The effect of the molecular structure on flexoelectric coupling in the chiral nematic phase†

H. J. Coles,* B. Musgrave, M. J. Coles and J. Willmott

SLCI, Department of Physics and Astronomy, University of Southampton, Southampton, Hampshire, UK SO17 1BJ. E-mail: hjc@lc.phys.soton.ac.uk; Fax: +44 2380 595359; Tel: +44 2380 595335

In order to understand the correlations between molecular structure and flexoelectric properties inherent in the electro-optic switching behaviour of chiral nematic liquid crystals, we have examined the properties of monomesogenic and bimesogenic achiral nematic materials doped with a low concentration (3–6% by weight) of a chiral additive. On comparing the properties of host nematogenic materials, specifically the monomesogens 7OCB and 7CB and the bimesogen CBO8OCB, we find that the cyanobiphenyl (CB) and oxycyanobiphenyl (OCB) mesogenic units undergo particularly strong flexoelectric coupling. In contrast with the behaviour of achiral nematic materials, however, we find that the inclusion of a significant transverse molecular dipole (7OCB) affects neither the sign of the flexoelectric coefficient nor its magnitude when compared with a similar material bearing a smaller transverse dipole (7CB). The values of the ratio of flexoelectric coefficient to elastic constant $\bar{e}/K$ are large and of similar magnitude in all three materials ($0.4 \leqslant \bar{e}/K \leqslant 0.6$ C N^{-1} m^{-1}). The bimesogenic mixture has the separate advantage of possessing a low dielectric anisotropy, which allows this material to exhibit a complete (2ϕ) optic axis rotation of 45° in a bipolar field of amplitude 6 V μm^{-1}. Additionally, we note that the occurrence of blue phases can be exploited to simplify the procedure required to align the chiral nematic phase in the uniaxial lying helix configuration for the flexoelectric electro-optic effect.

Introduction

Flexoelectric coupling[1] in the chiral nematic liquid crystal phase has provoked much interest in recent years. The associated optical switching effect, first reported by Patel and Meyer,[2] is the result of an in-plane rotation of the chiral nematic material's optic axis. The rotation is linear with electric field amplitude and can be independent of temperature.[3] These features, coupled with microsecond response times,[4] render the switching effect potentially viable for future use in electro-optical device and display applications. In this paper we propose to continue the theme of our earlier work by further investigating the correlations between molecular structure and flexoelectric properties. We have also examined the impact of the direction of the dipole moment in relation to the molecular long axis.

In order to observe unambiguously the flexoelectrically-induced electro-optic effect in a chiral nematic material, the helix axis must be aligned unidirectionally in the plane of the confining surfaces. In this configuration a short pitch chiral nematic phase has the macroscopic appearance of a birefringent crystal with negative uniaxiality: the optic axis of the sample lies normal to the average director plane of the phase. If the material is unperturbed, the optic axis lies collinear with the helix axis.

The perturbation caused by flexoelectric coupling between an electric field and a chiral nematic liquid crystalline material results in the appearance of a macroscopic polarisation as the director field is distorted to produce splay and/or bend deformation patterns. The induced polarisation **P** is related to the director **n** as follows

$$\mathbf{P} = e_s \mathbf{n}(\nabla \cdot \mathbf{n}) + e_b \mathbf{n} \times \nabla \times \mathbf{n} \tag{1}$$

where e_s and e_b are the flexoelectric coefficients of splay and bend, respectively. This expression employs the sign convention proposed by Rudquist and Lagerwall[5] and follows experimental work by Komitov *et al.*[6] Note that this definition of **P** differs from that generally employed in experimental work carried out on achiral nematic liquid crystals,[7] which returns a value for the bend flexoelectric coefficient of opposite sign to that defined in eqn. (1).

Flexoelectric coupling between an electric field applied across the sample as described above, in a direction normal to the confining surfaces and the helix axis, results in a flexoelectric deformation which causes a rotation of the director planes through an angle ϕ about an axis parallel to the applied field.[2] The optic axis, lying normal to the director planes, is therefore deflected from its unperturbed position by a rotation through ϕ, in the plane of the confining surfaces. The relationship between the amplitude E of the applied electric field **E**, the induced rotation and the material's flexoelectric and elastic coefficients is given[2] by

$$\tan \phi = \frac{\bar{e}E}{kK} \tag{2}$$

where

$$K = \frac{K_{11} + K_{33}}{2}, \quad \bar{e} = \frac{e_s + e_b}{2} \text{ and } k = \frac{2\pi}{P_0}. \tag{3}$$

The parameters K and $\bar{e}$ are the material's effective elastic and flexoelectric coefficients respectively. K_{11} and K_{33} represent elastic constants coupling splay and bend, respectively. P_0 is the length of the natural helical pitch of the phase and k is the modulus of its helical wavevector. It is possible for the relationship between $\tan \phi$ and E to be invariant with sample
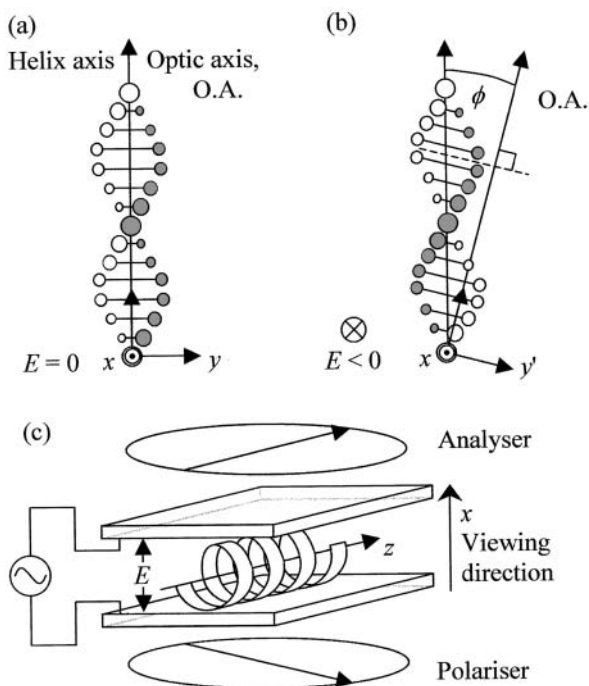
Fig. 1 In diagram (a) the directors of a right-handed helix are confined to the xy-plane, orthogonal to the helix and optic axes. In diagram (b) an electric field is applied along the $-x$ direction: the director plane and optic axis are rotated *via* flexoelectric coupling by an angle $+\phi$ about the x-axis. Diagram (c) illustrates the geometry required in order to view the birefringence switching effect.

temperature, and such behaviour has been observed in cases where the helical pitch is independent of temperature.[3,8,9] Fig. 1 illustrates the necessary alignment geometry of a chiral nematic material held in an electro-optic cell between crossed polarisers.

From the definition given in eqn. (3), the coefficient $\bar{e}$ is expected[10] to be a function of the dipolar flexoelectric coupling mechanism, as described by Meyer,[1] rather than the quadrupolar mechanism described by Prost and Marcerou.[11] Additionally, we note that owing to the sign change of e_b resulting from the alternative definition of flexoelectric polarisation employed in other work, the sum $e_s + e_b$ is equivalent to the "flexoelectric anisotropy" e^*, defined by the difference between the splay and bend coefficients, that is measured in work on achiral nematic liquid crystals.[7,16] Thus $e^*/K \equiv 2\bar{e}/K$.

The response time τ of the flexoelectric switching effect has been shown to be given[4] by

$$\tau = \frac{\gamma}{k^2 K} \quad (4)$$

where γ is the effective viscosity of the N* material phase, and is approximately equal to the twist viscosity γ_1. This relationship indicates that flexoelectric coupling to a short pitch (<1 μm) chiral nematic material should typically induce a response over a timescale of ~ 100 μs.[4] From eqn. (4) it is also clear that the response time should be independent of the applied field amplitude, although in practice it is generally found that there is a weak field dependence causing the response times to increase slightly as the field amplitude is decreased.[4,12] Measurements of response times as a function of sample temperature follow an Arrhenius-type relationship as response times decrease with increasing temperature.[12]

To date, no chiral nematic materials specifically optimised for flexoelectric switching have been developed. Such materials would exhibit a large rotation angle per unit applied field with a microsecond response time. In one study,[3] a short pitch chiral nematic material was reported to exhibit a large rotation of $\phi \approx 30°$: however, this measurement required an immoderately

large field to be applied across the sample (± 220 V across a 2 μm sample, or $E = 110$ V μm^{-1}). Short pitch materials with more reasonable attributes ($\phi \approx 10°$ in fields of 10 V μm^{-1}) have been examined,[8,9] although in these cases the magnitude of ϕ has ultimately been limited by the dielectric response of the materials in high fields (>10 V μm^{-1}). The dielectric coupling mechanism is a quadratic function of the applied field amplitude and is therefore dominated by flexoelectric coupling at low field amplitudes. At a sufficiently high field, however, dielectric coupling between an electric field and a material with positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$) causes the molecules to align parallel to the field, resulting in the complete unwinding of the helical structure. The critical field necessary to cause helix-unwinding is proportional to $P_0^{-1}(K_{22}/\Delta\varepsilon)^{-1/2}$,[13] where K_{22} is the twist elastic constant. At field amplitudes exceeding the critical value, flexoelectric coupling cannot induce an electro-optic switching effect because the optic axis associated with the helical structure no longer exists.

Our interest in flexoelectric switching in chiral nematic liquid crystals was stimulated by observations of the electro-optical properties of an homologous series of bimesogenic (estradiol-cyanobiphenyl) materials.[8,9] Our materials were systematically named mEsnCB, where Es denotes the chiral estradiol mesogen, CB denotes the cyanobiphenyl mesogen and m and n are integers giving the numbers of carbon atoms in the terminal and spacer aliphatic chains respectively. We have been particularly interested in understanding the structure–property correlations inherent in the behaviour of these bimesogens. It is difficult, however, to evaluate the separate contributions of the mesogenic units to the flexoelectric response by simply examining the properties of pure materials. In order to make a clear differentiation we examined the properties of various mixtures between an estradiol-cyanobiphenyl bimesogen (11Es5CB) and a cyanobiphenyl-containing monomesogenic nematogen, 4-hexyl-4′-cyanobiphenyl (6CB).[14] We found that the addition to the bimesogen of a large proportion of the monomesogenic material, up to 90% concentration by weight, caused only a slight reduction in the magnitude of the ratio $\bar{e}/K$ from its value in the pure bimesogen (from 0.5 C N^{-1} m^{-1} in pure 11Es5CB, to 0.4 C N^{-1} m^{-1} in a mixture containing a concentration of 90% by weight of 6CB). This observation leads us to surmise that the cyanobiphenyl unit's contribution to the flexoelectric coupling mechanism in the bimesogen is considerably stronger than that of the estradiol group.

In the present report we propose to advance our understanding by examining the flexoelectric properties of chiral nematic liquid crystals formed when *achiral* nematic liquid crystals, in particular monomesogens based on the cyanobiphenyl mesogenic unit, are weakly doped with a highly chiral additive. Such mixtures should allow the flexoelectric properties associated with the mesogenic unit to be identified unambiguously since the use of low concentrations of chiral additive (3 to 6% by weight) will allow the properties of the nematic hosts to dominate the mixtures' responses to electric fields. We shall compare the flexoelectric behaviour of the present mixtures with the behaviour, reported in earlier work, of the estradiol-cyanobiphenyl bimesogen-containing mixtures and pure materials, in an effort to determine whether or not the results gathered in the current work substantiate our inferences concerning the importance of the cyanobiphenyl unit.

The achiral monomesogens chosen for examination are the nematogens 7CB and 7OCB, members of the well-known nematogenic homologous series 4-cyano-4′-n-alkylbiphenyl (nCB) and 4-cyano-4′-n-alkoxybiphenyl (nOCB) respectively, where n is the number of methylene units in the terminal chain. The molecular structures of 7CB and 7OCB are illustrated for comparison in Figs. 2(a) and (b). Owing to the presence of the terminal nitrile group (-C≡N), these homologous series possess very strong terminal dipole moments, which act in a longitudinal direction along the conjugated biphenyl units.[15] In
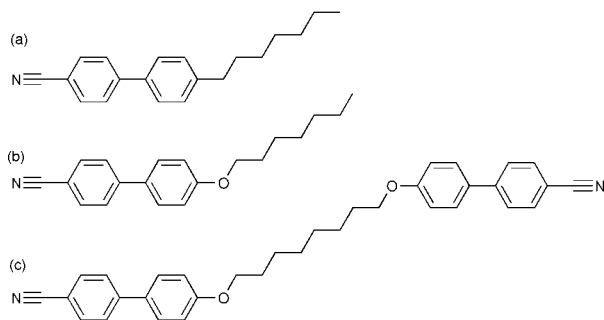
Fig. 2 The diagrams illustrate the molecular structures of (a) 7CB, (b) 7OCB, and (c) CBO8OCB

addition to this longitudinal dipole, the *n*OCB homologues possess a transverse component owing to the presence of the oxy linkage connecting the cyanobiphenyl unit to the terminal alkyl chain. Earlier measurements[16] of the flexoelectric properties of pure (undoped, achiral) homologues from these two series have indicated that their effective flexoelectric coefficients are opposite in sign, and quite different in magnitude. For instance,[16] the magnitude of the ratio $e*/K$ in 8OCB (reported to be -1.4×10^3 dyn$^{-\frac{1}{2}}$) is much larger than it is in 8CB (0.27×10^3 dyn$^{-\frac{1}{2}}$).‡ In addition, it has been found[7] that the magnitude of $e*/K$ is not very sensitive to alkyl chain length and varies little across an homologous series.

The difference between the flexoelectric properties of 8CB and 8OCB has been explained as follows:[16] adjacent 8CB molecules exhibit antiparallel ordering, owing to the dipolar interaction between the cyanobiphenyl moieties. The same antiparallel ordering is assumed to occur in 8OCB, with the macroscopic cancellation both of the longitudinal dipoles conferred on the molecules by the presence of the nitrile unit and of the transverse dipoles resulting from the presence of the oxygen atom. In a macroscopic bend configuration, however, the transverse oxygen dipoles become correlated, and it is to this bent configuration that the increase (and change in sign) of $e*/K$ in 8OCB, compared with 8CB, is attributed. This measurement confirms the prediction arising from the theoretical treatment[10] of flexoelectric coupling to nematic materials, which indicates that the dipolar contribution to the flexoelectric effect is dominated by transverse dipole moments. We are interested in discovering whether or not the difference in behaviour between the achiral materials is reflected in a difference between the forms of the flexoelectric switching effect once homologues from each series are doped with a chiral additive.

In addition to the work on monomesogenic materials, we have characterized the electro-optic properties of a mixture between the chiral agent and a bimesogenic material composed of two oxycyanobiphenyl mesogenic units separated by an alkyl spacer containing eight methylene units *i.e.* α,ω-bis(4-cyanobiphenyl-4′-yloxy)octane (denoted CBO8OCB). The structure of this molecule is shown in Fig. 2(c). With respect to its electro-optic behaviour, it is known that pure CBO8OCB has a lower dielectric anisotropy than monomesogens from the series *n*CB and *n*OCB.[17] In the present work we will discuss the flexoelectric behaviour of the chiral doped *n*CB and *n*OCB homologues in comparison with the switching properties of the similarly doped CBO8OCB bimesogen.

Experiment

The chiral additive used to dope the achiral nematogenic materials was supplied by Merck UK Ltd. and is named BDH1305. The helical twisting power of BDH1305 is high,

‡ 1 dyn $= 10^{-5}$ N.

57 μm^{-1}, extrapolated to the neat compound from solution measurements in the nematic material BL080 at 20 °C[18] and therefore it is often found that at low concentrations (3–6% by weight) this dopant produces short pitch chiral nematic phases that selectively-reflect visible light.

Electro-optic cells, nominally 5 μm and 7.5 μm thick, carrying conductive indium–tin oxide (ITO) coatings and surface alignment layers, are employed in order to characterise the chiral nematic mixtures. Rubbed polyimide films induce planar alignment, while a surface treatment of lecithin promotes homeotropic alignment.

The thermo-optic and electro-optic properties of the materials sealed in cells are evaluated by placing a sample cell between the crossed polarisers of a polarising microscope. A sample is mounted in an enclosed heating stage attached to a temperature controller. The material alignment necessary in order to view the flexoelectric switching effect is usually achieved in materials possessing positive dielectric anisotropy by applying an electric field while mechanically stimulating the material to flow. The electric field must be of sufficient amplitude to cause the helical structure to lie in the plane of the cell walls (*via* dielectric coupling), without unwinding the helical structure. The simultaneous mechanical manipulation process must be unidirectional because it is applied in order to produce uniaxial alignment of the lying helix: the helix axis tends to lie orthogonally across the direction of material flow.

Flexoelectric coupling to a periodic alternating electric field applied across the electrode gap induces periodic rotation of the optic axis of the sample. The rotation is detected as a modulation in the light intensity transmitted by the cell using a photodiode placed in the observation tube of the microscope. The signal from the photodiode is monitored using a digitising oscilloscope. Optic axis rotation angles and response times are measured as functions of temperature and applied field amplitude. The method employed to measure the deflection of the optic axis from the unperturbed lying helix position, which is described elsewhere,[9] allows measurements of ϕ to be made to within 0.3°. The response times of the materials are defined as the time taken for the responding photodiode signal, *i.e.* the transmitted intensity, to change from 0 to 90% when the polarity of a driving field of square waveform is reversed. It should be noted that this measurement, therefore, is of the characteristic time required for an electro-optic switch through 2ϕ (not ϕ). To ensure maximum contrast between the two extreme switched states, the response times are measured with the undisturbed optic axis lying at 22.5° to the transmission axis of one of the microscope's polarisers.

Results and discussion

Materials

Two-component mixtures between the chiral additive BDH1305 and the nematic liquid crystalline materials 7OCB, 7CB and CBO8OCB were prepared. Table 1 shows the transition temperatures of the mixtures and, for interest, the transition temperatures of the pure materials. Note that in addition to a chiral nematic phase (N*), the 7OCB mixture also displays blue phases (BP), which were identified *via* polarised optical microscopy. The 7CB mixture has the advantage of being mesomorphic at room temperature. The CBO8OCB mixture displays a mesophase at a significantly higher temperature than that of the monomesogens. The chiral nematic mesophase of this mixture is biphasic with the isotropic phase on cooling, until a sample temperature of 185 °C is reached. For this reason the electro-optic properties of the CBO8OCB mixture were investigated at a single temperature (183 °C) only.

Each mixture exhibits a chiral nematic phase with a right-handed helical structure. The wavelength λ of the light selectively reflected by each monomesogenic mixture's chiral

Table 1 Physical properties of the mixtures and the nematic host materials: the transition temperatures were measured using optical microscopy; the refractive index data, measured at 632.5 nm and at the reduced temperatures T_r indicated, are taken from references given in the text; reflected spectra were measured using a spectrometer; and pitch lengths are calculated as shown

Material	Transition temperature/°C	Refractive indices n_e and n_o $(T_r/°C)$	Reflected wavelengh λ/nm	Pitch $P_0 = 2\lambda(n_e+n_o)/ \pm 5$ nm $(T_r/°C)$
7OCB	Cr 54 N 74 I	$n_e = 1.660$ $n_o = 1.516(-7)$	—	—
7OCB+3% BDH 1305	Cr 55 N* 69 BP 70 I	—	662(−7)	415(−7)
7CB	Cr 30 N 42.8 I	$n_e = 1.674$ $n_o = 1.519(-6)$	—	—
7CB+4% BDH 1305	Cr <20 N* 37 I	—	470(−6)	295(−6)
CBO8OCB	Cr 175 N 205 I	—	—	—
CBO8OCB+3% BDH 1305	Cr168 N* (biphasic) 201 I	—	Near IR	≈700(−22)

nematic phase, and measured using a UV-Vis spectrometer, is also indicated in Table 1. The reflection properties of the mixtures are reasonably insensitive to variations in sample temperature (for example, in the 7CB mixture the reflected spectrum is centred on 658 nm close to the clearing temperature of the phase and it red-shifts by only 5 nm when the material is cooled by 14 °C). While the 7OCB and 7CB mixtures reflect visible light, the CBO8OCB mixture reflects infrared light (the reflection spectrum of the bimesogen mixture has not been measured). This increase in pitch is ascribed to increased elastic constants in the bimesogenic material in comparison with the monomesogens: a larger twist elastic constant opposes the formation of the helical structure that is imposed on the phase by the chiral additive.

Using the selective reflection wavelength data it is possible to estimate the helical pitch length of each monomesogenic material's phase: P_0 is evaluated using the relationship $\lambda = nP_0$, where n is the mean refractive index of a director plane and $n = (n_\parallel + n_\perp)/2$. The parameters $n_\parallel$ and $n_\perp$ are the microscopic refractive indices parallel and perpendicular to the director, respectively. In achiral nematic materials $n_\parallel$ and $n_\perp$ are related to the macroscopic ordinary and extraordinary refractive indices, n_e and n_o respectively, by $n_\parallel = n_e$, and $n_\perp = n_o$. As n_e and n_o have been measured in the pure monomesogens,[19,20] it is therefore possible to evaluate P_0 in the mixtures if it is assumed that the addition of a small quantity of chiral dopant has a negligible effect of the refractive properties of the nematogens. The refractive indices of the pure materials, measured at the reduced temperatures T_r indicated, and the pitch lengths of the chiral mixtures are given in Table 1. The reduced temperature is related to the measurement temperature T and the isotropic clearing temperature T_{clear} by $T_r = T - T_{clear}$.

The refractive indices n_e and n_o have been measured as functions of temperature in pure 7CB and 7OCB.[19,20] The values for the refractive index n calculated using these data are found to exhibit only a minor dependence on sample temperature over the range of interest to the present work; increases of less than +0.03 are noted as the samples are cooled from their clearing temperatures by 14 °C. Considering this observation, in conjunction with the small increases in selective reflection wavelengths noted over the same temperature ranges, it is clear that the helical pitch lengths of the mixtures vary little with temperature. Indeed, we find that the pitches of the

mixtures are invariant across the temperature ranges over which the selective reflection wavelengths have been measured.

As all three mixtures contain similar mesogenic groups, and therefore possess similar refractive properties, it is inferred that the pitch of the infrared-reflecting bimesogenic mixture is longer than those of the red- and blue-reflecting monomesogenic mixtures. On considering the visual appearance of this chiral nematic mixture and its textures, we estimate that its pitch is approximately 700 nm.

Dielectric coupling

Dielectric coupling to the mixtures proceeds as the electric field couples to the molecular dipole moments of the components. The dipole moment of the cyanobiphenyl group is large, calculated[15] to be of the order 19.4×10^{-30} C m (5.83 D), and acts along the major axis of the mesogen in the direction of the nitrile group (-C≡N). It is owing to the strength of this dipole that the values of the dielectric anisotropy of the pure achiral materials 7CB and 7OCB are positive and high,[19,21] as shown in Table 2. The dielectric anisotropy of the pure CBO8OCB achiral nematic material is also given in Table 2.[17] This material's dielectric anisotropy, while positive, is smaller than that of the monomesogenic materials. This diminution occurs because, in an extended conformation, the longitudinal dipole moments of the terminal mesogens are aligned anti-parallel. This arrangement reduces the longitudinal dipole moment acting along the molecule.

As with the achiral host nematic materials, the chiral nematic phases of the mixtures also display positive dielectric anisotropy. The critical fields required to unwind the helical structures of the mixtures are also given in Table 2. The decreased dielectric anisotropy of the bimesogenic material leads to a significant increase in the critical field required to unwind the helical structure, from ≈5 V μm^{-1} in the monomesogenic mixtures, to 18 V μm^{-1} in the CBO8OCB mixture. Furthermore, this increase in critical field appears despite the longer pitch of the bimesogenic system.

The critical field data presented in Table 2 come from electro-optic measurements made in 4 μm cells carrying rubbed polyimide (planar) alignment layers. The helix-unwinding fields of the monomesogenic mixtures were also evaluated in thicker cells (7 μm) using either rubbed polyimide or lecithin (homeotropic) alignment layers and, in each case, it was found that the choice of cell thickness or surface alignment treatment has little or no effect on the critical field for helix-unwinding.

Once a material has been suitably aligned in order to observe flexoelectric switching, the mechanical manipulation process is no longer required. However, owing to the effect of surface interactions, the uniform lying helix texture of the mixtures is not stable over time in cells treated with rubbed polyimide, unless an electric field is continuously applied in order to prevent a standing helix (Grandjean) texture from becoming established. The lying helix texture is much more stable in cells treated with lecithin. Indeed, we have found that in such a cell

Table 2 Dielectric properties of the host materials and mixtures. The relative dielectric anisotropy data $\Delta\varepsilon$ are taken from the references given in the text

Host material	Relative dielectric anisotropy $\Delta\varepsilon$ of host $(T_r/°C)$	Helix-unwinding field in mixture/ V μm^{-1} $(T_r/°C)$
7OCB	+8.8(−8)	5.2(−2)
7CB	+10.6(−8)	4.0(−1)
CBO8OCB	+3.3(−27)	18(−22)

the lying helix texture can be stored for days in the absence of an electric field, without showing evidence of any degradation in alignment.
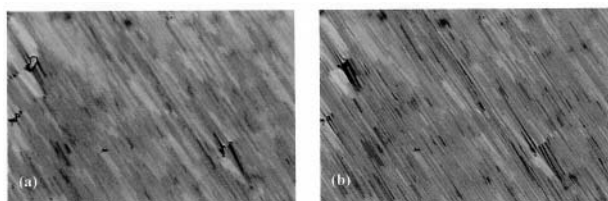
The appearance of blue phases introduces an interesting aspect to the discussion of the effects of dielectric coupling. In an unperturbed blue phase, helical structures can develop in all directions orthogonal to the director simultaneously, forming a "double twist" cylinder arrangement.[22] It has been observed previously[23,24] that on applying an electric field at a given frequency and a sufficiently high amplitude across a sample possessing positive dielectric anisotropy while it is in BPI (the highest ordered of the three blue phases), a non-turbulent chiral nematic structure is established in its focal conic form. This observation indicates that the propensity of this phase to allow the helical structure to propagate in all directions is overcome by the effects of dielectric coupling on the application of an electric field.

We have found that the occurrence of BPI is highly beneficial to the alignment process for flexoelectric switching. On testing several materials possessing blue phases in cells treated to promote planar molecular alignment (on one or both surfaces), we have found that it is usually possible to obtain the uniaxial lying helix geometry without the use of any mechanical manipulation: in each case excellent uniaxial lying helix alignment was obtained by simply holding the sample in the blue phase, while applying an electric field. [Our other test materials include chiral additive-doped 5OCB, 6OCB and a number of bimesogenic materials.] A uniaxial lying helix texture develops and is retained as the sample is cooled, in the presence of the field, into the chiral nematic phase. A cell treated to promote homeotropic alignment does not produce this uniaxial texture under the same experimental conditions; a scattering focal conic texture is obtained instead. It appears that the easy axis of a planar alignment layer acts to promote uniaxial alignment, by breaking the degeneracy of the helical structure propagating in BPI at all azimuths normal to the applied field direction. The helix axis of the spontaneously-aligned texture lies parallel, to within a couple of degrees, to the easy axis of the alignment layer. Fig. 3(a) is a photomicrograph of the uniformly lying helix texture spontaneously formed on the application of an electric field across the blue phase of the 7OCB mixture. Fig. 3(b) shows the same area after the sample was cooled into its chiral nematic phase with both mechanical shear and the same applied field.

The exploitation of blue phase-exhibiting chiral nematic liquid crystals has not been previously reported in this field of liquid crystal research. The ease with which a lying helix monodomain forms in these materials is potentially very useful and warrants further investigation.

Flexoelectric coupling

Each of the mixtures interacts strongly with an electric field *via* flexoelectric coupling, responding with $\tau \leqslant 120\,\mu s$ to exhibit a large optic axis rotation angle at a given applied field. The

response times and optic axis rotation angles of the 7OCB and 7CB mixtures were characterised as functions of applied field amplitude and temperature. The properties of the CBO8OCB mixture were examined as a function of applied field amplitude while the mixture was maintained at a constant temperature of 183 °C.

Fig. 4(a) shows the flexoelectrically-induced optic axis rotation angles ϕ of all three mixtures as a function of applied field amplitude E. Data sets were taken across the temperature range from $-12\,°C \leqslant T_r \leqslant -1\,°C$ for each of the monomesogenic mixtures. The behaviour of the these materials was invariant with temperature across this range; for this reason only a single data set is shown to exemplify the behaviour of each mixture. On comparing the responses of the three mixtures it is seen that the optic axis rotation angle at a given applied field increases as the helical pitch of the material increases, in agreement with the trend predicted by the theory [eqn. (2)]. Most significantly, however, the maximum rotation angles observed in the monomesogenic mixtures are limited to $\phi \leqslant 6°$ (before helix-unwinding occurs at $E \sim 5\,V\,\mu m^{-1}$), while in the CBO8OCB mixture much higher rotation angles are observed. We find that in the bimesogenic mixture a deflection of $\phi = 22.5°$ is measured at $E = 6\,V\,\mu m^{-1}$: *i.e.* a complete rotation through 45°, as required for maximum contrast in a birefringence switching regime, is observed when a $\pm 20\,V$
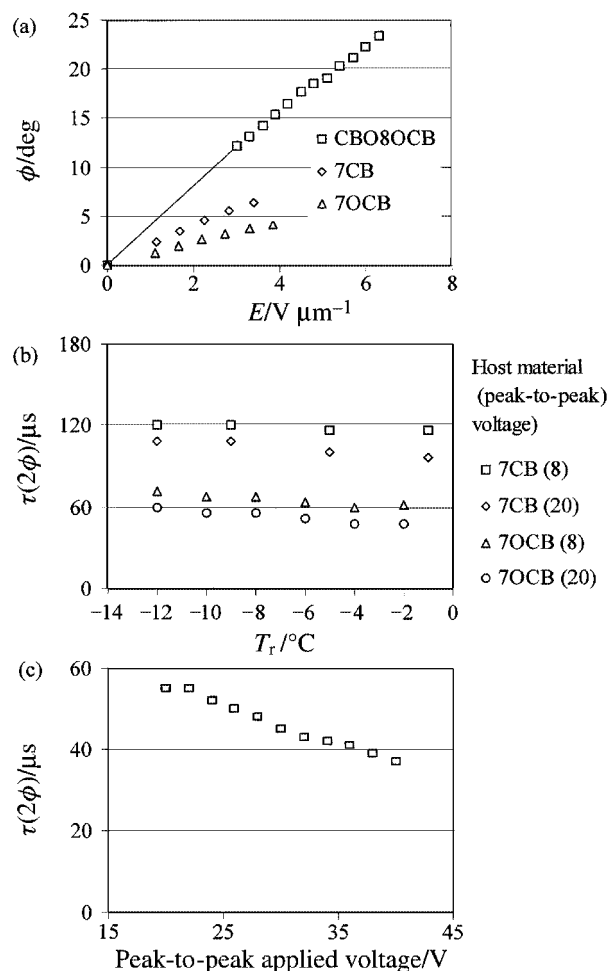
Fig. 4 The graph shown in (a) illustrates the angle of rotation of the optic axis ϕ as a function of the applied field amplitude E for the three mixtures. Graph (b) shows the variation in response time $\tau(2\phi)$ as a function of reduced temperature T_r of the monomesogenic mixtures containing 7CB and 7OCB. These samples were contained in 3.5 μm-spaced electro-optic cells. Graph (c) shows $\tau(2\phi)$ as a function of the peak-to-peak voltage applied across a 3.3 μm sample of the bimesogenic CBO8OCB mixture.

Fig. 3 Uniformly-lying helix textures in the 7OCB mixture. Photograph (a) shows the lying helix texture that is obtained, without mechanical shearing, on the application of an 80 Hz square waveform field of amplitude 2.5 V μm⁻¹, within the blue phase. Photograph (b) shows the same area of cell after cooling into the chiral nematic phase (the applied field is not altered). The image magnification is ×50 in each case.

Table 3 Flexoelectric properties of the chiral mixtures. The table shows: the gradients of linear regressions to tan ϕ *vs.* E; the values of the ratio $\bar{e}/K$; splay elastic constants K_{11} of the pure host materials at the reduced temperatures T_r indicated, which are taken from the references given in the text; and the effective flexoelectric constants $\bar{e}$

| Host material	Gradient of fit to tan ϕ *vs.* E/μm V^{-1}	$\bar{e}/K$/C N^{-1} m^{-1}	K_{11}/N (T_r/°C)	$\bar{e}$/C m^{-1} (T_r/°C)
7CB	3.3×10^{-2}	5.0×10^{-1}	4.9×10^{-12} (-7)	2.4×10^{-12} (-7)
7OCB	1.9×10^{-2}	4.0×10^{-1}	4.6×10^{-12} (-7)	1.8×10^{-12} (-7)
CBO8OCB	6.3×10^{-2}	$\approx 6 \times 10^{-1}$	13.3×10^{-12} (-7)	$\approx 8 \times 10^{-12}$ (-27)

bipolar signal is applied across a 3.3 μm sample of this mixture. This is a great improvement over any chiral nematic material previously examined. Indeed, the helical structure of the CBO8OCB mixture does not unwind until a critical field of 18 V μm^{-1} is reached, which indicates that even higher rotation angles are possible. The results illustrated in Fig. 4(a) are analysed in more detail below.

The flexoelectrically-induced electro-optic switching effect in the mixtures is fast. Fig. 4(b) illustrates the response times $\tau(2\phi)$, corresponding to a complete rotation through 2ϕ, measured in the monomesogenic mixtures as a function of temperature. Two data sets are shown for each mixture and were obtained by applying waveforms of differing peak-to-peak voltage across the cells. The behaviour of these mixtures is typical: a decrease in either the sample temperature or the applied voltage results in an increase in response time. Eqn. (4) indicates that a material with a shorter helical pitch exhibits a faster response time than a material of similar viscoelastic properties with a longer helical pitch. On comparing the behaviour of the mixtures we find that the 7CB mixture, which has a longer pitch than the 7OCB mixture, does exhibit longer response times-in broad agreement with the theory.

Fig. 4(c) shows the response time of the CBO8OCB mixture, measured at 183 °C as a function of applied peak-to-peak voltage. Again it is clear that the response times decrease as the voltage applied across the material is increased. Despite its increased pitch, however, the response of the bimesogenic mixture is faster than those of the 7OCB and 7CB mixtures: this diminished response time is likely to be attributable to the high temperature at which the measurements were made, as the viscosity of the phase appears to be very low at this temperature (see section Materials).

The gradients of linear regressions fitted to plots of tan ϕ *vs.* E are given in Table 3. Using these data and the helical pitch lengths reported in Table 1, the ratios $\bar{e}/K$ in the materials can be evaluated by applying eqn. (2): the results are included in the table. In each of the mixtures based on 7OCB and 7CB, the temperature invariance of both the helical pitch lengths and the relationships between tan ϕ and E, gives rise to temperature independent ratios $\bar{e}/K$. We note that the values of $\bar{e}/K$ in the three mixtures, ranging from 0.4 to 0.6 C N^{-1} m^{-1}, are similar to values measured in other BDH1305-doped monomesogens (see above) and estradiol-cyanobiphenyl bimesogens,[8,9] which range from 0.4 to 0.5 C N^{-1} m^{-1}: these are the highest values reported in any chiral nematic liquid crystals. This observation adds to the evidence suggesting that it is the presence of the cyanobiphenyl moiety in the estradiol-cyanobiphenyl bimesogens that governs their strong flexoelectric coupling mechanisms[14] (see section Introduction).

In passing, we note that the behaviour of BDH1305 doped monomesogenic nematic hosts such as 5CB, 5OCB and 6OCB is very similar to that of the 7CB and 7OCB mixtures discussed here: taking variations in helical pitch into account, neither the magnitudes of ϕ (E) nor the response times vary widely amongst these mixtures at a given applied field amplitude and reduced temperature. The maximum tilt angles observed before dielectric coupling destroys the helical structure are also very similar, at less than 8°. Additionally, on testing the electro-optic switching behaviour of several such mixtures in 4 μm and
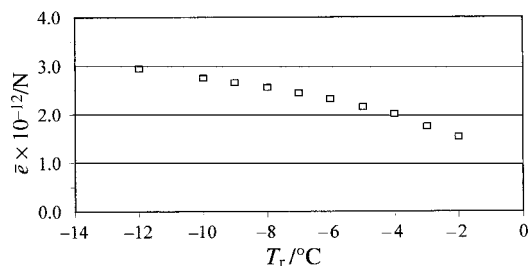
Fig. 5 The graph illustrates the variation in effective flexoelectric coefficient $\bar{e}$ as a function of reduced temperature T_r in the 7CB mixture.

7 μm cells carrying either rubbed polyimide or lecithin alignment layers, we have found that changing these boundary conditions does not alter the switching characteristics of the material examined.

If it is assumed[2] that the splay elastic constants K_{11} measured in the pure host materials[17,19,20] are approximately equal to their effective elastic constants K, it becomes possible to evaluate the (temperature dependent) flexoelectric coefficient. Fig. 5 shows $\bar{e}$ calculated as a function of reduced temperature, for the 7CB mixture. The effective flexoelectric coefficient exhibits the same temperature dependent behaviour as the splay elastic coefficient: although $\bar{e}/K$ is invariant with temperature, the value of $\bar{e}$ has quite a strong temperature dependence, decreasing in magnitude by a factor of 0.5 over 12 °C as the chiral nematic-to-isotropic transition is approached. The values of the coefficient $\bar{e}$, calculated for the mixtures at the particular reduced temperatures indicated, are shown in Table 3.

In order to identify the effect on flexoelectric coupling of increasing the magnitude of the transverse molecular dipole, we compare the values of the ratio $\bar{e}/K$ calculated for the 7OCB and 7CB mixtures: the ratio is a factor of 1.25 times *larger* in the 7CB mixture (at 0.5 C N^{-1} m^{-1}) than it is in the 7OCB mixture (0.4 C N^{-1} m^{-1}). This result does not tally with the observations made when comparing the properties of the pure achiral nematic materials 8CB and 8OCB, where it was found that the magnitude of the ratio $e*/K$ in 8CB is a factor of 0.19 times *smaller* than it is in 8OCB. We conclude that the presence of the transverse dipole in the oxycyanobiphenyl unit, which apparently plays such an important role in improving the response of the achiral nematic materials, does not strongly improve flexoelectric coupling in the chiral nematic phase. Moreover, the strong response of the 7CB mixture leads us to surmise that the longitudinal molecular dipole moment plays a significant part in governing the coupling mechanism.

The effective flexoelectric coefficient $\bar{e}$, which is determined for similar reduced temperatures in these mixtures, is found to be a factor of 1.33 times larger in the 7CB mixture (at 2.4×10^{-12} C m^{-1}) than it is in the 7OCB mixture (1.8×10^{-12} C m^{-1}). The sign of the effective flexoelectric coefficient is positive in both the 7CB and the 7OCB mixtures. In this, the behaviour of the chiral nematic mixtures deviates still further from that of the achiral monomesogens 8CB and 8OCB, which exhibit effective coefficients of opposite sign relative to one another. This leads to the inference that the

longitudinal molecular dipole moments may be of higher significance than transverse moments to a strong flexoelectric coupling mechanism in the chiral mesophases of the present mixtures.

The most obvious difference between the mixture based on CBO8OCB as a bimesogenic nematic host material and the monomesogenic 7CB and 7OCB mixtures is that dielectric coupling is significantly stronger in the monomesogenic materials: it is straightforward to see from Fig. 4(a) that dielectric coupling limits the magnitude of the switching of the optic axis to a much lower applied field amplitude in the monomesogenic mixtures than it does in the bimesogenic mixture. For this reason we suggest that the bimesogenic structure makes an excellent *template* for the design of molecules for flexoelectric coupling. Hence, a bimesogenic molecule containing mesogens that exhibit strong flexoelectric coupling mechanisms in other situations, substituted onto a spacer chain such that the lowest energy configuration has antiparallel aligned dipoles, will possess a low molecular dielectric anisotropy and should exhibit strong flexoelectric switching to a high field amplitude.

We must compare the relative strengths of the flexoelectric coupling mechanisms in our mixtures, separately from the dielectric coupling process, in order to come to some conclusion as to whether a bimesogenic molecular form can also improve the potency of flexoelectric coupling.

On comparing the values of the ratio $\bar{e}/K$ shown in Table 3, it can be seen that in the bimesogenic mixture the magnitude of $\bar{e}/K$ ($0.6 \text{ C N}^{-1} \text{ m}^{-1}$), though larger than has been previously reported in any chiral nematic material, is only slightly increased over its value in the monomesogenic mixtures. We note also that the CBO8OCB mixture also possesses a very large effective flexoelectric coefficient ($\bar{e} \approx 8 \times 10^{-12} \text{ C m}^{-1}$). No discussion is included here of the difference between the values of $\bar{e}$ determined for the bimesogenic material and those calculated for the monomesogens because the estimates presented here are made at widely different reduced temperatures. However it is clear that for CB080CB the role of the bimesogenic structure in increasing the absolute flexoelectric coefficient is almost hidden in the $\bar{e}/K$ comparison by the concomitant increase in $K_\parallel$.

The similarity of the values of $\bar{e}/K$ in the monomesogenic and bimesogenic materials indicates that the bimesogenic molecular form does not profoundly improve the flexoelectric coupling properties of the material *per se* (cf. eqn. (2) where tan ϕ/E is proportional to $\bar{e}/K$). Rather, the bimesogenic structure with its long aliphatic chain decouples effectively the terminal mesogens and allows them to interact with the electric field with a degree of independence. This supposition implies that the electric field couples to the large longitudinal dipoles acting along the terminal cyanobiphenyl groups, instead of interacting with the small dipole of the molecule as a whole. The similarity of the values of $\bar{e}/K$ in our mixtures also appears to indicate that the larger elastic constants measured in bimesogenic materials, compared with monomesogenic liquid crystals, are mirrored by a proportionate increase in the effective flexoelectric coefficient $\bar{e}$. Hence we infer that the structure–property relationships governing elastic constants also influence directly the flexo-electric coefficients of a material. It may be possible to observe parallels in the responses of both sets of parameters to changes in molecular structure.

Conclusions

In this work we have been chiefly concerned with a comparison of the properties of the cyanobiphenyl and oxycyanobiphenyl mesogenic units as contributors to the flexoelectric coupling mechanism in the chiral nematic phase. Examination of the behaviour of mixtures composed of the monomesogenic

materials 7CB and 7OCB doped with a chiral additive reveals strong similarities in their characteristic features: the magnitudes of the ratio of the effective flexoelectric coefficient to the mean elastic constant $\bar{e}/K$ are large and nearly equivalent, at $0.4 \text{ C N}^{-1} \text{ m}^{-1}$ in 7OCB and $0.5 \text{ C N}^{-1} \text{ m}^{-1}$ in 7CB. Very significantly, we find that the flexoelectric coefficients in these mixtures have the same sign. These observations lead us to surmise that the presence of a large longitudinal molecular dipole, found owing to the presence of the cyanobiphenyl group in both 7CB and 7OCB, might be of great importance to the design of a molecular structure for flexoelectric coupling in the chiral nematic phase. That the sign of $\bar{e}$ is the same in both materials indicates that the presence of a significant transverse molecular dipole on the oxycyanobiphenyl mesogen does not strongly affect the flexoelectric coupling mechanism. This does not agree with the observed behaviour of *achiral* nematic materials, where it has been found that the introduction of a transverse dipole on exchanging 8CB for 8OCB, reverses the sign of the flexoelectric coefficient measured.[16]

The properties of a bimesogenic mixture comprising the nematic host CBO8OCB doped with a chiral additive clearly illustrate that increases in the size of the maximum rotation of the optic axis are possible if materials possessing low dielectric anisotropy are utilised. Despite its increased pitch, the critical field required to unwind the helical structure of the bimesogenic mixture is at least three times larger than the fields required to unwind the 7CB and 7OCB mixtures. Thus larger optic axis rotation angles are observed in the bimesogenic mixture because higher fields may be applied across the lying helix texture. We note that it does not appear that the bimesogenic structure improves the degree of flexoelectric switching itself, as the value of $\bar{e}/K$ is, at $0.6 \text{ C N}^{-1} \text{ m}^{-1}$, only slightly higher in this mixture than it is in the monomesogenic mixtures. Instead the bimesogenic molecular structure allows the terminal mesogenic units to respond as strongly as they would if they were parts of monomesogenic molecules, rather than moieties in a bimesogen. However, we note that the absolute value of e is significantly increased (by a factor of 4), along with K in this system. We believe that the bimesogenic molecular structure is the key to developing new materials for the flexoelectric switching effect and are currently investigating the properties of room temperature bimesogenic materials.

We have discovered that the existence of blue phases promotes the easy formation of the uniaxial lying helix texture. We have examined several materials that exhibit blue phases and possess positive dielectric anisotropy. We find that such materials, when enclosed in cells treated with a planar alignment layer on at least one surface, spontaneously form a uniaxial lying helix texture when an alternating electric field is applied across the material while it is in BPI. No mechanical manipulation, such as a shearing process, is required in order to obtain a uniaxial texture. (The sole use within a cell of degenerate homeotropic alignment layers, however, does not aid the alignment process; a scattering multidomain focal conic texture is formed instead.) The uniaxial texture is retained as the sample is cooled into the chiral nematic phase under the applied field. With regard to the experimental conditions, we note that the amplitude of the electric field must not be so high that it causes the mesophase to adopt a homeotropic texture. The frequency of the waveform plays a part in relation to the ease with which the lying helix texture is adopted, although this dependence appears to vary from one material to another. It will be interesting to investigate a wider range of blue phase-exhibiting materials in order to discover whether the useful alignment behaviour is an inherent feature of materials possessing blue phases. The effects of a range of alignment layers should also be examined.

The results presented here show that the flexoelectric behaviour of chiral materials can be significantly different to that of related achiral nematic materials. This clear difference

requires further experimental investigation: the signs and magnitudes of the flexoelectric coefficients of a range of nematic materials in both chiral and achiral forms must be quantified and compared. For example, racemic mixtures can be compared with racemates, and achiral nematic materials can be compared with chiral additive-doped mixtures. If the results from such a study should confirm our observations, it will become imperative that a model is developed to explain the discrepancy.

Acknowledgements

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