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Rotational bias of an antiferroelectric liquid crystal studied by polarized Fourier transform infrared spectroscopy

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Experimental studies of the absorbance vs polarization angle of the incident ir beam on a cell have been carried out for several absorbance bands in the Sm*A* phase and in electrically induced ferroelectric states $F(+)$ and $F(-)$ of the SmC_A^* and SmC^* phases of an antiferroelectric liquid crystal. The various absorbance profiles are quantitatively analyzed in terms of the rotational bias parameters of the azimuthal distribution function of the transition moments located in the core of the molecule. The parameters so determined reproduce the profiles of the other transition dipole moments. The parameters of the distribution function for the rotational motion around the long molecular axis show the predominance of the quadrupolar bias relative to the polar bias in both SmC^* and SmC_A^* phases, while a significant quadrupolar bias is also seen in the Sm*A* phase. [S1063-651X(98)08712-1]

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I. INTRODUCTION

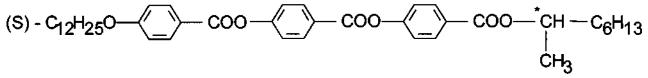
It is generally accepted that in both the SmC^* and SmC_A^* phases, the transverse permanent dipoles located near the chiral center play an essential role in the appearance of ferroelectricity or antiferroelectricity. In both cases, the rotation of the molecule around the long molecular axis is biased so the chiral part on the average is oriented along a particular direction to produce the spontaneous polarization. Nevertheless, the intermolecular interactions are different in ferroelectric and antiferroelectric phases. In the SmC^* phase, dispersion forces between the transverse permanent dipoles and the polarizable centers are the most likely reasons for the molecular tilt and the ferroelectric order as a consequence of the tilt may appear [1,2]. Antiferroelectricity in the chiral SmC_A^* phase appears due to the direct Coulomb interactions between the permanent dipoles in the adjacent layers [3]. Due to different types of interactions in antiferroelectric liquid crystals, the angle of rotational biasing is expected to be different in the SmC_A^* phase from that in the SmC^* phase. This has been confirmed for the carbonyl group close to the chiral center [4–6] using ir spectroscopy.

In this paper we investigate the orientational distribution function for the rotation of the molecule around its long molecular axis. A detailed analysis of various bands in the polarized Fourier transform infrared spectra of an antiferroelectric liquid crystal (AFLC) sample in the SmC_A^* , SmC^*, and Sm*A* phases is carried out to obtain this distribution function. We shall find that the quadrupolar bias is predominant in the SmC^* and SmC_A^* phases and is also present in the Sm*A* phase.

II. EXPERIMENT

An AFLC sample with homogeneous orientation was prepared between the optically polished ZnSe windows with the indium tin oxide (ITO) conductive layers. These windows were spin coated with polyimide solution (0.2% solution) and one of them was rubbed unidirectionally. Mylar foil was used as a spacer and the thickness of the cell was determined to be 4.8 μm through observation of ir fringes. The quality of the alignment has been tested using polarizing microscopy. The transition temperatures of the sample were found to be [7]

Cr 338 SmC_A* 371.7 Fi1 374.2 Fi2 376.2 SmC* 392 SmA 403 I



Fi1 and Fi2 are two ferrielectric phases, which have been characterized using polarization and dielectric measurements.

The infrared spectra were recorded using a Bio-Rad FTS-6000 spectrometer with 1-cm^{-1} resolution and these were averaged over 64 scans. An IR-KRS5 grid polarizer was used to polarize the ir beam. A special sample holder has been designed for the oblique transmission angle measurements. The arrangement allows the sample to be rotated out of the normal plane of incidence. Polarized ir spectra were measured as a function of the polarizer rotation angle.

III. RESULTS

The absorbance profiles $A(\omega)$ for several bands (Table I) as a function of the polarizer rotation angle have been measured at a temperature of 395 K in the Sm*A* phase and at temperatures of 380 K in the SmC^* phase and 345 K in the

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TABLE I. Assignments of several peaks in the ir spectrum.

Frequency (cm^{-1})	Assignments
2956	CH_3 asymmetric stretching
2927	CH_2 asymmetric stretching
2855	CH_2 symmetric stretching
1718	C═O stretching (chiral)
1740	C═O stretching (core)
1600, 1508	phenyl ring C—C stretching
1467	CH_2 scissors vibration
1380	CH_3 symmetric bending
1263	asymmetric C—O stretching
1201	aromatic CH in-plane deformation
764	C—C out-of-plane deformation

$\mathrm{Sm}C_A^*$ phase. In the Sm*A* phase, the absorbance of the bands with transition moments along the long molecular axis is maximal for the polarizer parallel to the smectic layer normal and consequently the absorbance of the perpendicular bands has maxima rotated by 90°. An electric field applied to the sample in the $\mathrm{Sm}C^*$ phase rotates the absorbance profiles through approximately the optical tilt angle either clockwise or anticlockwise depending on the polarity of the electric field. A similar rotation of the absorption profiles can be observed in the $\mathrm{Sm}C_A^*$ phase at a temperature of 345 K (Fig. 1) when an electric field greater than the threshold is applied. This transforms the system to the induced ferroelectric $[F(+)$ or $F(-)]$ states. It has been found [8,9] that the absorbance vs polarizer rotation angle dependence can be described by the formula

$$A(\omega)=-\log_{10}[10^{-A_{\parallel}}+(10^{-A_{\perp}}-10^{-A_{\parallel}})\sin^2(\omega-\omega_0)], \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the maximal and minimal values of the absorbance, ω is a polarizer angle, and ω_0 is the angle for which a maximal absorbance is obtained. $A_{\parallel}$ and $A_{\perp}$ can be related to the main components in laboratory frame as

$$\begin{aligned} A_Z&=A_{\parallel}\cos^2(\omega_0)+A_{\perp}\sin^2(\omega_0),\\ A_Y&=A_{\parallel}\sin^2(\omega_0)+A_{\perp}\cos^2(\omega_0),\\ A_{YZ}&=(A_{\parallel}-A_{\perp})\sin(\omega_0)\cos(\omega_0). \end{aligned} \tag{2}$$

The tilt angles found by fitting Eq. (1) to the data for different bands are listed in Table II. In both phases, the maximal tilt angle is observed for the phenyl stretching band (1600 cm^{-1}) and the value is in good agreement with that found from the optical tilt angle measurements. The tilt angle for most other bands except for the carbonyl group is approximately 5° lower than for the 1600-cm^{-1} band and this in turn agrees with the steric tilt angle determined from the data on the molecular length and the lamellar spacing determined using x-ray diffraction.

A simple explanation for the above finding can be given in terms of a steric model of the molecules tilted within their smectic layers (i.e., zigzag molecules in their all-trans conformations). In this model, the spontaneous polarization direction is fixed by a spatial configuration of the chiral center [9,10] and the lateral components of the dipole moments associated with it. The rigid aromatic cores may be packed up in a more tilted orientation in the plane of the smectic layer than the molecule as a whole. The model is able to qualitatively explain the behavior of some but not all bands. In general, such an inconsistency in the tilt angle of the various bands implies that a rotation of the molecule is biased around its long axis. The biasing for the carbonyl dipole moment was shown to exist [4–6] in ferroelectric liquid crystal (FLC) and AFLC materials.

IV. DISCUSSION

To describe the orientational distribution of the selected transition dipoles in the molecular system (Fig. 2) we use the polar angle β, which is measured from the z axis (long molecular axis), and the azimuthal angle γ, measured from the normal to the tilt plane. For the ferroelectric phase the absorbancies, A_Z, A_Y, and A_{YZ} in the laboratory system can be expressed in terms of $\langle\sin\gamma\rangle$ and $\langle\sin^2\gamma\rangle$ as [6]

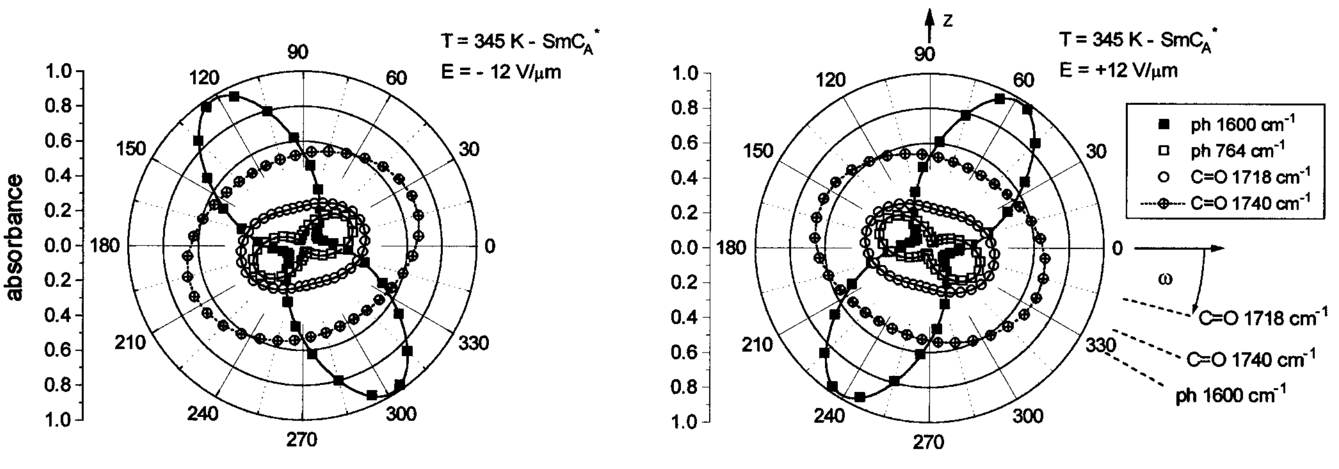

FIG. 1. Absorbance profiles $A(\omega)$ vs polarizer rotation angle ω for different transition dipole moments of the molecular core: ■, 1600 cm^{-1} phenyl in plane; □, 764 cm^{-1} phenyl out of plane; ○, 1718 cm^{-1} C═O near the chiral center; ⊕, 1740 cm^{-1} far from the chiral center. Solid lines and dashed line are calculated with the parameters from Table III.

TABLE II. Angular shift ω_0 (deg) of peak profiles with an applied electric field. For SmC_A^*, $E=12$ V/μm; for SmC^*, $E=6$ V/μm.

	Band	Phenyl	Phenyl	CH_2 symmetric	CH_2 asymmetric	CH_3 symmetric	C═O core	C═O chiral
	Frequency (cm^{-1})	1600	764	2928	2928	1380	1740	1718
T (K)	Phase							
345	SmC_A^* $F(+)$	−30.57	−25.18	−22.58	−26.75	−30.19	−23.34	−14.05
	$F(-)$	31.30	24.69	22.08	26.56	29.43	21.94	15.67
380	SmC^* $F(+)$	−25.70	−20.31	−18.61	−23.17	−24.95	−18.86	−13.63
	$F(-)$	25.29	20.85	17.95	23.94	25.11	19.26	13.11

$$\begin{aligned}A_Z&=k\{\cos^2\beta\langle\cos^2\theta\rangle-2\sin\beta\cos\beta\langle\sin\theta\cos\theta\rangle\langle\sin\gamma\rangle\\&\quad+\sin^2\beta\langle\sin^2\theta\rangle\langle\sin^2\gamma\rangle\},\\A_Y&=k\{\cos^2\beta\langle\sin^2\theta\rangle+2\sin\beta\cos\beta\langle\sin\theta\cos\theta\rangle\langle\sin\gamma\rangle\\&\quad+\sin^2\beta\langle\cos^2\theta\rangle\langle\sin^2\gamma\rangle\},\\A_{YZ}&=k\{\langle\sin\theta\cos\theta\rangle[\cos^2\beta-\sin^2\beta\langle\sin^2\gamma\rangle]\\&\quad+\sin\beta\cos\beta[\langle\cos^2\theta\rangle-\langle\sin^2\theta\rangle]\langle\sin\gamma\rangle\}.\end{aligned}\tag{3}$$

In these formulas, Jang *et al.* [6] have considered only the fluctuations of the tilt angle in the tilt plane. In the SmA phase the fluctuations in the tilt angle should be considered as doubly degenerate [11] and we had derived the formulas, which in the present notation become

$$\begin{aligned}A_Y&=0.5k\{\sin^2\beta[1-\langle\sin^2\theta\rangle\langle\sin^2\gamma\rangle]+\cos^2\beta\langle\sin^2\theta\rangle\},\\A_Z&=k\{\sin^2\beta\langle\sin^2\theta\rangle\langle\sin^2\gamma\rangle+\cos^2\beta\langle\cos^2\theta\rangle\}.\end{aligned}\tag{4}$$

The polar angle β of the bands under investigations is widely reported in the literature [4,6,11,12] and we have verified these values using the molecular modeling package. Since θ describes the orientation of the long molecular axis (z axis) in the laboratory system, the averages $\langle\cos^2\theta\rangle$ and $\langle\sin\theta\cos\theta\rangle$ provide information about the distributions of the long molecular axis.

In order to find the averages $\langle\cos^2\theta\rangle$ and $\langle\sin\theta\cos\theta\rangle$, one can use bands for which the transition dipole moments are well defined in the molecular system of the coordinates. In previous papers [4,6] the averages $\langle\cos^2\theta\rangle$ and $\langle\sin\theta\cos\theta\rangle$ were calculated for the phenyl C—C stretching band, based on the assumption that its polar angle $\beta\cong 0$. We suggest, however, that this cannot be fully justified in our case. Instead of using the C—C phenyl stretching vibration, it is better to use the out-of-plane (764-cm^{-1}) vibration to describe the orientational distribution of the long molecular axis since the tilt angle of the latter is close to the steric angle. Moreover, the apparent order parameter obtained for the 1600-cm^{-1} band is found to be significantly lower than for the 764-cm^{-1} band. This observation suggests that the para benzene axis is tilted from the long molecular axis by more than 20°. This was already reported in the literature [11,13] for phenyl rings with carboxyl linkage.

We carefully studied the possible conformations of the molecular structure using quantum orbital calculations and we found that the core of the molecule is not planar. The torsional angle $\angle C_k$—O—C_{ph}—C_{ph} (k denotes carbonyl and ph phenyl) found is about 55°, which agrees with the values reported for similar structures [14,15]. The other torsional angle $\angle C_{ph}$—C_{ph}—C_h—O is only about 5°, which again is in agreement with that reported in the literature. Hence we can consider the structure of the core with the phenyl rings rotated by about 50° to 60° with respect to each other. The polar angles of the dipole have been taken to be $\beta=24.4°$ for the phenyl stretching vibration (1600 cm^{-1}), $\beta=102°$ for the C—C out-of-plane vibration (764 cm^{-1}), and $\beta=61.4°$ for the carbonyl C═O stretching vibration.

A. The Sm*A* phase

In the SmA phase an assumption is commonly made that molecules are rotating freely around their long axis [4,6]. In such a case the transition dipole is uniformly distributed around the long molecular axis and we shall expect $\langle\sin\gamma\rangle=0$ and $\langle\sin^2\gamma\rangle=0.5$. The average $\langle\cos^2\theta\rangle$ can be simply related to the dichroism ratio N for any particular band as

$$N=\frac{A_Z}{A_Y}=\frac{\frac{1}{2}\sin^2\beta(1-\langle\cos^2\theta\rangle)+\cos^2\beta\langle\cos^2\theta\rangle}{\frac{1}{4}\sin^2\beta(1+\langle\cos^2\theta\rangle)+\frac{1}{2}\cos^2\beta\langle 1-\cos^2\theta\rangle}.\tag{5}$$

In this case the orientational order in the material is described by a single order parameter $S=0.5\langle 3\cos^2\theta-1\rangle$. Us-

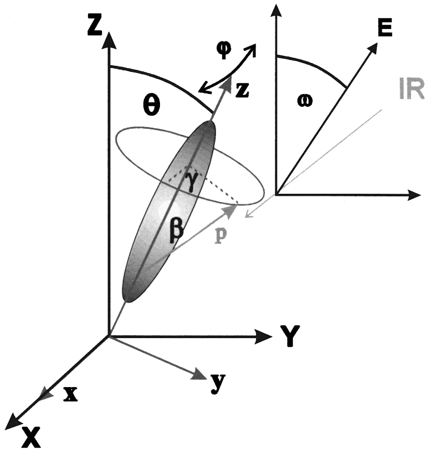

FIG. 2. Coordinate system used for absorbance components calculations (X,Y,Z) describes the laboratory frame, with Z taken as a normal to the smectic layer; (x,y,z) describes the molecular frame, where z is the long molecular axis and x coincides with X. The transition dipole moment **p** makes a polar angle β with the long molecular axis and its azimuthal angle is γ.

TABLE III. Calculated rotational bias parameters.

T (K)	Phase	a	b	$\lvert\gamma_0\rvert$	$\lvert\langle\sin\gamma\rangle\rvert$	$\langle\sin^2\gamma\rangle$
345	SmC_A^* $F(+)$	0.039	0.052	41°	0.081	0.486
	$F(-)$	0.036	0.065	39°	0.072	0.479
380	SmC^* $F(+)$	0.031	0.055	38°	0.050	0.478
	$F(-)$	0.032	0.047	37°	0.049	0.479
395	SmA					0.480

ing ir dichroism data, we independently determined values of $\langle\cos^2\theta\rangle$ for different transition dipole moments located in the core. However, we find that the values of $\langle\cos^2\theta\rangle$ obtained in this way are scattered more than the experimental error. Therefore, we conclude that the rotation around the long molecular axis is not free, i.e., $\langle\sin^2\gamma\rangle\neq 0.5$ ($\langle\sin\gamma\rangle=0$ remains valid because polar order is not present in the Sm*A* phase). It is reasonable to assume that γ angles of the C—C phenyl stretching dipole and the out-of-plane (764-cm^{-1}) vibration dipole moment differ by 90°. Using the experimental data of the dichroism ratio and the formulas (4) we find the values of $\langle\cos^2\theta\rangle=0.74$ and $\langle\sin^2\gamma\rangle=0.48$ for the C—C phenyl stretching dipole moment. The same value $\langle\sin^2\gamma\rangle=0.48$ has been obtained also for carbonyl dipole near the chiral carbon; see Table III. In the next step, the constant k in a set of equations (3) and (4) for each band has been obtained from the absorbance components in the Sm*A* phase using Eq. (4).

Effects similar to that of a nonisotropic rotation in the Sm*A* phase, using ir dichroism data, have already been observed in terms of the dispersion parameter D [11] or as differences in apparent order parameter S for dipoles belonging to the molecular core [16]. The nonexistence of the molecular free rotation of the short axis has also been pointed out in the Sm*A* phase through FLC dynamic studies by Lalanne, Buchert, and Kielich [17]. They observed a pretransitional slowing down far above the SmC^*-SmA phase transition temperature using the degenerate four-wave-mixing investigation on a chiral compound. This effect appears to be directly linked to the γ privileged direction evidenced by our ir experiments. This means that the rotation in the Sm*A* phase is largely modified near the SmC^* phase itself; the short molecular axis spends more time in some privileged directions.

B. The SmC_A^* and SmC^* phases

In order to solve this problem in the SmC_A^* and SmC^* phases we have simultaneously carried out a calculation for the three transition dipole moments located in the molecule core. These are the phenyl stretching vibration (1600 cm^{-1}), the C—C out-of-plane vibration (764 cm^{-1}), and the carbonyl C═O stretching vibration near the chiral center. We assume that the molecular core is rigid; hence the biasing parameters for the constituents of the core can be calculated as an entity. A number of variables have been reduced as we express the averages $\langle\sin\gamma\rangle$ and $\langle\sin^2\gamma\rangle$ in terms of the approximation for the azimuthal distribution function $f(\gamma)$ [6],

$$f(\gamma)=\frac{1}{2\pi}+a\cos(\gamma-\gamma_0)+b\cos[2(\gamma-\gamma_0)], \qquad (6)$$

$$\langle\sin\gamma\rangle=\int_0^{2\pi}\sin(\gamma)f(\gamma)d\gamma=\pi a\sin(\gamma_0),$$
$$\qquad (7)$$
$$\langle\sin^2\gamma\rangle=\int_0^{2\pi}\sin^2(\gamma)f(\gamma)d\gamma=\tfrac{1}{2}[1-\pi b\cos(2\gamma_0)],$$

where a and b indicate the degree of polar and quadrupolar biasing and γ_0 is the angle of biasing. We suggest that the transition dipole moments under consideration are expected to have the same degree of biasing (a and b) but different biasing angles. The difference in the biasing angles, however, should directly correspond to the torsional angles between components of the core. The overall distribution for all molecules is generally a linear combination of $[f(\gamma)+f(-\gamma)]/2$ and $[f(\pi-\gamma)+f(-\gamma+\pi)]/2$. For the positive polarization the first term is predominant while for the negative polarization the second term is.

The results of calculations are listed in Table III in terms of rotational bias parameters. The values of $\langle\sin\gamma\rangle$, $\langle\sin^2\gamma\rangle$, and γ_0 are related to the carbonyl dipole near the chiral carbon for the positive electric field. For a negative field the angle γ_0 turns into $\gamma_0+180°$. In all of the above cases the calculated parameters reproduce the experimental profile extremely well (see Fig. 1).

In the next step we use the averages $\langle\cos^2\theta\rangle$ and $\langle\sin\theta\cos\theta\rangle$ and the parameters a and b to reproduce the absorbance profiles of the remaining carbonyl groups centered at 1740 cm^{-1} and the symmetrical stretching CH$_3$ band of 1380 cm^{-1}. The absorbance profile of the 1740-cm^{-1} band (Fig. 1) is found to be a superposition of the two profiles, one with an angle $\omega_0=13.5°$ and the second with the angle $\omega_0=9°$ in the SmC_A^* phase. This reflects the fact that one of the C═O dipole moments is rotated with respect the second (around the long molecular axis) by a torsional angle of ~55° so they have different values of biasing angles γ_0. The calculated profile reproduces the experimental data quite well. For the CH$_3$ group, the polar angle is taken to be 109° and the best fit to the experimental data is obtained for γ_0 to be 262°. This corresponds to the torsional angle between the carbonyl group and the CH$_3$ group of about 220°, which is quite a reasonable value for the most probable conformation [18]. From the calculations, we obtain tilt angles of 25.0° for the SmC^* phase and 29.8° for the SmC_A^* phase, which are in good agreement with the experimental values (Table II).

Our result shows a slightly higher angle and the degree of biasing for the C═O transition dipole moment in the SmC_A^* phase than in the SmC^* phase, although the angles of biasing are very similar to that reported for the Ajinomoto compound [6]. The degree of polar biasing, the factor a, is found to be significantly lower than the factor b of quadrupolar biasing of the distribution function. These results differ from those obtained by Jang *et al.* [6]. We suppose that the main reason for the divergence in the results arises as the tilt fluctuations were assumed to lie in the tilt plane in the Sm*A* phase [6]. In our case, tilt fluctuations are not restricted to the tilt plane in the Sm*A* phase. We have found that the quadrupolar biasing of a similar order of magnitude as in the SmC^*

and SmC_A^* phases is also present in the SmA phase. The finding of a significant quadrupolar biasing reflected in the biasing parameter b of the distribution function may be of great significance in providing the microscopic basis of the electroclinic effect and the bistability and in explaining how the ferri- and ferrostates are induced in antiferroelectric liquid crystals.

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