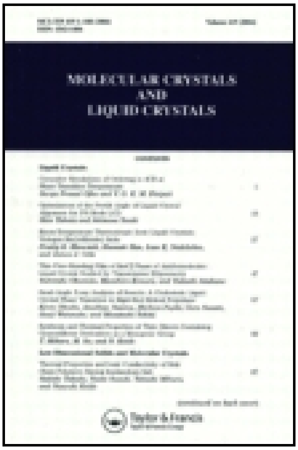

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Flexoelectro-Optic Properties of a Series of Novel Chiral Nematic Liquid Crystals

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Flexoelectro-Optic Properties of a Series of Novel Chiral Nematic Liquid Crystals

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We present a series of chiral nematic liquid crystal bimesogenic compounds based on estradiol as the chiral unit and the highly polarizable cyanobiphenyl as the terminal group. The mesophases have temperature ranges up to 40 °C wide, entering the isotropic phase at about 100 °C. We have observed the flexoelectro-optic effect and have found that the average flexoelectric coefficients of our materials are high ($\geq +5\times10^{-12}$ $\mathrm{Cm^{-1}}$). The electro-optic response times, for 0 to 90% of transmitted intensity, are of the order 1 ms.

Keywords: chiral nematic; flexoelectricity; flexoelectro-optic

INTRODUCTION

Chiral nematic materials are a continuing source of research interest. In recent years, attention has focussed on the flexoelectric switching phenomenon first observed in 1987 by Patel and Meyer.[1] This *flexoelectro-optic*[2] effect is linear with the amplitude of the applied electric field and hence has potential for display applications and for optical switches or modulators. One of the key molecular features of flexoelectric materials is their shape asymmetry: they are typically "drop"- or "banana"- shaped,[3] or a combination of these shapes. In this paper, we will describe a new series of bimesogenic compounds with a

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combined drop and banana[4] shape that exhibit exceptionally high flexoelectric coefficients. Other factors that affect the magnitude and the response time of the flexoelectro-optic effect include the helix pitch length, the mean elastic constant and the dielectric anisotropy of the material (see below).

The Flexoelectro-Optic Effect

An undisturbed chiral nematic material is usually described in a Cartesian frame of reference where the z-axis is parallel to the helical axis **h**. The director, $\hat{\mathbf{n}}$, is thus confined to the (x, y) plane, *i.e.* $\hat{\mathbf{n}} = (n_x, n_y, n_z) = (\cos\theta, \sin\theta, 0)$ where θ, taken to be zero when the director is parallel to the x-axis, is given by $\theta = kz$ and $k = 2\pi/P_0$. P_0 is the length of the undisturbed pitch and k is the helical wavevector of the material. Short pitch nematics have their macroscopic optic axis perpendicular to the director plane[5] and in such an undisturbed material the optic axis lies along **h**.

The theory of the flexoelectro-optic effect[1,6] commences with the free energy density, f, of a chiral nematic subject to an electric field:

$$f = \frac{1}{2}\left[\kappa_{11}(\nabla\cdot\hat{\mathbf{n}})^2 + \kappa_{22}(k + \hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \kappa_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2\right]$$
$$-\frac{\Delta\varepsilon}{8\pi}(\hat{\mathbf{n}}\cdot\mathbf{E})^2 - \mathbf{E}\cdot(e_s\hat{\mathbf{n}}\nabla\cdot\hat{\mathbf{n}} + e_b\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}}). \quad (1)$$

The first term in Eq. 1 gives the free energy density of the undisturbed chiral nematic. κ_{11}, κ_{22} and κ_{33} are the elastic constants of splay, twist and bend respectively. The second term is the contribution from the coupling between the electric field **E** and the dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$. Note that the dielectric coupling is quadratic in E. The third term describes the effect of the flexoelectric coupling[3] between the field and the material. The parameters e_s and e_b are the flexoelectric coefficients of splay and bend. In this paper we use the sign convention devised by Rudquist and Lagerwall.[7] Note that the flexoelectric coupling is linear in E and is therefore dominant at low fields.

The effect of the flexoelectric coupling is to rotate the director plane by an angle ϕ, about the field direction. The angle ϕ is taken to be positive when the rotation is in a right-hand sense about **E**. In consequence of the director plane's rotation, the optic axis of the material is also rotated through angle ϕ; see Figure 1. The direction and pitch of the helix are unaffected.

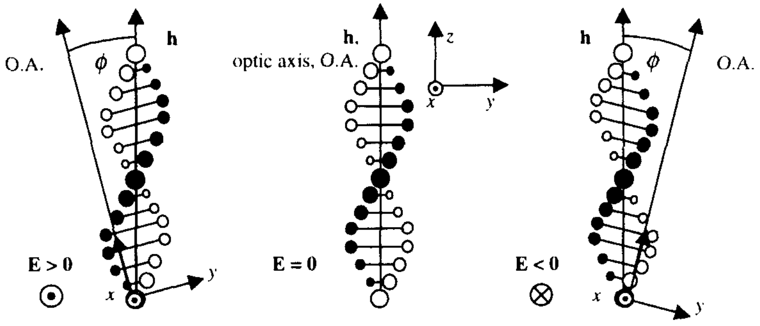

FIGURE 1 The effect of flexoelectric coupling between a field and a right-handed chiral nematic material. Splay and bend deformations appear in the rotated director plane.

The free energy density of the distorted chiral nematic (in the presence of a field) is minimized with respect ϕ. In the minimization, small angle approximations are made; it is also assumed that the unwinding of the helix due to the dielectric coupling can be neglected. The solution is given by

$$\tan\phi = \bar{e}E/k\bar{\kappa}\,, \qquad (2)$$

where $\bar{\kappa} = (\kappa_{11}+\kappa_{33})/2$ and $\bar{e} = (e_s+e_b)/2$ are the effective elastic and flexoelectric coefficients respectively.

The characteristic response time, τ, of flexoelectro-optic switching[8] is given by $\tau = \gamma_1/\bar{\kappa}k^2$, where γ_1 is the effective viscosity associated with helix distortion (no liquid flow) and, typically, $\gamma_1 \approx 0.01$ to 0.1 Nsm^{-2}.[9] It is clearly preferable to use short pitch chiral nematic materials with high elastic constants for fast flexoelectro-optic switching.

EXPERIMENTAL

The structure of the liquid crystal bimesogenic compounds synthesized for this work is shown in Figure 2. The series is systematically denoted *m Es n CB*, where *Es* denotes the chiral estradiol group, *CB* denotes the conjugated cyanobiphenyl group, and the integers *m* and *n* give the number of carbon atoms in the alkyl spacers as indicated.

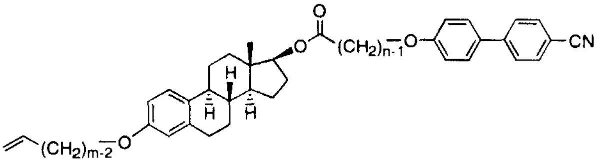

FIGURE 2 The structure of the series *m Es n CB*.

Table 1 shows the transition temperatures of the materials in the series, together with their pitch lengths. The transition temperatures were measured using differential scanning calorimetry. The pitch lengths, which were essentially temperature-independent, were measured using the Cano wedge technique at reduced temperatures ($T\text{-}T_{clear}$) of about –5 °C.

TABLE 1 The phase properties of the series *m Es n CB*.

Material	Transition, °C k → n*	Transition, °C n* → i	Pitch length, nm
11 Es 5 CB	68	95	595
5 Es 5 CB	91	105	320
11 Es 11 CB	42	82	280
5 Es 11 CB	71	87	210

The flexoelectric effect was observed in 4 μm thick specimens contained in glass cells treated with rubbed polyimide for planar alignment. The samples were examined on a hotstage held on the rotating sample stage of a polarizing microscope. Using the polarizing microscope and a series of filters, we determined that the helical sense of the materials is right-handed by observing the effect of the chiral nematic's optical rotatory power on the polarized light transmitted by the sample.

Transparent electrodes on the inner walls of the cell made it possible to apply fields across the samples. The waveforms of the applied fields were either triangle- or square-waves, usually in the frequency range 10 Hz – 1 kHz, and varied in amplitude from zero up to 15 Vμm^{-1}. All the materials have positive dielectric anisotropy: at high field amplitudes (~ 10 Vμm^{-1}) the molecules tend to align homeotropically along the applied field direction.

The flexoelectro-optic effect is best observed with the chiral nematic helix perpendicular to both the applied field and the viewing direction, that is, with the uniformly-lying helix[10] (ULH) form of the focal conic texture. One method successfully employed to obtain the ULH texture was to apply a field of just sufficient amplitude to cause the texture change from planar Grandjean to focal conic, while unidirectionally rubbing the cell. The rubbing promotes the uniform alignment of the disordered focal conic texture *via* a shearing action: the helical axis is forced to lie perpendicular to the rubbing direction.

The rotation angles of the optic axis were evaluated by holding the sample between crossed polarizers and measuring the half-angle between the two extinction positions. The response time was measured as the time elapsed between a change in the polarity of the applied field and the responding photodiode signal changing by 90% of its peak-to-peak amplitude, with the undisturbed optic axis aligned at 22.5° to the polarization of the incident light.

RESULTS AND DISCUSSION

The presence of the highly polarizable cyanobiphenyl unit as the end group confers a high dielectric anisotropy on the molecules and thus we might expect the behaviour of the present materials to deviate from that predicted by the theory. Figure 3 illustrates flexoelectro-optic response of 5 Es 5 CB, where the relationship between tanϕ and E is nonlinear even in moderate electric fields.

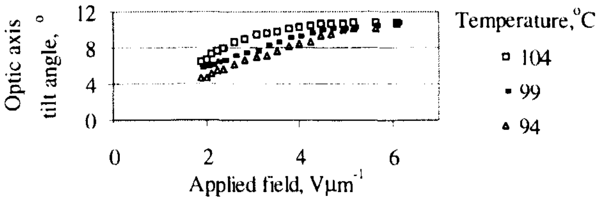

FIGURE 3 Optic axis tilt angle versus applied field for 5 Es 5 CB. The helix is completely unwound by fields in excess of 7 Vμm^{-1}.

However, two of the materials, 5 Es 11 CB and 11 Es 5 CB, do show a linear response, in reasonable agreement with theory, at low fields over short temperature ranges, as illustrated in Figure 4. The lines shown are linear regressions that were fitted to the data using Eq. 2 (for clarity, however, the y axis is plotted in terms of ϕ, rather than tanϕ).

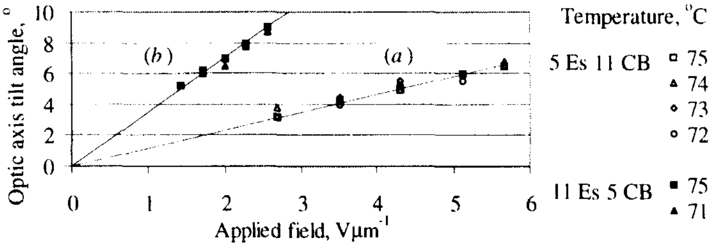

FIGURE 4 Optic axis tilt angle versus applied field for (*a*) 5 Es 11 CB and (*b*) 11 Es 5 CB.

Table 2 shows the effective flexoelectric coefficients obtained for the compounds 5 Es 11 CB and 11 Es 5 CB. We assume a reasonable value[11] for the average elastic constant, $\overline{K} \approx 10^{-11}$ N. The present materials have higher effective flexoelectric coefficients than any yet measured by this technique. Previous work[1,8,10] has concerned materials with $\bar{e} \leq 1.2\times10^{-12}$ Cm^{-1}.

TABLE 2 Flexoelectric coefficients of 5 Es 11 CB and 11 Es 5 CB.

Material	$\bar{e}/\bar{K}$, C(Nm)$^{-1}$	Effective flexoelectric coefficient, $\bar{e}$, Cm^{-1}
5 Es 11 CB	0.53	$+5.3\times10^{-12}$
11 Es 5 CB	0.52	$+5.2\times10^{-12}$

We have observed a strong flexoelectric response, with the optic axis tilting by up to 10° for applied fields of only 3 – 10 Vμm^{-1}, compared with the previous work where angles up to 10° were observed for fields of 28 – 40 Vμm^{-1}.[1,8,10]

The response times are faster at high fields and temperatures, as Figure 5 shows. The materials have longer switching times than those previously reported[2,8,10,12] (50 - 250 μs), an effect due in part to the viscosity of the present materials. Other contributing factors[12] include the temperature dependences of the pitch lengths and mean elastic constants, together with the helix-unwinding effect of the electric field, whereby the coupling between the field and the dielectric anisotropy tends to increase the pitch lengths of these materials.

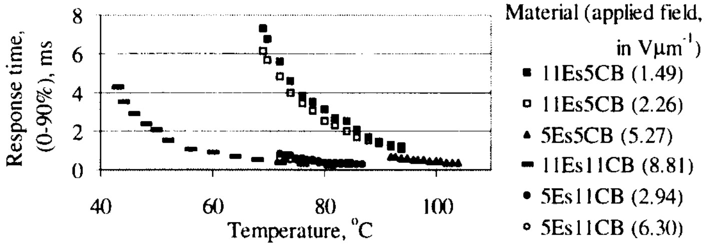

FIGURE 5 Response time versus temperature.

In addition to the shape asymmetry, the coupling between the estradiol and cyanobiphenyl moieties within these bimesogenic compounds is crucial in determining the flexoelectric properties of these materials. A short spacer, or "strong" coupling, leads to increased pitch lengths and hence to larger effective flexoelectro-optic tilt angles. A long spacer, or "weak" coupling, leads to decreased pitch lengths and hence faster (~300 μs) switching times. For all of the homologues, however, switching times faster than ~7 ms were recorded at low fields over, typically, a 15 – 40 °C temperature range (*cf.* Figure 5).

SUMMARY

We have presented a new series of bimesogenic chiral nematic materials that exhibit large flexoelectro-optic effects with millisecond (or faster) response times. The isotropic-to-nematic transition temperatures are relatively high (between 82 °C and 105 °C) but the flexoelectro-optic effect is exhibited over a 40 °C temperature range. In the present work we have concentrated primarily on the effect of the coupling alkyl chain. We are currently investigating modified variants of the non-chiral mesogenic unit with a view to further improving the flexoelectro-optic behaviour and reducing the isotropic-to-nematic transition temperatures whilst maintaining the shape asymmetry that appears to be important in these materials.

Acknowledgements

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