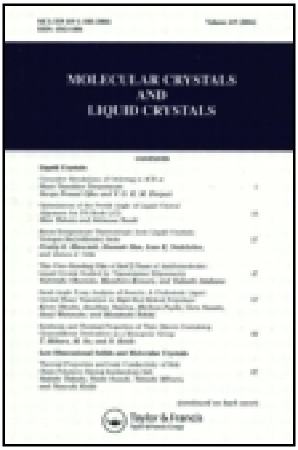

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FLEXOELECTRIC LIQUID CRYSTAL BIMESOGENS

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FLEXOELECTRIC LIQUID CRYSTAL BIMESOGENS

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Recently we have shown that short pitch chiral nematogenic bimesogens may be synthesized that couple weakly via the bulk dielectric anisotropy, but extremely strongly via the flexoelectric effect to give exceptional flexoelectric, room temperature, fast electro-optic switching characteristics. Typical switching times are 100 μs with bipolar switching angles of 90° at fields of 5 V μm^{-1}.

In the present work we show how changes to the molecular structure, namely replacing the ether linkages with ester groups, control the bulk flexoelectric switching properties of these bimesogenic nematic materials. Due to the strong monotropicity of the ester bimesogens, mixtures with the more enantiotropic ether linked bimesogens were made, and the effect on the flexoelectric coefficient behaviour investigated.

INTRODUCTION

In previous studies we demonstrated an integrated approach to molecular design for enhanced flexoelectric switching in the chiral nematic phase [1–3]. The flexoelectric-optic effect [4] in short pitch chiral nematic systems ($P < 1\,\mu$m) yields short optical response times of the order of $100\,\mu$s, and a temperature-independent optic tilt angle, which is linear with applied field amplitude [5]. This flexoelectric effect is observed in a parallel plate cell in which the helix of the twisted chiral nematic lies uniformly aligned parallel to the cell walls, known as the uniformly lying helix (ULH) texture, see Figure 1.

In the absence of a field the system is uniaxially birefringent with the optic axis in the same plane as the helix axis – see Figure 2(a). When a field is applied across the cell, i.e. normal to the helix axis, via ITO coated glass plates, a splay and bend deformation forms in the rotated director

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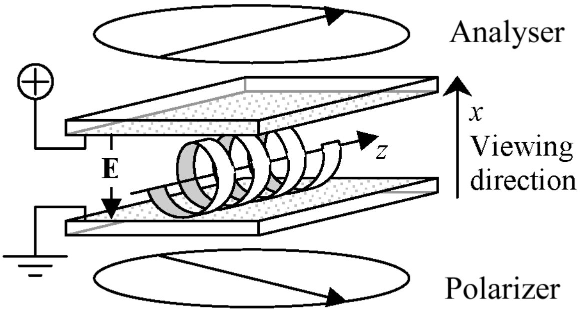


FIGURE 1 Schematic of the ULH flexoelectric cell geometry required to observe the birefringence switching effect.

plane – see Figure 2(b). The rotation of the optic axis is linear with, and follows the sign of E, and is related to the helical pitch of the phase through [4]

$$\tan\phi = (eEP)/(2\pi K), \tag{1}$$

where K and e are the effective elastic constant and flexoelectric coefficient of the phase, respectively: $K = (K_{11}+K_{22})/2$ and $e = (e_{\text{splay}} + e_{\text{bend}})/2$. The response time τ of the flexoelectric-optic switching is given by $\tau = P^2\gamma/(4\pi^2 K)$, where γ is the effective viscosity associated with the helix distortion [6].

Dielectric coupling must also be considered in the design of suitable materials. It is desirable to achieve a large deflection of the optic axis

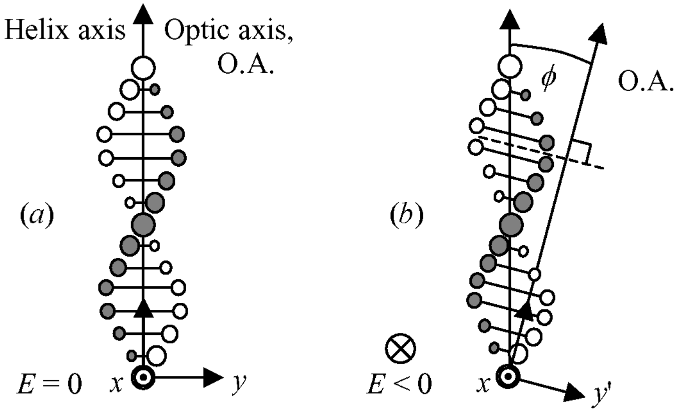
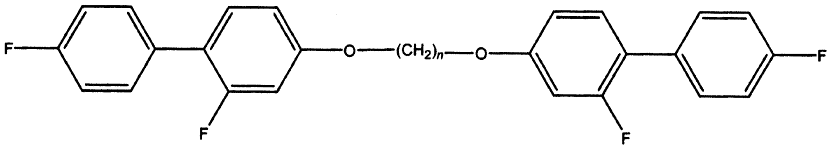


FIGURE 2 In (a) the directors of a right-handed helix are confined to the xy-plane, orthogonal to the helix and optic axes. In diagram (b) an electric field is applied along the -x direction: the director plane and optic axis are rotated via flexoelectric coupling by an angle $+\phi$ about the x-axis.

through an angle ϕ from the uniaxial geometry ($E = 0$, see Fig. 2(*a*)) before the dielectric coupling acts to realign the mean helical axis or unwind the axis completely to form a homeotropic nematic texture. Previous examples of flexoelectric switching [7] were demonstrated at low fields for materials with (usually) positive dielectric anisotropies. However, at higher fields dielectric coupling dominated this flexoelectric effect by causing the helix to unwind. In our integrated approach to molecular design [1–3] we reported materials with low dielectric anisotropies, which allowed the flexoelectric response to be extended to high field amplitudes. The approach was to design and synthesize ***symmetric*** bimesogenic molecules, such that the dielectric contributions of the two attached mesogenic moieties were minimised. These materials doped with chiral additives were found to exhibit a remarkable flexoelectric-optic response, where the optic axis was rotated through $2\phi = 45°$ in $<50\,\mu s$ on reversing the polarity of the field (amplitude $E = 6\,V\mu m^{-1}$). We have subsequently synthesized room temperature chiral nematic materials that exhibit outstanding switching behaviour of $2\phi \geq 90°$ at $E \approx 10\,V\mu m^{-1}$.

The bimesogens which exhibited this fascinating behaviour comprised of linking two mesogenic substituted-biphenyl moieties through a flexible alkyl spacer of varying chain lengths via ether groups – see structure **I**. As part of an ongoing investigation into how the molecular structure affects the flexoelectric optic switching properties we have synthesized a homologous series of liquid crystal bimesogens, similar in structure to series **I**, but where the ether (-O-) linkages have been replaced by ester (-COO-) groups – see structure **II**. In both series, *n* denotes the number of methylene units in the flexible alkyl spacer and are named **I***n* and **II***n*, respectively.



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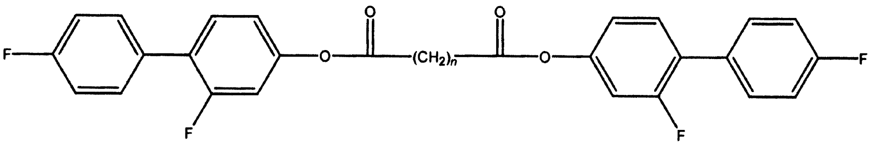

II

EXPERIMENTAL

The precursor 2,4′-difluorobiphen-4-ol was provided by Merck NBSC, U.K. Series I bimesogens were synthesized by coupling the precursor to a dibromoalkane via a standard Williamson etherification. Series II bimesogens were synthesized by coupling the precursor to an aliphatic α,ω-diacid using DCC and DMAP in DCM. Full experimental details will be published shortly.

The chiral additive used to dope the achiral nematogenic materials is commercially available from Merck, in this case BDH1281. This is a highly chiral dopant and at very low concentrations (3–5% w/w), can induce a helical pitch in the visible wavelength range. The electro-optic cells of approximately 5–7.5 μm thickness were coated with ITO and surface-alignment layers. The thermo-optic and electro-optic properties of the materials were determined by placing the sample cell, enclosed in a Linkam TMS90 hot stage connected to a temperature controller, between the crossed polarisers of an Olympus BH-2 polarising optical microscope (POM).

Alignment of the series **II** bimesogens (with positive dielectric anisotropy) was accomplished by mechanically stimulating the cells in a unidirectional mode whilst simultaneously applying an electric field, yielding a helix axis that lies orthogonal to the rubbing direction.

A rotation of the optic axis of the system is induced via flexoelectric coupling to an applied periodic alternating electric field, monitored by a photodiode detector recording the modulation in the light intensity transmitted by the cell. This rotation angle, and the response times are recorded as a function of applied field amplitude and temperature. For a detailed description of the method used to determine the optic axis deflection see reference [3]. Response times are taken as the time for the responding photodiode signal to increase from 0 to 90 per cent when the polarity of the driving square waveform field is reversed. In order to maximise the contrast between the two switched states, response times are measured with the undisturbed optic axis lying at 22.5° to the transmission axis of one of the microscope polarisers.

RESULTS AND DISCUSSION

The transition temperatures for the series **II** homologues are listed in Table 1. In this series of compounds the number of methylene units, n, in the spacer were $n = 9$–12 and 14. From these results we see this series possesses solely the nematic phase, which was recognised by its schlieren texture exhibiting both two and four point singularities and which flashed when subjected to mechanical stress. Figure 3 shows the effect of varying

TABLE 1 Transition Temperatures for the Series **II** Bimesogens. Parentheses Denote a Monotropic Transition

	Transition temperatures/°C				
n	Cr		N		I
9	•	93	(•	67)	•
10	•	109	(•	85)	•
11	•	99	(•	70)	•
12	•	110	(•	81)	•
14	•	108	(•	79)	•

the number of methylene units *n* in the flexible spacer on the liquid crystal behaviour for series **II**. We see that that there is a dramatic odd-even effect for both the liquid crystal-to-isotropic transitions and melting temperatures, typical of bimesogenic materials. As anticipated, the homologues with an even *n* lie on a curve above the odd *n* homologues due to the greater length-to-breadth ratio of the even *n* homologues in their all-*trans* conformation, allowing the mesogens to lie approximately parallel. It is also evident that the liquid crystal phases occur well below the melting point, by approximately −29°C.

Because of this strong monotropic nature, it was not possible to observe a chiral nematic mesophase over any meaningful temperature range.

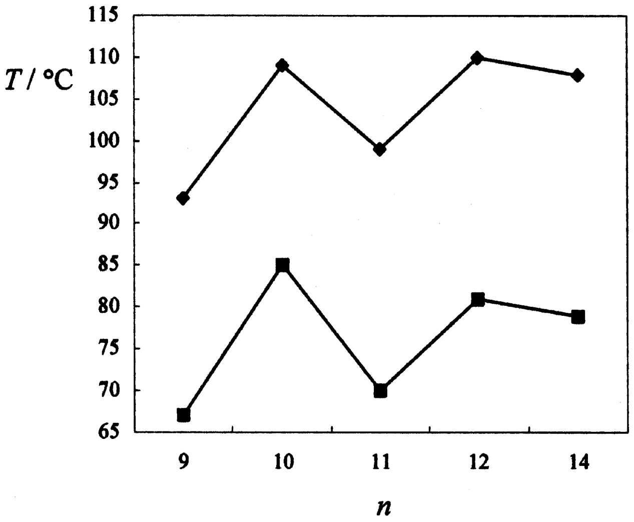

FIGURE 3 Transition temperatures for the series **II** bimesogens. [◆ = Cr-I; ■ = (N-I)]

A BDH-1281 doped mixture between the $n = 9$ and 11 homologues was prepared although the mesophase persisted only very close to the clearing transition and therefore measurements of the flexoelectric properties were made at a single reduced temperature of –2°C ($T_{NI} = 66$°C). It was found that the value of e/K of the mixture (2 $CN^{-1}m^{-1}$) was twice as high as those recorded in the series **I** bimesogens previously reported [1–3], which typically ranged from 1.0 to 1.2 $CN^{-1}m^{-1}$ on cooling from –5° to –25°C, or any of the other systems studied. However, being so close to T_{NI}, the result is likely to be affected by pre-transitional effects.

Thus, in order to gain a further insight into the properties of these series **II** ester-linked bimesogens, a series of mixtures with the more enantiotropic series **I** ether-linked bimesogens was investigated. These mixtures contained varying proportions of two ‘base’ two-component mixtures of homologues from the ether-linked and ester-linked bimesogenic series. The mixtures were then doped with a $\leq 3\%$ w/w concentration of BDH-1281. Thus the mixtures contained five constituent materials.

The ester series **II** two-component base mixture contained a 50% w/w concentration of **II**9 in **II**11. It should be noted that the exact proportion of one homologue in the other for these base mixtures is unlikely to be of great importance since such close homologues (i.e. similar in size and shape) are likely to have similar flexo-elastic properties. The ether series **II** base mixture contained a 25% w/w concentration of **II**9 in **II**11. In order to simplify the notation, the relative concentrations of the base nematic mixtures are quoted in the form $x\%$ series $\mathbf{II}_{(\mathrm{ester})} : y$ series $\mathbf{I}_{(\mathrm{ether})}$.

Figure 4 shows the electro-optic responses for one of the mixture studied (50:50 mix) measured at a shifted temperature of −10°C. The relationship between ϕ and E in this mixture is linear, in agreement with

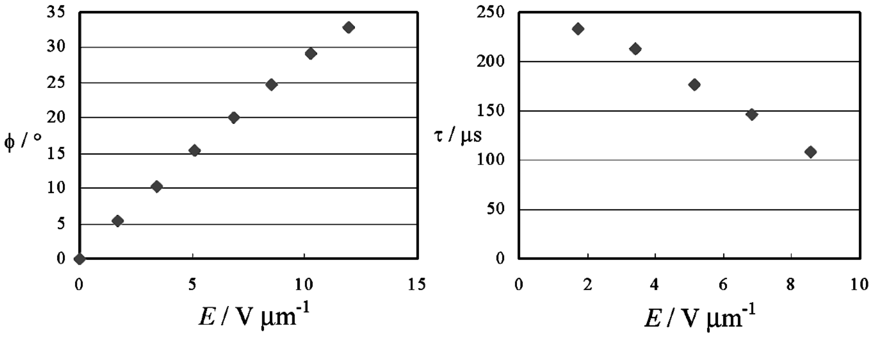

FIGURE 4 Behaviour of the 50:50 system ($T_r = -10$°C) typical of all the mixtures studied.

Eq. (1), and is typical of all the mixtures studied. The values of ϕ at a given field are similar to those observed for the series **I** bimesogens previously reported [1–3]. Furthermore, the values of ϕ recorded before helix unwinding are similarly high, owing to the low dielectric anisotropy of these bimesogenic systems. The response times for the 50 : 50 system are also given in Figure 4. As E is increased the value of $\tau_{(0-90)}$ decreases, in agreement with previous observations. These materials respond very quickly to variations in applied field amplitude, and these values are typical of all the mixtures studied.

The study of these materials were begun in the expectation that the typical value of *e*/*K* would increase proportionately with an increasing concentration x of the series **II** bimesogens which possess higher *e*/*K* ratios, in the series **I** : series **II** mixture. It was hoped that such results could be extrapolated to give an alternative measure of the behaviour of the $x = 100\%$ material as a function of temperature. Such an extrapolation might not only give a more accurate estimate of the typical value of *e*/*K* in this material than the single value that it was possible to measure directly, without pre-transitional effects distorting the results, but also to reveal the behaviour of the flexoelectric coefficient in mixtures.

However, instead of proportionate behaviour, the dependence of *e*/*K* on the relative concentrations $x : y$ appears to be discontinuous. Figure 5 shows the variation in the flexoelectric coefficient as a function of shifted temperature T_r for the mixtures. Figure 6 shows the dependence of *e*/*K* on the concentration of series $\mathbf{II}_{(\mathrm{ester})}$ in series $\mathbf{I}_{(\mathrm{ether})}$ at a fixed reduced temperature of −15°C. It is clear that the 0 : 100 and 20 : 80 mixtures lie in

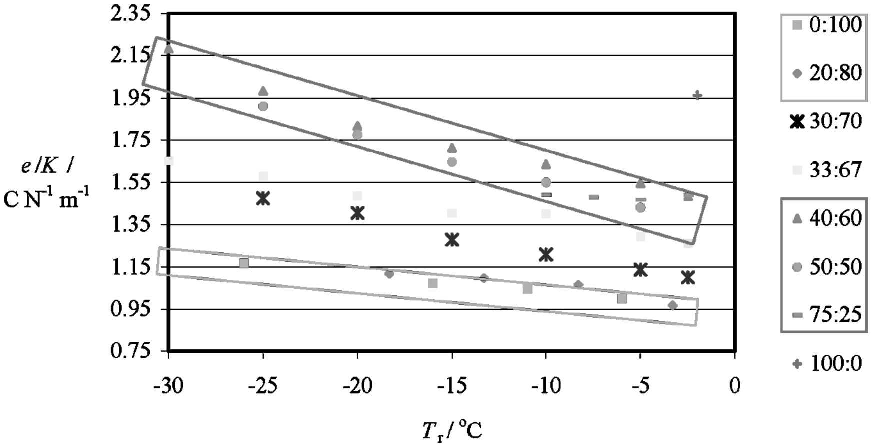

FIGURE 5 *e*/*K* data for the *x*% series $\mathbf{II}_{(\mathrm{ester})}$: y series $\mathbf{I}_{(\mathrm{ether})}$ mixtures. (See COLOR PLATE II)

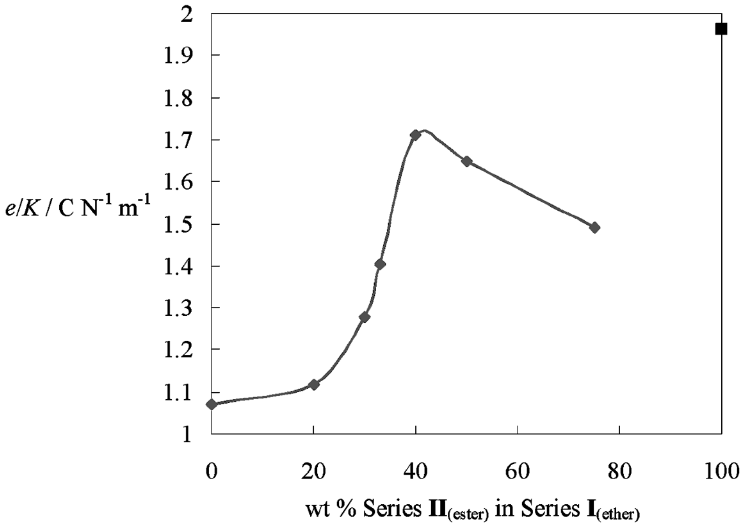

FIGURE 6 The dependence of *e*/*K* on the weight per cent of series $\mathbf{II}_{(\mathrm{ester})}$ in series $\mathbf{I}_{(\mathrm{ether})}$.

one group with lower values of *e*/*K*, and the 40 : 60, 50 : 50 and 75:25 mixtures in another with *e*/*K* values in the range 1.4 to 2.0 $\mathrm{CN^{-1}m^{-1}}$. The critical transition behaviour for the mixtures is exhibited by the data sets 30:70 and 33:67, which have intermediate values for *e*/*K* lying between the grouped data sets.

The initially recorded data point for the 100% series **II** system is also shown in Figures 5 and 6. However, the new data would indicate that this single data point is spurious since it lies well away from the curve drawn in Figure 6, presumably due to the pre-transitional effects alluded to earlier. Also, it seems likely that *e*/*K* for this mixture would traverse the same range of values exhibited by the higher group over the range of reduced temperatures shown. Hence, the original aims of this study may be fulfilled, although not by extrapolating proportional relationships between the concentration of the series **II** ester mixture and the values of *e*/*K* exhibited by the mixture with series **I** as was originally envisaged.

If this critical behaviour is demonstrable in other mixtures, it has consequences for future work on flexoelectricity. For example, mixtures can be made between materials with differing typical *e*/*K* values, yet the mixture may retain the larger coupling constant of the high *e*/*K* material even though the low *e*/*K* material (which may be chosen to enhance other desirable properties, such as a low viscosity) may be present at high concentrations.

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