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Molecular arrangement in a chiral smectic liquid crystal cell studied by polarized infrared spectroscopy

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The structure of the chiral smectic C phase (SmC*) of the mesogen MHP10CBC in a homogeneously aligned thin cell, that exhibits V-shaped-like switching in a certain frequency range, was studied using polarized Fourier-transform infrared spectroscopy and optical microscopy. The molecular orientational distributions were analysed quantitatively in terms of dichroic parameters of the absorbance profiles, by taking into account the orientational properties of the transition moments for several phenyl and carbonyl bands. The polar angles of the transition moments, with respect to the molecular long axis and their azimuthal orientational parameters used in calculations, were determined from the infrared dichroic data for helical and electrically unwound structures in a thicker cell of this material. For a sufficiently thin cell in the SmC* phase at zero electric field, the results on the azimuthal orientational distribution of the director over a ferroelectric liquid crystal cone, with respect to the substrate normal, are in agreement with the model of a partly twisted SmC* structure. The voltage-dependent dichroic parameters in relation to the direction and the degree of the preferable orientation of the molecules in a sample are compared for the SmC* and the SmC_A* phases.

1. Introduction

The V-shaped switching in thin cells of ferroelectric liquid crystals (FLCs) has great potential for use in active matrix LC displays with appropriate grey scale [1–3]. The phenomenon of V-shaped switching of a cell inserted between crossed polarizers was studied for sufficiently thin cells (thickness of 1–2 μm) of the Tokyo mixture of three chiral smectic compounds [1–3, 4–7]. The electro-optic response of such a cell under an applied electric field is characterized by high extinction at zero field, a linear increase of transmittance with field up to a saturated value, and a rather large contrast ratio up to 150. In addition to the properties of an FLC material, a signifi-

cant role of the surface conditions on the appearance of V-shaped switching is discussed in various papers [1–3, 4–7].

Several models have been proposed [1–8] for explaining the origin of V-shaped switching, but there is still no single model that is fully accepted. An important question of current discussions on this theme is the molecular arrangement in the cell at zero electric field. The model of a random azimuthal orientation of the directors on an FLC cone and a probable Langevin-like director reorientation under a field in a SmC*-like liquid crystalline phase [1, 7] assumes that the correlation among the smectic layers is sufficiently reduced at zero field due possibly to frustration between ferro- and antiferroelectricity. The models reported in [2, 8] consider a uniform molecular orientation at zero field and a collective

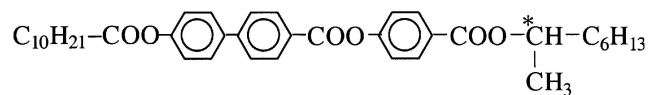
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(as a block) reorientation of molecules under a field. A rather uniform molecular orientation in the cell is assumed in [4] to be the result of almost total compensation of the molecular orientational twisted states near the surfaces by twisting of the smectic layers. However in a number of studies [3, 5, 6] the existence of a twisted structure in cells with V-shaped response was confirmed experimentally. The model proposed in [3] assumes the existence of a partly twisted SmC* structure where the molecular orientation is uniform in the bulk of a cell and considerably twisted in thin surface regions near both substrates. Such a structure is supposed to be stabilized by the electrostatic interactions of the bulk polarization charges and the polar surface interactions. A small twisted state of SmC* reported in [5, 6] was explained by the effect of the in-plane anchoring interaction between the LC and the rubbed surfaces. The molecular arrangement in the chiral smectic LC cells showing V-shaped switching has been studied using a variety of experimental techniques including optical methods such as polarized microscopy, optical spectroscopy, attenuated total reflection ellipsometry and Raman scattering [1–3, 4–7].

In this paper, we study the molecular orientational distribution in a homogeneously aligned cell of the FLC compound MHP10CBC in its chiral smectic C phase (SmC*) at zero electric field using polarized Fourier-transform infrared (FTIR) spectroscopy. For sufficiently thin cells of this material, switching as a block with an electro-optic response similar to V-shaped in a certain frequency range was observed. The dichroic behaviour for the various phase states of the cell under different electric fields is analysed for several characteristic absorption bands. The orientations of the respective transition moments in a molecule and the orientational distributions of the molecules in a cell are taken into account. For a cell in the ferroelectric SmC* phase and the antiferroelectric smectic C_A (SmC_A*) phase, the voltage dependences of the phenyl band dichroic parameters characterizing the degree and the direction of the preferable orientation of molecules were obtained and compared. A combined analysis of the dichroic data for several characteristic absorption bands was used to investigate the molecular arrangement in the SmC* cell at zero field.

2. Experimental

The structural formula and the phase sequence on cooling (°C) of the chiral smectic LC MHP10CBC used are as follows:



I 140.1 SmA* 115.1 SmC* 108.1 SmC₇* 103.5 SmC_A* (57.8 SmI_A*) 62.7 Cr

Homogeneously aligned samples were prepared between two polished CaF₂ substrates coated with a thin conducting layer of indium tin oxide and a sufficiently thick aligning layer of nylon 6,6 rubbed in one direction. The cell thickness of 2 μm was achieved using dielectric balls embedded in UV-curable adhesive as spacers. Cells of 2.9 and 6 μm thicknesses were obtained using mylar film spacers. The cell thickness was confirmed by monitoring the interference fringes in the IR transmittance spectrum of an empty cell. The LC material in its isotropic phase was filled into a cell and then cooled to the temperatures corresponding to smectic phases.

The homogeneity of the sample structure and the cell switching were examined using a polarizing optical microscope. For electro-optical measurements, the microscope was fitted with a photodiode detector and one of the crossed polarizers was set along the smectic layer normal as found for SmA*. A triangular waveform signal of a frequency in the range 0.02 to 100 Hz was applied across the cell for the switching measurements.

A Bio-Rad FTS-60A spectrometer equipped with an MCT detector and a wire grid polarizer was used for measuring polarized spectra in the wavenumber (ν) range 1000–4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹. Spectra were measured by a transmission method at normal incidence of the IR radiation onto the cell for a set of angles of polarizer rotation about an axis parallel to the IR beam axis. A signal-to-noise $S/N > 2000$ was achieved by the averaging of 16 scans. The orientations of the LC molecules and the vibrational transition moments with respect to the cell substrates and the polarization plane of the IR radiation are shown schematically in figure 1. Spectral measurements were carried out for SmA* at 125°C for zero electric field as well as for SmC* at 111°C and for SmC_A* at 95°C for d.c. fields in the range 0–5 V μm⁻¹. The temperatures were recorded in the middle of the temperature intervals of the studied phases.

3. Results and discussion

3.1. Electro-optic response and microscopy measurements

The microscopy studies showed the SmC* structure at 111°C to be helix-free for cells of 2 and 2.9 μm thickness. In particular, no defect lines were observed during the switching of the cell under an electric field. Furthermore, the orientational order for the tilted phase SmC* at 111°C was found to be similar to that for the orthogonal phase SmA* at 125°C, as the colour of the sample was almost free from change during the phase transitions between these two phases on cooling or heating at zero field. An electro-optic response similar to V-shaped was observed for SmC* at 111°C in the cells of 2 and 2.9 μm thickness under a triangular a.c. signal in the frequency range 0.02–0.2 Hz. Figure 2 shows an almost linear increase in the transmittance with

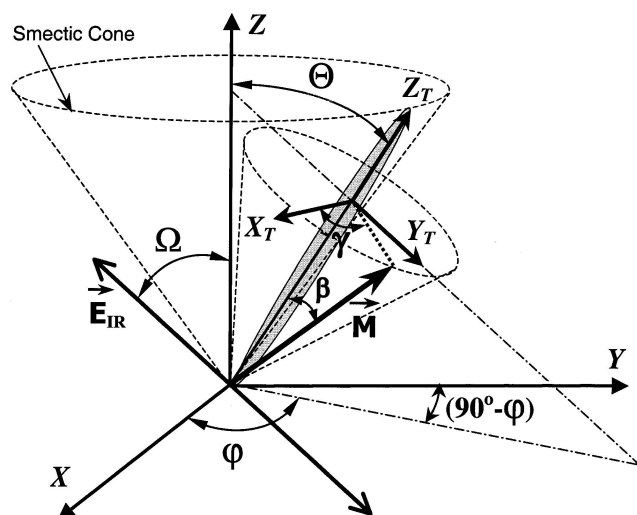


Figure 1. A schematic illustration of the orientations of a cell, the molecules and transition moments with respect to the laboratory frame (X, Y, Z): X axis is along the IR radiation propagation direction and is normal to the cell substrates; Z axis is normal to the smectic layers in the bookshelf geometry; Ω is the angle between the Z axis and the electric vector \mathbf{E}_{IR} of the polarized IR radiation. (X_T, Y_T, Z_T) being the molecular frame: its Z_T axis is parallel to the molecular long axis and makes the polar angle Θ with Z axis; (Y_T, Z_T) plane is parallel to the molecular tilt plane and makes the azimuthal angle φ with X axis. The transition moment \mathbf{M} of a vibration is characterized by its polar angle β with respect to the molecular long axis and its azimuthal angle γ measured from the normal to the tilt plane.

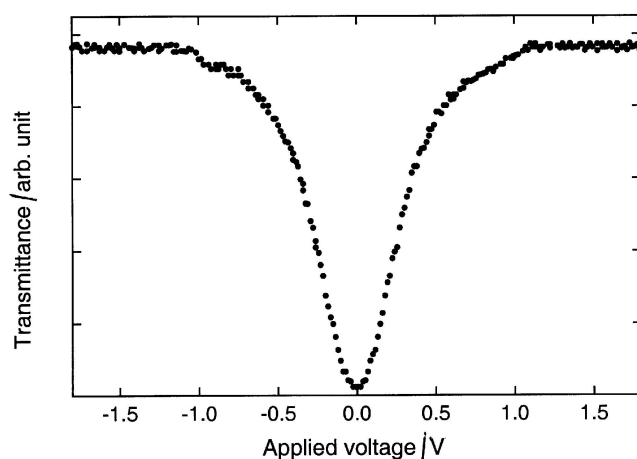


Figure 2. Electro-optic response of $2\mu\text{m}$ cell at 111°C for a triangular wave voltage of frequency 0.1 Hz . One of the crossed polarizers is set along the smectic layer normal.

voltage for a $2\mu\text{m}$ cell for the amplitude (U) ranging from 0 to 0.4 V , and a saturation in transmittance for $U \approx 1\text{ V}$ for a frequency of 0.1 Hz . The ratio of the maximal saturated transmittance to that for zero field

was found to be ~ 30 . In contrast, the cell of $6\mu\text{m}$ thickness in the SmC^* phase at 111°C was found to be helical for zero field and its switching was observed not to be V-shaped.

3.2. IR dichroism

Examples of polarized IR spectra from a $2.9\mu\text{m}$ cell are shown in figure 3. Here we studied the phenyl ring C-C stretching band at 1604 cm^{-1} , and the bands at 1718 , 1740 and 1760 cm^{-1} ; these correspond to the stretching vibrations of C=O groups attached close to the chiral centre, between the phenyl and biphenyl groups, and close to the hydrocarbon tail $\text{C}_{10}\text{H}_{21}$, respectively. The peak intensity A is determined as the difference in the absorbance at a band maximum and at a baseline level. A standard curve-fitting procedure was used for resolving the partly overlapping carbonyl bands. The absorbance profiles (i.e. the dependences of the peak intensity A on the polarizer rotation angle Ω) for higher dichroic bands of the $2.9\mu\text{m}$ cell in several states are shown in figures 4 and 5. For a certain band, the absorbance profile $A(\Omega)$ can be described by the equation [9, 10]:

$$A(\Omega) = -\log_{10} [10^{-A_{\text{max}}} + (10^{-A_{\text{min}}} - 10^{-A_{\text{max}}}) \times \sin^2(\Omega - \Omega_{\text{max}})] \quad (1)$$

where the angles Ω_{max} and $\Omega_{\text{max}} + 90^\circ$ correspond to the maximal, A_{max} , and minimal, A_{min} , values of the peak intensity, respectively. To find A_{max} , A_{min} and Ω_{max} for an absorbance profile, equation (1) was fitted to the experimental data. The angle Ω was set to 0° for the polarization direction corresponding to $\Omega_{\text{max}1604}$ of the phenyl absorbance profile for SmA^* at zero field. The dichroic ratio R is defined as $R = A_{\text{max}}/A_{\text{min}}$. The dichroic parameters obtained for four bands from the $2.9\mu\text{m}$ cell in

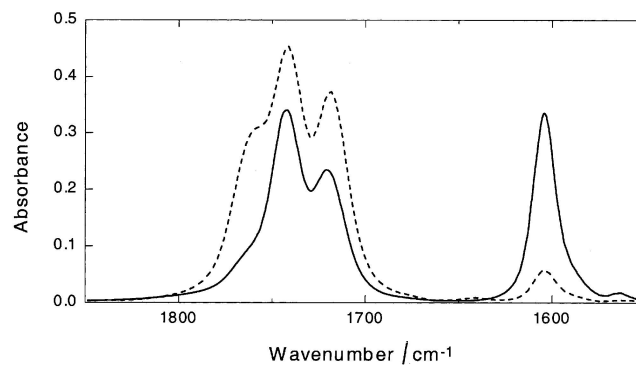


Figure 3. The IR absorption spectra of SmA^* in the $2.9\mu\text{m}$ cell at 125°C and zero electric field in the region $1550\text{--}1850\text{ cm}^{-1}$ for the electric vector of the polarized IR radiation parallel (solid line) and perpendicular (dashed line) to the smectic layer normal in the cell. Band assignments: 1604 cm^{-1} C-C stretch from phenyl ring; 1718 , 1740 , 1760 cm^{-1} C=O stretch.

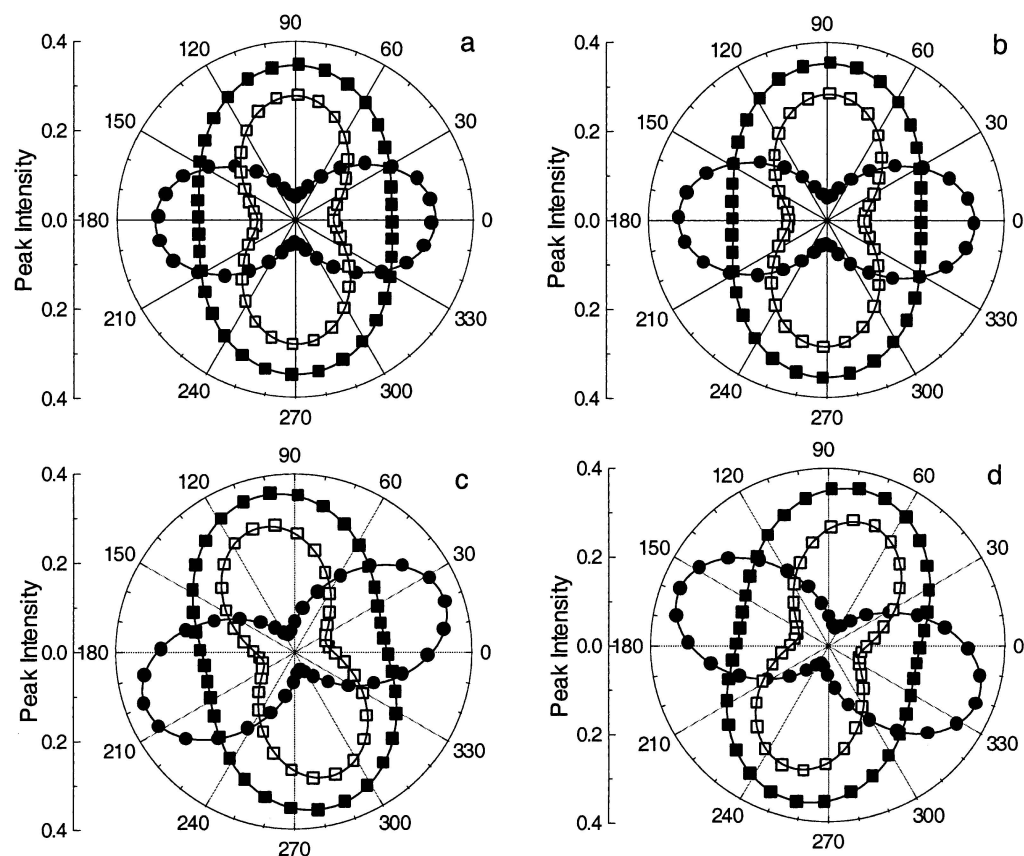


Figure 4. Polar plots of the absorbance profiles $A(\Omega)$ for the bands at 1604 (●), 1718 (■) and 1760 cm^{-1} (□) for the 2.9 μm cell with SmA* at 125°C for zero field (a) and SmC* at 111°C for fields of 0 (b), 4 $\text{V } \mu\text{m}^{-1}$ (c) and -4 $\text{V } \mu\text{m}^{-1}$ (d). Lines are fits of equation (1) to the experimental data.

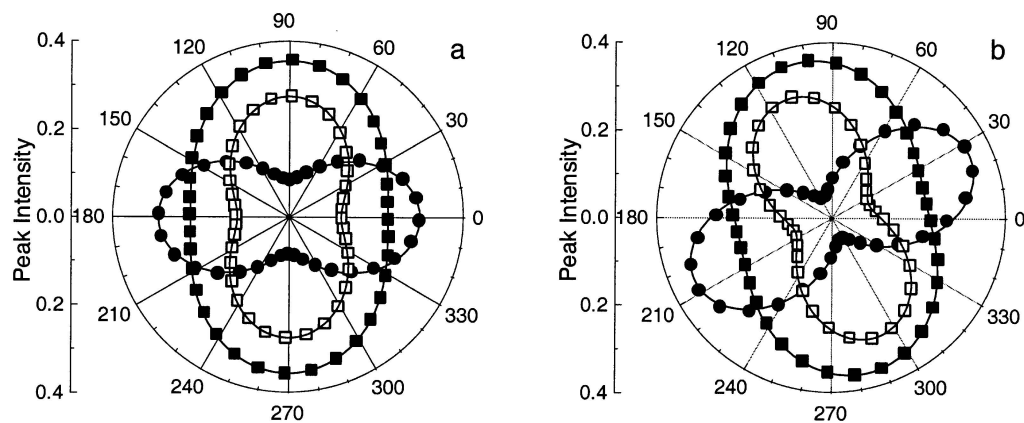


Figure 5. Polar plots of the absorbance profiles $A(\Omega)$ for the bands at 1604 (●), 1718 (■) and 1760 cm^{-1} (□) for the 2.9 μm cell at 95°C: for state 2 (SmC_A*) at zero field (a) and for a switched state for a field of 5 $\text{V } \mu\text{m}^{-1}$ (b). Lines are fits of equation (1) to the experimental data.

the SmC* and SmC_A* phases at zero field are given in table 1. The absorbance profiles of three higher dichroic bands for several phase states of the sample are shown in figures 4 and 5. The voltage dependences of $\Omega_{\text{max}1604}$ and R_{1604} for SmC* and SmC_A* in the 2.9 μm cell are shown in figure 6.

From molecular modelling for MHP10CBC, the polar angle β_{1604} for the phenyl ring C–C stretching vibration was found to be $\sim 15^\circ$. Due to rotational distribution of the LC molecules about their long axes (distribution through γ shown in figure 1), the average orientation of the phenyl transition moments under discussion is almost

Table 1. Fitting parameters Ω_{\max} (degrees) and R for the phenyl and the carbonyl absorbance profiles for SmC* at 111°C and SmC_A* at 95°C in the 2.9 μm cell for zero field.

Band/cm ⁻¹	SmC* at 111°C		SmC _A * at 95°C	
	Ω_{\max}	R	Ω_{\max}	R
1604	-1.4	6.57	-0.2	3.48
1718	90.6	1.68	89.7	1.58
1740	89.8	1.33	89.8	1.37
1760	90.1	3.42	89.8	2.32

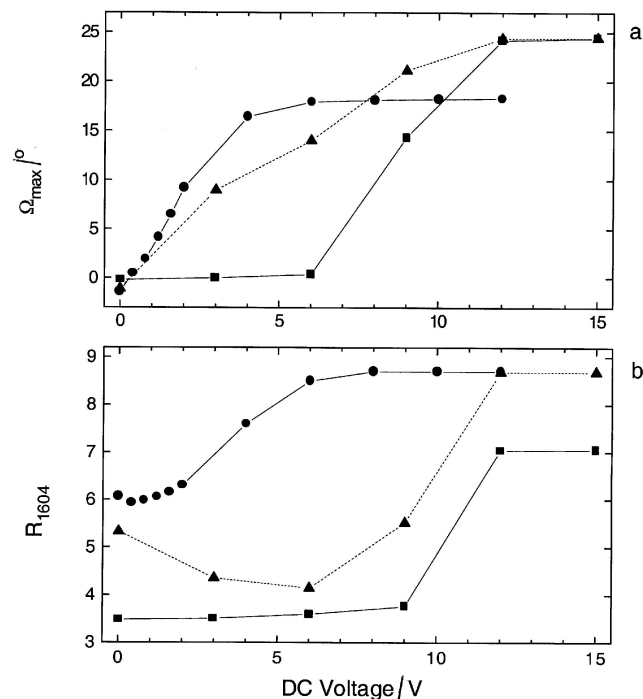


Figure 6. The voltage dependences of $\Omega_{\max1604}$ (a) and R_{1604} (b) for the 2.9 μm cell with SmC* at 111°C (●), state 1 (a coexistence of SmC* and SmC_A* at zero field) at 95°C (▲), and state 2 (SmC_A* at zero field) at 95°C (■).

parallel to the molecular long axis. The direction and the degree of preferable orientation of the molecules can be characterized in terms of $\Omega_{\max1604}$ and R_{1604} ,

respectively. The orientational order parameter $\langle P_2 \rangle$ can be found from R_{1604} by the formula $\langle P_2 \rangle = (R_{1604} - 1) / (R_{1604} + 2)$. As seen from figures 4 and 6 and table 1, for the 2.9 μm cell and SmC* at zero field, $\Omega_{\max1604}$ is close to 0°, similar to that for SmA*. For SmC* at zero field, the parameters $R_{1604} = 6.57$ and $\langle P_2 \rangle = 0.65$ are slightly greater than for SmA* for which $R_{1604} = 5.84$ and $\langle P_2 \rangle = 0.62$. Such relative values of $\langle P_2 \rangle$ for SmA* and SmC* in the cell can be connected with the existence of a sufficiently extended and rather uniform region in the bulk of the SmC* cell and with different temperature-dependent distributions of molecules through the tilt angle θ for these two phases. These results on the orientational order for SmC* and SmA* at zero field are in agreement with those obtained from microscopy studies. We note here that for the SmC* and SmA* phases of the Tokyo mixture in thin cells at zero field, similar results on $\langle P_2 \rangle$ and R for the phenyl band were reported [2].

As seen from figures 4 and 5, the absorbance profiles for all carbonyl band show $\Omega_{\max} \approx 90^\circ$ for all phases for zero field. For the switched states of the 2.9 μm cell with SmC* and SmC_A* (as well as for an unwound SmC* structure in the 6 μm cell—see table 2), the absorbance profiles for the bands at 1718 and 1760 cm⁻¹ show Ω_{\max} shifting in the same direction as the phenyl profile does with respect to the case for zero field. For the low dichroic band at 1740 cm⁻¹, the angular shift of the profile is small and opposite to the shifts for the other bands (see tables 1 and 2). Such dichroic behaviour can be explained by different orientational functions of the transition moments for different bands in a molecule. For each band, the direction of the angular shift of the profile is dependent on the polarity of the field. It is important to note that for a sample under a saturating field, the angular shifts of the carbonyl absorbance profiles are different from that of the phenyl profile. The asymmetry of the carbonyl absorbance profiles with respect to the major axes of the phenyl profile is connected [11] with the rotational biasing of molecules about their long axes in the FLC material studied.

Table 2. Fitting parameters Ω_{\max} (degrees) and R for the various absorbance profiles for a 6 μm cell with SmC* at 111°C for a helical structure at $U_{\text{d.c.}} = 0$ V and for an unwound structure at $U_{\text{d.c.}} = 18$ V. Parameters β (degrees), $\langle \sin \gamma \rangle$ and $\langle \sin^2 \gamma \rangle$ were obtained for the vibrational transition moments from experimental dichroic data for MHP10CBC in its SmC* phase at 111°C.

Band/cm ⁻¹	$(U_{\text{d.c.}} = 0 \text{ V})$		$(U_{\text{d.c.}} = 18 \text{ V})$		β	$\langle \sin \gamma \rangle$	$\langle \sin^2 \gamma \rangle$
	Ω_{\max}	R	Ω_{\max}	R			
1604	0	6.12	20.4	8.69	14.4	0.025	0.489
1718	90.8	1.74	101.6	1.74	62.9	0.074	0.476
1740	91.3	1.31	88.1	1.27	57.8	0.078	0.492
1760	90.1	4.23	108.2	4.68	77.0	0.046	0.381

The 2.9 μm cell of MHP10CBC exhibits substantially different voltage dependences of the dichroic parameters of the phenyl band for the SmC^* and SmC_A^* phases, as shown in figure 6. For SmC^* , for low fields in the range 0 to $\sim 0.7 \text{ V } \mu\text{m}^{-1}$, the value of $\Omega_{\text{max}1604}$ increases almost linearly with voltage, while R_{1604} remains approximately constant. On further increasing the field, $\Omega_{\text{max}1604}$ and R_{1604} exhibit a monotonous increase followed by saturation for fields of ~ 2 to $2.5 \text{ V } \mu\text{m}^{-1}$. The maximum angular shift of the phenyl absorbance profile with respect to that for zero field is $\sim 19.3^\circ$. This is close to the molecular apparent tilt angle of $\sim 20^\circ$ measured using polarizing optical microscopy. For the SmC_A^* temperature range, the structure and related IR dichroic behaviour of a thin cell were found to be dependent on the history of temperature cycling because of the rather slow rate at which the phase transitions occur in the compound studied. This effect can be due to a partial suppression or retardation of phase transitions by the substrates during cooling of the sample from SmC^* to SmC_A^* . This is illustrated in figures 6(a) and 6(b) through the voltage dependences of $\Omega_{\text{max}1604}$ and R_{1604} for the 2.9 μm cell in two different phase states at 95°C .

State 1 of the sample was obtained after slow cooling of the cell from 111 to 95°C and waiting for one hour at this temperature. State 2 was established on further cooling of the sample from 95 (state 1) to 55°C (SmI_A^*) for a short duration of about 10 min followed by heating to 95°C at zero field. On the basis of the IR dichroic data, state 2 of the LC sample can be considered as SmC_A^* . For zero field, R_{1604} and $\langle P_2 \rangle$ for state 2 are substantially lower than for SmC^* at 111°C , see table 1 and figure 6(b), due to the anticlinic and the synclinic director orientations in SmC_A^* and SmC^* , respectively. Moreover for the state 2, the value of $\Omega_{\text{max}1604}$ remains almost constant and close to zero for a field in the range 0 to $2 \text{ V } \mu\text{m}^{-1}$, see figure 6(a). A distinct voltage threshold exists at $U_{\text{d.c.}} \approx 6 \text{ V}$ above which an increase in $\Omega_{\text{max}1604}$ with voltage occurs. R_{1604} remains almost constant for fields in the range 0 to $3 \text{ V } \mu\text{m}^{-1}$ and increases for higher fields. Saturation of $\Omega_{\text{max}1604}$ and R_{1604} takes place for $U_{\text{d.c.}} \approx 12 \text{ V}$. Such a type of voltage dependence of Ω_{max} for the phenyl band is typical of SmC_A^* as it is qualitatively similar to the characteristic voltage dependences of the apparent tilt angle [12] and the macroscopic spontaneous polarization [13] for the SmC_A^* phases of various FLCs. However, for state 1, the voltage dependence of $\Omega_{\text{max}1604}$ is found to be thresholdless, although the rate of increase in $\Omega_{\text{max}1604}$ with voltage is approximately half that for SmC^* for the low voltage region see figure 6(a). From this comparison it is possible to conclude that state 1 at 95°C can represent a coexistence of SmC^* and SmC_A^* which appears to be due to the slow rate of the phase transitions occurring

in a thin cell of MHP10CBC on cooling. For state 1 of the initial sample, R_{1604} decreases with increasing voltage and approaches the values of R_{1604} for the initial state 2 (SmC_A^*) in the low voltage range from 0 to 6 V (figure 6). This behaviour can be connected with a relative increase in the partial content of areas with anticlinic director order for the sample in the initial state 1 under the field. The procedure described involving additional cooling and heating of the cell yields the pure SmC_A^* . We note here that the slow rate of phase transitions in thin cells of the Tokyo mixture is considered in [3] to be an important factor for the occurrence of V-shaped switching for temperatures in the range corresponding to the SmC_A^* phase.

3.3. Structure in the SmC^* cell at zero field

We use the experimental data on IR dichroism of several characteristic absorption bands and the orientational parameters of the corresponding transition moments for analysing the molecular arrangement in the 2.9 μm thin cell with the SmC^* phase and zero field. From the expressions for the components M_Y and M_Z of the transition moment (see figure 1) of a band for arbitrary angles Θ , φ , γ and β [14], it is possible to obtain the following expressions for the absorbances $A_Y = \langle M_Y^2 \rangle$, $A_Z = \langle M_Z^2 \rangle$ and $A_{YZ} = \langle M_Y M_Z \rangle$ for IR radiation propagating along the X axis:

$$\begin{aligned} A_Y = & k \{ \sin^2 \beta \langle \cos^2 \gamma \rangle + \langle \sin^2 \varphi \rangle (\cos^2 \beta \langle \sin^2 \Theta \rangle \\ & + \sin^2 \beta \langle \cos^2 \Theta \rangle \langle \sin^2 \gamma \rangle - \sin^2 \beta \langle \cos^2 \gamma \rangle \\ & + 2 \sin \beta \cos \beta \langle \sin \Theta \cos \Theta \rangle \langle \sin \gamma \rangle) \\ & - 2 \sin \beta \langle \sin \varphi \cos \varphi \rangle (\cos \beta \langle \sin \Theta \rangle \langle \cos \gamma \rangle \\ & + \sin \beta \langle \cos \Theta \rangle \langle \sin \gamma \cos \gamma \rangle) \} \end{aligned} \quad (2)$$

$$\begin{aligned} A_Z = & k \{ \cos^2 \beta \langle \cos^2 \Theta \rangle + \sin^2 \beta \langle \sin^2 \Theta \rangle \langle \sin^2 \gamma \rangle \\ & - 2 \sin \beta \cos \beta \langle \sin \Theta \cos \Theta \rangle \langle \sin \gamma \rangle \} \end{aligned} \quad (3)$$

$$\begin{aligned} A_{YZ} = & k \{ \langle \sin \varphi \rangle [(\cos^2 \beta - \sin^2 \beta \langle \sin^2 \gamma \rangle) \langle \sin \Theta \cos \Theta \rangle \\ & + \sin \beta \cos \beta \langle \sin \gamma \rangle (\langle \cos^2 \Theta \rangle - \langle \sin^2 \Theta \rangle)] \\ & + \langle \cos \varphi \rangle [\sin^2 \beta \langle \sin \Theta \rangle \langle \sin \gamma \cos \gamma \rangle \\ & - \sin \beta \cos \beta \langle \cos \Theta \rangle \langle \cos \gamma \rangle] \} \end{aligned} \quad (4)$$

where k is a constant for a certain band. Equations (2), (3) and (4) are different from those given in Ref. 14, because there only the unwound case is considered. The averaging of functions in these equations is carried out over all possible orientations of the individual transition moments over the sample. This approach makes it possible to account for the molecular distributions through Θ , φ and γ . It is important to note that the parameter $\langle \sin^2 \varphi \rangle$ that characterizes the molecular distribution through φ can be used for examining the possible structural models.

For example, for both a helical structure and a structure with a random azimuthal orientation through φ , the distributional density $f(\varphi)$ is constant for all values of φ , and $\langle \sin^2 \varphi \rangle = 0.5$. For a uniform orientation with $\varphi = 0^\circ$ for all molecules, $\langle \sin^2 \varphi \rangle = 0$. We determine the value of $\langle \sin^2 \varphi \rangle$ for the $2.9 \mu\text{m}$ cell from IR dichroic data and then draw a conclusion about a possible structure at zero field.

For normal incidence of the polarized IR radiation on the cell, we consider two dichroic ratios $R_{Y,Z}$ and $R_{YZ,Z}$ defined by the relations $R_{Y,Z} = A_Y/A_Z$ and $R_{YZ,Z} = A_{YZ}/A_Z$. For a certain band at a wavenumber ν , we obtain two equations:

$$R_{Y,Z}(\Theta, \varphi, \gamma_\nu, \beta_\nu) = A_Y/A_Z \quad (5)$$

$$R_{YZ,Z}(\Theta, \varphi, \gamma_\nu, \beta_\nu) = A_{YZ}/A_Z \quad (6)$$

where $R_{Y,Z}$ and $R_{YZ,Z}$ are expressed as functions of Θ , φ , γ_ν and β_ν using equations (2–4). Numerical values of A_Y , A_Z and A_{YZ} , in the right hand sides of equations (5) and (6), are calculated through the fitting parameters Ω_{\max} , A_{\max} and A_{\min} for this band using the relations [11, 14]:

$$A_Y = A_{\min} \cos^2 \Omega_{\max} + A_{\max} \sin^2 \Omega_{\max} \quad (7)$$

$$A_Z = A_{\min} \sin^2 \Omega_{\max} + A_{\max} \cos^2 \Omega_{\max} \quad (8)$$

$$A_{YZ} = (A_{\min} - A_{\max}) \sin \Omega_{\max} \cos \Omega_{\max}. \quad (9)$$

For the analysis of the distributions of LC molecules through the angles φ and Θ using equations (2–4) and the IR dichroic data for certain vibrations, it is necessary to know the parameters β , $\langle \sin \gamma \rangle$ and $\langle \sin^2 \gamma \rangle$ dependent on the structure of a molecule and the orientational distribution of molecules through γ . The use of the data for a switched $2.9 \mu\text{m}$ cell for the determination of these parameters is insufficient due to a possible presence of a thin region with a twisted SmC* structure close to one of the substrates. The reason for this is that the saturated value of $\Omega_{\max 1604}$ for this cell (19.3° and -19.5° for fields of 4 and $-4 \text{ V } \mu\text{m}^{-1}$, respectively) is somewhat less than for the $6 \mu\text{m}$ cell with an unwound structure (20.4° and -20.2° for fields of 3 and $-3 \text{ V } \mu\text{m}^{-1}$, respectively). For a certain vibration, β is considered to be the same for all molecules and the parameters $\langle \sin \gamma \rangle$ and $\langle \sin^2 \gamma \rangle$ (related to the rotational biasing of the FLC molecules about their long axes) are supposed to have approximately the same values for both zero and saturating fields for SmC* at a given temperature.

We determined the parameters β , $\langle \sin \gamma \rangle$ and $\langle \sin^2 \gamma \rangle$ for the transition moments from the experimental dichroic data of the $6 \mu\text{m}$ cell in two well defined structural states at zero and saturating fields (see table 2). For the $6 \mu\text{m}$ cell we considered a system of 16 equations comprising equations (5) and (6) for each of the four studied bands

for both a helical structure for zero field and an unwound structure for a field of $-3 \text{ V } \mu\text{m}^{-1}$. In relations (2) and (4) we used $\langle \sin^2 \varphi \rangle = 0.5$ and $\langle \sin \varphi \cos \varphi \rangle = \langle \sin \varphi \rangle = \langle \cos \varphi \rangle = 0$ for a helical structure, and $\varphi = 90^\circ$ for an unwound structure. We note here that for each band, equation (6) for a helical structure is reduced to $A_{YZ}/A_Z = 0$ and is satisfied with good accuracy for the determined value of Ω_{\max} . The residual system of 12 equations was solved using a package MATHCAD 2000 to find the parameters β , $\langle \sin \gamma \rangle$, $\langle \sin^2 \gamma \rangle$ for each band and also the parameters $\langle \cos^2 \Theta \rangle$ and $\langle \sin \Theta \cos \Theta \rangle$ for both helical and unwound states.

At the first step of this calculation procedure, the initial values of β and $\langle \sin \gamma \rangle$ for a certain C=O band were obtained by solving a system of equations (5) and (6) for an unwound structure using the procedure reported in [14] with the approximation $\beta_{1604} = 0^\circ$ and $\langle \sin^2 \gamma \rangle = 0.5$ for each band. Then the system of 12 equations was solved using, as initial values, the angles β for the C=O vibrations found from the previous step, $\beta_{1604} = 14^\circ$ (in accordance with the molecular structural analysis), $\langle \sin \gamma \rangle = 0.08$ (close to the values obtained on the previous step) and $\langle \sin^2 \gamma \rangle = 0.5$ for all the bands. The obtained values of β , $\langle \sin \gamma \rangle$, and $\langle \sin^2 \gamma \rangle$ for the bands studied are given in table 2. The values of β determined for the carbonyl vibrations agree with the polar angles of the corresponding C=O bonds with respect to the molecular long axis estimated from the molecular structural analysis. Reasonable values of the parameters characterizing the averaged distributions of molecules through Θ were obtained: $\langle \cos^2 \Theta \rangle = 0.8$, $\langle \sin \Theta \cos \Theta \rangle = 0.3$ for zero field and $\langle \cos^2 \Theta \rangle = 0.83$, $\langle \sin \Theta \cos \Theta \rangle = 0.27$ for the field of $3 \text{ V } \mu\text{m}^{-1}$. The difference in the values for the two states can be connected with a partial suppression of the soft mode (fluctuations of molecules in the tilt planes) by the field.

Then we determined the value $\langle \sin^2 \varphi \rangle \approx 0.18$ for SmC* in the $2.9 \mu\text{m}$ cell at zero field by solving a system of three equations (5) for the higher dichroic bands at 1604 , 1718 and 1760 cm^{-1} with unknown parameters $\langle \cos^2 \Theta \rangle$, $\langle \sin \Theta \cos \Theta \rangle$ and $\langle \sin^2 \varphi \rangle$. The parameters Ω_{\max} and R for this state of the $2.9 \mu\text{m}$ cell with SmC* (see table 1) and the parameters β , $\langle \sin \gamma \rangle$ and $\langle \sin^2 \gamma \rangle$ (see table 2) found in the previous state were used in the calculations. The analysis of possible values of $\langle \sin^2 \varphi \rangle$ for various molecular orientational distributions over an FLC cone shows that the models of a random azimuthal orientation, a helical structure, a perfect uniform orientation and even the model of a small twisted structure cannot explain the value $\langle \sin^2 \varphi \rangle \approx 0.18$ determined for the cell studied that exhibits $\Omega_{\max 1604} = 0^\circ$ for zero field.

To simulate a probable molecular arrangement for the $2.9 \mu\text{m}$ at zero field we used a simplified version (dashed curve 4 in figure 7) of the molecular distribution in φ

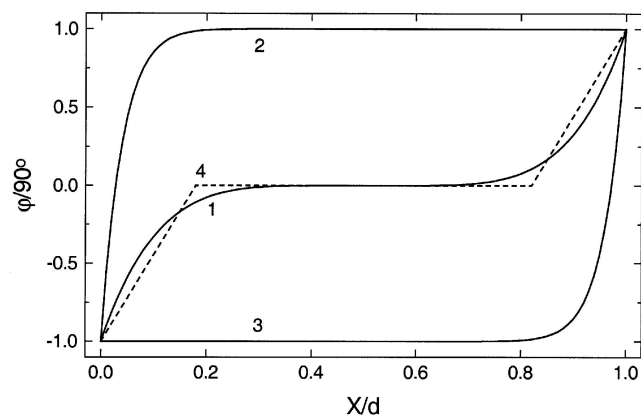


Figure 7. Possible distributions of the molecular orientational angle φ as a function of the X coordinate normalized by the cell thickness d for zero (1), high positive (2) and high negative (3) fields for a twisted SmC* structure in the cell [3], and the schematic molecular distribution $\varphi(X)$ used in simulations for zero field (dashed line 4).

through the cell thickness assumed in [3] (solid curve 1 in figure 7) for a twisted SmC* structure at zero field. For curve 4, $\varphi = 0^\circ$ for all molecules in the region of thickness d_h in the central part of the cell. In the regions of equal thickness $d_{t1} = d_{t2} = (d - d_h)/2$ close to both substrates, the structure is twisted and φ is assumed to vary linearly with the X coordinate from -90° to 0° for $0 \leq X \leq d_{t1}$ and from 0° to 90° for $(d - d_{t2}) \leq X \leq d$ with the same slope. (Note that in figure 1, φ is measured from the normal to the substrates, so its value is shifted by 90° with respect to values of φ used in [3].) For the molecular distribution in φ corresponding to curve 4 in figure 4, we get $\langle \sin^2 \varphi \rangle = (1 - d_h/d)/2$. For the value of $\langle \sin^2 \varphi \rangle \approx 0.18$ determined for the cell, it is possible to obtain $d_h/d \approx 0.64$. Hence the IR dichroic properties of the $2.9 \mu\text{m}$ cell with SmC* at zero field can be connected with the possible existence of a homogeneous region (with $\varphi = 0^\circ$ for molecules) occupying about 64% of the cell thickness and regions of twisted structure in the vicinity of the substrates.

4. Conclusions

Polarized FTIR spectroscopy and microscopy studies show that a homogeneously aligned sample of the FLC material MHP10CBC, in a sufficiently thin cell that exhibits an electro-optic response similar to V-shaped switching, the SmC* structure is neither helical nor totally uniform at zero field. A procedure is developed where the azimuthal orientational distribution of molecules in a cell can be determined. A combination of the

dichroic properties of such a cell for zero field is in agreement with the model of the SmC* structure being homogeneous in the bulk of the cell and twisted in the vicinity of the substrates. The thickness of the region with a uniform molecular orientation was estimated using the parameter $\langle \sin^2 \varphi \rangle$. For the SmC* and SmC_A* phases in the cell, the voltage dependences of Ω_{max} for the phenyl band (the corresponding transition moment is almost parallel to the molecular long axis) are different and agree qualitatively with the typical voltage dependences of the molecular apparent tilt angle for these phases.

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