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Optical and electro-optical properties of bimesogenic organosiloxane antiferroelectric liquid crystals with molecular tilt approaching 45 degrees

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We have studied the optical and electro-optical properties of three different bimesogenic siloxane materials. The dimers are symmetrical and the two mesogenic groups are connected by a siloxane unit containing three Si atoms and methylene spacers. The mesogens contain F, Cl and Br substituents, respectively, laterally attached to the phenyl ring lying closest to the chiral centre of the mesogen. These materials each exhibited a broad temperature range antiferroelectric phase and large molecular tilt, which is almost temperature-independent. We have shown that, at low temperatures, the molecular tilt in the antiferroelectric phase is the same as the apparent molecular tilt in the field-induced ferroelectric state and is close to 45°. It was found that the antiferroelectric phase of these compounds, aligned in such way that the dimeric molecules were lying in a plane parallel to the confining substrates, exhibited very low in-plane birefringence. For this reason, samples of the compounds inserted between crossed polarizers in the antiferroelectric state exhibited an extremely dark state, with contrast ratios as high as 1000:1, which did not change noticeably on rotating the sample between the crossed polarizers. It was shown that the optically isotropic siloxane moiety did not contribute to the optical properties, viz. birefringence or tilt angle, but served to enhance the promotion of the antiferroelectric phase and the temperature independent properties. We also showed the existence of a linear electro-optic response in the pretransitional region of the antiferroelectric phase of these compounds over a moderate range of fields.

1. Introduction

Organosiloxane low molar mass (LMM) liquid crystals have attracted considerable interest because their electro-optic properties are similar to those of classical LMM liquid crystals, demonstrating fast switching times in the nematic [1], smectic A [2], smectic A* [3], smectic C* [4–6] and smectic C_A* [7, 8] phases. Characteristically such materials exhibit a high mobility of their side groups, temperature independent layer spacing, tilt angles and good mechanical properties associated with the microscopic self assembly of the siloxane moieties. Over the last decade such LMM organosiloxane monomesogens and bimesogens have become the subject of intensive investigation since this class of liquid crystal materials has shown a number of extraordinary macroscopic and microscopic properties. Macroscopically, such materials have been incorporated

into devices based on, for example, light scattering [9], birefringence [1, 3–8, 10], dichroism [11], fluorescence [12], photochromism [13] and optical nonlinearity [14]. Microscopically it has been shown that the siloxane moiety may be controlled to induce de Vries type behaviour and SmA* phases in materials that otherwise only exhibited SmC* phases [15]. Depending on their siloxane content, we have shown [7] that these moieties may be used to control the synclinc (ferroelectric) or anticlinc (antiferroelectric) nature of the phase using the same bimesogenic groups. It should be noted that that the anticlinc state may be stabilized by more subtle effects including entropic ones [16]. One particularly interesting property of these materials, exhibiting ferroelectric [6] or antiferroelectric [8] phases, is the large molecular tilt that may readily attain ~45°, depending on the ability of the mesogen to ‘accommodate’ in its 2-dimensional packing with the siloxane moieties [17–19]. In most of these siloxane bimesogens the molecular tilt is temperature-independent over a broad temperature

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interval. Further, the siloxane bimesogens are materials that can easily be uniformly aligned in a ‘bookshelf’ geometry, without chevron defects, with the smectic layers being normal to the confining surfaces, and with switching times of the order of 10s to 100s of μs . Such materials, which show good mechanical stability, are therefore very interesting for applications in photonics, for instance as optical phase modulators and beam steering devices, in LCOS devices and indeed complex displays [20].

In particular, we have shown that the siloxane spacer linking two mesogenic molecules in such bimesogens may give rise to ferroelectric or antiferroelectric phases depending on the number of Si atoms in the siloxane units [6, 8]. In the latter references it should be noted that the mesogenic groups used are naturally ferroelectric, i.e. the constituent mesogenic groups do not normally exhibit an antiferroelectric phase. We have shown that the antiferroelectric nature arises from a molecular ‘templating’ effect due to the ‘bent’ shape adopted by the siloxane moiety (for moieties incorporating 3 or 5 Si atoms). For siloxane moieties containing 2 or 4 Si atoms a ‘linear’ shape is adopted and a ferroelectric phase is formed. Strictly it will be the direction of the final siloxane group’s bonds, linking the alkyl spacer chains to the mesogens, which defines these configurational properties. This templating effect is not limited to chiral bimesogens. In a parallel study we used achiral SmA phase-forming bimesogens, based on azo and stilbene compounds, to induce antiferroelectric properties in otherwise ferroelectric monomesogens [21]. These achiral siloxane bimesogens showed the same odd–even effect in the molecular templating. Since discovering this effect, in siloxane based helielectric compounds, we have used a variety of other mesogens, including those containing perfluorinated end chains and have always observed the same odd–even templating effect [10, 22].

In the present work we have studied the optical and the electro-optical properties of three siloxane bimesogens exhibiting a broad temperature antiferroelectric (AF) phase, with high molecular tilt, and high spontaneous polarisation \mathbf{P}_s in the field-induced

ferroelectric phase (F). We compared their characteristics with those of other similar siloxane bimesogens that have been recently studied [23, 24] and show that the compounds studied in this work have a potential for applications.

2. Experimental

The siloxane bimesogens studied in this work have the following general structure:

The homologues Br11-3-11Br, Cl11-3-11Cl and F11-3-11F are the materials whose properties were investigated; Br, Cl and F refer to the halogen substituent, 11 refers to the number of methylene spacers and 3 refers to the number of Si atoms in the siloxane moiety. The phase sequences and transition temperatures were determined by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and from electro-optic response observations. Cells with a gap of $4\mu\text{m}$ and a polyimide alignment layer, unidirectionally rubbed, were filled with the liquid crystal material in the isotropic phase. The tilt angle was determined by optical microscopy, as half the angle between two positions of optical extinction when the sample was switched between crossed polarizers. The spontaneous polarization was evaluated with an accuracy of $\pm 3\text{nC cm}^{-2}$ using the current pulse technique. All the materials displayed a broad smectic C_A^* phase with a high spontaneous polarization, of the order of 100nC cm^{-2} , and a high tilt, close to 45° . A summary of the measurements is given in the table [8]. The layer spacing was only very weakly dependent on temperature. The threshold field $\mathbf{E}_{\text{th}}^{\text{AF-F}}$ for inducing the AF–F transition was from $7\text{V}\mu\text{m}^{-1}$ near to the I–Sm C_A^* phase transition, to $20\text{V}\mu\text{m}^{-1}$ near to the Sm C_A^* –Cr phase transition temperature [25].

Measurements of the birefringence (Δn) of the AF phase, with and without applied fields, were carried out by means of a Berek Compensator (U-CBE, Olympus). A relatively high frequency electric field (5–20 kHz) was applied to the sample in order to unwind completely the helical order in the AF phase. In-plane switching of the effective optic axis in the pretransitional region of the AF phase was measured as half the angle between two

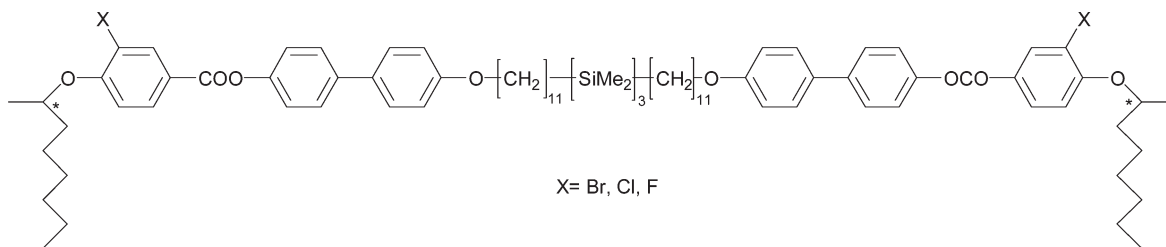


Table. Physical properties of the organosiloxane materials at a fixed shifted temperature of -20°C below the clearing point.

Compound	Clearing temp./ $^{\circ}\text{C}$	Mesophase	Melting temp./ $^{\circ}\text{C}$	$P_s/n\text{C cm}^{-2}$	Tilt angle/degrees
F11-3-11F	121	SmC_A^*	51.2	101	40.4
Cl11-3-11Cl	110	SmC_A^*	55.2	119	41.7
Br11-3-11Br	106	SmC_A^*	50	135	43.5

positions of optical extinction when the sample was switched between crossed polarizers.

3. Results and discussion

Optical and electro-optical studies of the compounds were carried out in cells containing these materials aligned in the horizontal antiferroelectric state, the so called HAF state [27]. In the HAF state the bimesogenic molecules lie in a plane parallel to the confining substrate (figure 1). With no applied electric field across the samples, a non-uniform texture was obtained, consisting of large size domains, most of which possessed uniform HAF alignment, i.e. with smectic layer normals lying along a preferred direction. There were also large circular (or part-circular) domains with HAF texture in which the normal to the smectic layers was aligned locally along the radius of the domain.

The uniformity of the HAF texture in the samples was found to improve substantially on applying an electric field with low frequency ($f \approx 10\text{ Hz}$) during the transition from the isotropic to the AF phase. The strength of the applied field was chosen to be higher than the threshold field $E_{\text{th}}^{\text{AF-F}}$ for inducing the AF-F transition. In the AF phase of the samples, the presence of a deformed helical molecular order was observed. Obviously, the cell gap thickness of $4\mu\text{m}$ was larger than that which would produce unwinding of the helix (known as stabilization by surface/liquid crystal interactions) in the AF phase. A high frequency electric field

(10–100 kHz) was applied to the sample in order completely to unwind the helical order in the AF phase. At this frequency, we verified optically that the applied electric field induced neither the Fréedericksz nor the AF-F transitions in the AF phase. The applied field only suppressed the helical molecular order in the AF phase and thus stabilized the HAF texture.

Photomicrographs of a cell containing the compound Br11-3-11Br, aligned in the HAF texture are shown in figure 2. The sample was oriented between crossed polarizers with the smectic layer normal oriented at 45° with respect to the transmission direction of the polarizers. The photographs are taken at 50°C , i.e. deep in the AF phase, before (a) and after (b) applying a high frequency electric field for helix unwinding. The brightness of the photographs in figures 2(a) and 2(b) was electronically enhanced in order to demonstrate the sample texture and to analyse it. In reality, the AF state in the field-off state appeared very dark indeed and barely changed on rotating the sample between the crossed polarizers, thus indicating an extremely low in-plane birefringence of the AF phase [23, 27]. In figure 2(a), the presence of traces of incompletely unwound helical order can be seen. The applied electric field, however, removes the helix and stabilizes the HAF texture, which in turn results in a decrease of the in-plane birefringence Δn of the sample [27]. This is demonstrated in figure 2(b). The photographs of figures 2(c) and 2(d) were taken after inserting a λ -first order red plate between the crossed polarizers with its

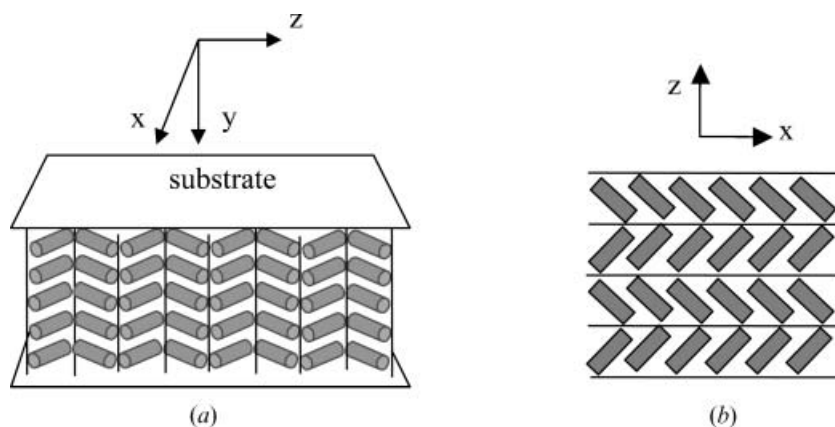


Figure 1. Schematic of the horizontal anti-ferroelectric (HAF) state of the dimeric molecules.

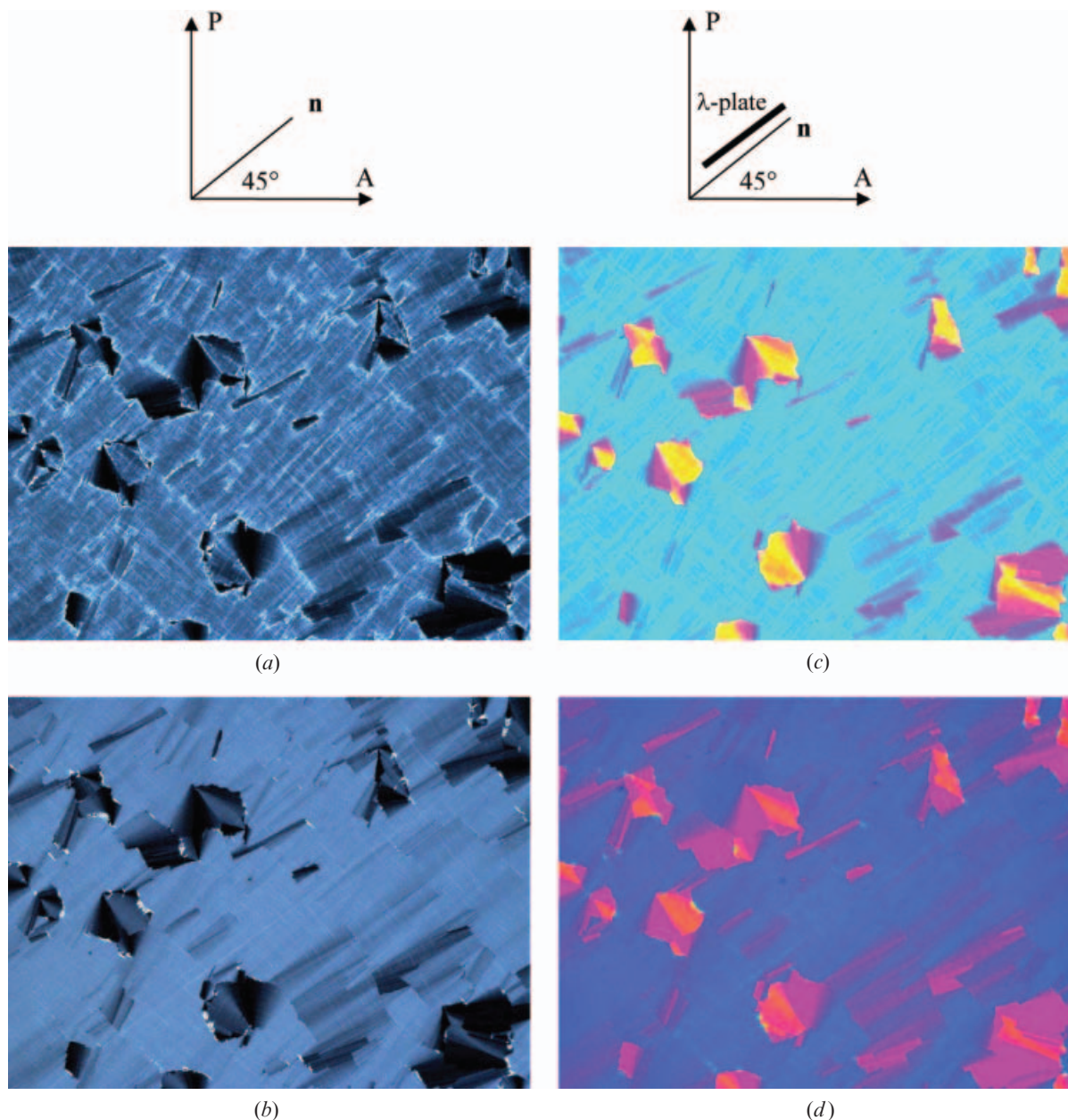


Figure 2. Photomicrographs of a cell containing the compound Br11-3-11Br, aligned in HAF texture with no electric field (*a* and *c*) and with a $33 \text{ V } \mu\text{m}^{-1}$, 5 kHz stabilizing electric field applied (*b* and *d*). In (*c*) and (*d*) a λ -first order red plate was inserted to emphasize the regions with small Δn .

slow axis oriented at 45° with respect the polarizers. As can be seen, the total phase retardation of the sample and the λ -plate, and hence Δn of the AF phase, decreases on applying a stabilizing field which is clearly indicated by the decrease of the level of the interference colour. This was confirmed by performing direct measurements of the in-plane Δn of the samples in the AF phase. Even though the sample texture is not quite uniform, as seen from the photographs, there are

enough large areas with uniform HAF alignment to allow measurements of the optical, as well as of the electro-optical, properties of the sample to be carried out.

In figure 3 the temperature dependence of Δn for the compound Br11-3-11Br and Cl 11-3-11Cl are given. The values of Δn of the electrically stabilized HAF state of the compounds at low temperatures were found to be very low, in the range 0.005–0.008 at 50°C . It was also

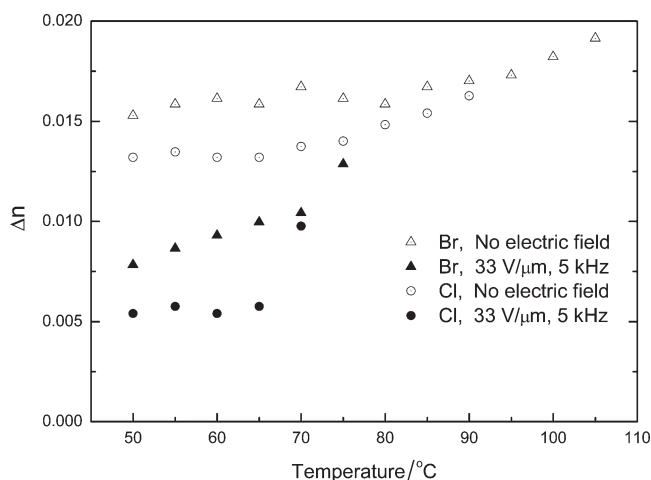


Figure 3. Temperature dependence of the birefringence Δn , for the compounds Br11-3-11Br and Cl11-3-11Cl.

found that Δn of the electrically stabilized HAF texture appeared to be lower than that without the stabilizing field.

At normal incidence of the light, Δn of the HAF state is $\Delta n_{z-x} = n_z - n_x$, where n_z and n_x are the refractive indices along and perpendicular, respectively, to the smectic layer normal and they are given by [28, 29]

$$\begin{aligned} n_x^2 &= n_e^2 \sin^2 \theta + n_o^2 \cos^2 \theta \\ n_z^2 &= n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta \end{aligned} \quad (1)$$

where n_o and n_e are the ordinary and the extraordinary refractive indices, respectively. According to equation (1), the in-plane birefringence Δn_{z-x} becomes zero (i.e. the HAF state exhibits isotropic optical properties), when the molecular tilt θ reaches 45° . Such isotropic optical properties ($\Delta n = 0$) of an AFLC, aligned in the HAF texture with molecular tilt of 45° , were first predicted by de Meyere *et al.* [28].

The low birefringence measured for the samples containing the bimesogenic siloxanes, aligned in HAF texture, indicates that the molecular tilt in the AF phase of these materials at low temperatures approaches 45° , and the optical properties of the HAF state become almost isotropic, i.e. $\Delta n \approx 0$. The optically isotropic HAF state appears totally black between crossed polarizers (the quality of the black state is only limited by the polarizer quality). Indeed the contrast ratio for the switched F state relative to the field free AF state was of the order of $10^3:1$, see figure 4. Figures 4(a) and 4(b) illustrate the field-off black state of the sample containing Br11-3-11Br with a multi-domain HAF texture on rotation between crossed polarizers. It can be seen that there is virtually no variation in the dark state in the sample. The very small variations are caused

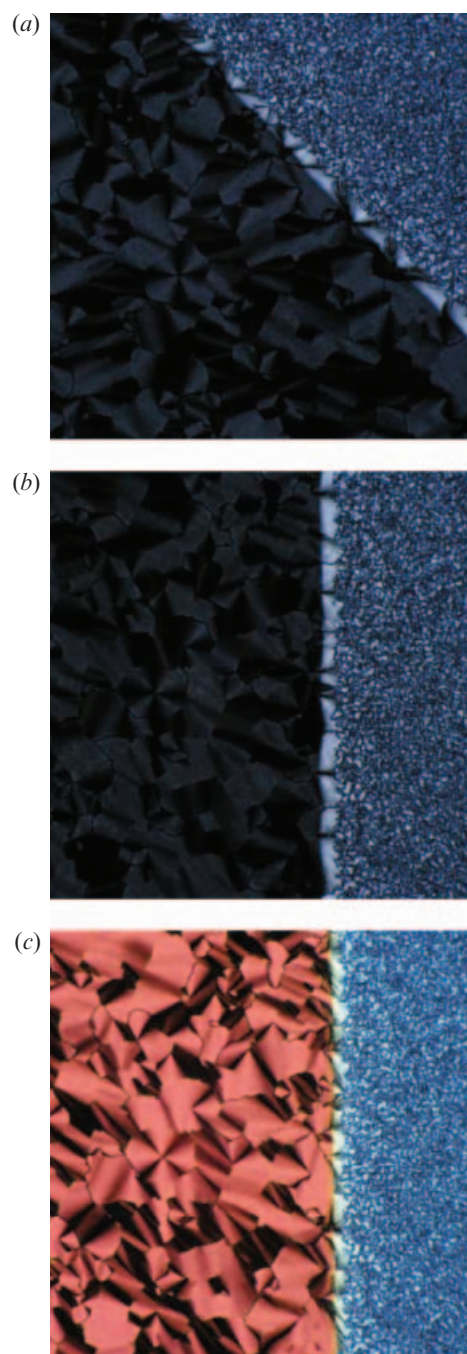


Figure 4. Photomicrographs of the field-off AF black state (a, b) of the Br11-3-11Br sample with a multi-domain HAF texture, and the field-switched F state (c). As shown by the position of the electrode edge on (a) and (b), the sample between crossed polarizers has been rotated through $\sim 45^\circ$. The texture with no field applied exhibits the same level of dark state whatever the angle of rotation.

by the local in-plane variation of the smectic layer direction. This is because the molecular tilt in the compound is not exactly 45° . Figure 4(c) shows the F

switched state in these multi-domain HAF textures with the same crossed polarizer direction as in (b). A similar optical appearance was exhibited by samples of the other two bi-mesogenic compounds.

We also measured Δn for the field-induced ferroelectric state. Δn values at $T=50^\circ\text{C}$ were 0.109, 0.092 and 0.093 for Br11-3-11Br, Cl11-3-11Cl and F11-3-11F, respectively. From the measurements of Δn in the field-induced F state we estimated the following values of n_o and n_e for the compounds:

$$\text{Br11-3-11Br} \quad n_o = 1.51; n_e = 1.62$$

$$\text{Cl11-3-11Cl} \quad n_o = 1.51; n_e = 1.60$$

$$\text{F11-3-11F} \quad n_o = 1.51; n_e = 1.60.$$

Then from the values of $\Delta n_{z-x} = n_z - n_x$, measured in the AF phase aligned in the HAF texture (electrically stabilized), and the estimated values of n_o and n_e , from equation (1) we calculated the molecular tilt θ in the AF phase at $T=50^\circ\text{C}$ (see figure 5). Comparing these values with the θ_{pp} measured in the field-induced F state at the same temperature, we found:

Br11-3-11Br

$\theta \approx 43^\circ$ in AF phase (calculated); $\theta_{pp} = 43.5^\circ$ (measured in F state)

Cl11-3-11Cl

$\theta \approx 43^\circ$ in AF phase (calculated); $\theta_{pp} = 41.7^\circ$ (measured in F state)

F11-3-11

$\theta \approx 40^\circ$ in AF phase (calculated); $\theta_{pp} = 40.4^\circ$ (measured in F state).

Hence, we may conclude that at temperatures some $60\text{--}70^\circ\text{C}$ below the clearing points (i.e. at 50°C) the molecular tilt angle in the AF phase of the bimesogenic

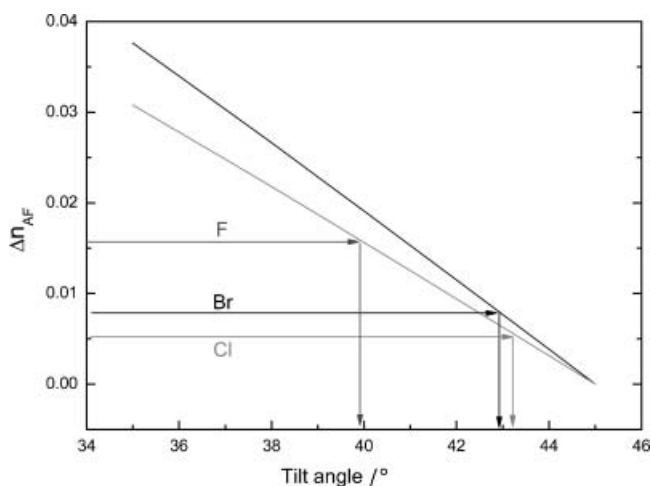


Figure 5. Graphical representation of equation (1) for Br11-3-11Br, Cl11-3-11Cl and F11-3-11F.

siloxanes is almost the same as the apparent tilt in the field-induced F state in these compounds, which is in accordance with what was found in [23], and both angles are close to 45° . However, this might not be the case at higher temperatures. To determine whether the molecular tilt in the AF phase at higher temperatures is also the same as in the field-induced F state, a stable HAF texture in the samples at these temperatures is required. Unfortunately, it is very difficult to obtain a HAF state of our compounds by means of high frequency electric field at temperatures higher than 70°C . One possible solution could be the use of cells with a very small cell gap, less than $1\ \mu\text{m}$. Such studies are in progress.

Another monomeric AFLC mixture possessing a molecular tilt of about 42° and, thus, low in-plane birefringence (0.019), has been reported [30]. However, neither this mixture nor the bimesogenic siloxanes studied in this work exhibit exactly 45° molecular tilt in the AF phase and, hence, these materials do not possess in-plane birefringence of exactly zero, i.e. they do not exhibit totally isotropic optical properties when aligned in the HAF state. However the Br11-3-11Br compound with a tilt angle of 43.5° and a $\Delta n = 0.005\text{--}0.008$ gives an almost totally black state on rotation between crossed polarizers [26]. Recently we have synthesized, and studied, a further bimesogenic siloxane AFLC, in which the molecular tilt was found to reach 53° [23]. Due to the weak temperature dependence of the molecular tilt in this compound, it was possible to study the optical properties of the HAF state at exactly $\theta = 45^\circ$ and to confirm experimentally, as predicted by de Meyere, the totally *isotropic* optical properties of this state when $\theta = 45^\circ$.

In the pretransitional region of the AF phase, i.e. the region that occurs for applied electric fields $\mathbf{E} < \mathbf{E}_{th}^{AF-F}$, a linear-like electro-optic response at moderate electric fields was observed. The response was found to be due to: (a) in-plane switching of the effective optic axis, which in the field-off state is lying along the smectic layer normal; and (b) out-of-plane switching of the bimesogen, due to the Fréedericksz transition in the AF phase, which in its turn resulted in a change in Δn of the sample. This switching is regarded as a field-induced transition from the HAF to the vertical antiferroelectric (VAF) state, in which the tilt plane formed by the bimesogen (antiferroelectric pair) and smectic layer normal is oriented perpendicular to the sample substrates.

It was found that the field-induced in-plane deviation of the optic axis is a linear function of the applied electric field at moderate electric fields. This is demonstrated in figure 6, and values as high as $15\text{--}18^\circ$ were

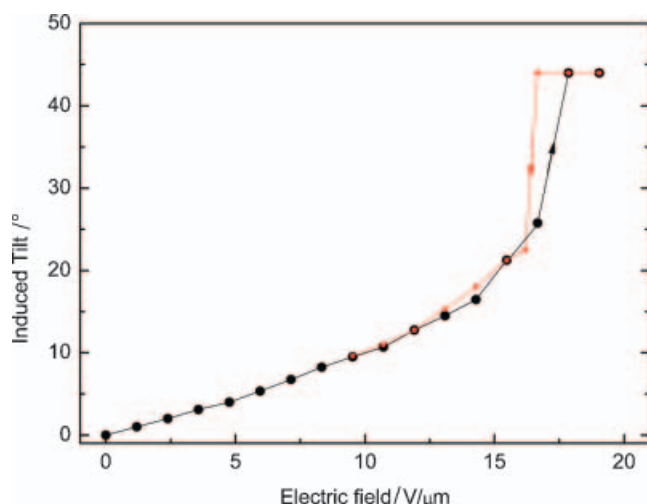


Figure 6. Electric field dependence of the induced in-plane deviation of the optic axis measured in Br11-3-11Br at 50°C with increasing (black) and decreasing (red) voltage.

achieved in all the compounds for applied fields of 10–15 $\text{V}\mu\text{m}^{-1}$. The origin of the field-induced deviation of the sample optic axis is not the electroclinic (soft mode) effect, even though it exhibits some similarities to this effect. A possible origin of the field-induced deviation of the sample optic axis is presented in [24]. Generally speaking, it is due to the deformation of the antiferroelectric order that takes place under an applied electric field.

We have also found that, in the pretransitional region, Δn of the sample is changed by the applied electric field. The field-dependence of Δn measured in Br11-3-11Br at 50°C is shown in figure 7. Starting with

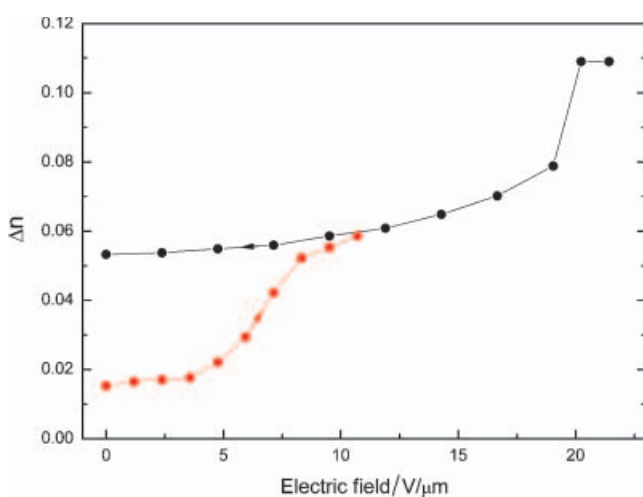


Figure 7. The electric field dependence of Δn in the pretransitional region measured in Br11-3-11Br at 50°C with increasing (red) and decreasing (black) voltage.

the HAF state subjected to a stabilizing electric field of $U=33\text{ V}\mu\text{m}^{-1}$ and $f=10\text{ kHz}$, Δn was measured to be 0.0078. After switching the stabilizing field off, Δn jumped to the value of 0.015, due to partial relaxation of the helical order. On applying a d.c. field, it was found that, up to $4\text{--}4.5\text{ V}\mu\text{m}^{-1}$, Δn changed very little and that this change was completely reversible with the electric field. However, if the applied electric field was increased above $4.5\text{ V}\mu\text{m}^{-1}$, Δn started to increase rapidly and the sample texture also started to change. Bright domains with higher birefringence appeared and stayed after the removal of the electric field. The texture change was found to stay for some time after removing the applied field. The textural change seems to be a result of the field-induced transition from the HAF state to the vertical state [29]. Such a hysteretic behaviour of

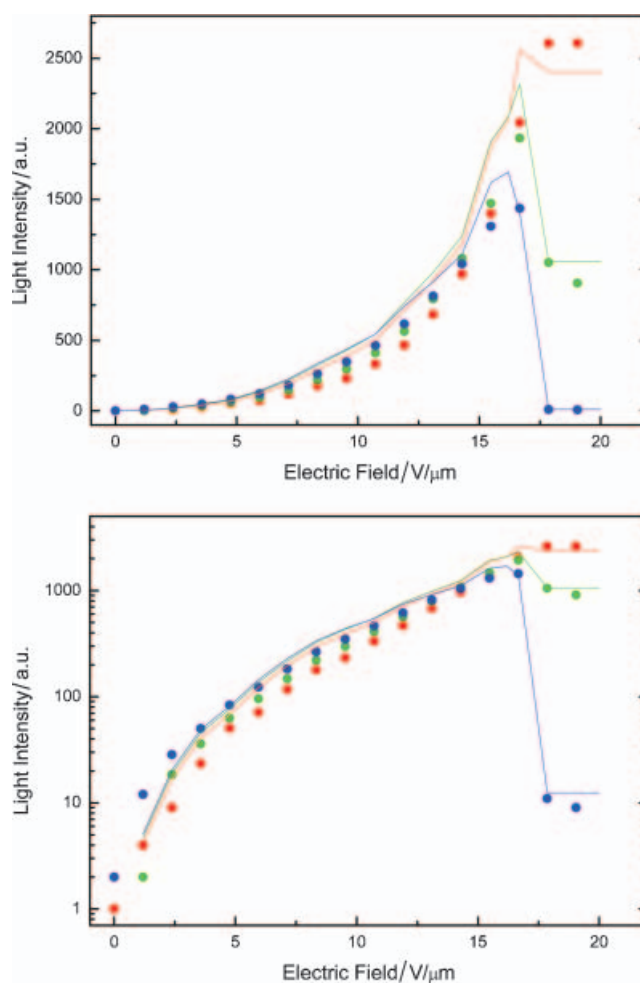


Figure 8. Electro-optic response measured (dots) and calculated (lines) from equation (2) for Br11-3-11Br sample. Cell thickness $4.2\mu\text{m}$ and $\lambda=630, 550$ and 450 nm for red, green and blue colour, respectively. The only fitting parameter was $I_0=4200\text{ a.u.}$ The electro-optic response is presented in linear and logarithmic scales.

Δn , as a function of the applied electric field, is shown in figure 7.

Both effects, i.e. the field-induced in-plane deviation of the sample optic axis and the field-induced changes of Δn which take place in the pretransitional region, result in changes of the intensity of the light transmitted through the cell. For normal incidence of the light the transmitted light intensity through the sample, aligned in the HAF state and placed between crossed polarizers, is given by:

$$I = I_0 \sin^2 2\varphi \sin^2 \pi d \Delta n / \lambda \quad (2)$$

where φ is the field-induced deviation of the optic axis and Δn is the birefringence of the sample. Δn in the pretransitional region, where the Fréedericksz transition takes place, changes from $\Delta n_{z-x} = n_z - n_x$, in field-off condition, to $\Delta n_{z-y} = n_z - n_y$, when an electric field is applied. The field-induced change of Δn in this region was found to be about 0.06 for our compounds and to a large extent to take place over a narrow field interval.

We inserted the values of Δn in equation (2), as a function of the applied electric field, and the values of the field-induced deviation of the sample optic axis, both measured in the pretransitional region. The fitting curve of the transmitted light intensity using equation (2) and the experimentally detected light intensity as a function of the applied electric field is shown in figure 8. As clearly seen for both, the experimental and the fitted curves are quite similar. Hence, we may conclude that in the pretransitional region of the AF phase of our compounds, two switching mechanisms are contributing to the electro-optical response: (a) the field-induced in-plane deviation of the sample optic axis, giving rise to the amplitude modulation; and (b) the field-induced transition from the HAF to the VAF state, giving rise to phase modulation of the light transmitted intensity.

4. Conclusions

In this paper we present the results of a study on the optical and electro-optical properties of three symmetric bimesogenic siloxane materials, in which two mesogenic groups are connected by a siloxane unit consisting of three Si atoms, and the benzoate ester mesogens were laterally substituted with F, Cl or Br. It was found that these materials, which exhibited an AF phase over a broad temperature range, possessed a large molecular tilt angle in the AF phase close to 45° . Moreover, we have confirmed, at least for low temperatures, that the molecular tilt in the AF phase is the same as the apparent tilt angle in the field-induced F state. As a result of the large tilt angle in the AF phase, the samples containing bimesogenic siloxanes, aligned in the HAF

texture, were found to exhibit a state with extremely low and virtually negligible birefringence. Such a state appeared dark, almost totally black, when the sample was inserted between crossed polarizers, i.e. a contrast ratio of $10^3:1$. The dark state obtained did not change noticeably on rotating the sample between the polarizers, thus demonstrating a very low in-plane birefringence that was measured to be in the interval 0.005–0.008 for the compounds under investigation. In the field-induced F state, the birefringence Δn the compounds was found to be in the interval 0.109–0.092. Hence, switching from AF state to F state would give a change in the Δn of about 0.1. Such a large change of Δn could have a potential for applications such as phase modulators or beam steering devices. On the other hand, the linear electro-optic response detected in the pretransitional region of the AF phase might be a candidate for application in light intensity modulation devices. An important advantage of the bimesogenic siloxane AFLCs, studied in this work, compared with monomeric AFLCs exhibiting molecular tilt close to 45° , is that the molecular tilt in the bimesogenic siloxanes is temperature independent over a broad temperature interval. This makes the bimesogenic siloxane AFLCs very attractive for applications in LCOS displays and photonic devices.

The bimesogenic siloxane AFLCs reported in this work, have been known since 1996 [6–8, 20] to have a high tilt angle of $\sim 45^\circ$ and were observed to exhibit a truly black AF state between crossed polarizers [31]. Here we have re-measured these materials and clearly established that the in-plane birefringence is indeed extremely small. This is in accord with the de Meyere *et al.* [28] predictions in 1996; therefore these materials behave optically as might be expected for a ‘conventional’ 45° tilt AF mesogen not containing siloxanes. This is contrary to suggestions, recently, that a monomeric AFLC mixture with a tilt angle approaching 45° (in fact 42°), represents a new class of materials [32] possessing isotropic optical properties between crossed polarizers. There would appear to be no need to redefine these materials as orthoconic [33] since, as predicted [28], any 45° tilt AFLC material, properly aligned, will show the same optical isotropic properties as those demonstrated here. This is a general property of an AFLC material with an optically measured tilt angle close to 45° .

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