants are independent of the wave vector of the fluctuation mode (q). While this is likely to be true for q less than some critical wave vector q_c, at higher q the elastic constants will depend on the wavelengths of the fluctuation. The response of the director fluctuations to an applied field could therefore be more complicated than that predicted by the simple theory. Another factor which is neglected is the effect of the cell walls on the fluctuation mode spectrum. Our results show that the sample thickness is a critical factor in determining the optical response of the liquid crystal film. It is assumed that the film thickness determines the minimum value of the fluctuation mode wave vector, but it is possible that surface forces will partially quench some of the other modes leading to a non-modular dependence of induced birefringence on field strength.

The result for the enhancement to the measured order parameter from director fluctuation quenching given in Eq. (10) is for a value of ξ such that $q_{\min} \ll \xi^{-1} \ll q_{\max}$. If these conditions are not fulfilled then the full Eq. (9) must be used, although we still neglect any q-dependence of the elastic constants. Rearranging Eq. (9) gives:

$$\langle S_{zz}^{(\mathrm{lab})}\rangle = S'\left[1 + \frac{3kTS_0}{2\pi^2 K\xi S'}\left(\tan^{-1}\xi q_{\max} - \tan^{-1}\xi q_{\min}\right)\right] \tag{15}$$

where

$$S' = S_0\left[1 - \frac{3kT}{2\pi^2 K}\left(q_{\max} - q_{\min}\right)\right]$$

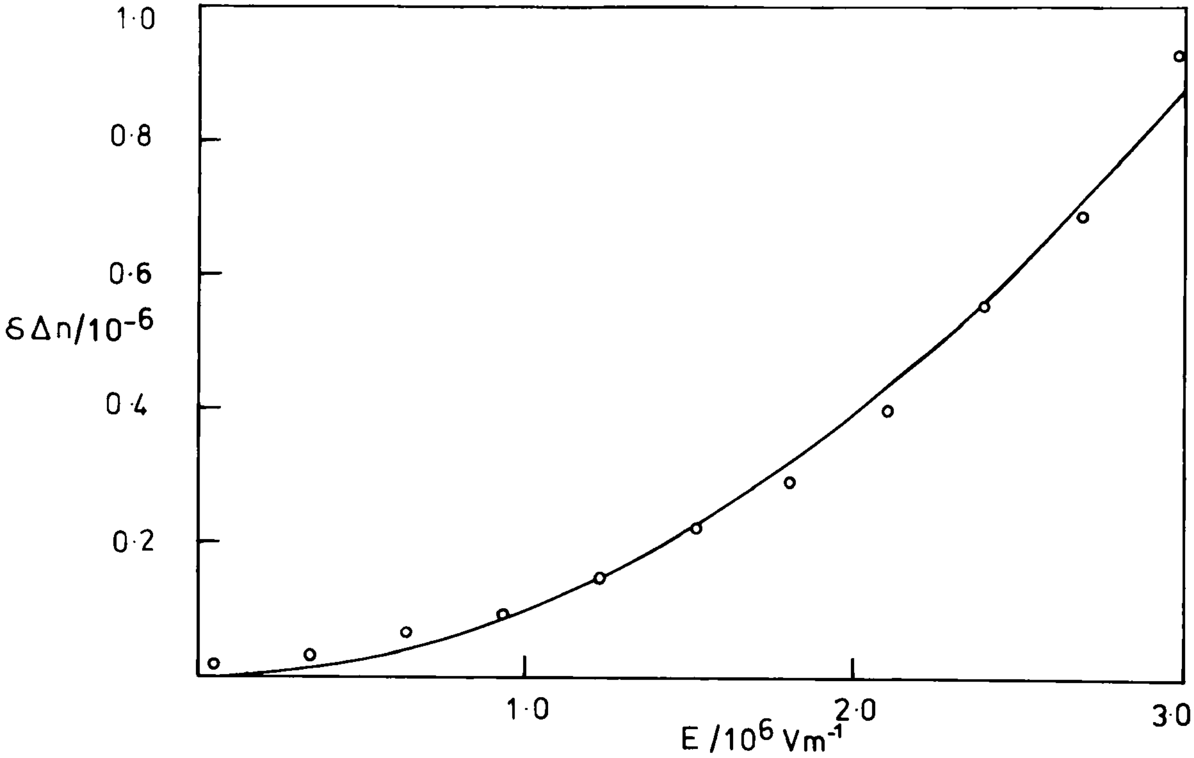

FIGURE 4 Electric field-induced birefringence as a function of field strength for smectic 8CB (D = 24 μm) at 25°C.

the quantity S' is the local molecular order parameter renormalised by thermally excited director fluctuations in the absence of an external field. Warner[2] suggests that the ratio S'/S_0 could be significantly different from unity; examination of NMR evidence suggests that an estimated value of $S'/S_0 = 0.65$ for PAA (p-azoxyanisole) could be conservative. To compare our experimental results of electrical field-induced birefringence with values predicted by Eq. (15), we use the following relation between refractive indices and the order parameter:

$$\left(\frac{n_e^2 - n_o^2}{\overline{n^2} - 1}\right) = \text{Const.}\ \langle S_{zz}^{(\text{lab})}\rangle_E \tag{16}$$

For small induced changes in refractive indices, $\overline{n^2}$ is independent of field strength, and:

$$n_e(E) = n_e + \frac{2n_o\delta\Delta n(E)}{(n_e + 2n_o)}$$

$$n_o(E) = n_o - \frac{n_e\delta\Delta n(E)}{(n_e + 2n_o)} \tag{17}$$

combining Eqs. (15), (16), and (17) leads to an expression for $\delta\Delta n(E)$:

$$\delta\Delta n(E) = \frac{(2n_o + n_e)(n_e^2 - n_o^2)kTS_0(\tan^{-1}\xi q_{\text{max}} - \tan^{-1}\xi q_{\text{min}})}{4\pi^2 n_e n_o K\xi S'} \tag{18}$$

The field dependence of the induced birefringence predicted by Eq. (18) is quadratic at low field strengths, but becomes modular at higher field strengths in agreement with the experimental observations. Our experimental results in Figure 3 have been fitted to Eq. (18) by allowing q_{max} and $q_{\text{min}} = 2\pi/\alpha D$ to be adjustable parameters, and it is clear that the theory is capable of explaining the observed squared dependence of induced birefringence on field strength at low fields. However we can only achieve quantitative agreement by selecting suitable values for the scaling parameter α and the short distance cut-off for director fluctuations ($l = 2\pi/q_{\text{max}}$). Values for α, q_{max}, l and other constants required for the calculations are collected in the table. Both parameters α and q_{max} appear to depend on cell thickness, which is surprising, although q_{max} may tend to a limit for thick cells. The small values of α are also surprising, and correspond to larger values of q_{min} than would be determined by the cell dimensions alone.

TABLE

Parameters used in calculations

Cell thickness	$q_{\max}/10^9$ m	α	l/nm
15 μm	3.0	0.033	2.09
55 μm	6.5	0.028	0.97
111 μm	7.6	0.017	0.83

$K = 5.5 \times 10^{12}$ N
$\Delta\epsilon = 12.25$
$n_e = 1.695$; $n_0 = 1.531$

Quenching of long-wavelength modes by the walls could account for this, but it is difficult to understand how the effect could increase for thicker cells.

The experiments described in this paper were designed to measure the effect of electric fields on the local nematic order, however we find that in the nematic phase the induced birefringence is dominated by quenching of director fluctuations. Continuum theory provides a qualitative interpretation of our results, but quantitative agreement between theory and experiment is lacking at present. The introduction of two parameters into continuum theory allows us fit the experimental data extremely well, but the physical significance of the parameters is not clear. Measurements on cells of different thicknesses indicate that the walls strongly influence the electro-optic response of the nematic film, and the parameters $q_{\max}$ and α provide a measure of this effect. However a proper theoretical interpretation of these experiments will require the inclusion of wall-anchoring energy in the continuum theory expression for the free energy and also make allowance for the q-dependence of the elastic constants.

Acknowledgments

One of us (TFW) thanks the SERC and Ministry of Defence for a CASE Research Studentship, and we are grateful to Dr. M. Warner of the Rutherford Laboratories for valuable discussions.

References

1. T. E. Faber, *Proc. Roy. Soc.*, **A353**, 247 (1977).
2. M. Warner, *Mol. Phys.*, **52**, 677 (1984).
3. P. G. de Gennes, "*The Physics of Liquid Crystals*," Oxford University Press (Oxford, 1974), p. 103.

4. B. Malraison, Y. Poggi, and E. Guyon, *Phys. Rev.*, **A21**, 1012 (1980).
5. J. Hanus, *Phys. Rev.*, **178**, 420 (1969).
6. J. Shen and C. Woo, *Phys. Rev.*, **A24**, 493 (1981).
7. P. Palffy-Muhoray and D. A. Dunmur, *Phys. Lett.*, **91A**, 121 (1982).
8. Y. Poggi and J. C. Filippini, *Phys. Rev. Lett.*, **39**, 150 (1977).
9. M. Françon and S. Mallick, "*Polarisation Interferometers*," Wiley (London, 1971), p. 141.
10. B. B. Kosmowski, M. E. Becker, R. A. Cremers, and D. A. Mlynski, *Mol. Cryst. Liq. Cryst. Lett.*, **72**, 17 (1981).