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Siloxane antiferroelectric liquid crystalline dimer exhibiting two field-free zero birefringent states

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We studied the optical and electro-optical properties of a siloxane antiferroelectric liquid crystalline dimer exhibiting a large molecular tilt that reached a maximum value of 53°. When the molecular tilt angle in the antiferroelectric phase exceeded 45°, it was found that the field-free position of the slow vibration direction, which corresponds to the largest refractive index, flipped from a position along the smectic layer normal, to a position perpendicular to it. When the tilt angle became 45°, a zero birefringent state, which was theoretically predicted by de Meyere in 1996, was also found to occur twice in the antiferroelectric phase of the siloxane dimer.

1. Introduction

The motivation for the strong interest in liquid crystal science over the past three decades is primarily the great potential of liquid crystalline materials for applications as an electro-optically active medium in display devices. Today efforts among display engineers are focused on, for example, display concepts and materials giving shorter response times, grey scale capability, high contrast, low energy consumption, easy processing and manufacture.

Since their discovery, antiferroelectric liquid crystals (AFLCs) have been considered to be very promising materials for displays [1, 2]. Compared with ferroelectric liquid crystals (FLC), AFLCs can be aligned more easily and their electronic driving is simpler since there is no need for d.c. compensation. In both AFLC and FLC displays, however, the dark field-free state suffers substantially from local misalignment of the liquid crystal layer, usually caused by the preparation process and/or by the electronic driving of the displays. AFLCs aligned in the bookshelf geometry, with the smectic layers perpendicular to the confining substrates, the so-called horizontal antiferroelectric (HAF) state, are of particular interest. In this type of alignment the smectic layer normal and the tilt plane containing the antiferroelectric (AF) pair are parallel to the substrate [3]. In AFLC displays aligned in the HAF state and with a molecular tilt of $\theta=45°$, the existence of any misaligned domain in the liquid crystal layer will no longer deteriorate the dark field-free state, and thus reduce the image contrast. This is because the field-free state between crossed polarizers, as predicted by de Meyere *et al.* [4], would be 'totally dark' for any in-plane direction of the smectic layer normal between the polarizers, provided that the AFLC is aligned in the HAF state. This is because the in-plane birefringence, Δn, of the AFLC sample becomes *zero*. The *totally* black field-free state exhibited by the AFLC with a tilt of $\theta=45°$ aligned in the HAF state is one of the most important prerequisites for achieving high contrast images in displays.

Siloxane AFLC dimeric materials, with a molecular tilt close to $\theta=45°$, and thus capable of displaying high contrast images, were first reported by Coles and coworkers, who synthesized and studied such materials [5–9]. An AFLC dimeric material whose molecular tilt in the field-induced ferroelectric (F) state exceeded 45° was recently reported by Nishiyama *et al.* [10]. However, the optical properties of this material were not studied and it is not clear whether the molecular tilt angle in the AF phase of their AFLC dimer is the same as the apparent tilt θ_{app} in the field-induced F state. An optically isotropic state in liquid crystals of bent-core molecules, i.e. a state with $\Delta n=0$, which was achieved after treatment with an electric field, was recently reported [11].

In this work, we present investigations on the optical and electro-optical properties of a siloxane AFLC

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dimeric material that exhibits a large molecular tilt. The molecular tilt of this material reached a maximum value of 53°.

2. Experimental

2.1. *Sample preparation*

The AFLC material studied in this work is a siloxane dimer shown in figure 1. The phase behaviour of the dimer was identified by combining polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction on aligned samples and electro-optical measurements and will be further described together with the synthesis of several similar materials in a separate paper. The phase transition temperature was taken as the maximum point in the DSC enthalpic peaks at a heating rate of $5^\circ\mathrm{C\,min^{-1}}$. The phase sequence of the dimer is given in figure 1. Robinson *et al.* have studied a similar siloxane dimer [8, 9]. However, there are two important structural differences between the latter and the dimer studied in this work. Our siloxane AFLC dimer has no lateral Cl group in the mesogenic structure and the direction of the internal ester in the three-ring core of the mesogen is reversed, which together with the removal of the Cl group in the mesogenic structure greatly changes the electron density in the core near the chiral group. Our current studies indicate that for the related unfluorinated dimers these two changes cause an increase of spontaneous polarization $\mathbf{P}_s$ of more then 300%. Accordingly, the $\mathbf{P}_s$ of the field-induced F state of our AFLC dimer increased substantially compared with the one exhibited by the dimer reported in [8, 9].

In the field-induced F state, the compound exhibited a large $\mathbf{P}_s$ of more than $800\,\mathrm{nC\,cm^{-2}}$. Such a high $\mathbf{P}_s$ is due partly to the fluorination and the increased order in the two columnar antiferroelectric phases, but also to the structural effects already described.

Conventional sandwich cells of the EHC (Japan) type were used in the experiments. The liquid crystal material was introduced into the cell gap in the isotropic phase by capillary force. The cell gap was measured to be about 4 μm. The optical and electro-optical studies of the samples were carried out in a set-up consisting of polarizing microscope, photodetector, digital camera, function generator with amplifier, and oscilloscope. The microscope is equipped with a Mettler thermostage FP52 and FP5 control unit allowing temperature control within 0.1°C. The position of the direction of the *slow* vibration of the sample, corresponding to the largest refractive index, was identified by means of a λ first-order red plate [12]. The inner surface of the cell substrates was covered by a thin unidirectionally rubbed polyimide layer that gives a uniform planar alignment with very low pretilt (less than 2°). The alignment of the samples was inspected in the polarizing microscope between crossed polarizers.

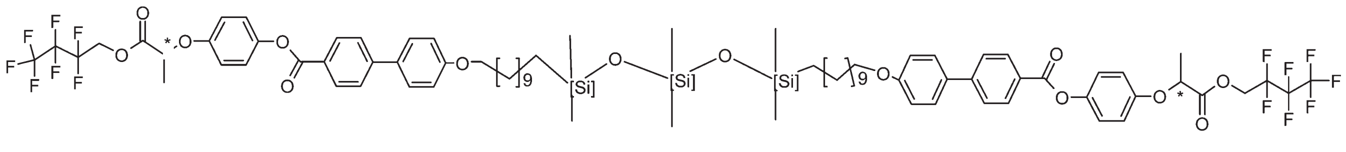
2.2. *Measurement of the molecular tilt and* Δn

The apparent tilt θ_{app} in the field-induced F state, which is the switching cone angle of the molecules, was measured instead of the molecular tilt θ in the AF phase. These two tilt angles could in principle have different magnitudes but, as we shall see, they are the same when the molecular tilt in the AF phase of the siloxane dimer studied in this work at a field-free condition becomes $\theta = 45^\circ$.

The θ_{app} was measured from the electro-optic response as half the angle between two extinction positions of the cell between crossed polarizers, measured at fully switched F states corresponding to different field polarities of the applied electric field. The transmitted light intensity I through the sample placed between the crossed polarizers is given by:

$$I = I_0 \sin^2 2(\Psi + \theta_{\mathrm{app}}) \sin^2 \pi d \Delta n / \lambda \qquad (1)$$

where Ψ is the angle between the transmission direction of the polarizer and the direction of the slow vibration of the sample. Δn is the sample birefringence, and λ is the wavelength of the incident light. First, $(\Psi + \theta_{\mathrm{app}})$ is set to zero at one field polarity, giving I a minimum (dark state). At the other field polarity, the sample is rotated to find $I_{\min}$ again. The angle of rotation of the



Highly ordered phase **79°C** AFLC *columnar 1* **102°C** AFLC *columnar 2* **133.5°C**

$\mathrm{SmC_A}$ **145°C** SmA **150°C** Iso

Figure 1. Structure and phase sequence, measured on heating the siloxane AFLC dimer; in E.H.C cells on cooling, the temperature range of the columnar 1 phase is broader.

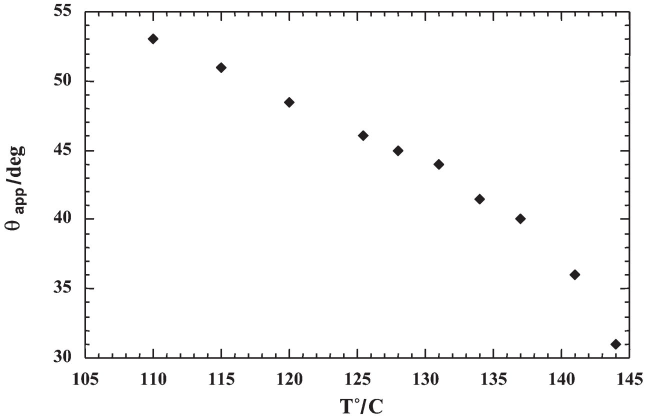


Figure 2. Apparent tilt angle θ_{app} measured in the field-induced F state, at saturated ferroelectric switching, as a function of temperature. For temperatures below 110°C, voltages near the dielectric breakdown of the cells are required in order to induce the F state.

sample will then simply correspond to $2\theta_{\mathrm{app}}$. The temperature dependence of the θ_{app} exhibited by the siloxane AFLC dimer studied in this work is given in figure 2.

The birefringence of the field-induced F state of the sample at $T=128$°C was estimated from the interference colour of the field-induced F state, using the Michel–Lévy chart, to be $\Delta n=0.16$.

3. Results and discussion

3.1. *General optical behaviour of the material*

It was found that the siloxane AFLC material in the experimental cells did not exhibit a pronounced helical molecular order. Moreover, it was found that the unidirectionally rubbed polyimide layer deposited on the inner surface of the cell substrates was reasonably efficient in aligning the siloxane material in a state that is referred to as the HAF state. In the HAF state, the plane containing the dimeric molecule and the smectic layer normal is parallel to the substrate plane (figure 3). Depending on the filling conditions, temperature treatment and subsequent treatment with an electric field, two kinds of cells were obtained, one with uniform and another with degenerate HAF alignment, respectively. The cells with the degenerate (polydomain) texture consisted of a set of large focal conic domains, possessing essentially a HAF alignment, whose preferred in-plane direction of the smectic layer normal varied from one domain to another, i.e. the samples exhibited an HAF texture with a degenerate in-plane orientation of the smectic layer normal. In the uniformly aligned samples, the HAF texture showed uniform in-plane orientation of the smectic layer normal everywhere. Samples of both kinds, with a uniform and a degenerate in-plane HAF state, were studied. The samples exhibiting a polydomain texture were of special interest since in this case there was no need to rotate the sample between the crossed polarizers. Thus the *zero* birefringence (black) state can be detected directly.

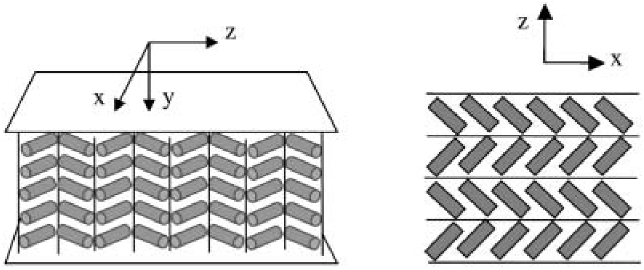


Figure 3. Schematic representation of the horizontal antiferroelectric (HAF) state [3] with the co-ordinate system used in this work. In the HAF state the molecular tilt plane, *xz*, contains the dimer molecules and the smectic layer normal.

Optical properties of samples aligned in a polydomain or in a uniform HAF texture were first studied in the field-free state. Figure 4 shows a sequence of photomicrographs of the sample with a polydomain HAF texture taken at different temperatures with and without a λ first-order red plate. The transmitted light intensity and the contrast between the dark state (in which the local position of the direction of the slow vibration is oriented parallel to one of the crossed polarizers) and the bright state (with the direction of the local slow vibration oriented 45° with respect to the polarizer) were found to decrease continuously as the temperature was reduced from 144 to 128°C and finally to become zero at 128°C. This is due to the reduction of the in-plane birefringence of the AF state with decreasing temperature. A decrease in the birefringence of the AF phase of (*R*)-MHPOBC at decreasing temperatures was also reported in [13].

At $T=128$°C, the siloxane AFLC dimer sample with a polydomain HAF texture, exhibiting degenerate in-plane orientation of the smectic layer normal, appeared totally black (not shown in figure 4) between the crossed polarizers, regardless of the local position of the smectic layer normal. The sample with a uniform HAF texture was also found to exhibit a superior black state that was independent of the position of the sample smectic layer normal between the crossed polarizers. These observations indicate that the in-plane birefringence of the samples filled with siloxane dimer oriented in the HAF texture, regardless of whether they are uniform or multidomain, is zero at temperature $T=128$°C. As we shall see later, the reason for the appearance of the field-free totally black state

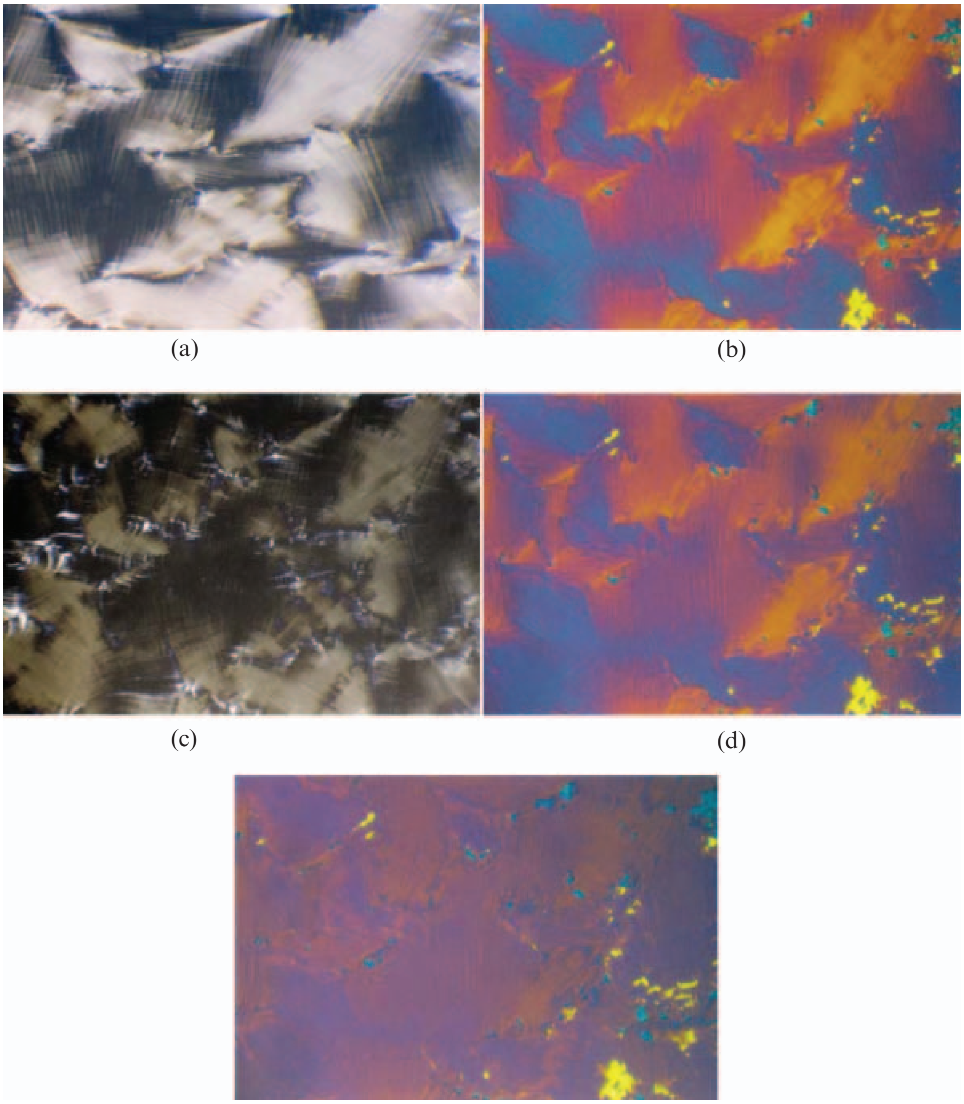

(a) (b) (c) (d) (e)

Figure 4. Photomicrographs of a cell with a polydomain HAF texture of the siloxane AFLC dimer taken between crossed polarizers at temperatures (*a*) $T=136^\circ$C and (*c*) $T=132^\circ$C before inserting a λ first-order red plate, and after (*b*) and (*d*), respectively. Photomicrograph (*e*) is taken when approaching close to $T=128^\circ$C, at which temperature the molecular tilt of the dimer is 45°. At $T=128^\circ$C, the sample exhibited a totally black state, i.e. $\Delta n=0$, and therefore the interference colour of the λ plate, which is red, did not change, see figure 6(*c*). Despite the polydomain texture and disturbances from the local defects in the HAF alignment, the decreasing difference in the interference colour of the differently oriented domains when approaching close to 128°C is clearly seen.

at $T=128^\circ$C is that the molecular tilt θ in the AF phase aligned in the HAF texture is 45°. On inserting a λ first-order red plate between the sample and the analyser the black state, i.e. the state with zero birefringence, became reddish, as seen in figure 4, and hence more easily shown and analysed. Only the local defects in the HAF texture were visible, whereas the rest of the area, even though the in-plane orientation of the smectic layer normal varied locally, exhibited a relatively homogeneous colour, indicating unambiguously that the AF phase of the siloxane dimer possesses a zero birefringence state.

The apparent tilt angle θ_{app} was measured as a function of the temperature (cf. figure 2). It was found that θ_{app} increased with temperature and reached a maximum value of 53° at $T=110^\circ$C. At lower temperatures, however, very high voltages were required and close to the electrical breakdown of the cell in order to measure the θ_{app}. Thus the measurements of θ_{app} were only performed to 110°C.

To measure θ_{app} in the vicinity of 45°, additional experiments were carried out in which a λ first-order red plate was used. For instance, the magnitude of the θ_{app} at $T=128$°C was confirmed to be 45° by studying the electro-optic response of a cell with uniform HAF alignment inserted between crossed polarizers. The sample was oriented between the polarizers with the direction of the slow vibration of one of the field-induced F states at 45° with respect to the transmission direction of the polarizer. In this setting, the electro-optic response of the sample at $T=128$°C was found to be quadratic, figure 5 (*a*); i.e. the switching states corresponding to the different polarity of the applied electric field had the same optical appearance between crossed polarizers. In general, there are two possible reasons for such a response; first, the switching is of dielectric origin (non-polar and therefore quadratic), or second, the switching is ferroelectric with a cone angle of 90°. (The ferroelectric switching, even though polar, will, in the case of $\theta_{app}=45$°, result in 90° switching of the direction of the slow vibration. Hence, the two field-induced F states, corresponding to the different field polarities, will be optically indistinguishable between crossed polarizers.) In order to distinguish between these two possibilities for the quadratic electro-optic response detected at $T=128$°C, a λ first-order red plate was inserted between the sample and the analyser, oriented with its slow vibration direction at a position of 45°, i.e. along the slow vibration direction of one of the field-induced F states. If the electro-optic response was of dielectric origin, i.e. if it was non-polar and, moreover, an out-of-plane type of switching, the quadratic character of the response would not change after the insertion of the λ red plate. However, if the response is due to ferroelectric (in-plane) switching, the intensity of the transmitted light would then be dependent on the polarity of the electric field applied. This is because the direction of the slow vibration of the sample in this experimental arrangement will switch between two different positions, parallel and perpendicular to the direction of the slow vibration of the λ first-order red plate. This in turn, will result in an increase and a decrease, respectively, of the total phase retardation of the sample and the λ-plate, depending on the field polarity, as observed experimentally; cf. figure 5 (*b*). Hence, it is confirmed by the quadratic electro-optic response detected at $T=128$°C that the θ_{app} in the field-induced F state is 45°. As we shall see later, the molecular tilt θ in the AF phase has the same magnitude as θ_{app} in the field-induced F state, i.e. 45°. This is because at $T=128$°C the AF phase aligned in the HAF state exhibits zero birefringence in field-free conditions, thus indicating that the θ in the AF phase at this temperature is also 45°.

The temperature dependence of Δn of an AFLC sample with a uniform HAF texture was studied on cooling from $T=144$°C. The sample was oriented with its smectic layer normal at 45° with respect to the polarizers. The changes in Δn were estimated from the changes in the interference colour of the sample investigated in the polarizing microscope with an inserted λ first-order red plate. On lowering the temperature below 144°C it was found that Δn started to decrease quickly and became zero at 128°C, as mentioned previously. On further decreasing the temperature below $T=128$°C, Δn first started to increase and became saturated at $T=90$°C. When the temperature was decreased below $T=90$°C, Δn fell, reaching zero at $T=73$°C, then increased again when the temperature was decreased even further. Hence, at $T=73$°C, the sample exhibited zero in-plane birefringence a second time, which indicated that θ had again become 45°. A further decrease of the temperature resulted in an increase in Δn, due most probably to a decrease in the molecular tilt below 45°.

The position of the direction of the slow vibration of the AF phase in the sample with a uniform HAF texture, corresponding to the largest refractive index, was defined by means of a λ first-order red plate. The sample and λ-plate were placed between the crossed polarizers. The sample was oriented with the smectic layer normal along the direction of the slow vibration of the λ-plate, which in turn was oriented 45° with respect to the transmission direction of the polarizer. As is known, in the case of typical AFLCs (with tilt angles usually in the range 23°–35° [14, 15], i.e. lower than 45°), the direction of the slow vibration of the HAF state is directed along the smectic layer normal. Figure 6 shows a sequence of photomicrographs illustrating the optical appearance of the AF phase, uniformly oriented in the HAF state, at different temperatures. In the experimental arrangement, in which the smectic layer normal is oriented along the direction of the slow vibration of the λ-plate, if the direction of the slow vibration lies along the smectic layer normal then the phase retardation of the sample will be added to the phase retardation of the λ plate. Hence, the interference colour of the λ-plate, which is red, will increase in level to blue–green. As seen in figure 6 (*a*), the interference colour detected at temperatures higher than $T=128$°C is blue, thus indicating that the direction corresponding to the largest refractive index coincides with the smectic layer normal. If the sample is rotated 90°, thus making the smectic layer normal perpendicular to the slow axis of the λ-plate, the phase retardation of the sample will now subtract from the phase retardation of the λ-plate, which results in a decrease in the level of the interference colour to

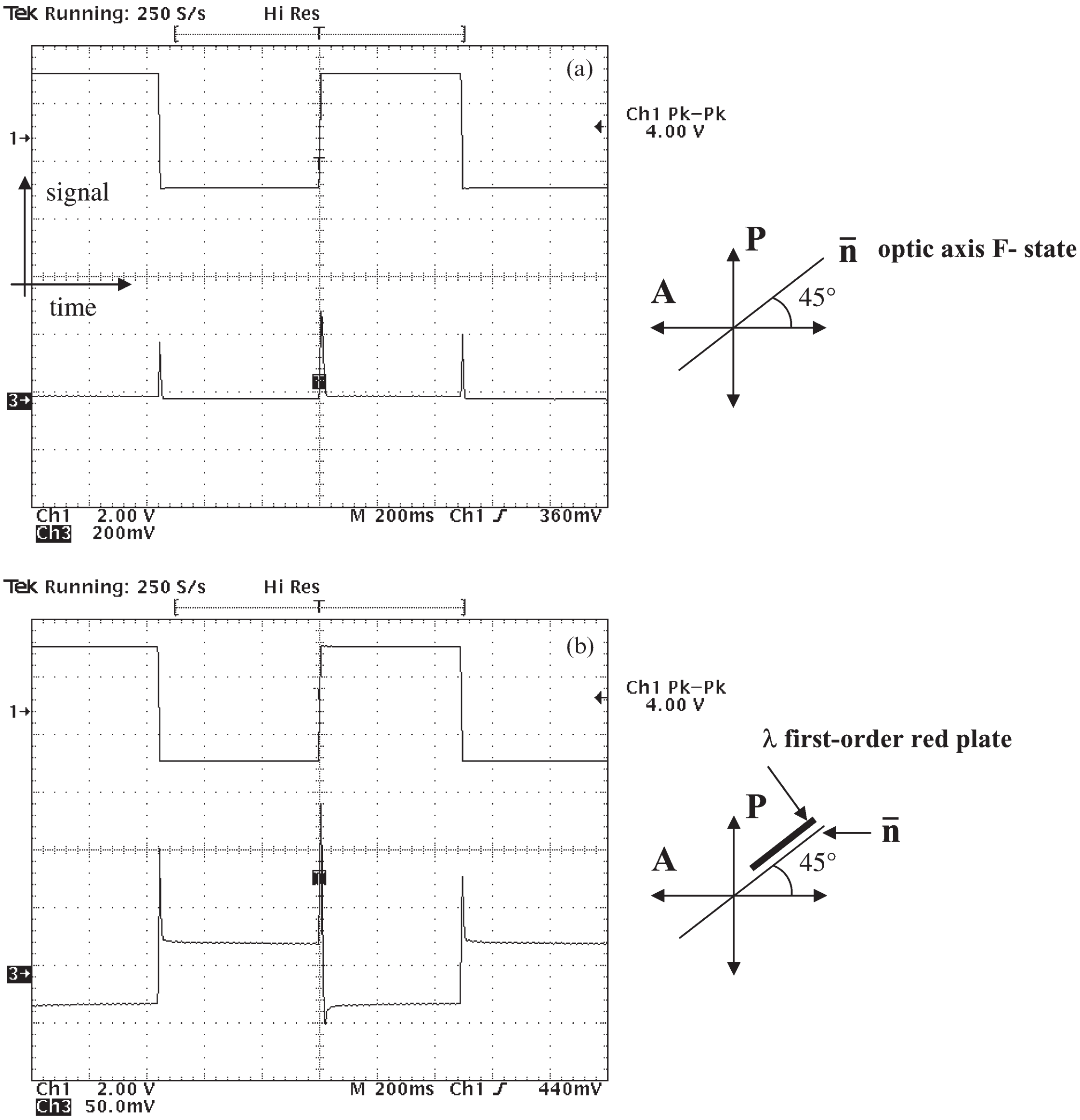


Figure 5. Electro-optic response of a cell with a uniform HAF texture at $T = 128°C$ (trace 3) between crossed polarisers (*a*) before and (*b*) after inserting a λ first-order red plate (trace 1 is the applied voltage form). The cell was oriented with the optic axis of one of the field-induced F states at 45° with respect to the polarizer. Before inserting the λ-plate, the response was quadratic. This changed to linear in the presence of the λ-plate, hence indicating an in-plane ferroelectric switching.

yellow. This, as seen in figure 6 (*b*), was found experimentally. Returning the sample to the initial arrangement, with the smectic layer normal directed along the direction of the slow vibration of the λ-plate, and reducing the temperature below 128°C in the interval $73°C < T < 128°C$, the interference colour appeared to be yellow, figure 6 (*d*)). This change in the interference colour indicates a flip of the direction of the slow vibration of the sample from a position parallel to the slow axis of the λ-plate, detected at temperatures $T > 128°C$, to a position perpendicular to it at lower temperatures. Hence, in the temperature interval $73°C < T < 128°C$, the direction of the slow vibration of the HAF state is perpendicular to the smectic layer normal. If we define Δn as the difference in refractive index between vibrations parallel and perpendicular to the layer normal, we can thus conclude that Δn is negative in the interval $73°C < T < 128°C$. At temperatures below 73°C, the interference colour changed to blue, figure 6 (*f*), thus indicating a reverse flip of the direction of the slow vibration from a position perpendicular to the smectic layer normal to a position parallel to it. At temperatures 128°C, figure 6 (*c*), and 73°C,

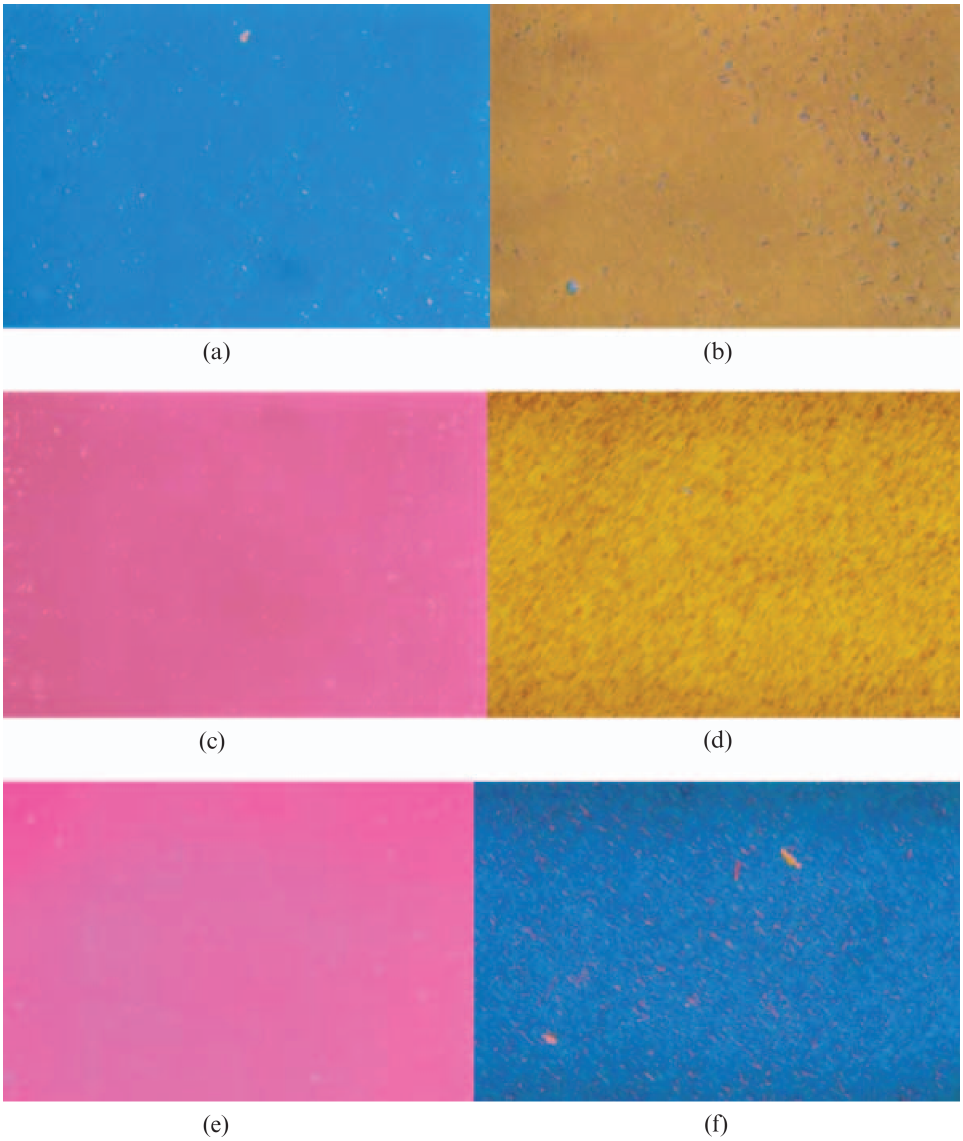


Figure 6. Microphotographs of the siloxane AFLC dimer aligned uniformly in the HAF state at different temperatures. (*a*) $T=132°C$, (*b*) $T=132°C$ (the cell is notated 90°), (*c*) $T=128°C$, (*d*) $T=115°C$, (*e*) $T=73°C$, (*f*) $T=68°C$. For explanations of the colour changes see the text.

figure 6 (*e*), as mentioned previously, $\Delta n=0$, and hence the interference colour of the cell and the λ plate will be that of the λ-plate, i.e. first-order red.

3.2. *Optical properties of the HAF state*

The molecules of nematic liquid crystals possess orientational but not positional order. Nematic liquid crystals, due to molecular rotational symmetry, are optically uniaxial. Their optical properties can be described in terms of the optical indicatrix which, in this case, is a prolate ellipsoid whose long axis is oriented parallel to the preferred direction of alignment of the liquid crystal molecules. The three principal axes of the optical indicatrix correspond to the ordinary n_o (two short axes) and extraordinary n_e (one long axis) refractive indices, respectively.

The molecules in the smectic liquid crystals are arranged in layers, i.e. they have a positional order in addition to the orientational one, forming two-dimensional liquids. In the orthogonal smectic phases, the molecules are oriented along the smectic layer normal and they, like the nematics, possess uniaxial optical properties. The molecules of each smectic layer in the tilted smectic phases are oriented at a fixed angle θ (tilt angle) with respect to the layer normal. This tilt may have the same sign in the adjacent smectic layers, i.e. tilted smectic phases of this kind possess a *synclinic* molecular order. The tilted smectics are biaxial and their optical properties can be described by a triaxial ellipsoid with three mutually perpendicular principle radii corresponding in length to the three principal indices [16]. In the tilted smectics with *synclinic* molecular order, such as smectic C, the principal optical plane of the optical ellipsoid containing the two optic axes coincides with the molecular tilt plane formed by the long molecular axis and the smectic layer normal. In general, the degree of the biaxiality in tilted smectics is very low and they can be considered with a good approximation as optically uniaxial. In this case, the long molecular axis, which is also the acute bisectrix of the two optic axes of the biaxial indicatrix, takes the role of the optic axis. Hence, the optic axis in tilted smectics appears to be tilted with respect to the smectic layer normal at an angle approximately equal to the molecular tilt, θ.

When the constituent molecules of the tilted smectics are chiral, i.e. the mirror symmetry of the phase is broken then each smectic layer exhibits a spontaneous polarization, P_s, directed along the smectic layer and perpendicular to the molecular tilt plane, containing the molecules and the smectic layer normal. The chiral tilted smectic liquid crystals with a *synclinic* molecular order form the class of FLCs. In the FLC, the *c*-director (the projection of the long molecular axis onto the plane of the smectic layer), due to the chirality in the field-free condition, might form a helix with an axis along the smectic layer normal and with a pitch in the micrometer range. However, in thin samples, a helical molecular order with the helix axis lying along the substrates may be efficiently suppressed by the solid surface–liquid crystal interactions at the boundaries. Monostable or multistable configurations are then obtained, and these can be switched by an electric field applied parallel to the smectic layers, which in turn gives rise to a distinct electro-optic response.

Antiferroelectric liquid crystals (AFLCs) belong to the general class of tilted chiral smectic liquid crystals in which the molecular tilt angle in adjacent smectic layers has the opposite sign, the so-called *anticlinic* molecular order. In AFLCs, the *c*-directors of adjacent layers are almost antiparallel. As a result of the anticlinic molecular order in AFLCs, the $\mathbf{P}_s$ vectors of the adjacent smectic layers are nearly antiparallel. This leads to a macroscopic $\mathbf{P}_s = 0$ (figure 7). Hence, the AFLCs do not exhibit a macroscopic $\mathbf{P}_s$. As with the FLCs, the AFLCs, because of chirality, exhibit a long range helical structure in addition to the short range anticlinic molecular order. Also, as in the case of synclinic FLCs, the helical structure can be suppressed by the surfaces of the confining substrates. The siloxane dimer studied in this work was successfully surface-stabilized in the cells with a gap of 4 μm, indicating that the material possesses a long pitch, if any. AFLCs, like FLCs, are biaxial but with the principal optical plane, which contains the two optic axes (optical axial plane), perpendicular to the molecular tilt plane [17–19] (see figure 8). The direction of the slow vibration in the HAF state coincides with the smectic layer normal and acts as an effective optic axis of the AFLC. An external electric field applied along the smectic layers at $\mathbf{E} > \mathbf{E}_{th}$ will align the $\mathbf{P}_s$ of the adjacent smectic layers along the field direction and thus will induce a transition to the F state (see figure 7). The field-induced AF to F transition was first reported by Chandani *et al.* [1, 2] and soon became of great scientific and technological interest. The field-induced transition from the AF to F state, so-called three-state switching, results in a substantial change in the position of the direction of the local slow vibration as well as of the birefringence of the AFLC sample. The field-induced AF–F transition, however, is *always* preceded by a pre-transitional phenomenon described widely in the literature [20–24]. The character

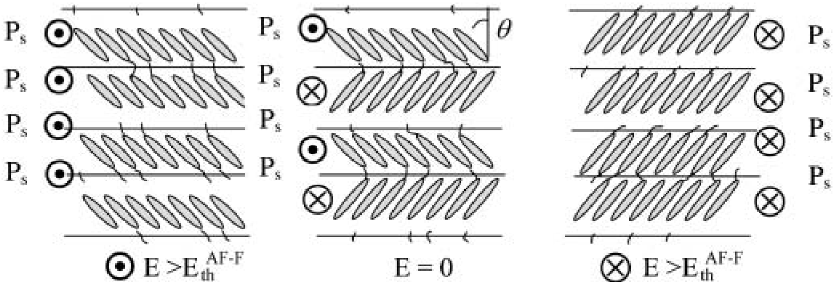


Figure 7. Schematic presentation of the field-induced F state on applying an electric field along the smectic layers, i.e. perpendicular to the sample substrates, when the AFLC is oriented in the HAF state. A sufficiently high electric field, $\mathbf{E} > \mathbf{E}_{th}^{AF}$, will transform the anticlinic order of AFLC to synclinic (field-induced F state) due to coupling between the spontaneous polarization $\mathbf{P}_s$ of the smectic layers and the applied field.

of the pre-transitional effect depends strongly on the material properties [25].

Consider an AFLC sample aligned in the HAF state (cf. figure 3) and light impinging the sample at normal incidence. Figure 8 schematically illustrates the molecular tilt plane containing the dimeric molecules and the smectic layer normal. The biaxial optical properties of the AFLC are represented by the indicatrix ellipsoid, which, for tilt angles in the range $20° < \theta < 37°$, typical for most AFLC materials [14, 15], has a prolate form. In the HAF state, the acute bisectrix of the two optic axes of the biaxial indicatrix is parallel to both the substrates and the smectic layer normal and represents the direction of the in-plane slow vibration. If the acute bisectrix Bxa is along the direction of maximum refractive index, i.e. the z-axis, the biaxiality has a positive sign. This occurs when the angle between the two optic axes $2V < 90°$. If it is along the direction of the lowest refractive index, i.e. the y-axis $\equiv$ Bxo, the biaxility then has a negative sign [12].

AFLCs possess an anticlinic molecular order with a periodicity that is several orders of magnitude smaller than the wavelength of the incident light. Hence, the impinging light will not see the anticlinic structure. The optical properties of an AFLC can therefore be presented as the optical properties of a uniform medium consisting of two synclinic structures with molecular tilts of $-\theta$ and $+\theta$.

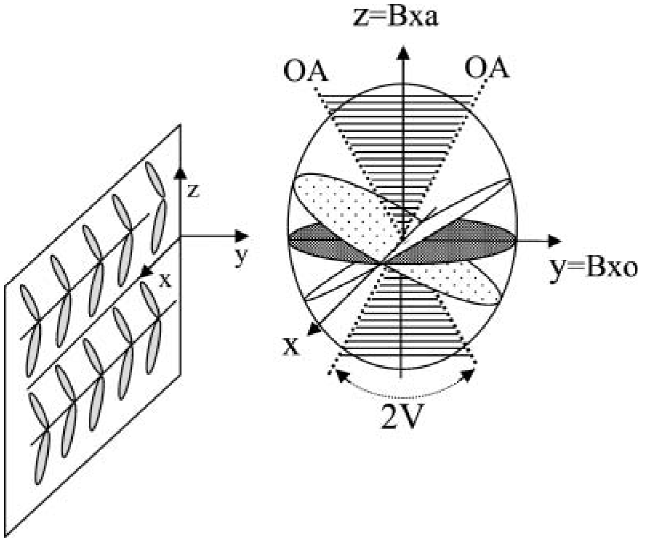


Figure 8. Schematic representation of the optical properties of AFLCs aligned in the HAF state; *xz* is the molecular tilt plane containing the dimers and the smectic layer normal. The optical properties of the HAF state are represented by a biaxial indicatrix whose principal optical plane, containing the two optic axes, is perpendicular to the molecular tilt plane. These axes make an angle $2V$ which is a measure of the degree of biaxility. See text for discussion of biaxiality.

The optical properties of AFLCs with an unwound helix are well described by de Meyere *et al.* [4]. In the co-ordinate system with the z-axis directed along the smectic layer normal, the x-axis lying in the tilt plane of the AFLCs, and the y-axis perpendicular to it (cf. figure 8), the optical properties of the *single* synclinic structure can be described by the dielectric tensor [4]:

$$\varepsilon_{\text{syncl}}(\theta) = \begin{pmatrix} \varepsilon_\perp \cos^2\theta + \varepsilon_\parallel \sin^2\theta & 0 & (\varepsilon_\parallel - \varepsilon_\perp)\sin\theta\cos\theta \\ 0 & \varepsilon_\perp & 0 \\ (\varepsilon_\parallel - \varepsilon_\perp)\sin\theta\cos\theta & 0 & \varepsilon_\perp \sin^2\theta + \varepsilon_\parallel \cos^2\theta \end{pmatrix} \tag{2}$$

where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are the dielectric constants, parallel and perpendicular, respectively, to the long molecular axis. The optical properties of an AFLC with an unwound helix will then be represented by the effective dielectric tensor:

$$\varepsilon_{\text{anticl}} = \frac{1}{2}\left[\varepsilon_{\text{syncl}}(+\theta) + \varepsilon_{\text{syncl}}(-\theta)\right] = \begin{pmatrix} \varepsilon_\perp \cos^2\theta + \varepsilon_\parallel \sin^2\theta & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\perp \sin^2\theta + \varepsilon_\parallel \cos^2\theta \end{pmatrix} \tag{3}$$

for optical frequencies, $n_\perp^2 = n_o^2 = \varepsilon_\perp$ and $n_\parallel^2 = n_e^2 = \varepsilon_\parallel$, where n_o and n_e are the ordinary and extraordinary refractive indices, respectively. If n_x and n_z are the refractive indices in the tilt plane, which in the HAF state is parallel to the substrates, n_x and n_z are the refractive indices perpendicular to and along the smectic layer normal of the AFLC, respectively, while n_y is the refractive index along the y-axis, which is perpendicular to the smectic layer normal and the tilt plane, i.e. to the glass substrates. A simple model gives [4, 26]:

$$\begin{aligned} n_x &= \left(n_o^2 \cos^2\theta + n_e^2 \sin^2\theta\right)^{\frac{1}{2}} \\ n_y &= n_o \\ n_z &= \left(n_o^2 \sin^2\theta + n_e^2 \cos^2\theta\right)^{\frac{1}{2}} \end{aligned} \tag{4}$$

where, for molecular tilt angles of $\theta < 45°$, $n_y < n_x < n_z$, whereas, for $\theta > 45°$, $n_y < n_z < n_x$. An AFLC sample oriented in the HAF state will exhibit in-plane birefringence (i.e. in the *XOZ* plane, $\Delta n_{z-x} = n_z - n_x$ (cf. figure 8). De Meyere concluded from equation (4) that *for* $\theta = 45°$, $\Delta n_{z-x} = 0$, and he predicted that *in an ideal AFLCD the alternating state is totally dark* ***in whatever position between two perpendicular polarizers!!*** Hence, an AFLC sample with a HAF alignment will exhibit at normal light incidence an optically zero birefringent state when the molecular tilt is $\theta=45^\circ$, which our experiment has indeed shown to occur at 128 and 73°C.

The maximum light transmission intensity I_m through a birefringent sample at normal light incidence is achieved when the sample optic axis, i.e. the direction of the slow vibration, is oriented at 45° with respect to the transmission direction of one of the polarizers. Then from equation (1) we can write:

$$I_m = I_o \sin^2 \pi d \Delta n / \lambda \qquad (5)$$

The birefringence of the sample aligned in the HAF state is $\Delta n = n_z - n_x$. Setting the position of the direction of the slow vibration at 45° with respect to the crossed polarizers at normal incidence of the light, I_m will be zero, i.e. a totally black state, when $\Delta n = 0$. Such a black state was indeed found at $T=128^\circ$C and at $T=73^\circ$C. Moreover, the quality of the black state was independent of the in-plane position of the smectic layer normal between the crossed polarizers, thus indicating that the in-plane birefringence is indeed $\Delta n = n_z - n_x = 0$ and the sample is in the HAF state.

A few AFLC compounds with molecular tilt angles close to 45° have been studied previously. Siloxane bimesogenic AFLCs with molecular tilt angles in the interval 40.4°–43.5° were reported in [6–9]. It was also recently found that some materials exhibited a very low in-plane birefringence of $\Delta n \approx 0$ (Δn was measured in the interval 0.005–0.008, which is very low indeed in comparison with other liquid crystals) [6, 7]. A monomeric AFLC mixture possessing a molecular tilt of about 42°, and thus a low in-plane birefringence ($\Delta n = 0.019$) when aligned in the HAF state, was reported in [27]. However, neither this mixture nor the bi-mesogenic siloxanes studied in [6, 7] possess exactly a 45° molecular tilt in the AF phase and, hence, these materials are not capable of exhibiting a zero birefringent (totally black) state, i.e. $\Delta n = 0$, when aligned in the HAF state. To our knowledge the siloxane dimer studied in this work is the first AFLC material that has been proven to exhibit a molecular tilt of $\theta=45^\circ$ at field-free conditions in a sample aligned in the HAF state in which a *totally* black state, i.e. a state with $\Delta n = 0$, was detected. Such a black state was found to occur at two different temperatures in this compound.

It is easy to understand from equation (4) that at $\theta=45^\circ$ the HAF state of the AFLC sample becomes *negative uniaxial*, since $n_x = n_z$ and n_x, $n_z > n_y$. This means that the optical indicatrix of an AFLC sample with a molecular tilt of $\theta=45^\circ$, aligned in the HAF state, will have the form of an oblate ellipsoid with the optic axis perpendicular to the confining substrates, i.e. along the *y*-axis (cf. figure 8). Hence, in the case of normal incidence of the light, the AFLC sample exhibiting $\Delta n_{z-x} = n_z - n_x = 0$ will behave as negatively uniaxial with an optic axis corresponding to the smallest refractive index, n_o. Our samples containing the siloxane dimer aligned in the HAF state are found to exhibit a totally black state at $T=128$ and 73°C when inserted between crossed polarizers. The in-plane changes in the position of the smectic layer normal of the samples do not affect the quality of the black state at all. Hence, at these temperatures, the AFLC sample aligned in the HAF state behaved as a negative uniaxial optical plate with its optic axis oriented perpendicular to the sample substrates.

The changes in the optical properties of the HAF state with the molecular tilt θ are illustrated in figure 9, where values of $n_o = 1.51$ and $n_e, = 1.67$ (which are typical values for the field-induced F state [28]) are inserted in equation (4). As seen, for $\theta < 35^\circ$ and for $\theta > 55^\circ$, the optical biaxiality is positive, while it is negative for $35^\circ < \theta < 45^\circ$ and for $45^\circ < \theta < 55^\circ$. At 45°, at which the Δn of the HAF state becomes zero (figure 10), the optical indicatrix of the sample is represented by a negative uniaxial ellipsoid (cf. figure 9). If we now follow the position of the slow vibration direction in the sample plane (*xz*-plane), we will find that this axis flips from a position parallel

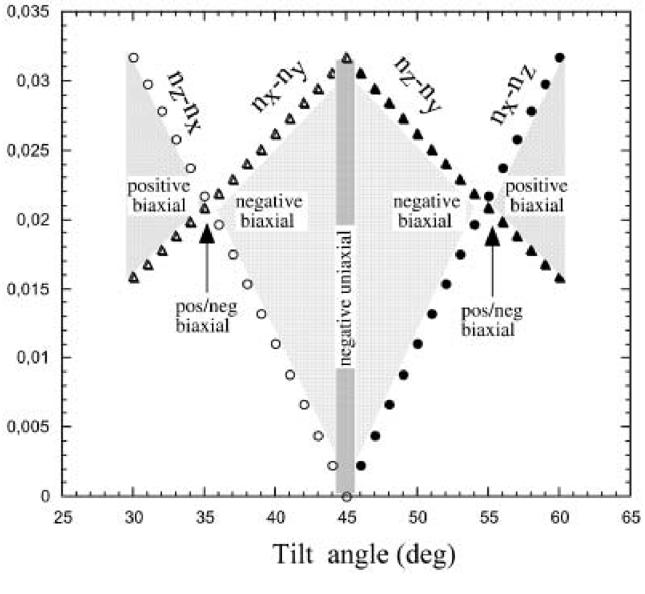


Figure 9. Schematic representation of the optical properties of AFLCs, aligned in the HAF state. Refractive indices n_z and n_x are given by equation (4) where ordinary n_o and extraordinary n_e refractive indices are assumed to have values of 1.51 and 1.67, respectively [28]. See text for detailed discussion.

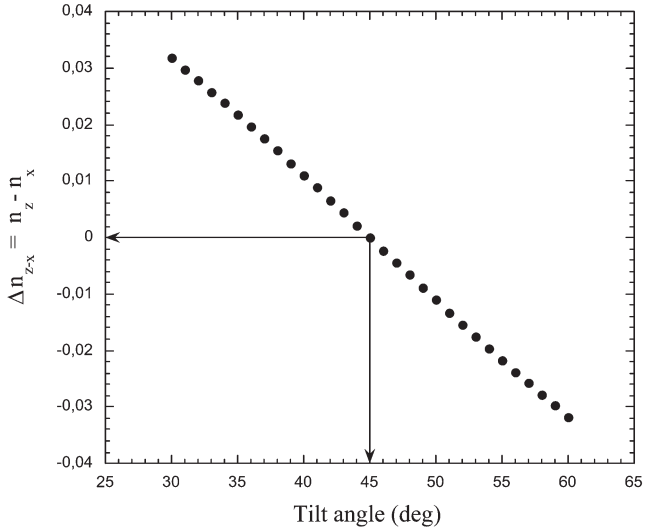


Figure 10. Dependence of the birefringence, $\Delta n = n_z - n_x$, of AFLCs aligned in the HAF state as a function of the molecular tilt θ. Refractive indices n_z and n_x are given by equation (4) (see figure 9). At a molecular tilt of $\theta = 45°$ Δn changes its sign, which corresponds to a flip of 90° of the direction of the slow vibration in the xz-plane (see figure 11).

to the smectic layer normal, oriented along the z-axis, to a position perpendicular to it, i.e. it becomes parallel to the x-axis, when $\theta < 45°$ (see figure 11). This flip of the direction of the slow vibration in the HAF state between two orthogonal directions, as described already, has experimentally been found to take place in the siloxane dimer studied in this work.

In the HAF state, an external electric field **E** applied along the smectic layers of the AFLCs orient the $\mathbf{P}_s$ of the adjacent smectic layers along the field direction and, hence, may induce a ferroelectric (F) state when the field strength is higher than E_{th}^{AF-F}, the threshold for the field-induced AF–F transition. The principal optical plane of the biaxial indicatrix of the field-induced F state containing the two optic axes now becomes parallel to the substrates, i.e. it rotates 90° with respect to that of the field-free HAF state. The acute bisectrix of the F state which, as mentioned before, is regarded as the effective optic axis of this state, will lie in the plane of the substrates and be tilted at angle θ with respect to the smectic layer normal. By changing the field polarity, the effective optic axis will swing in the plane of the sample at angle $2\theta_{app}$. The case of $\theta = 45°$ is of particular interest. In this case, applying an electric field across the AFLC sample, i.e. perpendicular to the sample substrates, will switch the direction of the slow vibration between two mutually perpendicular positions, lying in the sample plane and corresponding to the optic axis of the field-induced F states; whereas the

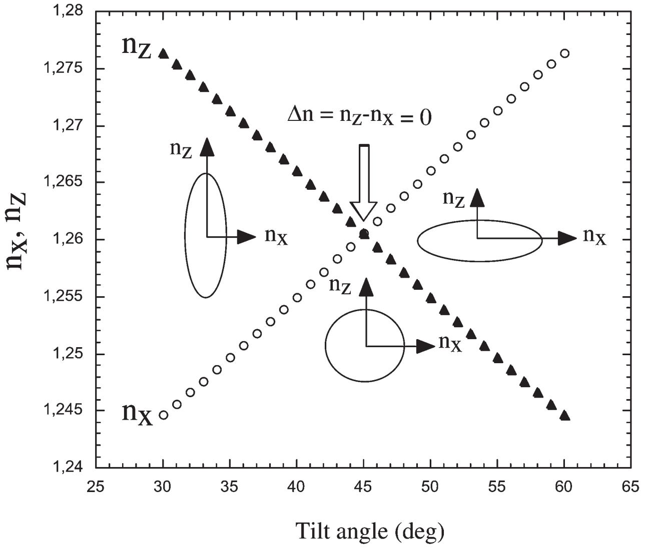


Figure 11. Schematic representation of the n_z and n_x of the HAF state, as a function of the molecular tilt, θ. Refractive indices n_z and n_x are given by equation (4) (see figure 9). For $\theta < 45°$, the slow vibration direction in the sample plane, i.e. the xz-plane, is along the z-axis. At $\theta = 45°$, $n_z = n_x$, i.e. $\Delta n = n_z - n_x = 0$ and, hence, HAF exhibits negative uniaxial properties, since $n_y < n_x$, n_z, with the optic axis of the indicatrix perpendicular to the sample substrates. At $\theta > 45°$, the slow vibration direction of the sample plane is now along the x-axis, i.e. it flips 90°.

sample at field-free conditions will exhibit negative uniaxial properties characterized by a zero in-plane birefringent state and optic axis perpendicular to the substrates (see figure 12).

On applying an electric field with strength **E** above $\mathbf{E}_{th}$, the sample in the AF phase was switched to the F state (figure 13). $\mathbf{E}_{th}^{AF-F}$ was found to increase strongly with decreasing temperature and very high fields indeed were needed to switch the sample to the F state for temperatures below 115°C. For electric fields $\mathbf{E} < \mathbf{E}_{th}$, a pre-transitional behaviour was detected that was similar to that of another siloxane liquid crystal dimer recently studied by ourselves [25]. A particularly interesting feature of the pre-transitional state observed in the experimental cells in this study is the optical appearance, which is much brighter than that of the field-induced F state. In figure 13 are shown (*a*) the field-induced F state, (*b*) the pre-transitional state and (*c*) the relaxation to the AF state from the pre-transitional AF state (the photomicrographs are taken at $T = 128°C$). As can be seen, the contrast between the AF state (the black regions) and the pre-transitional AF state (the large bright regions of the transient texture) when the field is switched off is extremely high.

This study and others we have carried out on AFLC

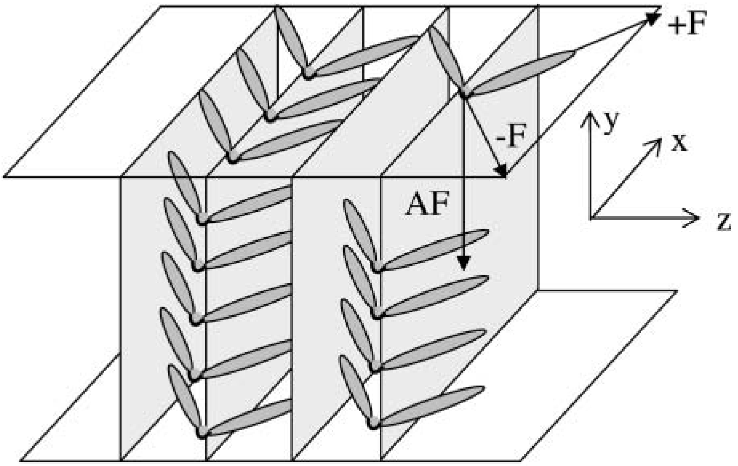
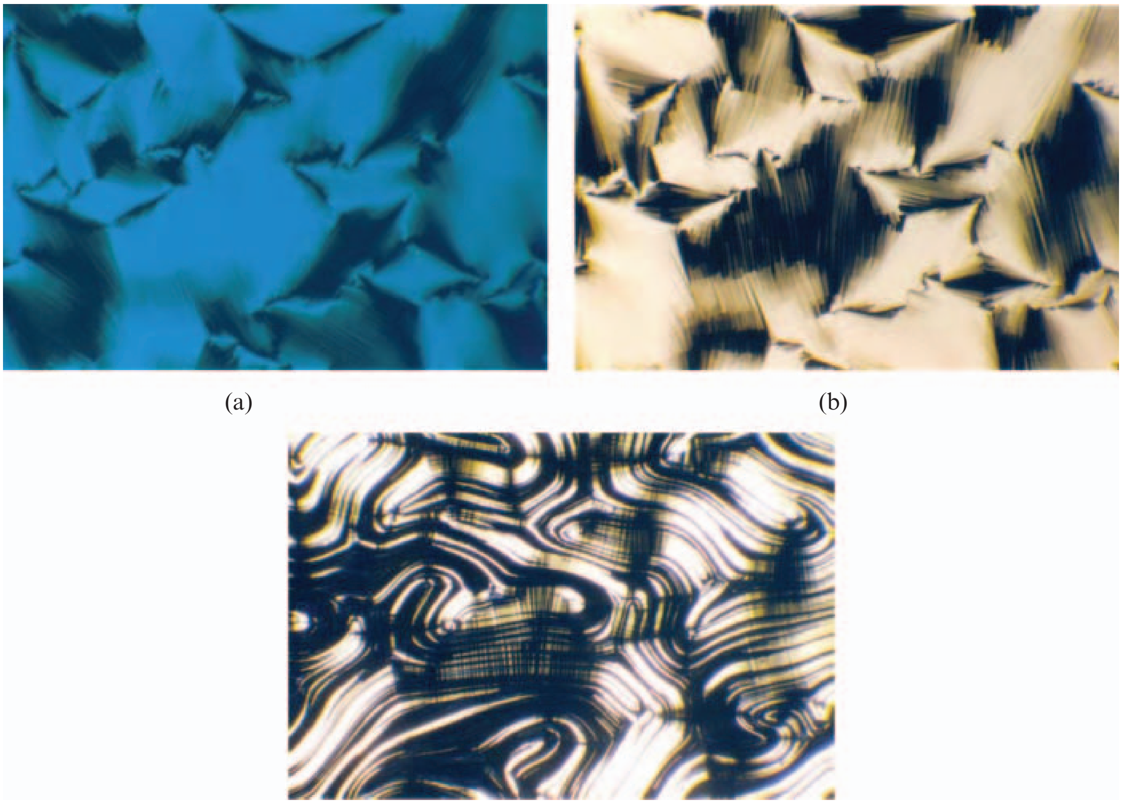


Figure 12. Schematic representation of the switching of the siloxane AFLC dimer by an electric field applied across the sample, i.e. along the y-axis (see also figure 3 and 8).



(a) (b)

(c)

Figure 13. Photomicrographs of a cell with a polydomain HAF texture of the siloxane AFLC dimer taken between crossed polarizers at temperature $T=128^\circ$C, at which the molecular tilt θ of the dimer is 45°. (*a*) On applying a sufficiently high electric field across the cell, the F state is induced. (*b*) At lower field strength, a pre-transitional behaviour was detected. The pre-transitional state in the experimental samples appeared to be quite bright. After removal of the field, the field-induced F state and the pre-transitional state relaxed to the field-free state, which is totally black. Photomicrograph (*c*) illustrates the contrast between the pre-transitional (bright) and the relaxed (black) states. As seen, the contrast is extremely high and the quality of the black state does not depend on the local variation of the smectic layer normal in the polydomain texture.

siloxane dimeric materials have shown that these compounds possess quite remarkable and attractive properties. Despite the zero birefringent states that the AFLC sample aligned in the HAF state was found to exhibit in this study, other siloxane dimers studied by ourselves have shown a peculiar pre-transitional behaviour [25]. It was found in some of these materials that the field-induced AF–F transition, which is usually of the first order characterized by nucleation and propagation of finger-like solitary waves, is instead continuous and, hence, appeared to be of second order. In general, in the pre-transitional region of these siloxane dimers, the field-induced deviation of the effective sample optic axis was found to be a linear function of the applied electric field, and in some cases exceeded 20°. The apparent tilt angle in these materials was also found to be close to 45°. Hence, the siloxane AFLC dimers that combine the properties of AFLCs with a molecular tilt of 45°, as excellent dark state, with those of AFLCs exhibiting a second order field-induced AF–F transition, with grey scale capability, seem to be very attractive materials for high performance display applications.

The switching from the AF state to the F state results in large changes in the birefringence. Changes of Δn of this kind have potential for applications in photonics, such as phase modulators or beam steering devices. On the other hand, the linear electro-optic response detected in the pre-transitional region of the AF phase might be a candidate for applications in light intensity modulation devices. The bi-mesogenic siloxane AFLCs have in general an important advantage compared to monomeric AFLCs. The molecular tilt in the bimesogenic siloxanes caused by the siloxane bridging unit is often temperature independent over a broad temperature interval. This makes the bi-mesogenic siloxane AFLCs very attractive for applications in displays and photonic devices.

4. Conclusions

In this work we experimentally found that the siloxane AFLC dimer, aligned in the HAF state, exhibited two field-free zero birefringent states, at 128 and at 73°C. These states were found when the molecular tilt of the field-free AF state became 45°, and they were optically totally black regardless of the sample position between crossed polarizers. It is also confirmed that the apparent tilt angle θ_{app} measured in the field-induced F state at 128°C had the same magnitude (i.e. 45°) as the molecular tilt θ in the field-free AF state at this temperature. An interesting observation was the flip of the direction of the slow vibration, i.e. the direction corresponding to the largest refractive index, found to occur twice, specifically at 128 and 73°C, i.e. at the same temperatures at which the field-free in-plane birefringence of the AF state became zero.

The AFLC siloxane dimer studied in this work exhibited an extraordinarily large molecular tilt of 53° in the AFLC phase. The temperature dependence of the molecular tilt of this dimer made it possible to study the optical and electro-optical properties of the AFLC dimer when the molecular tilt becomes 45°, as well as when the molecular tilt is larger or smaller but close to 45°. Due to the temperature dependence of the tilt angle as well as to the high transition temperatures, this siloxane AFLC dimer might be regarded as an AFLC material of only scientific interest. However, similar AFLC siloxane dimers studied previously by Coles and his co-workers as well as by ourselves [6, 7, 25, 29] possess properties that in many cases are superior to those exhibited by monomeric AFLCs. First of all, it should be noted that these siloxane dimers generally have a considerably more stable AF phase due to the siloxane unit. The siloxane dimers, even though they are single compounds and not mixtures, exhibited an AF phase over a broad temperature interval. Their molecular tilt is usually large and in some cases is very close to 45°. In contrast to the molecular tilt of monomeric single compounds, the temperature dependence of the molecular tilt of the siloxane dimers in the AF as well as in the F phase is generally comparatively minor, which is in fact a great advantage, especially in terms of display applications [6, 7, 25, 29]. The promising properties of siloxane dimers imply that we might find attractive AFLC characteristics in the general class of liquid crystal dimers. Moreover, it seems possible by appropriate molecular design to synthesize AFLC materials exhibiting a field-induced AF–F transition of second instead of first order, which means that the field-induced AF–F transition becomes continuous [25], i.e. thresholdless (similar to V-shaped switching) [19]. AFLC dimeric materials possessing $\theta = 45°$ in a broad temperature interval that includes room temperature, and exhibiting second order field-induced AF–F transition, will be ideal candidates for high contrast display devices with grey scale capability and temperature independent performance.

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