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Study of the molecular tilt angle and the order parameter of a ferroelectric liquid crystal mixture using IR spectroscopy

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We report measurements of the molecular tilt angle of a ferroelectric liquid crystal mixture (ZLI 3654), using infra-red spectroscopy, and of the optical tilt angle using polarizing microscopy. The molecular tilt angle is found to be approximately the same for different molecular vibrations. The second rank orientational order parameter for the axis of molecular vibrations of different groups of the molecule for homogeneously aligned samples have been determined as a function of temperature. The order parameter depends slightly on the sample thickness and is about 8 per cent higher for a lower thickness ($\sim 7\,\mu$m) compared to a higher thickness ($\sim 12\,\mu$m). The order parameter does not change significantly at the S_C^*–S_A transition. The order parameter of S_C^* is found to be unaffected by the application of a constant electric field. The order parameter for the alkyl chain is found to be about three times lower than for the molecular core.

1. Introduction

Ferroelectric liquid crystals have attracted considerable attention due to their wide range of applications in electro-optical devices. It is known that in the bookshelf geometry the application of a constant electric field fixes the direction of the director relative to the layer normal. When this field is reversed the director is switched on to a new position making the same tilt angle with the layer normal, as before. For this geometry the director always lies in the plane of the glass plate or the optical window [1, 2] as the case may be. However, the molecular mechanism responsible for this switching is not yet fully understood.

Here we report investigations of the second rank orientational order parameter and of the tilt angle as a function of temperature in the S_A and S_C^* phases of a ferroelectric liquid crystal mixture (E. Merck ZLI 3654) using infra red spectroscopy. The results are compared with those determined using polarizing microscopy. This is perhaps the first time that IR spectroscopy has been used to determine the molecular tilt angles; here the term molecular tilt angle is defined as the angle between the transition dipole moment and the rubbing direction. The latter direction is coincident with the layer normal in S_A phase. The advantage over polarizing microscopy is that not only can the average value of the molecular tilt angle be determined, but also the order parameter for different parts of the macromolecule. Polarizing microscopy makes possible a determination of the optical tilt angle only. Intermolecular interactions and the shape of the molecule play a dominant role not only in establishing the liquid-crystalline phases but also in determining the transition temperatures. The intermolecular interactions are known to

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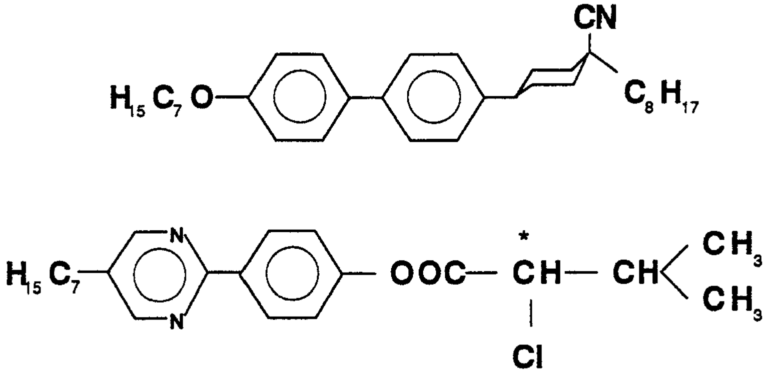
affect the shape and the frequency of the vibrational bands. A systematic study of IR spectroscopy is therefore likely to further the understanding of the molecular mechanisms responsible for the phase transitions and for the switching in a S_C^* phase.

2. Experimental

The basic chemical constituents of ZLI 3654 mixture and the transition temperatures are given in figure 1. A homeotropically aligned sample of approximate thickness 25 μm was prepared between KRS5 windows. We find that if we clean the windows with acetone then a good homeotropically aligned sample is obtained as confirmed by polarizing microscopy. The cell was filled under a dry nitrogen atmosphere and good alignment was achieved by cooling the sample slowly from its isotropic phase. The alignment was checked using a polarizing microscope. It may be mentioned that the director for the case of a homeotropically aligned sample may not be normal to the cell windows throughout the sample volume. The structure is helical, and a number of turns of the helix within the cell thickness will determine to what degree the homeotropically aligned sample may be considered as uniaxial. In our case no birefringence has been observed which indicates the presence of a complete pitch in the sample. The purpose of the measurements on a homeotropic aligned sample is to find the correct band assignment.

Homogeneously oriented samples were prepared between optically polished silicon windows. These were spin coated by nylon 6/6 (0·2 per cent solution in methanol) to obtain a uniform layer about 0·2 μm thick. Both windows were subsequently rubbed in antiparallel directions. Mylar foils of 7 and 12 μm were used as spacers. The distances between windows were confirmed by interference fringe measurements. The cells were filled at a temperature above the clearing point using the capillary effect. Since it was not possible to confirm the alignment of the sample between silicon windows using polarizing microscopy, a similar sample was prepared between two glass plates, in the manner just described. Polarizing microscopy was then used to confirm the homogeneous alignment of such an aligned sample.

The temperature accuracy and set point stability were 0·5°C and 0·1°C, respectively. Infrared absorption spectra were recorded with a Digilab FTS60A spectrometer, with 0·5 cm^{-1} resolution. A SpecAc IR-KRS5 polarizer was used to polarize the IR beam.



−30°C S_C^* 62°C S_A 76°C N* 86°C I*

Figure 1. Molecular structures of the components in the ZLI 3654 mixture and its transition temperatures.

3. Results and discussion

3.1. *Band assignment*

The IR spectra of ZLI 3654 of the chiral smectic C phase, for homeotropic and homogenously oriented samples, are shown in figures 2 and 3. The main absorption bands are assigned to the characteristic vibrational modes, taking account of the direction of their vibrational transition dipole moments. We have chosen those vibrational bands which correspond to the molecular vibrations of the core. These are complex bands which appear around 1607 cm^{-1}, 1498 cm^{-1} and 1432 cm^{-1} they correspond to the benzene ring C–C stretching vibrations. The complex bands around

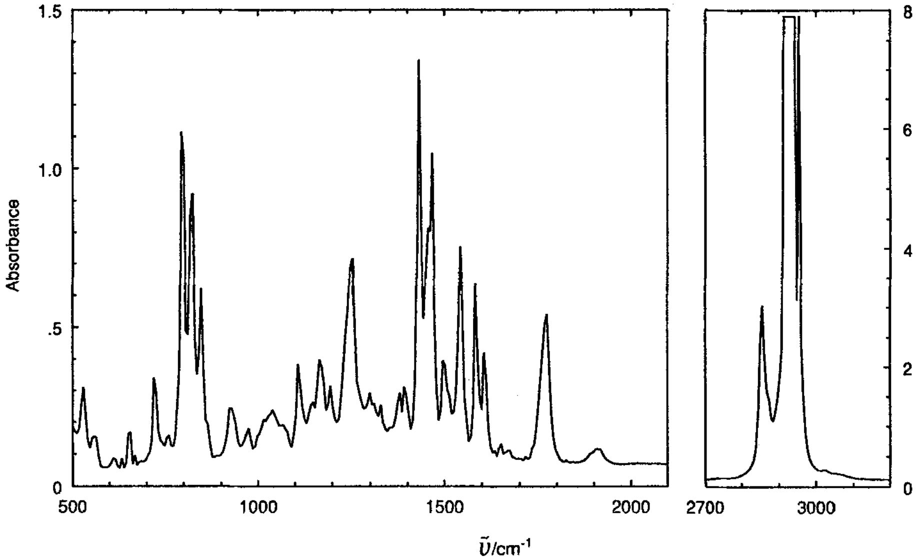


Figure 2. FTIR spectrum of the homeotropically aligned ZLI 3654 mixture at 30°C.

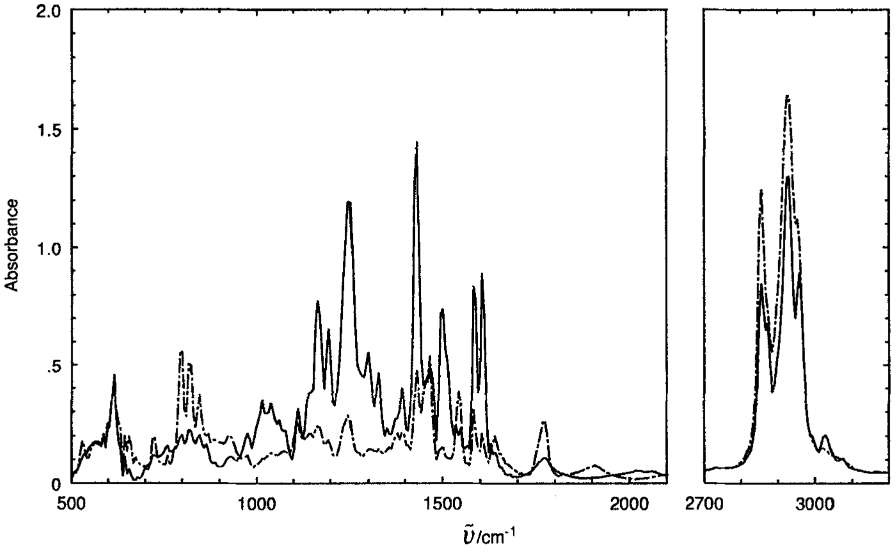


Figure 3. Polarized FTIR spectrum of the homogeneously aligned ZLI3654 mixture at 30°C. Solid line, 0°; dotted line, 90° (angle in both cases is measured with respect to the rubbing direction).

$800\,\mathrm{cm}^{-1}$ (range 860–$780\,\mathrm{cm}^{-1}$) are connected with the C–H aromatic out-of-plane vibrations. We have also chosen the CH_2 and CH_3 stretching vibrations of the alkyl chains; that is the complex band in the range 2800–$3000\,\mathrm{cm}^{-1}$. The band centred at $650\,\mathrm{cm}^{-1}$ for the homeotropically aligned sample corresponds to C–Cl vibrations situated close to the chiral centre of the molecule. The C=O stretching vibration at $1771\,\mathrm{cm}^{-1}$ is strong and can be measured for these samples.

3.2. *Second rank orientational order parameter*

The dichroism ratio R is defined as

$$R=\frac{\int A_{\parallel}\,d\omega}{\int A_{\perp}\,d\omega}, \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the director respectively. According to Neff *et al.* [3] the dichroism ratio can be expressed as

$$R=\frac{\cos^2\alpha\langle\cos^2\beta\rangle+0{\cdot}5\sin^2\alpha\langle\sin^2\beta\rangle}{0{\cdot}5\cos^2\alpha\langle\sin^2\beta\rangle+0{\cdot}25\sin^2\alpha\langle 1+\cos^2\beta\rangle}, \tag{2}$$

where β is the angle between the molecular axis which is along the core of the molecule and the optical axis, and α is the angle between the molecular axis and the direction of the vibrational transition moment. This formula can be simplified on assuming that the transition dipole moment is directed along the long molecular axis, i.e. $\alpha=0$; this gives

$$R=\frac{1+2S_2}{1-S_2}, \tag{3}$$

where S_2 is the second rank orientational order parameter

$$S_2=1/2\langle 3\cos^2\beta-1\rangle.$$

If the transition dipole moment is oriented perpendicular to the long molecular axis, i.e. $\alpha=90°$, the expression for R can be simplified to

$$R=\frac{2(1-S_2)}{2+S_2}. \tag{4}$$

Figure 4 shows the temperature dependence of the order parameter obtained for the $12\,\mu\mathrm{m}$ sample thickness for the three vibrations that are parallel to the molecular core ($1607\,\mathrm{cm}^{-1}$, $1498\,\mathrm{cm}^{-1}$ and $1432\,\mathrm{cm}^{-1}$ lines). The vibrations normal to the core are the C–H aromatic out-of-plane (centred at $800\,\mathrm{cm}^{-1}$) and the CH_2, CH_3 stretching vibrations (centred at around $2900\,\mathrm{cm}^{-1}$). The C=O vibration, centred at $1771\,\mathrm{cm}^{-1}$, is assumed to be directed at an angle of $\alpha\sim 71°$ [4] to the molecular long axis.

The order parameter for the $7\,\mu\mathrm{m}$ sample thickness was found to be 6–8 per cent higher than that for $12\,\mu\mathrm{m}$. This is due presumably to a strong suppression of the helix [5] by the smaller thickness of the sample. The surface effects tend to align the molecules in the bulk with those on the surfaces better for a lower sample thickness. The consequence of this is that surface effects play a dominant role in fixing the position of the director. The temperature dependences of the order parameter are observed to be very similar for the two sample thicknesses. We observed a drop in the IR dichroism ratio close to the cholesteric phase transition due to the formation of a cholesteric helix.

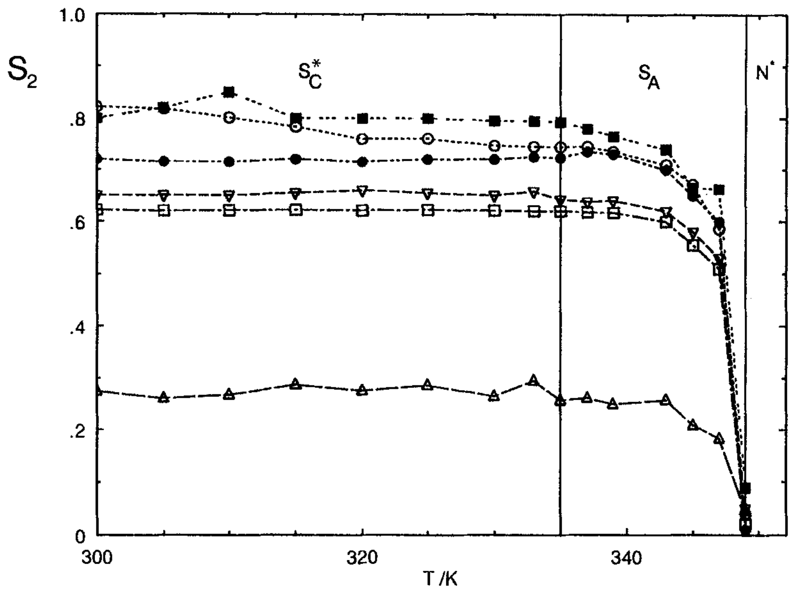


Figure 4. Temperature dependence of the second rank orientational order parameter for the 12 μm homogeneously aligned sample for: benzene ring, C–C parallel stretching vibrations: 1607 cm^{-1}, ●—···—●; 1498 cm^{-1}, ∇——∇; 1432 cm^{-1}, □—·—□; and perpendicular C–H out-of-plane bending vibrations 860–780 cm^{-1}, ○·····○; C=O stretching vibration 1771 cm^{-1} (for $\alpha = 71°$), ■··· ···■; and CH_3 and CH_2 stretching vibrations of alkyl chain 3100–2900 cm^{-1}, △——△.

For the 7 μm thick cell, the drop in the IR dichroism occurs 1°C below that for the 12 μm thick sample. This can easily be explained in terms of the temperature dependence of the cholesteric pitch. The order parameter for the vibration belonging to the molecular core was found to be approximately $0{\cdot}7 \pm 0{\cdot}1$. The value is relatively high and shows a good ordering of the molecular core. However, we find that there is a systematic decrease in the value of the order parameter with an increase in the absorption of the bands. This may result from the local field effect, however a quantitative calculation is not yet possible [6]. At the smectic A–cholesteric phase transition the order parameter tends to go to zero because of an averaging effect of the helical structure which appears in the cholesteric phase. The CH_2, CH_3 stretching vibrations of the alkyl chain show a small value of the order parameter ($S_2 \cong 0{\cdot}3$) (see figure 4). The latter is an indication of a large disorder in the alkyl chain due to conformational averaging. Similar results have also been obtained for the alkyl chain in non-chiral liquid-crystalline samples using NMR [7].

We do not observe any change in the value of the order parameter for the chiral smectic C–smectic A transition for any of the vibrations that have been studied. We shall discuss this later.

3.3. *Effect of an electric field on* S_C^* *phase: a determination of the molecular tilt angle*

The experimental arrangement for the study of the effect of an electric field on the IR absorbance for ferroelectric liquid crystal switching is shown in figure 5. When a constant electric field, E, of approximately 1 V μm^{-1} is applied across the sample we observe a significant decrease in parallel absorbance, $A_{\parallel}$ and, at the same time, we observe an increase in perpendicular absorbance, $A_{\perp}$. This is shown in figure 6. The IR spectra were recorded as a function of the polarization angle of the incident beam in order to determine the angle at which the maximum absorbance occurs. This was found to lie at an angle θ to the rubbing direction; this angle is close to the measured tilt angle found by using polarizing microscopy. Next the electric field was reversed ($-E$) and the procedure was repeated. The angle between the two absorbance maxima, divided by 2, is defined as the molecular tilt angle for the particular molecular vibration under investigation. The results for benzene ring stretching vibrations 1607 cm^{-1}, 1585 cm^{-1} and 1432 cm^{-1}) and for the optical measurement using polarizing microscope are shown in figure 7. For the optical tilt angle measurement, we used approximately the same thickness as for the IR measurements. The optical cell consisted of two ITO

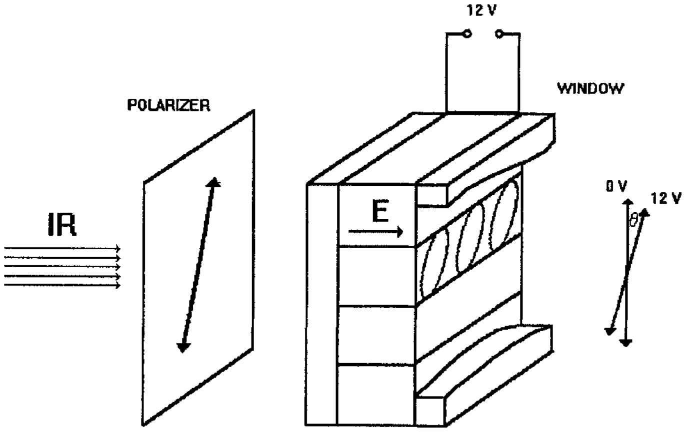


Figure 5. Experimental set-up for the study of effect of an electric field on the IR absorbance.

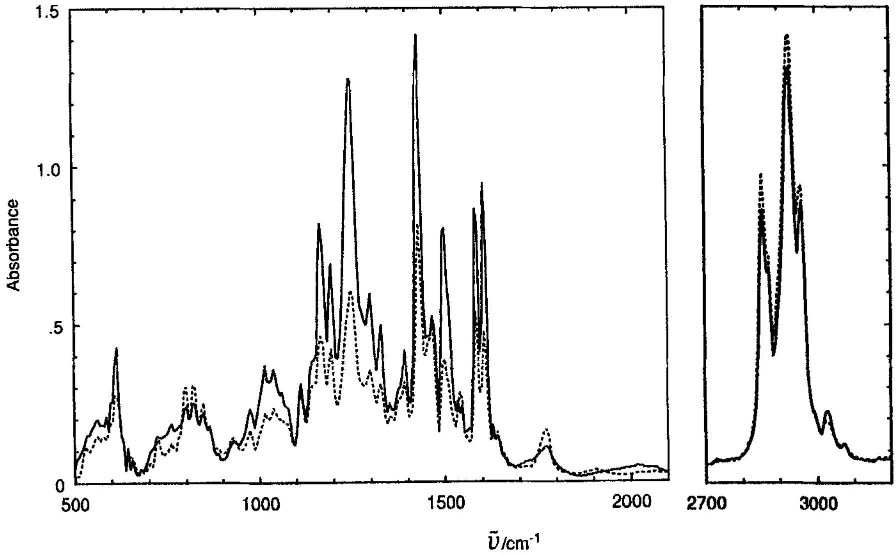


Figure 6. Polarized FTIR spectrum of homogeneously aligned sample (thickness 12 μm) with electric field (12 V) at 30°C; solid line with $+E$ (polariser adjusted to obtain maximum absorption of parallel bands); dashed line-spectra with $-E$.

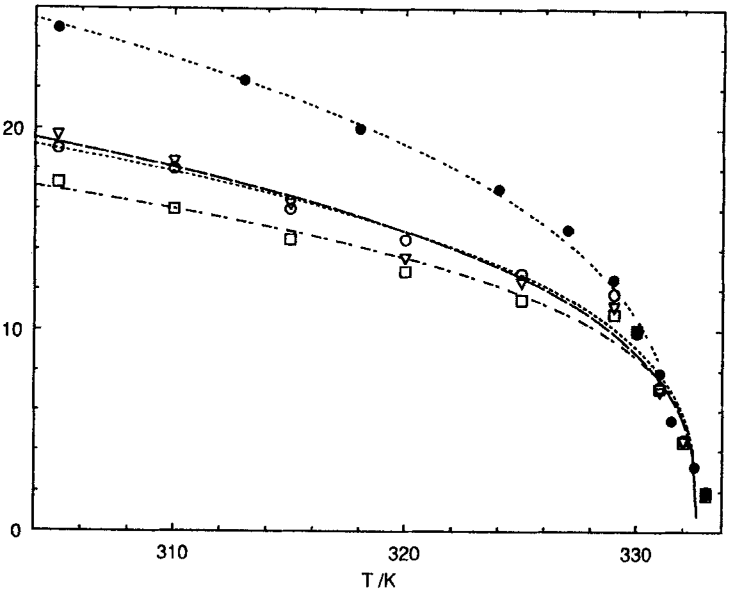


Figure 7. Temperature dependence of the tilt angle obtained from polarizing microscopy, ● ··· ··· ●; and from FTIR measurements: 1430 cm^{-1}, □–· –· □, 1585 cm^{-1}, ▽– – –▽; 1600 cm^{-1}, ○ ······ ○; (sample thickness 12 μm). The measured tilt angle has been fitted to the equation $\theta \sim (T_{S_C^* S_A} - T)^{\alpha}$; $\alpha = 0{\cdot}31 \pm 0{\cdot}02$; $T_{S_C^* S_A}$ is found to be 60°C compared to 62°C specified by E. Merck.

coated glass plates. The voltage across the sample (1 V μm^{-1}) was the same in both cases. We find a close agreement between the molecular and optical tilt angles at temperatures close to the S_C^*–S_A transition. At a temperature 5°C below the transition, the molecular tilt angle starts to depart from the optical one. In the S_C^* phase, the molecular tilt angle for the molecular core is somewhat lower than for the optical one. This is not surprising in view of the fact that a bigger change in the position of the director with temperature is expected to be brought about by the large mobility of the alkyl chains. It is interesting to note, however, that no significant discrepancy is observed among the molecular tilt angles measured for different vibrational bands that are linked to the molecular core. This provides indirect evidence of the reliability of the technique for calculating the molecular tilt angles. However, it is quite probable that the sample for the IR measurements was not a monodomain as the IR beam covered an area of approximately 2·5 cm^2 compared to 0·16 cm^2 for the optical cell.

The important observation is that no discontinuity in the order parameter S_2 at the S_C^*–S_A phase transition is observed (see figure 4). At first sight this may seem surprising. A similar observation has recently been reported by Zgonik *et al.* [8] on 4′-(2S,3S)-2″-chloro-3″-methylpentyl-oxyphenyl-4-decyloxy thiobenzoate (10.S.Cl Isoleu) synthesized by Tweig *et al.* [9], who did not observe any discontinuity in S_2 at the S_C^*–S_A transition. Zgonik *et al.* [8] explain their observation by assuming that in the S_A as in the S_C^* phase, the long molecular axes are also tilted with respect to the layer normal. But unlike the S_C^* phase there is no order among the long axes within a layer in the S_A phase. The latter observation explains that why the average tilt angle in the S_A phase is zero but S_2 in the direction of the layer normal is largely unaffected by the local disorder in a layer. Apart from the local order in a layer in the S_C^* phase, the tilt angle of a molecule does not change abruptly at the phase transition. The idea of a tilted orientation in the S_A phase was advanced, presumably for the first time, by Loesche and Grande [10]. Their conclusion was based on measurements of the angular dependence of the proton NMR linewidth in smectic phases. Raman scattering allows for the measurement of S_2 and S_4. Jen *et al.* [11] and Miyano [12] obtained low values of S_4 for S_A phases. For S_4 equal to zero, namely

$$S_4 = \tfrac{1}{8}\langle 35\cos^4\beta - 30\cos^2\beta + 3\rangle = 0, \tag{5}$$

we find that $\langle\beta\rangle = 30{\cdot}6°$. This value of β gives $S_2 = 0{\cdot}6$ which is close to the experimental value for some of the vibrational bands. Our observations will therefore reinforce the view held by some authors that molecules in the S_A phase are already tilted with respect to the layer normal. Their long axes may lie on a cone with a constant angle in a layer and this trend extends to different layers. At the S_C^*–S_A phase transition temperature, not only are the long axes aligned in each layer but also linkage between successive layers is established at the same time due to the chirality of the molecules.

As expected we find that the order parameter is largely unaffected by the application of an external field because the cone angle is unaffected by the magnitude of the weak external field. This would also suggest that surface effects play a dominant role in fixing the position of the director.

4. Conclusions

The molecular tilt angles for the different vibrational bands of the molecular core of a ferroelectric liquid crystal agree closely with the optical tilt angle for temperatures within about 5°C of the S_C^*–S_A phase transition. At temperatures lower than about 5°C below the transition, the molecular tilt angles start departing from the optical ones. In all cases the molecular tilt angle for the molecular core is lower than the optical one. This shows that the alkyl chains play an important role in the molecule orientation of a ferroelectric liquid crystal. No discontinuity in S_2 has been observed at the S_C^*–S_A phase transition. This observation suggests that in the S_A like the S_C^*, the molecules are already tilted with respect to the layer normal. In the S_C^* phase, local order among the molecules within a layer and a linkage between the molecules in successive layers due to their chirality do not seem to affect the order parameter.

References

[1] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.

[2] Clark, N. A., and Lagerwall, S. T., 1984, *Ferroelectrics*, **59**, 25.

[3] Neff, V. D., Gulrich, L. W., and Brown, G. H., 1965, *Proceedings International Conference of Liquid Crystals*, Kent State University. Brown, G. H., Dienes, G. J., and Labes, M. M. (editors) (Gordon & Breach), p. 21.

[4] Mitchell, A. D., and Cross, L. C. (editors), 1958, *Tables of Interatomic Distances and Configuration in Molecules and Ions* (The Chemical Society, Special publication No. 11).

[5] Brunet, M., and Isaert, N., 1988, *Ferroelectrics*, **84**, 25.

[6] Blinov, L. M., 1983, *Electrooptical and Magnetooptical Properties of Liquid Crystals* (Wiley–Interscience).

[7] Guo, W., and Fung, B. M., 1991, *J. chem. Phys.*, **95**, 3917.

[8] Zgonik, M., Rey-Lafon, M., Destrade, C., Leon, C., and Hguyen, H. T., 1990, *J. Phys., France*, **51**, 2015.

[9] Twieg, R. J., Betterton, K., Hguyen, H. T., and Hinsberg, W., 1989, *Ferroelectrics*, **91**, 243.

[10] Loesche, A., and Grande, S., 1974, *18th Ampere Congress*, Nottingham. Loesche, A., and Grande, S., 1976, *IV Ampere Int. Summer School*, Pula, Yugoslavia, p. 467.

[11] Jen, S., Clark, N. A., Pershan, P. S., and Priestley, E. B., 1977, *J. chem. Phys.*, **66**, 4635.

[12] Miyano, K., 1978, *J. chem. Phys.*, **69**, 4807.