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Short Communication

Microscopic ordering in smectic phases of liquid crystals

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Résumé. — On a étudié par spectroscopie d'absorption infrarouge l'ordre orientationel dans les phases smectiques d'un matériau cristal liquide ferroélectrique, le décyloxy-4-thiobenzoate de [(2S, 3S)-chloro-2-méthyl-3-pentanoyloxy]-4'-phényle, en abrégé $\overline{10}$.S.C1Isoleu. Deux types d'échantillons orientés, l'un homéotrope, l'autre en configuration Clark-Lagerwall, ont été préparés et plusieurs bandes intenses en infrarouge, caractéristiques des différentes parties et orientations des molécules, ont été choisies. Les résultats montrent que l'inclinaison des parties centrales (cœurs) des molécules varie très peu de la phase S_A à la phase S_C^*, ce qui implique que les cœurs des molécules sont déjà inclinés dans la phase S_A. Leurs axes, qui sont désordonnés sur un cône dans la phase S_A, s'alignent mais restent sur ce cône quand on passe en phase S_C^*en abaissant la température. Ce modèle est en accord avec quelques résultats antérieurs.

Abstract. — Orientational order in smectic phases of a ferroelectric liquid-crystalline material 4'-(2S, 3S)-2''-chloro-3''-methylpentanoyloxyphenyl-4-decyloxy thiobenzoate, abbreviated $\overline{10}$.S.C1Isoleu, was examined by IR absorption spectroscopy. Oriented samples were prepared in both bookshelf and homeotropic alignment geometry. Several stronger IR vibrations were selected characterizing different parts and orientations of the molecules. Results show that the molecular tilt of the core parts of the molecules changes very little from the S_A to the S_C^* phase implying that the core parts of the molecules are already tilted in the S_A phase. Axes of the core parts, that are disordered on a cone in the S_A phase, start to align with each other but remain on this cone on lowering the temperature into the S_C^* phase. The model agrees with some previous results.

1. Introduction.

Molecular ordering in liquid crystal (LC) phases is the basic phenomenon leading to a great variety of different LC structures [1]. As such, it has been widely studied by several spectroscopic techniques and main features of the different phases are indeed understood, but much remains

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to be done. Important details in orientational distribution functions are still missing as well as knowledge regarding the shape of the molecules and the relative ordering of different atomic groups.

In this letter we present new results on the molecular ordering in the smectic A (S_A) and ferroelectric smectic C_* (S_C^*) phases of 4'- (2S, 3S)-2"-chloro-3"-methylpentyloxyphenyl-4-decyloxy thiobenzoate, abbreviated $\overline{10}$.S.C1Isoleu [2]. The material belongs to the recently synthesized family of LCs which are chemically stable, have relatively broad S_C^* phase and have high spontaneous polarization. The structure of the material is shown in figure 1. As the S_C^* phase is an interesting phase from a fundamental and an application point of view, a better understanding of molecular form and functionality of different molecular parts is necessary to allow the use of molecular engineering to improve the properties of materials.
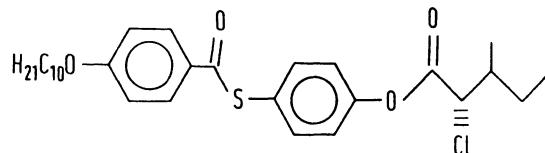

Fig. 1. — Molecule of the $\overline{10}$.S.C1Isoleu liquid crystal.

2. Molecular order.

A typical mesogenic molecule is composed of a quasi rigid central part and one or two more flexible aliphatic chains or end groups. A commonly accepted picture of a smectic phase shows orientationally ordered molecules arranged in layers, changing their orientational order at the $S_A - S_C^*$ phase transition [1]. In the S_A phase long molecular axes are suppposedly orthogonal to smectic layers and begin to tilt away from this direction on crossing the phase transition temperature. The long molecular axis usually refer to average axis of all of the molecule. As most spectroscopic techniques measure the orientation of the axes of the central molecular parts one must be careful in interpretation of the results. A well established fact is that the LC order is mostly connected with ordering of the central molecular parts while aliphatic chains are quite disordered [3,4].

The orientational order in a smectic layer can be described by an orientational distribution function, which-taking molecules as rigid bodies-is a function of all three Euler angles [5]. Any spectroscopic technique applied to measure this function can give only certain approximations. The IR absorption due to a single molecule is proportional to $(\mathbf{E} \cdot \mathbf{p}_i)^2$ where $\mathbf{E}$ is the optical electric field and $\mathbf{p}_i = \dfrac{\partial \mathbf{M}}{\partial Q_i}$ is the change of the molecular dipole moment $\mathbf{M}$ due to a vibrational mode characterized by the normal coordinate Q_i. Instead of the orientation of the whole molecule, we will study the orientational distribution of dipoles $\mathbf{p}_i$ that characterize the molecular parts at which some molecular vibration is localized. The distribution of $\mathbf{p}_i$ is a function of just two Euler angles β and γ defined in figure 2. The laboratory coordinate system is defined with the z axis normal to the smectic layer and the x axis normal to z and to the direction of spontaneous polarization in the ferroelectric S_C^* phase. In the uniaxial S_A phase the distribution depends just on β, but in S_C^* we have to study the dependence on γ too. We expand the orientational distribution function

$D_i(\beta, \gamma)$ of a particular vibrating dipole p_i in a series of spherical harmonics, consistent with the local symmetry of the S_C^* phase.

$$D_i(\beta, \gamma) = \frac{1}{4\pi}\left[1 + 3A_i\sin\beta\,\sin\gamma + 5B_i\,P_2(\cos\beta) + \frac{15}{4}C_i\sin2\beta\,\cos\gamma + \frac{15}{4}D_i\sin^2\beta\,\cos2\gamma + \right.$$

$$\left. + \frac{15}{4}E_i\sin2\beta\,\sin\gamma + \frac{15}{4}F_i\sin^2\beta\,\sin2\gamma\right] + ..., \qquad (1)$$

where A_i, B_i, C_i, D_i, E_i, and F_i are the expansion coefficients and serve as order parameters with the maximum value of 1 in completely ordered systems. A_i measures the polar order and can be nonzero in the ferroelectric phase. If the dipole p_i is chosen so that it is aligned along the molecular major axix, B_i is the usual order parameter $\langle P_2(\cos\beta)\rangle$ in the S_A phase with $P_2(\cos\beta)$ being the Legendre polynomial. In general, coefficients B_i measure the order relative to the z axis. A maximum value of 1 means that all of the dipoles are parallel to the z axis and minimum value of -0.5 shows the dipoles are orthogonal to z and may be disordered otherwise. C_i, D_i, E_i and F_i are four other parameters measuring the quadrupolar order.
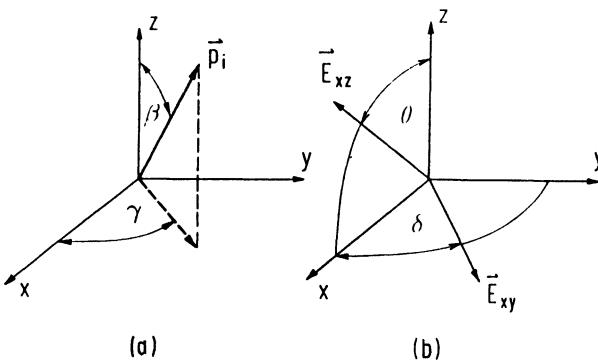

Fig. 2. — (a) shows orientation of the induced molecular dipole moment p_i in the laboratory frame with z axis normal to the smectic layers and y axis parallel to ferroelectric polarization in the S_C^* phase. (b) defines the angles δ and θ that measure the orientation of the optical electric field in the x-y and x-z planes respectively.

Let us first calculate the contribution to absorption coefficient for the arbitrarily oriented dipole p_i and the incident field E in experimentally accessible principal planes of the laboratory coordinate system. We write the components of p_i as $|p_i|$ $(\sin\beta\,\cos\gamma, \sin\beta\,\sin\gamma, \cos\beta)$ and the components of the incident electric field polarized in the x-z plane as $|E|(\sin\theta, 0, \cos\theta)$ where θ is the angle between the z axis and the electric field direction, as seen in figure 2. The contribution $(E_{xz} \cdot p_i)^2$ then equals:

$$\left(\frac{E_{xz} \cdot p_i}{|E||p_i|}\right)^2 = \frac{1}{3} + \frac{2}{3}P_2(\cos\beta) + \left[\frac{1}{2}\sin^2\beta\,\cos2\gamma - P_2(\cos\beta)\right]\sin^2\theta + \frac{1}{2}\sin2\beta\,\cos\gamma\,\sin2\theta \quad (2)$$

An analogous expression for the case with the electric field in the x-y plane, where it is written as $|E|(\cos\delta, \sin\delta, 0)$ with δ the angle between the x axis and E_{xy} (Fig.2), equals:

$$\left(\frac{E_{xy} \cdot p_i}{|E||p_i|}\right)^2 = \frac{1}{3} - \frac{1}{3}P_2(\cos\beta) + \frac{1}{2}\sin^2\beta\,\cos2\gamma\,\cos2\delta + \frac{1}{2}\sin^2\beta\,\sin2\gamma\,\sin2\delta \qquad (3)$$

To calculate the measured absorption coefficient we then multiply the absorption of a single molecule ((2) or (3)) with the distribution function (1) and integrate over $d\gamma$ and $d(\cos\beta)$. The resultant absorption coefficients normalized to the absorption in the isotropic phase, where the distribution is isotropic, are :

$$\frac{A_{zz}^i}{A_{\text{iso}}^i} = 1 + 2B_i + \left[\frac{3}{2}D_i - 3B_i\right]\sin^2\theta + \frac{3}{2}C_i\sin2\theta \tag{4}$$

and

$$\frac{A_{xy}^i}{A_{\text{iso}}^i} = 1 - B_i + \frac{3}{2}D_i\cos2\delta + \frac{3}{2}F_i\sin2\delta \tag{5}$$

As seen, only second order coefficients can be deduced from IR absorption measurements. No information is obtained on the A_i coefficients which are the ones that distinguish the ferroelectric from the nonferroelectric S_C phase.

In an IR absorption experiment for a birefringent medium, the incident beam should be polarized in one of the two eigen polarization direction for the selected direction of propagation. Therefore , only two angles corresponding to the eigen polarizations are allowed for δ and θ in the previous expressions.

3. Experimental.

The phase transition temperatures of $\overline{10}$-S·C1Isoleu measured on heating are $T_{XC} = 54°\text{C}$, $T_{CA} = 66°\text{C}$, and $T_{AI} = 74°\text{C}$ corresponding to transitions between the crystal, S_C^*, S_A, and isotropic phases respectively.

Disordered samples for the IR spectroscopy were prepared by heating the powder in vacuum between two rough CsI plates until it melted and formed a film approximately 5 μm thick. A homeotropically oriented sample of a thickness of around 5μm was prepared between two ZnSe optically polished plates coated with lecithin. The cell was also filled in vacuum and good alignment in S_A phase was obtained by slowly cooling the sample from the isotropic phase. The alignment was checked under a polarizing microscope. The transition to the S_C^* phase was clearly detected by noting the reduction of optical extinction between crossed polarizers. The low birefringence observed proved that the direction of the pitch was normal to the ZnSe plates and that the smectic layers were not perturbed by crossing the $S_A - S_C^*$ phase transition.

Homogeneously aligned samples were prepared between Si polished plates with indium-tin-oxide electrodes and poly-vinyl alcohol alignment coating. One of the plates was mounted in a slide to allow shearing the two plates. This proved to be necessary in order to obtain good alignment in the S_A phase. In the ferroelectric phase an electric field was needed in order to produce good bookshelf orientation. A typical voltage of 5 to 10 V was applied to the electrodes when the sample thickness was around 5 μm. The sample could not be checked optically but similar cells were prepared using glass plates and procedure was devised leading unequivocally to well-oriented samples. Cells with glass plates were used also for Raman measurements. Different cells for temperature regulation were used in the study with an accuracy and stability of better than 1 K.

The first measurements were directed toward band assignments in the IR and Raman spectra. Infrared absorption spectra were taken, depending on the availlability of the instruments, with a Nicolet 740 and Brucker 113 Fourier transform spectrometers. Some intermediate products in the synthesis and Br-Cl substituted chiral chain samples were investigated, the results for which will be presented elsewhere. No bands directly associated with the vibrations near the chiral centres

could be observed. The aliphatic C−H stretching domain presents a complex group of bands as well in the IR as in the Raman spectrum. Besides C=O stretching vibrations at frequencies 1762 cm⁻¹ (IR only) and 1672 cm⁻¹ and C−S stretching at 900 cm⁻¹ , all other stronger bands are associated with para-substituted benzene-ring vibrations.

Seven characteristic dipoles were selected for the determination of the molecular orientation. The choice was made upon a compromise between following criteria : the respective vibration should be well localized with predictable direction of the induced dipole moment, their IR absorption bands should be strong enough and well isolated from the neighbouring bands. Four of the dipoles are directed predominantly along the long axis of the molecular core. These are the bands around 1600 cm⁻¹, 1163 cm⁻¹ and 1015 cm⁻¹ that are all complex bands with complicated substructure and correspond to benzene ring C−C stretching and C−H bending in-plane vibrations and the 900 cm⁻¹ C−S stretching vibration. Three of the studied bands characterize vibrating dipoles making large angles with the molecular major axis. These are two C=O vibrations at around 1762 cm⁻¹ and 1672 cm⁻¹, and a complex band at about 839 cm⁻¹ connected with the ring C−H out-of-plane bending. For all the bands the integral of the absorbance was taken over the relevant spectral region. The ratios R^i_{xy} were calculated as :

$$R^i_{xy} = \frac{\int A^i_{xy}\,d\omega}{\int A^i_{iso}\,d\omega} \tag{6}$$

and analogously R^i_{xz} too.

The measurements in homeotropically oriented samples were used to determine parameters B_i. The layer structure was not perturbed at the $S_A - S_C^*$ phase transition as mentioned previously but the helical structure with approximately ten pitch periods was present in the sample. The polarized IR beam was directed normally to the cell. Different incident polarizations gave identical absorption spectra and therefore the average of the absorption (5) over δ was obtained. The parameters B_i were calculated from the absorption spectra as $B_i = 1 - R^i_{xy}$. Figure 3 shows the temperature dependence of the seven parameters. As seen in the figure these parameters do not change much at T_{AC} and stay nearly constant throughout the S_C^* phase.

To determine the other two coefficients C_i and D_i, measurements in a cell with bookshelf orientation were performed. In the S_A phase the results confirmed previously obtained values for B_i. Their absolute values were few percent smaller and the difference was attributed to a poorer sample orientation. In the S_C^* phase the IR absorption spectra were taken at several angles θ. The extrema in the absorbances were found when θ coincided with the optical tilt angle showing no measurable dispersion of the optical indicatrix orientation from the visible into the IR region. Due to a less reliable quality of the sample orientation only the strongest band, centered at 1600 cm⁻¹, was investigated and no precise temperature dependence was measured. The corresponding saturated value (10 K below T_{AC}) of the parameter C_i was found to be 0.4 ± 0.1 and the absolute value of D_i is smaller than 0.05.

4. Discussion.

We explain the continuity of parameters B_i by a specific ordering of molecules at the $S_A - S_C^*$ phase transition. Orientation of a single molecule relative to the smectic layer does not change
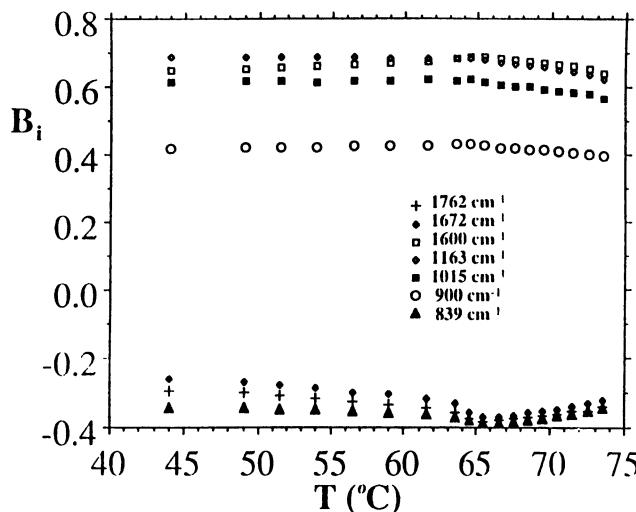
Fig. 3. — Temperature dependence of the order parameters B_i for the seven molecular dipole moments associated with different molecular vibrations. Center frequencies are marked in the figure. Phase transition temperatures on cooling are $T_{AI} = 74°C$ and $T_{CA} = 66°C$.

significantly at this phase transition. We can claim this for the core part of the molecules which was characterized by the studied IR vibrations. The long axes of the core parts of the molecules are disordered on a cone in the S_A phase and start to align with each other on passing the phase transition temperature. The tilt angle of the molecules therefore does not change at the phase transition. In this picture the parameter C_i associated with the induced dipole moment p_i aligned along the molecular axis is the primary microscopic order parameter which characterizes the non-ferroelectric S_C phase. This is also valid for the ferroelectric S_C^* phase where the parameter A_i measuring the polar order of a permanent dipole transverse to the long molecular axis is proportional to the spontaneous polarization. It is generally accepted that the spontaneous polarization is only a secondary order parameter [4] and so A_i is a secondary microscopic order parameter of the S_C^* phase.

Parameters B_i characterizing the orientation of the long molecular axis are gradualy diminishing in the S_C^* phase. The molecular tilt therefore slowly increases when cooling this phase. Typical tilt angle β_i calculated from $B_i = (3\cos^2\beta_i - 1)/2$ for the dipole vibrating at 1600 cm^{-1} is increasing from 27° at T_{AC} to 29°.

The idea of a tilted orientation in the S_A phase is not new. To our knowledge the first indication of this kind of ordering is the work by Loesche and Grande [6]. Their conclusion was based on the measurements of the angular dependence of the proton NMR linewidth in the smectic phases. In Raman scattering one is also measuring the orientational order of the molecular core part as all studied vibrations are modulating the polarizability of benzene rings. In addition to $\langle P_2(\cos\beta)\rangle$ the technique also permits the determination of $\langle P_4(\cos\beta)\rangle$. The results on $\langle P_4(\cos\beta)\rangle$ obtained by Jen et al. [5] and also others [7] in the S_A phase were considered to be anomalously low in comparison with predictions obtained from Maier Saupe mean field theory. In the picture of the average molecular orientation orthogonal to smectic layers this would mean a relatively large disorder. The authors already gave an explanation that the preferential molecular orientation is

tilted away from the layer normal. If we then suppose that the tilt distribution function is rather narrowly centred around the average molecular tilt, that is around an angle of 30°, it is not surprising to find a relatively low contribution of $\langle P_4(\cos\beta)\rangle$ to the series expansion of the orientational distribution function, since $P_4(\cos\beta)$ is zero at 30.5°.

In support of this model we should also repeat that the tilt angle of the core part and of the aliphatic chains not need to be the same. Evidence was presented that this difference in tilt is important in explaining the appearance and sign of the spontaneous polarization in the S_C^* phase [8,9]. In most cases it seems that the tilt angle of the core part is larger. Judging from the Raman and IR spectra the molecular conformation does not change on going from S_A to S_C^* phase therefore the tilt of the core part in S_A is also expected.

The strongest evidence mentioned usually against such a picture of molecular ordering is the dependence on temperature of the smectic layer thickness d. In materials where no association of molecules is observed d is usually constant in the S_A phase and start to diminish on crossing T_{AC}. Such a behaviour is also measured in our LC. The diminishing of d in the S_C^* phase is usually attributed to the appearance of tilted molecular orientation. But in many cases of smectic phases the value of d is significantly shorter than that estimated for the most extended molecular configuration l [10]. The difference is typically a little less than 10% . In our material the layer thickness in the S_A phase was measured to be 3.072 nm, and is 2.845 nm 10 K below T_{AC}. The length of the extended molecule was estimated to be $l = 3.3$ nm. Various interpretations of this mismatch include interpenetration of liquid-like hydrocarbon chains in the neighbouring layers or the departure of the configuration of the terminal alkyl chains from their fully extended trans conformation. Nevertheless, the most obvious explanation is the tilted molecular orientation [11]. Taking the steric tilt angle as $\arccos(d/l)$ we get 21.5° in the S_A phase and 30.5° 10 K below the transition. Even if the steric tilt angle defined in this way may not be accepted with great confidence the values for the tilt angle in the S_C^* phase agree quite well with our IR results (29° for the 1600 cm^{-1} vibration). If we then take the molecular tilt to be around 30° in both smectic phases we can attribute the increased layer thickness in the S_A phase solely to increased disorder of the molecular positions along the direction of the layer normal.

5. Acknowledgements.

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