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A study of the electroclinic effect in the smectic A* phase of mixtures with strongly chiral alkoxybiphenyl-phenyl carboxylate dopants

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A detailed investigation has been reported of the electroclinic behaviour in the smectic A* phase of eleven mixtures made up of a commercial achiral smectic C host and strongly chiral alkoxybiphenyl-phenyl carboxylate dopants. A new technique was used to measure the induced tilt angle as a function of electric field and temperature. For all the mixtures, the electroclinic response followed a Curie–Weiss type temperature dependence for measurements performed well away from the smectic A* to smectic C* phase transition temperature. The strength of the electroclinic response was evaluated for each mixture by determining the temperature independent ratio k/a (i.e. the electroclinic coupling susceptibility, k divided by the susceptibility coefficient controlling the induced tilt, a). Analysis of the results showed that k/a of the mixtures was dependent on the type and position of the electronegative or polar substituents that affected the net dipole moment of the chiral dopants. In fact, the value of k/a was largest when fluorine was replaced by hydrogen in the lateral position and at the chiral centre. Furthermore, relatively short alkyl chains (e.g. C_6H_{13}) at the chiral centre were preferred to longer ones (e.g. $C_{10}H_{21}$) for a larger electroclinic response.

1. Introduction

Tilted chiral smectic liquid crystals such as the chiral smectic C (S_C^*) type have ferroelectric properties which offer fast speed, high contrast, and bistable electro-optic switching characteristics when the intrinsic helical structure of these materials is suppressed [1, 2]. Ferroelectric liquid crystals have two stable states with opposite spontaneous polarization, P_S, which can be switched from one state to the other on a time scale of a few microseconds with a small external electric field applied. However, in orthogonal chiral smectic liquid crystals such as the chiral smectic A (S_A^*) type, the P_S is zero, but in these materials there exists a different switching mechanism which is typically 100 times faster. This is due to a phenomenon first reported by Garoff and Meyer [3, 4] in the late seventies known as the electroclinic (or soft mode ferroelectric) effect which results from the induction of a molecular tilt, θ, relative to the layer normal on applying an electric field in the direction parallel to the layer planes. A symmetry argument at the molecular level describes the origin of this effect [4].

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The molecular long axis or director $\hat{\mathbf{n}}$ in the S_A^* phase lies in the direction parallel to the normal of the smectic layers. On application of a d.c. electric field, the natural behaviour of the molecules to rotate freely about their long axes is biased due to the tendency of the transverse component of the permanent dipole moment $\boldsymbol{\mu}$ to orient along the electric field, E. For an achiral system, the plane containing $\hat{\mathbf{n}}$ and $\boldsymbol{\mu}$ is a mirror plane, but if the molecules are chiral, all mirror symmetry is eliminated. Hence, the free energy is no longer symmetric about the $\hat{\mathbf{n}}$ and $\boldsymbol{\mu}$ plane, resulting in an induced tilt perpendicular to that plane. The linear coupling between the polarization and the induced tilt represents the electroclinic response of the S_A^* phase [4].

The electroclinic effect can also be observed in higher ordered non-tilted chiral phases, e.g. S_B^*, E* [5, 6]. Furthermore, a very small electric field-induced tilt of the optic axis in long pitch chiral nematics has been observed [7, 8] and can be linked to the build up of smectic order which has the effect of quenching the local helical structure in the phase. Most studies of the electroclinic effect have been carried out in the S_A^* phase, because the induced tilt angle is relatively large in this

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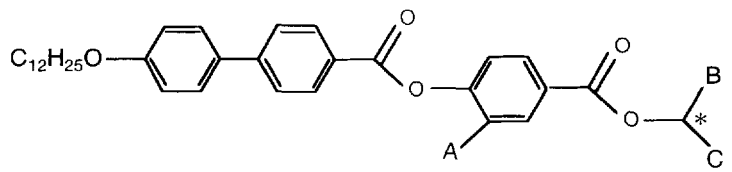
phase, and for a large number of materials, the S_A^* phase is exhibited over a wide temperature range. Since the magnitude of the electroclinic response is highly dependent on the strength of the coupling between tilt angle and polarization, in order to maximize the electroclinic response, compounds have been designed to exhibit a large P_S [9]. The induced tilt can be as large as $\sim 20°$ [10, 11], but typically is $\leqslant \sim 10°$ [9, 12, 13] for a reasonable applied electric field (i.e. $\sim 10\ V\ \mu m^{-1}$). The relatively small induced tilt available can be compensated by using more than one electroclinic cell and/or other optical components so that it is possible to construct devices which provide full transmitted light modulation [13], and perform logic operations based on three different polarization states [14]. An electroclinic device in conjunction with a suitable photosensor can be used as an optically addressed spatial light modulator which has generated interest recently for many potential applications (e.g. optical data processors, image amplifiers) [15]. The electroclinic response varies continuously with the field and does not show bistability so that continuous grey scale or even colour scan applications are possible [13, 16]. Switching behaviour and the electro-optic response of the electroclinic effect have been investigated in detail by Abdulhalim and Moddel [17]. A summary of the basic principles and experimental background of the electroclinic effect is provided by Andersson *et al.* [18]. The potential and limitations of using the electroclinic effect in device applications is reviewed by Davey and Crossland [19].

For fundamental research, the electroclinic effect can be used as a probe for studying the critical behaviour of the $S_A^* \rightarrow S_C^*$ phase transition [20, 21]. One recent study by Glogarova *et al.* [22] reported how the electroclinic parameters were influenced by chirality. In their work, the left and right-handed versions of a S_C^* material were mixed to change the substance's chirality. In our work, we have aimed at developing the electroclinic effect as a method for investigating the chiral strength of molecules by establishing quantitative relationships between electroclinic phenomena and structure of chiral molecules. Hitherto, little work involving structure–property correlations of the electroclinic effect has been performed [10, 23]. Bahr *et al.* [24] have reported results for an homologous series of liquid crystals and showed that the electroclinic response was increased slightly as the length of the terminal alkyl chain was increased, as well as showing odd–even behaviour. In this paper, we report electroclinic measurements on mixtures with a commercial achiral S_C host doped with strongly chiral alkoxybiphenyl-phenyl carboxylate materials. Some of these dopants exhibit antiferroelectric and ferrielectric phases, and their structures are illustrated in the table. We show how the electroclinic response is influenced by the molecular structure of these dopants and discuss the possible reasons for the structure–property relationships

Phase behaviour of the alkoxybiphenyl-phenyl carboxylates.



Compound number (Absolute config.)	A	B	C	Phase transition temperature/°C											
				I		S_A^*		S_C^* (ferro)		$S_{C_\gamma}^*$ (ferri)			$S_{C_A}^*$ (antiferro)		Cr
1(*S*)	H	CH_3	C_6H_{13}	●	131·7	●	122·0	●	107·8	●			—	37·3	●
2(*S*)	F	CH_3	C_6H_{13}	●	107·5	●	89·5	●	81·9	●	79·0	●	31·0		●
3(*R*)	H	CH_3	C_8H_{17}	●	124·0	●	113·9	●	93·5	●	43·1	●	35·9		●
4(*R*)	F	CH_3	C_8H_{17}	●	100·1	●	85·7	●	59·3	●	46·9	●	32·2		●
5(*R*)	F	CH_3	$C_{10}H_{21}$	●	95·6	●	80·9	●				—	34·7		●
6(*R*)	H	C_2H_5	C_8H_{17}	●	93·8	●	84·0	●	83·9	●		—	38·9		●
7(*R*)	F	C_2H_5	C_6H_{13}	●	73·6	●	59·9	—		···		●	<23·6[a]		●
8(*S*)	H	CH_2F	C_6H_{13}	●	120·6	●	112·5	●	68·0	●	56·1	●	55·5		●
9(*S*)	H	CH_2F	$CH_2OC_6H_{13}$	●	132·4	●	114·5	●		—		···	60·9		●
10(*S*)	F	CH_2F	C_6H_{13}	●	94·4	●	76·3	●		—		—	44·9		●
11(*S*)	F	CH_2F	$CH_2OC_6H_{13}$	●	105·5	●	85·3	●		—		—	47·4		●

Data recorded by thermal polarizing microscopy at a cooling rate of $-2°C\ min^{-1}$.
[a] Thermal equilibrium could not be maintained.

observed. Furthermore, we discuss how the electroclinic measurements were performed using a new experimental arrangement.

2. Theory

To interpret our experimental results presented later, we need to consider the mean field theory which can be used to describe the main features of the electroclinic effect. The Landau free energy density of the S_A^* phase in the presence of an electric field applied parallel to the smectic layers can be written to fourth order in θ as [4, 25]:

$$G = G_0 + \tfrac{1}{2}A\theta^2 + \tfrac{1}{4}B\theta^4 + \tfrac{1}{2}\chi_p^{-1}P^2 - PE - \frac{1}{8\pi}\varepsilon_0 E^2 - \eta\theta P. \tag{1}$$

The first three terms are the beginning of the Landau series expansion where G_0 represents the contribution to G for the S_A^* phase without the electric field applied. For a racemic mixture, A is zero at the phase transition temperature (T_0) so that $A \propto (T - T_0)$, and B is a temperature independent constant. The following three terms of the series describe the electrostatic free energy, where P is the component of the average molecular polarization parallel to E, ε_0 is the dielectric constant without contributions from the permanent dipole moment, and χ_p is the generalized susceptibility. Finally, the last term shown in equation (1) represents the electroclinic coupling between P and θ to first order, where η is the electroclinic coupling constant. Only the terms PE and $\eta\theta P$ in equation (1) depend on the chirality of the system.

We can minimize with respect to P, by setting $\partial G/\partial P = 0$, and obtain the result:

$$P = \chi_p(E + \eta\theta) \tag{2}$$

which can be substituted for P in equation (1) to give:

$$G = G_0 + \tfrac{1}{2}(A - \chi_p\eta^2)\theta^2 + \tfrac{1}{4}B\theta^4 - \chi_p\eta E\theta - \frac{1}{8\pi}(\varepsilon_0 + 4\pi\chi_p)E^2. \tag{3}$$

In the coefficient of θ^2, the appearance of the extra term $\chi_p\eta^2$ represents a shift in the phase transition from T_0 due to the coupling of P and θ [3, 4]. Hence, for a chiral mixture, if we set $A' = A - \chi_p\eta^2$ for simplicity, then $A' = a(T - T_c)$, where a is a constant and T_c is the temperature of the $S_A^* \rightarrow S_C^*$ phase transition. Now, if E is the only independent variable, we can minimize G with respect to θ by setting $\partial G/\partial\theta = 0$ and obtain the result:

$$A'\theta + B\theta^3 - \chi_p\eta E = 0 \tag{4}$$

At sufficiently small fields and correspondingly small θ, the induced tilt is always linearly proportional to E, so that equation (4) can be simplified to:

$$\theta = \frac{\chi_p\eta E}{A'} \tag{5}$$

However, on approaching close to T_c the contribution of the $B\theta^3$ term in equation (4) increases substantially with an increasing field, which implies non-linear behaviour of θ. In fact, for large fields and for temperatures close to T_c, θ is expected to be proportional to E^α, where α lies in the range $\frac{1}{3} \leqslant \alpha < 1$ [26]. For a.c. electric fields, the induced tilt angle is modulated, and it has been suggested [14] that close to T_c, the a.c. electroclinic response may include contributions from the molecular tilt (soft mode) and changes in the azimuthal angle (Goldstone mode) as the tilt angle changes sign. In this work, we have only used d.c. fields for measuring the electroclinic response, and so there will be no contributions from the Goldstone mode. Hence, we used the following expression to analyse our results:

$$\theta = e_c E \tag{6}$$

and the electroclinic coefficient, e_c is given by:

$$e_c = \frac{k}{a(T - T_c)} \tag{7}$$

where $k = \chi_p\eta$. Physically, a can be thought of as a susceptibility coefficient controlling the tilt of $\hat{\mathbf{n}}$. Glogarova *et al.* [22] inferred from their results that a was chirality independent, but it was shown that η varied linearly with substance chirality. This suggests k may give a measure of the chiral strength of a material. However, the magnitude of the ratio k/a gives a temperature independent measure of the electroclinic strength for a particular material. Therefore, it is important to be aware that a large electroclinic response may be due to a strong coupling between P and θ (large k) or an easy to tilt S_A^* phase (small a). Hence, ideally, it would be useful to measure both k and a to determine which is the dominant parameter controlling the strength of the electroclinic response. In fact, it is possible to measure k by performing simultaneous measurements of θ/E and the relative dielectric constant as a function of temperature [21]. To obtain values of k it is necessary also to perform dielectric measurements on the corresponding racemic mixture to take into account the polarization due to other causes (e.g. orientation). Unfortunately in this work, the corresponding racemic mixtures were not available, but since we were most interested in the overall electroclinic strength of the materials and how structural differences influenced this strength, the measurement of k/a was sufficient for our purposes. Furthermore, we have assumed that a of the S_C host is not modified by the chiral dopant and is not likely

to change significantly for relatively low dopant concentrations.

3. Experimental details

Earlier work to measure the electroclinic effect has either used manual signal nulling with a polarizing microscope [10, 27], or more commonly and accurately, synchronized detection of a modulated optical signal provided by a rotating analyser [28] or induced by the sample with an a.c. electric field applied, e.g. [25, 29, 30]. In our set-up for measuring the electroclinic response shown in figure 1, the polarized light originating from a 5 mW He–Ne laser (632·8 nm) source was modulated using a strain-induced birefringence device known as a photoelastic modulator. The optical elements were positioned at particular angles as shown in figure 1. On using matrix methods, the transmitted intensity (I) detected at the photodiode and measured by an EG&G, model 5210, lock-in amplifier can be expressed as:

$$I = \tfrac{1}{2}I_0\{1 - \tfrac{1}{2}[1 + \cos\delta_S]\cos(2\rho_{A_r} + \delta_M) - \tfrac{1}{2}[1 - \cos\delta_S]\cos(4\theta - 2\rho_{A_r} + \delta_M)\} \quad (8)$$

where δ_M is the modulator retardation, ρ_{A_r} is the angle of rotation of the analyser, and the sample retardation δ_S can be expressed as:

$$\delta_S = \frac{2\pi\Delta n d}{\lambda} \quad (9)$$

where d is the sample thickness and Δn is the birefringence of the sample. Since δ_M varies sinusoidially with time as $\delta_M = D\sin\omega t$, where D is a proportionality constant, and if $x = 2\rho_{A_r}$ or $x = 4\theta - 2\rho_{A_r}$ then:

$$\cos(x + \delta_M) = \cos x\cos(D\sin\omega t) - \sin x\sin(D\sin\omega t) \quad (10)$$

This can be expanded as a series in Bessel functions containing terms dependent on the fundamental frequency (ω), the second harmonic (2ω), and other higher harmonics:

$$\begin{aligned}\cos(x + \delta_M) &= \cos x\left[J_0(D) + 2\sum_{l=1}^{\infty} J_{2l}(D)\cos 2l\omega t\right] \\ &\quad - \sin x\left[2\sum_{l=0}^{\infty} J_{2l+1}(D)\sin(2l+1)\omega t\right] \\ &= J_0(D)\cos x - 2J_1(D)\sin\omega t\sin x \\ &\quad + 2J_2(D)\cos(2\omega t)\cos x - \ldots \end{aligned} \quad (11)$$

Hence, on considering only the fundamental frequency signal, the expression in (10) can be written as:

$$\cos(2\rho_{A_r} + \delta_M) = -2J_1(D)\sin\omega t\sin(2\rho_{A_r}) \quad (12)$$

or

$$\cos(4\theta - 2\rho_{A_r} + \delta_M) = -2J_1(D)\sin\omega t\sin(4\theta - 2\rho_{A_r}) \quad (13)$$

Substituting expressions (12) and (13) in equation (8) gives a useful general equation for detection at the fundamental frequency:

$$I = \tfrac{1}{2}I_0J_1(D)\sin\omega t\{[1 + \cos\delta_S]\sin(2\rho_{A_r}) + [1 - \cos\delta_S]\sin(4\theta - 2\rho_{A_r})\} \quad (14)$$

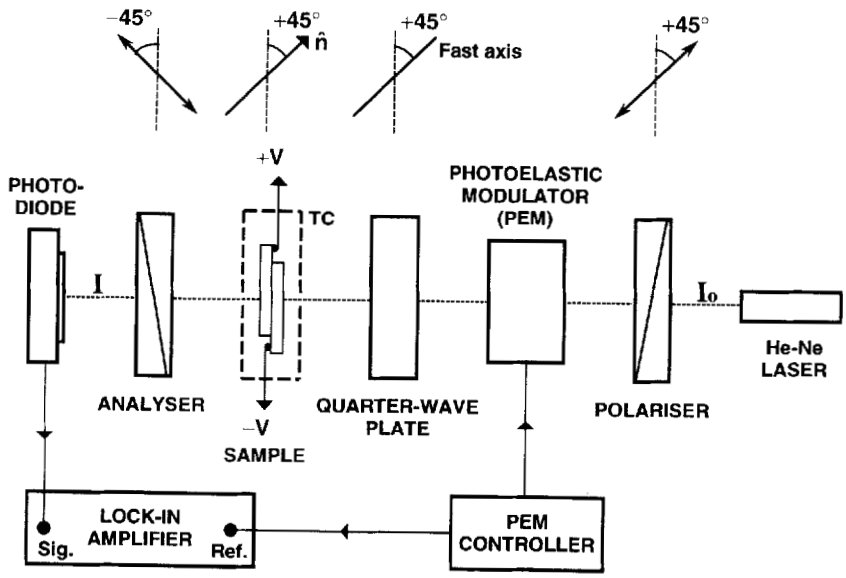


Figure 1. Experimental set-up for studying the electroclinic effect as a function of electric field and temperature.

where $J_1(D)$ is the first order Bessel function and is optimized (i.e. $J_1(D) = 0{\cdot}582$) by setting the peak-to-peak retardation of the modulator to 371 nm. Figure 2 illustrates how the ω signal measured by the lock-in amplifier, corresponding to the intensity in equation (14), varies as a function of ρ_{A_r} for a fixed δ_S and various induced tilts. If $\rho_{A_r} = 0°$, equation (14) can be simplified to:

$$I_{\rho_S=\theta+45°} = \tfrac{1}{2}I_0 J_1(D)(1 - \cos\delta_S)\sin\omega t \sin 4\theta \quad (15)$$

If θ is replaced by $\theta' = \theta - \rho_S$ in equation (15), where ρ_S is the angle of rotation of the sample stage, the fundamental frequency signal is zero when $\rho_S = \theta$. Hence, θ could be determined by measuring the angle of rotation of the sample stage when the ω signal is nulled for a particular d.c. voltage applied to the sample. However, this manual method of measuring the induced tilt angle tended to be subjective and time consuming.

We decided on a method for automatic measurement of the induced tilt angle by measuring a ratio of intensities. This method required no additional optics and the precision in measuring the induced tilt angle was better than $\pm 0{\cdot}01°$. Now, if the sample stage is rotated by $22{\cdot}5°$ from the ω signal null position with no electric field applied to the sample so that $\theta = 0°$, equation (15) can be written as:

$$I_{\rho_S=67{\cdot}5°} = \tfrac{1}{2}I_0 J_1(D)(1 - \cos\delta_S)\sin\omega t \quad (16)$$

On dividing equation (15) by equation (16) we obtain an expression which can be used to evaluate θ on measuring a ratio of intensities (i.e. $I_{\rho_S=\theta+45°}$ and $I_{\rho_S=67{\cdot}5°}$) and without the need for continuously rotating the sample stage:

$$\theta = \tfrac{1}{4}\sin^{-1}\left(\frac{I_{\rho_S=\theta+45°}}{I_{\rho_S=67{\cdot}5°}}\right) \quad (17)$$

This was confirmed by reproducing some of the results obtained manually. During the experiment, $I_{\rho_S=67{\cdot}5°}$ was measured initially by rotating the sample stage by $22{\cdot}5°$ from the position in figure 1 and recording the magnitude displayed on the lock-in amplifier. As this was the maximum value of the ω signal, the error in determining this value was very small. The sample stage was returned to $\rho_S = 45°$ and the residual voltage was noted from the magnitude displayed, but usually this value was too small to be significant. With no voltage applied to the sample cell, only a second harmonic (2ω) signal was detected at the photodiode. On applying d.c. voltages to the sample in $\sim 2{\cdot}5$ V steps, controlled by a Viglen PC, an increasing ω signal corresponding to the induced tilt appeared at the photodiode as well as the 2ω signal. Knowing $I_{\rho_S=67{\cdot}5°}$ the PC evaluated and recorded θ as a function of electric field at a particular temperature. This procedure was repeated at each temperature. In this technique, the application of only d.c. fields to the sample avoided the formation of the striped texture exhibited on applying a.c. fields, as reported by Pavel and Glogarova [31]. This domain formation can cause erroneous readings in the tilt angle due to the reduced birefringence and increased light scattering [32]. The d.c. fields may induce a very small ionic charge in the

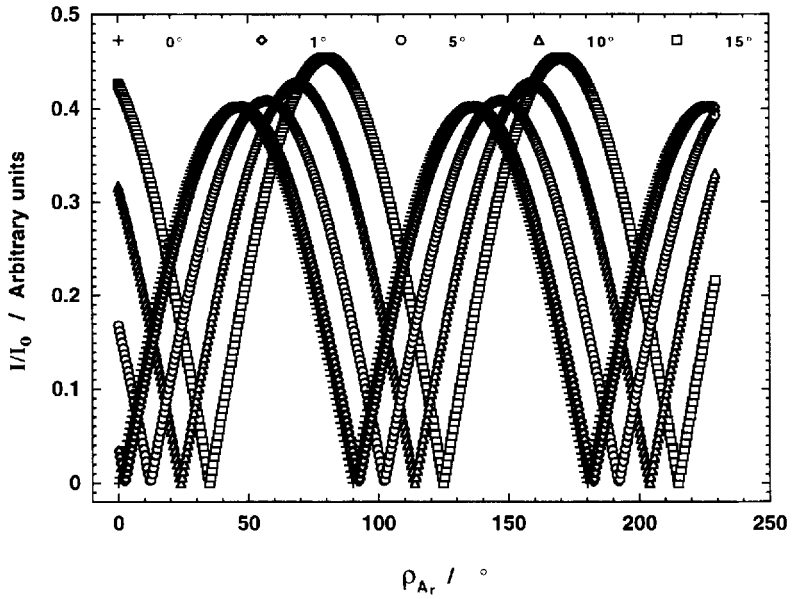


Figure 2. Plots of the magnitude of the fundamental frequency signal as a function of ρ_{A_r}, described by equation (14) for a fixed value of $\Delta n = 0{\cdot}2$ and varying θ.

bulk and result in possible screening effects. However, we have shown that these effects are insignificant by reproducing the electroclinic results for Merck mixture 764E [25] determined by a.c. fields without the formation of the striped texture.

Most of the electroclinic measurements were performed using commercial cells made of two indium–tin oxide glass plates separated by a spacer of 5 or 7·5 μm thickness. The inner surfaces of these plates were coated with polyamide and buffed to induce planar alignment in the sample. Although different cell thicknesses were used, this should not influence the electroclinic behaviour, because the effect has been established to be cell thickness independent [33]. However, for very thin cells (i.e. ~1 μm), the surface alignment may constrain the effect [34]. The cells were filled with the liquid crystal sample by capillary action. The temperature stability of the sample cell in the cell holder system was better than ±0·05°C and the sample cell was maintained at constant temperature for ~5 min before performing each run as a function of voltage.

Measurements of T_c were performed to normalize the electroclinic results. By using the set-up in figure 1, the sample was cooled with a small sinusoidal a.c. field applied (i.e. ~6 Vp-p at ~10 Hz). As the sample progressed from the S_A^* phase to the S_C^* phase, a strong switching fundamental frequency signal appeared on the oscilloscope connected to the signal input of the lock-in amplifier. The temperature at which the switching occurred suddenly was measured and denoted as T_c.

4. Results and discussion

To perform a reliable study of the electroclinic effect in the S_A^* phase, it is essential that the alignment of the materials in this phase is of the highest quality. Normally, excellent alignment in the S_A^* phase can be obtained by cooling slowly from the N* phase to the S_A^* phase. However, the N* phase is absent from all of the alkoxybiphenyl-phenyl carboxylate chiral dopants in the table. As expected, the alignment for these materials was poor when using commercial cells with either polyamide or polyimide aligning layers, and cooling slowly from the isotropic phase to the S_A^* phase, with or without applying electric fields having a wide range of frequencies and magnitudes. Nevertheless, it has been reported that some S_A^* materials can be aligned successfully just by cooling slowly from the isotropic phase to the S_A^* phase [24]. In fact, good alignment for one of the compounds was obtained in certain regions of a 7·5 μm thick cell which was constructed in the laboratory with polyamide aligning layers. Electroclinic results determined from a well-aligned region are shown in figure 3 for compound **4(*R*)**. Results at the lower temperature are non-linear, most likely due to the measurements being made close to T_c. At 95·9°C, the results are linear and $e_c \sim 0{\cdot}38^\circ\,V^{-1}\,\mu m$ was obtained on performing a linear least-squares fit.

To satisfy the phase behaviour requirements necessary to perform reliable electroclinic measurements, we used a two component system of a S_C host SCE12(base), composed of fluorophenyl-biphenyl carboxylates doped with the guest chiral compounds. The chiral dopants were completely miscible in the host at a concentration of ~5 per cent weight fraction (w/w). All the mixtures exhibited the N*, S_C^*, and S_A^* phases. The presence of the S_C^* phase below the S_A^* phase ensured a large induced effect in the S_A^* phase and T_c could be used to normalize the electroclinic results. Since SCE12(base) has relatively

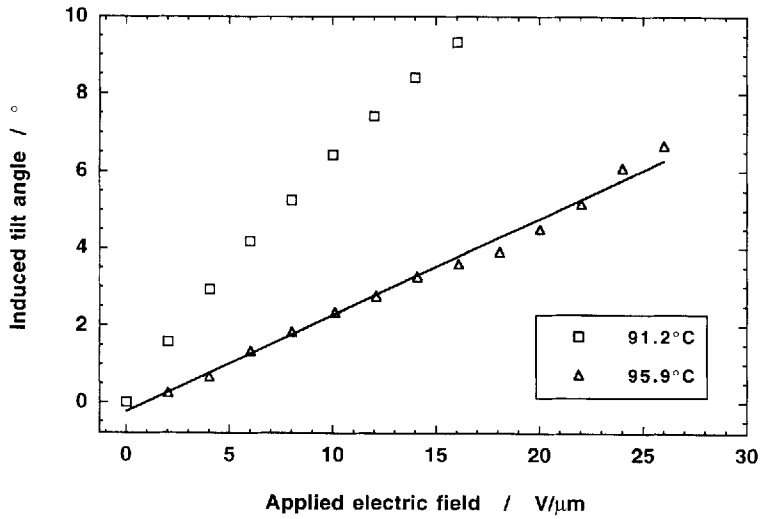


Figure 3. Graph of induced tilt angle as a function of electric field at two temperatures for compound **4(*R*)**. For this material measurements were performed by manual means (see §3). The solid line represents the least-squares fit of the experimental data at 95·9°C.

low phase transition temperatures [i.e. $T(S_C \rightarrow S_A) = 64°C$ and $T(N \rightarrow S_A) = 80°C$], the resulting mixtures correspondingly exhibited low phase transition temperatures and were therefore less likely to degrade while making electroclinic measurements. In figure 4 measurements of T_c of the mixtures are presented. Chiral com-

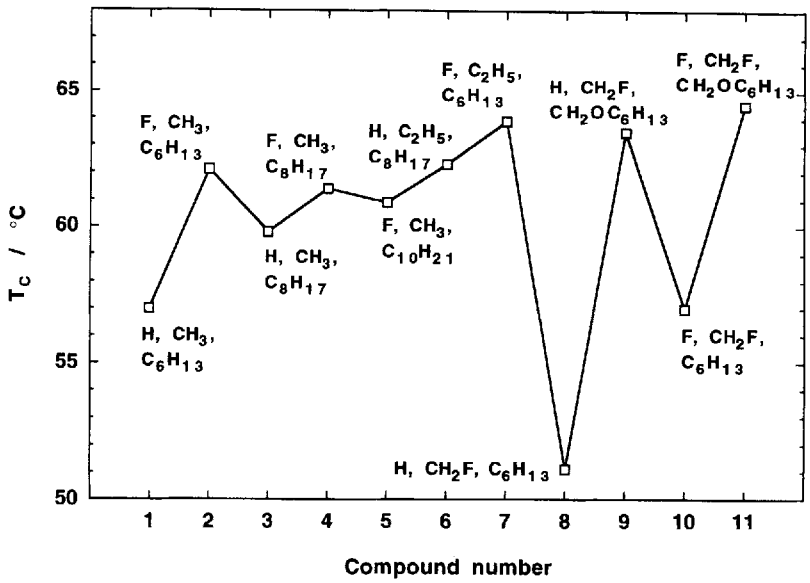


Figure 4. Variation of T_c for the mixtures of the strongly chiral alkoxybiphenyl-phenyl carboxylate compounds doped in SCE12(base) at a concentration of ~5 per cent (w/w). Substituents refer to the positions on the general structural formula in the table at A, B, and C, respectively.

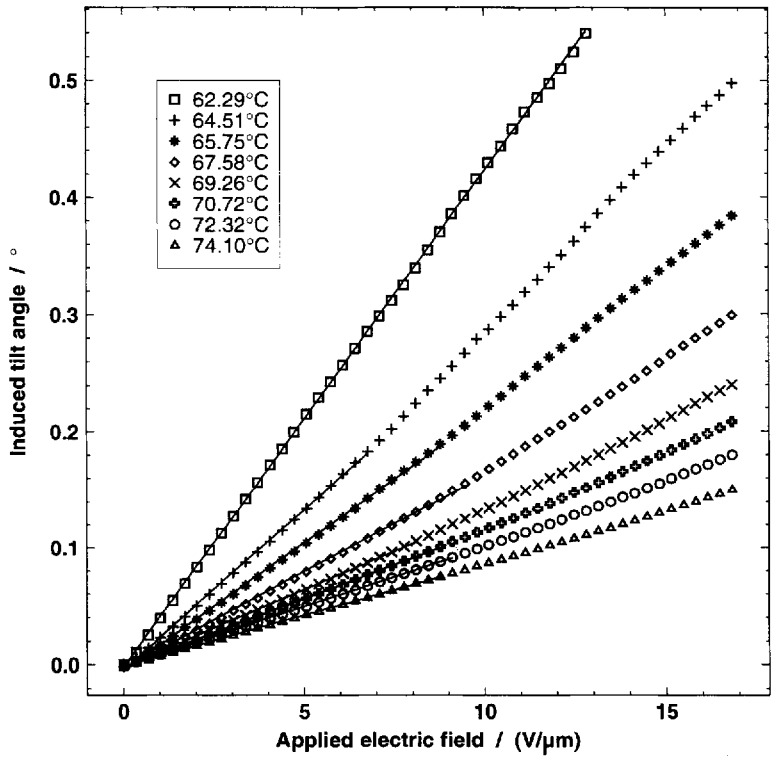


Figure 5. Graph of the induced tilt angle as a function of electric field and temperature for the mixture 5·4 per cent (w/w) compound **3**(***R***)/94·6 per cent (w/w) SCE12(base). The solid lines represent linear least-squares fits to the experimental data.

ponents with fluorine in the A position induce higher T_c in the mixtures than those with H in that position. As the alkyl chain at C becomes longer, T_c increases if H is in the A position, but decreases slightly if F is in that position. In the B position, CH_2F tends to lower T_c significantly when there is a C_6H_{13} group at C. However, the strong positive influence on T_c of $CH_2OC_6H_{13}$ at C compensates for the negative influence of CH_2F.

Electroclinic measurements were performed on all eleven mixtures in the commercial planar aligning cells. Excellent alignment was obtained for the mixtures in the S_A^* phase. Figures 5 and 6 show typical measurements of the electroclinic response as a function of electric field. Linear least-squares data fits were performed to evaluate the gradients (i.e. e_c) of the results in the linear regions for $E \leqslant \sim 10\,V\,\mu m^{-1}$ and at temperatures of $T - T_c \geqslant \sim 5°C$ as a function of temperature. In figure 7, these results for the mixtures are presented and all show Curie–Weiss type temperature dependence, i.e. e_c is inversely proportional to the normalized temperature. Deviation from linearity tended to occur for data points near T_c. Most of these results are omitted from figure 7, since we are interested only in the linear regions. The gradients (i.e. k/a) of the linear graphs in figure 7 give a temperature independent measure of the electroclinic strength of the mixtures.

Figure 8 shows how the structure of the chiral dopants affect k/a. The values of k/a for the mixtures are relatively small (i.e. $k/a \sim 0{\cdot}03$–$0{\cdot}22° V^{-1}\,\mu m\,°C$) because of the low chiral dopant concentration. By making a crude extrapolation, the pure chiral materials may have $k/a \sim 1$–$4\,V^{-1}\,\mu m\,°C$. Recently, using the half leaky guided mode technique, compound C7 [34] was determined to have a smaller value of k/a (i.e. $\sim 0{\cdot}48\,V^{-1}\,\mu m\,°C$). Bahr *et al.* [24] have reported values of k/a for an homologous series of pure chiral compounds (i.e. $k/a \sim 2{\cdot}6$–$3{\cdot}1° V^{-1}\,\mu m\,°C$) which are within the approximate range for those of the pure alkoxybiphenyl-phenyl carboxylates. On the whole, the electroclinic response is increased significantly when F is replaced by H in the A position or when CH_3 is replaced by CH_2F in the B position. For example, the value of k/a for compound **1**(*S*) is almost twice that of compound **2**(*S*). This may be explained by the strongly electronegative F reducing the effectiveness of the CO dipole moment. However, replacing the alkyl chain at C with $CH_2OC_6H_{13}$ increased the electroclinic response, minimizing the negative influence of F in the A position. For example, compounds **9**(*S*) and **11**(*S*) have values of k/a in the range $\sim 0{\cdot}11$–$0{\cdot}13° V^{-1}\,\mu m\,°C$, whereas k/a for compound **10**(*S*) has dropped to $\sim 0{\cdot}04° V^{-1}\,\mu m\,°C$. This may be due to the lone pairs on the oxygen of

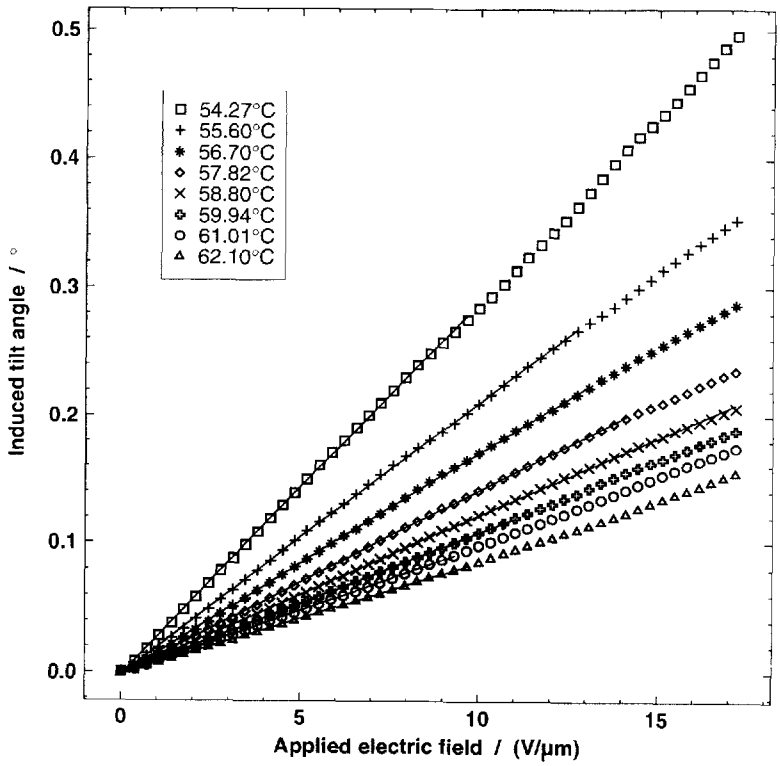


Figure 6. Graph of the induced tilt angle as a function of electric field and temperature for the mixture 5·5 per cent (w/w) compound **8**(*S*)/94·5 per cent (w/w) SCE12(base). The solid lines represent linear least-squares fits to the experimental data.

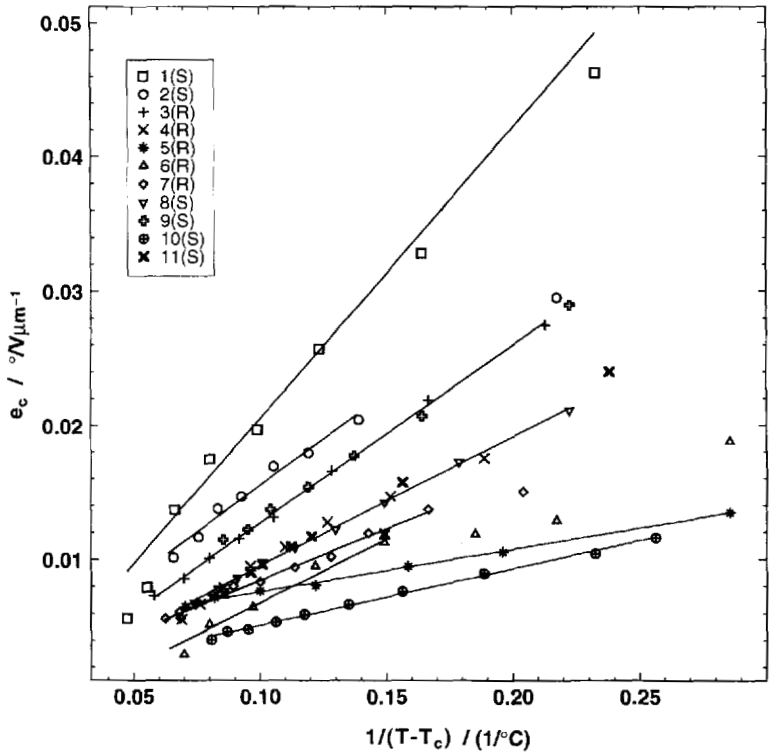


Figure 7. The influence of the reciprocal normalized temperature on e_c for all the mixtures with host SCE12(base) doped with the strongly chiral alkoxybiphenyl-phenyl carboxylate compounds. The solid lines represent the linear least-squares fit to the experimental data.

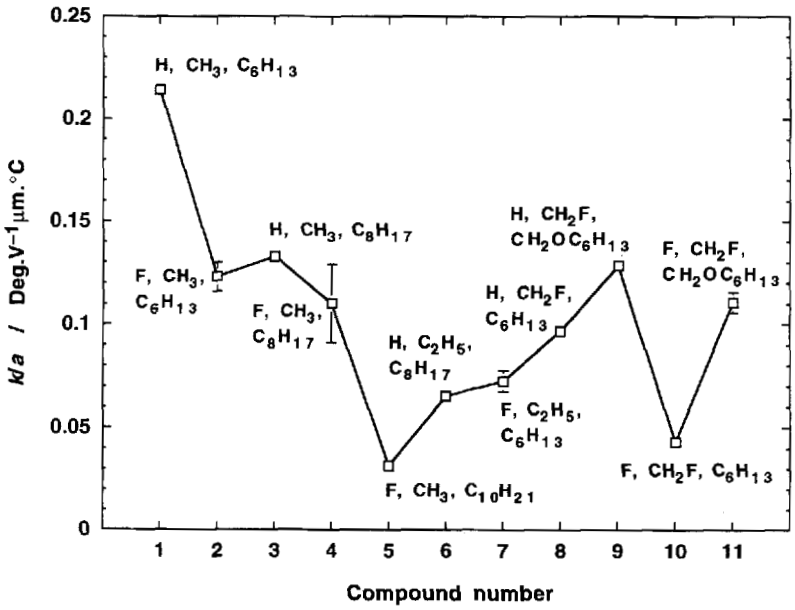


Figure 8. The effect of the structure of strongly chiral alkoxybiphenyl-phenyl carboxylate compounds doped in SCE12(base) on k/a. Substituents refer to the positions on the general structural formula in the table at A, B, and C, respectively.

$CH_2OC_6H_{13}$ and the CO dipole at the chiral centre combining to give a larger net dipole moment component. As the alkyl chain length increases at either the B or C positions, the electroclinic response decreases. However, the opposite would have been expected, since lengthening the alkyl chain at B or C should increase

the steric hindrance to the rotation of the asymmetric centre about the long axis of the molecule and so should increase the response.

5. Conclusion

We have reported an alternative method for automatic measurement of the electric field-induced tilt angle in the S_A^* phase and applied this technique successfully for measuring the electroclinic behaviour of mixtures of a S_C host doped with strongly chiral compounds. In the pure electroclinic switching regime, the soft mode response of the mixtures was modelled well by a typical Curie–Weiss type temperature dependence. We have demonstrated that the magnitude of the electroclinic effect was dependent on the net dipole moment component of the dopant chiral molecules, determined by the position and type of electronegative or polar substituent attached. Analysis of the structure–property relationships showed that the dopants without a lateral fluorine, and relatively short alkyl chains at the chiral centres tended to induce the largest electroclinic response. Furthermore, we have established that the magnitude of the electroclinic response does not always give a reliable measure of the chiral strength of a material, since it is important to take into account the achiral effects contributing to the net dipole moment component, as well as the ease of tilt as measured by a, to determine the true molecular chiral influence on the electroclinic effect. However, the structure–property work presented in this paper will help in designing improved electroclinic materials for the future.

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