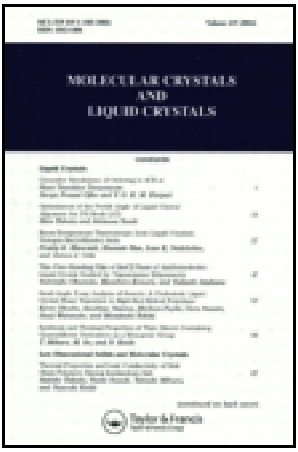


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Field-Induced Biaxiality in Nematics

D. A. Dunmur [a], K. Szumilin [a b] & T. F. Waterworth [a]
[a] Department of Chemistry, The University, Sheffield, S3 7HF, U. K.
[b] Paper presented at the 11th International Liquid Crystal Conference, 30 June-4 July, 1986, Berkeley, CA

Version of record first published: 28 Mar 2007.

To cite this article: D. A. Dunmur, K. Szumilin & T. F. Waterworth (1987): Field-Induced Biaxiality in Nematics, Molecular Crystals and Liquid Crystals, 149:1, 385-392

To link to this article: http://dx.doi.org/10.1080/00268948708082993

*Mol. Cryst. Liq. Cryst.*, 1987, Vol. 149, pp. 385–392

Printed in the United States of America

# Field-Induced Biaxiality in Nematics†

D. A. DUNMUR, K. SZUMILIN‡ and T. F. WATERWORTH
*Department of Chemistry, The University, Sheffield, S3 7HF, U.K.*

(*Received August 18, 1986*)

It is shown that optical biaxiality can be induced in a nematic liquid crystal of negative dielectric anisotropy by an electric field applied normal to the director axis. The origin of the biaxiality is attributed to differential quenching of fluctuations. Results are presented for two materials, and are in qualitative agreement with the predictions of continuum theory.

*Keywords: nematic phases, biaxiality, field effects, dielectric anisotropy*

## INTRODUCTION

The molecules that form liquid crystal phases are rarely rod-like, and are more realistically depicted as laths having a long molecular axis and two different short axes. Such molecular structures are expected[1,2] to give rise to optically biaxial fluid phases in which both the long and short molecular axes are orientationally ordered. So far no single-component low molecular weight biaxial nematic phase has been identified, although some polymer liquid crystals (both main-chain[3] and side-chain[4]) have been shown to be biaxial. It has been predicted[5–8] that mixtures of rod-like and disc-like molecules may form biaxial nematic phases, but there has been no experimental confirmation of this. More complex lyotropic systems[9,10] e.g. potassium laurate:decanol:$D_2O$ do exhibit biaxiality, but the detailed structure of this phase has yet to be determined. The lack of macroscopic biaxiality in most systems examined must be attributed to cylindrical

---

†Paper presented at the 11th International Liquid Crystal Conference, Berkeley, CA, 30 June–4 July, 1986.

‡Permanent address: Institute of Physics, Warsaw Technical University, 00-662 Warsaw, Poland.

averaging of interactions between molecules so they behave as cylinders or ellipsoids of revolution. However the averaging of local biaxiality is not always complete, and local biaxial order may be detected by n.m.r.[11] or linear dichroism.[12]

Application of external fields to a uniaxial liquid crystal is predicted[13] to lead, under certain circumstances, to induced macroscopic biaxiality. For example a nematic liquid crystal consisting of molecules having a negative electric or magnetic susceptibility anisotropy will become biaxial on application of an electric or magnetic field perpendicular to the axis of molecular alignment, as illustrated in Figure 1. Calculations using Maier-Saupe or Landau-de Gennes theories[14] suggest that the effect is small. For normal molecules and achievable field strengths the field-induced biaxial order parameter is of the order of $10^{-7}$.

There is however another source of induced biaxiality in liquid crystals, which results from differential quenching of director fluctuations. In an aligned liquid crystal the director will not be fixed,

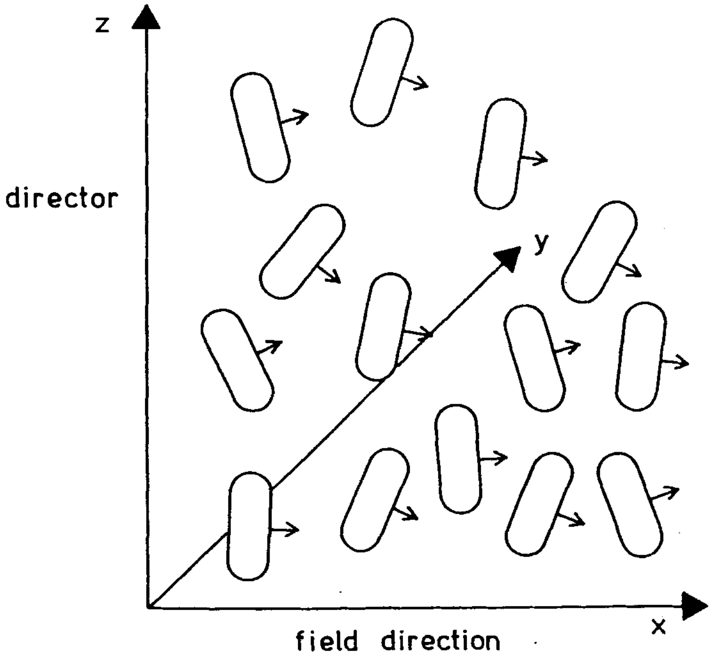


FIGURE 1 Schematic of the interaction of a nematic liquid crystal of negative susceptibility anisotropy with a field normal to the director axis.

but will fluctuate about some average orientation. Measurements of any anisotropic physical property will be the intrinsic anisotropy of the material renormalised by the director fluctuations.[15] Application of a field parallel to the director of a material of positive susceptibility anisotropy will partially quench the fluctuations and cause an increase in the anisotropy. Thus the intensity of scattered light is reduced by external fields,[16] and it has been demonstrated that the birefringence of a liquid crystal can be increased through fluctuation quenching by magnetic[17] and electric fields.[18] For materials of negative susceptibility anisotropy, application of a field perpendicular to the director will cause differential quenching of fluctuation modes in the plane perpendicular to the director, and so leads to induced biaxiality. This paper reports the first observation of the effect for electric fields applied to materials of negative dielectric aniosotropy; recently a similar experiment using magnetic fields has been reported.[19]

## THEORY

The orientational order at a point *r* in a nematic liquid crystal can be defined by the ordering matrix:

$$S_{\alpha\beta}(\mathbf{r}) = \frac{1}{2} S_o(3n_\alpha(\mathbf{r})\, n_\beta(\mathbf{r}) - \delta_{\alpha\beta}) \tag{1}$$

where $S_o$ is the Maier-Saupe order parameter defined with respect to a local director $\mathbf{n}(\mathbf{r})$. Averaging over time and spatial fluctuations of $\mathbf{n}$ gives the ordering matrix in a principal axis system as:

$$\langle S_{\alpha\beta}\rangle = \begin{bmatrix} -\frac{1}{2}(Q - P) & O & O \\ O & -\frac{1}{2}(Q + P) & O \\ O & O & Q \end{bmatrix} \tag{2}$$

$$Q = S_o(1 - \frac{3}{2}\langle n_x^2 + n_y^2\rangle) \tag{3}$$

and

$$P = \frac{3}{2} S_o \langle n_x^2 - n_y^2\rangle \tag{4}$$

It is clear that the biaxial order parameter P is non-zero if the mean square amplitude of director fluctuations in the $x$-$y$ plane is non-uniform.

Application of continuum theory and use of equipartition for director fluctuation modes gives[20]:

$$\langle n_x^2 + n_y^2 \rangle = \frac{k_B T}{\pi^2 k} [q_{max} - q_{min} - \zeta^{-1}(\tan^{-1} \zeta\, q_{max} - \tan^{-1} \zeta\, q_{min})] \quad (5)$$

where the coherence length $\zeta = (k/\Delta\chi F^2).^{1/2}$ k is an average elastic constant, $\Delta\chi$ is the susceptibility anisotropy and F is the field strength. $q_{max}$ and $q_{min}$ are wave-vectors of short and long wavelength cut-offs for the fluctuation mode spectrum. A similar result can be obtained[21] for the differential fluctuation amplitudes, such that:

$$\langle n_x^2 - n_y^2 \rangle = - \frac{k_B T}{2\pi^2 k} \zeta^{-1} [\tan^{-1} \zeta\, q_{max} - \tan^{-1} \zeta\, q_{min}] \quad (6)$$

Apart from a numerical factor the difference between the uniaxial (Eq. (5)) and biaxial (Eq. (6)) results is the zero field contribution to the uniaxial fluctuations which causes the effective anisotropy of the sample to be reduced. The values assumed for the cut-offs $q_{max}$ and $q_{min}$ are critical in determining the magnitude of the fluctuation amplitudes predicted by Eqs. (5) and (6). Various suggestions have been made for fixing the short wavelength cut off: it is often assumed to correspond to an intermolecular separation,[20] or a critical distance which defines the limit of applicability of continuum theory.[22] $q_{min} = 2\pi/D$ is fixed by the minimum sample dimension, which is usually the cell thickness D. We have found recently[21] that a choice of anisotropic boundary conditions for $q_{min}$, which more closely models the experimental situation, can influence the results significantly.

The same field-dependence is predicted by Eqs. (5) and (6) for both uniaxial and biaxial quenching of director fluctuations. At low field strengths and for thin samples a quadratic dependence on field strength is predicted, but under normal conditions Eqs. (4) and (6) yield:

$$P = \frac{3S_o k_B T}{8\pi k} \left[\frac{\Delta\chi F^2}{k}\right]^{1/2} \quad (7)$$

This result is valid for $\zeta q_{max} \to \infty$, and $\zeta q_{min} \to 0$.

## EXPERIMENTAL

The sample configuration used to measure the biaxiality induced in liquid crystals of negative dielectric anisotropy is illustrated in Figure 2. Application of an electric field perpendicular to the director (planar alignment) causes the extraordinary refractive index along the director ($n_e$) to increase, while the ordinary refractive indices $n_o$ and $n_{o'}$ become different. The induced biaxiality may be measured by detecting the changes in refractive indices using a sensitive modulation technique previously described.[18] The sample is illuminated by light plane polarised at 45° to the vertical axis. To detect the biaxiality it is necessary to measure the ellipticity of the emergent light as a function of the angle of incidence ($\psi$). For normal incidence the ellipticity expressed as a phase angle is:

$$\xi(0) = \frac{2\pi D}{\lambda}(n_e - n_o) \tag{8}$$

For the liquid crystal film rotated by angle $\psi$ about a vertical axis, the ellipticity becomes:

$$\xi(\psi) = \frac{2\pi D}{\lambda}\left(n_e\left[1 - \frac{\sin^2\psi}{n_{o'}^2}\right]^{1/2} - n_o\left[1 - \frac{\sin^2\psi}{n_o^2}\right]^{1/2}\right) \tag{9}$$

If there was no biaxiality in the film, then $n_o = n_{o'}$ and:

$$\xi(\psi)' = \left[1 - \frac{\sin^2\psi}{n_o^2}\right]^{1/2} \xi(0) \tag{10}$$

Thus the ellipticity due to induced biaxiality can be obtained as the difference of Eqs. (9) and (10). Assuming that the biaxiality is small, and writing $n_o = n_o(0) + \delta y$ and $n_{o'} = n_o(0) + \delta x$, we obtain:

$$\xi(\psi)\left[1 - \frac{\sin^2\psi}{n_o^2}\right]^{-1/2} - \xi(0) = \frac{\sin^2\psi}{n_o^3}\left[1 - \frac{\sin^2\psi}{n_o^2}\right]^{-1}(n_e\delta x - n_o\delta y) \tag{11}$$

Measurement of $\xi(\psi)$ at normal and oblique incidence enables the optical biaxiality expressed as $(n_e\delta x - n_o\delta y)$ to be determined.

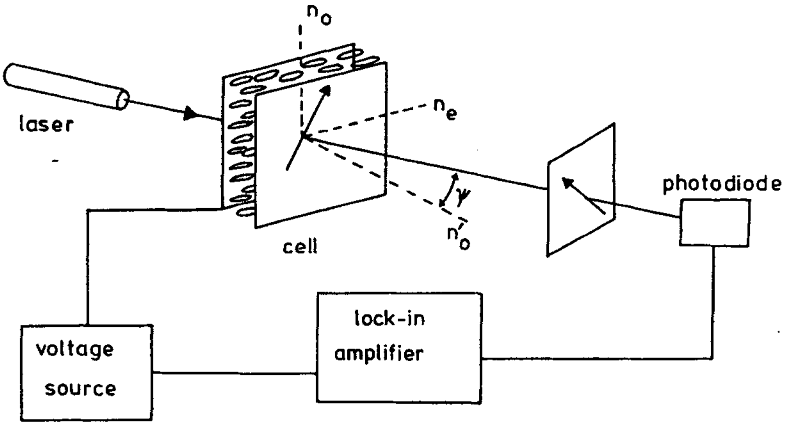


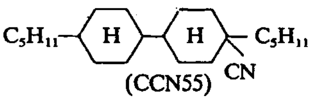
FIGURE 2 Experimental arrangement for the measurement of biaxiality induced in a liquid crystal of negative dielectric anisotropy.

## RESULTS AND DISCUSSION

We have measured the biaxiality induced in two nematic liquid crystals of negative dielectric anisotropy as a function of electric field strength. The material properties and structures are given in the table: the temperatures quoted refer to the measurement conditions. The induced biaxiality plotted in Figure 3 for CCN55 and FDE55 exhibits the linear dependence on field strength predicted by Eq. (7). For CCN55 the plot does not extrapolate to zero at zero applied field. This could be a result of a non-linear field response at low fields as observed[18] in positive materials, but is more probably attributable to an alignment correction. It would be interesting to compare the measured biaxiality with that predicted by Eqs. (6) or (7), but data on the

TABLE I

Material properties

| Compound | $T_{NI}$ | dielectric anisotropy | refractive indices | |
|---|---|---|---|---|
| | | $\Delta\epsilon(T)$ | $n_e(T)$ | $n_o(T)$ |
| <br>(CCN55) | 64°C | −5.4 (50°C) | 1.49(50°C) | 1.46(50°C) |
| <br>(FDE55) | 37°C | −0.75 (22°C) | 1.53(22°C) | 1.47(22°C) |

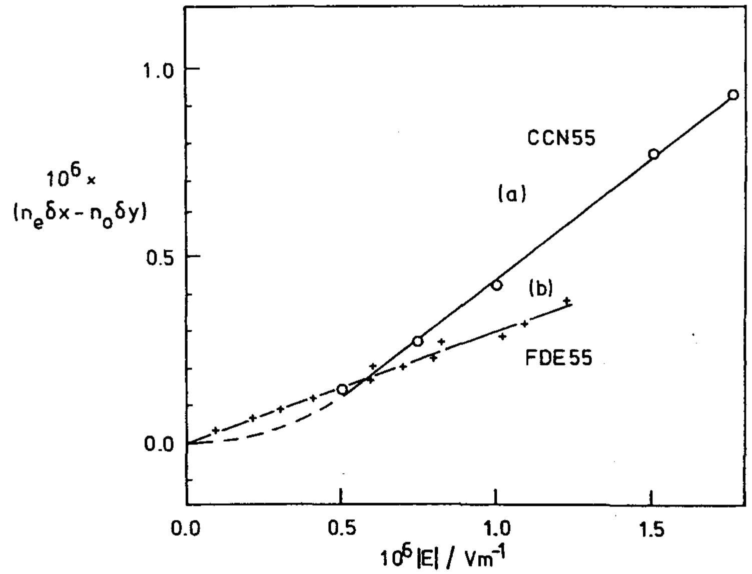


FIGURE 3 Induced biaxiality ($n_e\delta x - n_o\delta y$) plotted as a function of electric field strength.
(a) CCN55 – $\psi$ = 25°; D = 20μm
(b) FDE55 – $\psi$ = 20°; D = 25μm

required physical properties of the materials studied is not available. Equation (7) indicates that the electric field-induced biaxiality should depend on $(\Delta\epsilon/k)^{1/2}$: the ratio of the slopes in Figure 3 is 2.13, which compares with the value of $[\Delta\epsilon(\text{CCN55})/\Delta\epsilon(\text{FDE55})]^{1/2} = 2.68$.

In conclusion, we believe that we have observed electric field-induced biaxiality in two nematic liquid crystals of negative dielectric anisotropy. The effect is shown to vary linearly with applied field strength, and its magnitude is approximately proportional to $(\Delta\epsilon)^{1/2}$. These observations and the size of the effect suggest that the induced biaxiality arises from differential quenching of director fluctuations.

## Acknowledgments

We are grateful to the U.K. Science and Engineering Research Council for financial support. TFW thanks the SERC for the award of a CASE studentship with the Royal Signals and Radar Establishment, Malvern, and we are indebted to the University of Sheffield Academic Development Fund for the award of a bursary to K.S. Our thanks are also due to Dr. R. Eidenschink, E. Merck, for supplying us with a sample of CCN55.

## References

1. M. J. Freiser, *Phys. Rev. Lett.*, **24**, 1041 (1970).
2. G. R. Luckhurst and S. Romano, *Mol. Phys.*, **40**, 129 (1980).
3. C. Viney, G. R. Mitchell and A. H. Windle, *Mol. Cryst. Liq. Cryst.*, **129**, 75 (1985).
4. H. Finkelmann, F. Hessel and R. P. Herr, this conference.
5. R. Alben, *J. Chem. Phys.*, **59**, 4299 (1973).
6. Y. Rabin, W. E. McMullen and W. M. Gelbart, *Mol. Cryst. Liq. Cryst.*, **89**, 67 (1982).
7. R. G. Calfisch, Z.-Y. Chen, A. N. Berker and J. M. Deutch, *Phys. Rev.*, **A30**, 2562 (1984).
8. P. Palffy-Muhoray, J. R. de Bruyn and D. A. Dunmur, *J. Chem. Phys.*, **82**, 5294 (1985).
9. L. J. Yu and A. Saupe, *Phys. Rev. Lett.*, **45**, 1000 (1980).
10. A. M. Figueiredo Neto, A. M. Levelut, L. Liebert and Y. Galerne, *Mol. Cryst. Liq. Cryst.*, **129**, 191 (1985).
11. N. A. P. Vaz and J. W. Doane, *J. Chem. Phys.*, **79**, 2470 (1983).
12. M. G. Clark and F. C. Saunders, *Mol. Cryst. Liq. Cryst.*, **82**, 267 (1982).
13. P. Palffy-Muhoray and D. A. Dunmur, *Mol. Cryst. Liq. Cryst.*, **97**, 337 (1983).
14. T. F. Waterworth, Thesis, University of Sheffield (1985).
15. M. Warner, *Mol. Phys.*, **52**, 677 (1984).
16. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **7**, 325 (1969).
17. Y. Poggi and J. C. Filippini, *Phys. Rev. Lett.*, **39**, 150 (1977).
18. D. A. Dunmur, T. F. Waterworth and P. Palffy-Muhoray, *Mol. Cryst. Liq. Cryst.*, **124**, 73 (1985).
19. A. Seppen, G. Maret, A. G. M. Jansen, P. Wyder, J. J. M. Janssen and W. H. de Jeu, *Springer Proc. Phys.*, **11** (Biophys. Eff. Steady Magn. Fields) p. 18 (1986).
20. B. Malraison, Y. Poggi and E. Guyon, *Phys. Rev.*, **A21**, 1012 (1980).
21. K. Szumilin and D. A. Dunmur, to be published.
22. D. W. Berreman, *J. Chem. Phys.*, **62**, 776 (1975).