

Molecular tilt angle and order parameter of low molar mass ferroelectric liquid crystal using IR spectroscopy

T. S. Perova[†], A. Kocot, and J. K. Vij

Trinity College, University of Dublin, Department of Electronics
and Electrical Engineering, Dublin 2, Ireland

R. Zentel

Universitat Mainz, Institute für Organische Chemie, Germany

ABSTRACT

Fourier transform infrared spectroscopy (FTIR) of a ferroelectric liquid-crystalline material: 4-(3)-(S)-methyl-2-(S)-chloropentanoyloxy-4'-octyloxy-biphenyl has been investigated in the wavenumber range 450-4000 cm^{-1} for various temperatures and as a function of direct bias voltage in its SmC^* phase. Samples prepared in both homeotropic and homogeneous alignments have been studied. The order parameter was calculated for several isolated IR vibrations which are characteristic of different parts and orientations of molecules. The dependence of the molecular tilt angle on direct bias voltage and temperature has similar characteristics to those obtained from electro-optic measurements.

1. INTRODUCTION

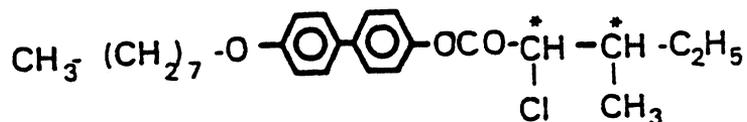
Ferroelectric liquid crystals (FLC) have attracted considerable attention due to their wide range of applications in electro-optical devices¹. Various methods have been used for investigating the switching mechanisms in ferroelectric liquid crystal cell. However, the molecular mechanism responsible for this switching is not yet fully understood. Infrared spectroscopy is ideally suited for these investigations since information about different parts of the molecule can be revealed through studies of the intensity and frequency of the various vibrational bands. Zgonik et al.² examined the orientational order in smectic phases of a ferroelectric liquid-crystalline material (abbreviated as 10.S.C11soleu) by IR absorption spectroscopy. Their results showed that the molecular tilt of the core changes only slightly in going from the SmA to the SmC^* . This has been interpreted in terms of cores that have already been tilted in the SmA phase. The reorientations of a FLC under applied electric field have also been studied. Kocot et al.³ used IR spectroscopy for the first time for determining the molecular tilt angle of a FLC material. The molecular tilt angle was defined as the angle between the transition dipole moment of the vibrational bands belonging to the central part of the molecule and the rubbing direction.

In this paper, we report results of investigations into of the second rank orientational order parameter and of the molecular tilt angle as a function of the applied direct bias voltage in SmA and SmC^* phases for a ferroelectric low molar mass LC: 4-(3)-(S)-methyl-2-(S)-chloropentanoyloxy-4'-octyloxy-biphenyl (designed as ZT) using IR spectroscopy. The results are compared with those obtained by using polarizing microscopy.

2. EXPERIMENTAL

The chemical constituent of ZT and the transition temperatures are given in Fig.1. Samples were oriented both in the homeotropic and the homogeneous configurations between a set of two Si and also two ZnSe windows. The alignment achieved on ZnSe windows was confirmed using polarizing microscopy. The purpose of experiments on a homeotropic aligned sample is to determine the correct assignment of the vibrational band and the phase transition behaviour.

A homeotropically aligned samples of approximate thickness 12 μm were prepared between two ZnSe windows. Both ZnSe windows were spin coated with 1% solution of ZLI 3334 Merck compound dissolved in methanol. Samples with



Crystal - 322 K - Smectic C* - 328 K - Smectic A - 338 K - Isotropic

Fig. 1. Structure of ZT liquid crystal

homogeneous orientation were prepared between the optically polished silicon windows. These were spin coated by nylon 6/6 (0.2 percent solution in methanol) to obtain a uniform layer about 0.2 μm thickness. Both Si windows were rubbed subsequently in antiparallel directions. Mylar foils of 6 μm were used as spacers for homogeneously oriented sample. Distances between the windows were checked through interference fringe measurements. The cells were filled at a temperature above the clearing point due to the capillary effect. Since it was not possible to check whether the alignment of the sample between a set of two silicon windows using polarizing microscopy was truly homogeneous, a similar sample was prepared between two glass plates in the manner analogous to that just described. The alignment determined by means of polarising microscopy was found to be homogeneous and it was reasonable to assume that the alignment was similarly homogeneous between a set of two Si windows.

The accuracy and the set point stability in temperatures were 0.5 $^{\circ}\text{C}$ and 0.1 $^{\circ}\text{C}$, respectively. The infrared spectra were recorded using a Digilab FTS 60A spectrometer, with 0.5 cm^{-1} resolution. An IR-KRS5 polarizer was used to polarize the IR beam.

3. RESULTS AND DISCUSSION

The polarized IR spectra of a chiral SmC* phase of homogeneously aligned samples of ZT are shown in Fig. 2. The absorption bands are assigned to the characteristic vibrational modes taking into account the direction of the vibrational transition dipole moments. For the purpose of this paper, we considered a few chosen vibration bands: C=O stretch vibrations $\nu = 1767 \text{ cm}^{-1}$ and two C-C benzene ring vibrations ($\nu=1497$ and $\nu=1608 \text{ cm}^{-1}$).

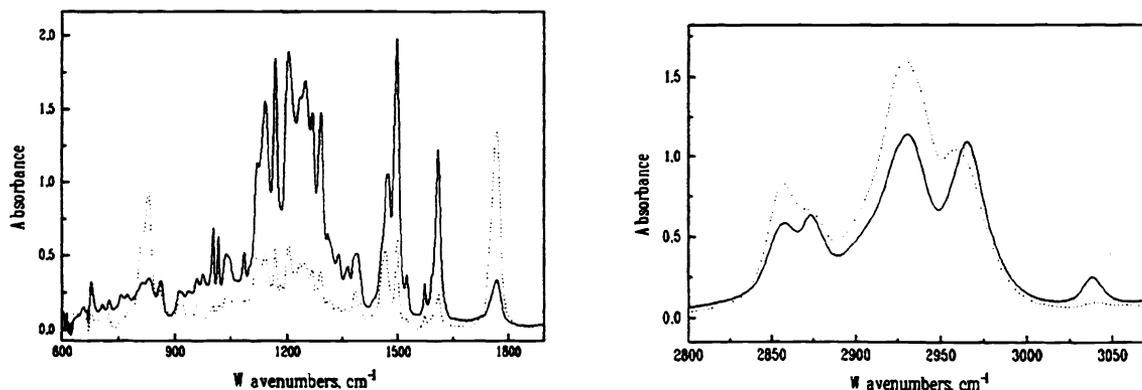


Fig. 2. Polarized FTIR spectrum of the homogeneously aligned ZT liquid crystal at $T=323\text{K}$. Solid line, 0° ; dotted line 90° .

3.1. IR spectra for different phase

FTIR spectra were recorded for homogeneous and homeotropic aligned samples in the temperature range of 300-350 K. The temperature dependence of the peak intensity and the frequency maximum of several bands are shown in Figures 3-5. The intensity and the peak position change significantly for the mesogen groups [benzene, biphenyl ($1608, 1497, 1202, 830 \text{ cm}^{-1}$), and ester (1767 cm^{-1}) and slightly for alkyl groups ($2960, 2932, 1460 \text{ cm}^{-1}$ etc) at the occurrence of the phase transition from crystalline to SmC^* phase. This is interpreted in terms of a significant conformational change for the entire FLC molecule. Very minor changes in the spectra during SmC^* to SmA phase transition were observed. However, a noticeable difference in the peak intensity and the peak position is observed during the SmA -I phase transition temperature. Figures 3-5 show that noticeable reorientations of the molecules start occurring at the temperature a few degrees above I- SmA phase transition and these stop at the temperature a few degrees below this transition temperature.

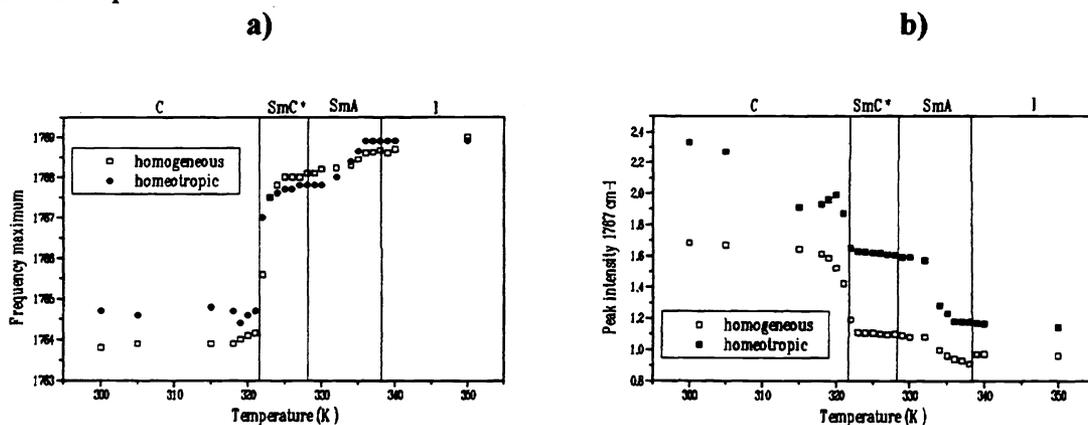


Fig. 3. Temperature dependences of frequency maximum (a) and peak intensity of C=O vibration.

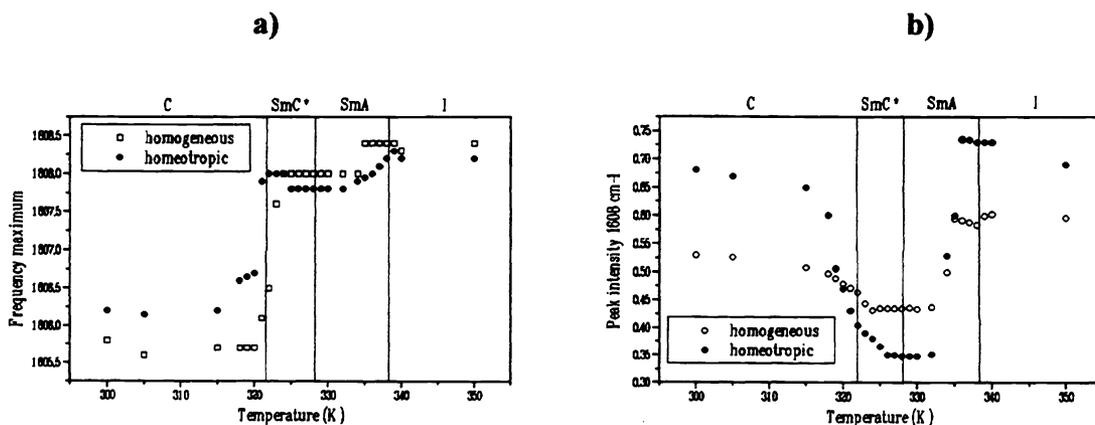


Fig. 4. The same as in Fig.3. for benzene ring C-C stretching vibration.

Figures 3-5 also show that both types of molecular orientations show similar characteristics in terms of both the peak intensity and the frequency maximum of the IR bands. For the C=O stretching vibrations, we observe a more complicated contour of the band than that for an isolated C-C benzene stretching vibrations (at 1608 cm^{-1}) and C-H aromatic out of plane vibration at 830 cm^{-1} (see Fig. 6). Since these groups play an important role in the switching process, a detailed analysis of the C=O band should be carried out. This band has been deconvoluted into its constituent vibrations.

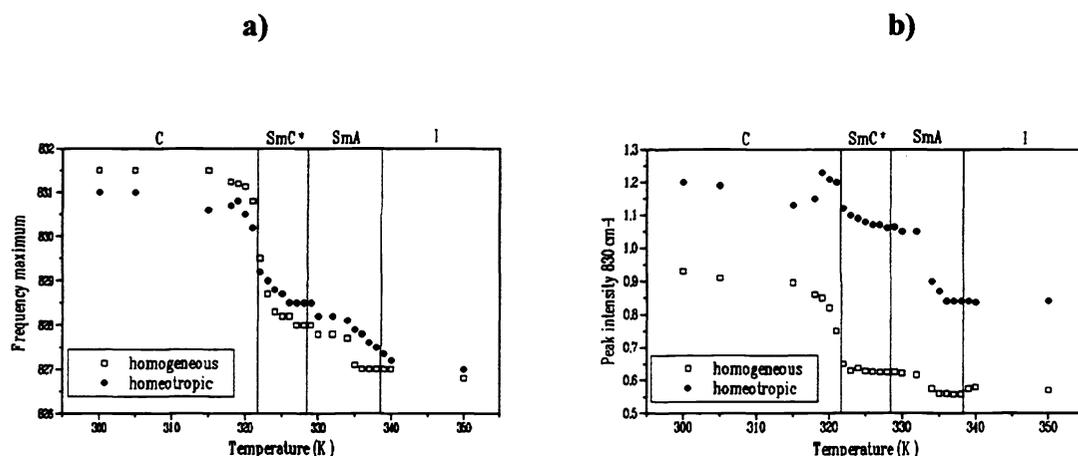


Fig. 5. The same as in Fig.3 for C-H aromatic out of plane vibration.

The analysis of the C=O stretching vibration suggests the existence of three possible conformations for the ester groups of the FLC molecule; the relative populations of which may vary significantly as a function of temperature (see Figs. 7 a and 7 b). One of the conformers exists primarily in the crystalline state, the other one exists primarily in the SmA and the isotropic phase. The relative populations of these two conformers are approximately equal in the SmC* phase. One of

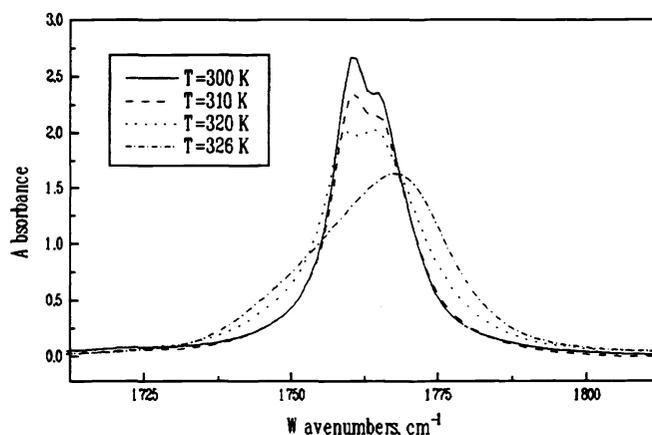


Fig. 6. FTIR spectrum of homogeneously aligned ZT LC at different temperatures.

the constituent bands exists only in crystalline phase and changes dramatically during the phase transition from the crystalline to the SmC* phase. This band completely disappears at the temperature of 325 K. These observed conformations correspond to different angles of the C=O bond with respect to the benzene ring. Kardan et al.⁴ have shown through the calculations that C=O stretching vibrational frequency varies when this angle changes. Hence for the SmC* phase we must consider that C=O band consists of 2 bands with frequency maxima at $\sim 1770 \text{ cm}^{-1}$ and $\sim 1758 \text{ cm}^{-1}$. Moreover from the dependence of the frequency maximum on temperature we see that the orientation of one of these two conformational bands (1770 cm^{-1}) is quite stable when the temperature changes while the frequency maximum of the other decreases when the temperature increases. This means that for the FLC molecules studied here, there is a preferable orientation for the C=O bond with respect to the mesogenic group. Possibly this gives rise to an

interesting behaviour of this molecule with respect to other carbonyl group containing LC molecules (see, for example⁵⁻⁷). This interesting behaviour has also been observed during the measurements of dichroism on applied electric field (see the next section and our paper to be published later⁸).

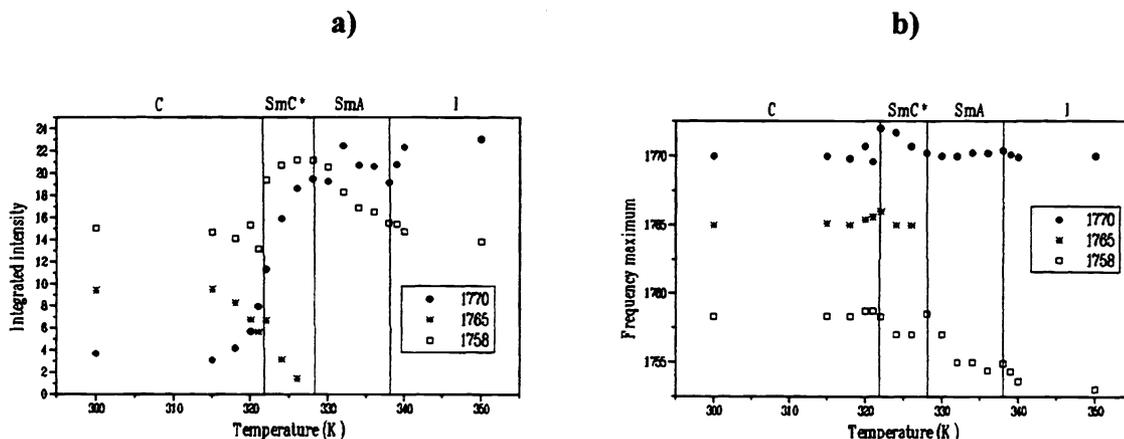


Fig. 7. The dependences of parameters of deconvolution (intensity (a) and frequency maximum (b)) of C=O band on different temperatures..

3.2. IR Dichroism Measurements

In this section we present the results of IR measurements for a homogeneously aligned sample for parallel and perpendicular polarisation with reference to the rubbing direction. These measurements allow us to evaluate the order parameter of the FLC system.

The second rank orientational order parameter S_2

$$S_2 = \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle$$

can be expressed in terms of the dichroism ratio, R^3 :

$$R = \frac{(1 + 2S_2)}{(1 - S_2)} \quad (5)$$

if transition dipole moment is directed along the long molecular axis, i.e. $\alpha = 0$ and

$$R = \frac{2(1 - S_2)}{(2 + S_2)} \quad (6)$$

if $\alpha = 90^\circ$,

where the dichroism ratio R is defined as

$$R = \frac{\int A_{\parallel} dv}{\int A_{\perp} dv} \quad (7)$$

(A_{\parallel} and A_{\perp} absorbances parallel and perpendicular to the director respectively). Here 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.

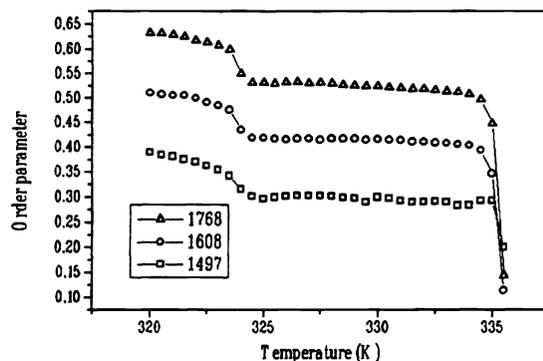


Fig. 8. The dependence of the order parameter on the temperature of homogeneously aligned sample.

The order parameter has been calculated for several stronger and isolated IR vibrations. These are characteristic of different parts and relative orientations of molecules. Figure 8 shows the temperature dependence of the order parameter for a sample of 6 μm thickness for three vibrational bands. As is seen from Fig. 8 the order parameter for the bands that have been investigated decreases slowly from the crystalline to the SmC^* phase, it does not change at the SmC^* - SmA phase transition and exhibits a sharp decrease at the temperature close to the isotropic phase transition temperature. The maximum value of the order parameter has been found for the C=O and the C-H out of plane bands. For the two benzene ring vibrations, the order parameter is somewhat less. For the alkyl group the order parameter was 2.5 times lower than for the central core. However this value of order parameter may not imply that alkyl chain is disordered, since the value of order parameter for C=O and CH_3 stretching vibrations behaviour makes it possible to conclude that at least a short alkyl chain for this LC material is quite ordered.

We observed interesting behaviour 2° K above the C- SmC^* transition temperature. This behaviour is observed in the temperature range 324-325 K. The phase transition temperature from the crystalline to SmC^* phase for this material is 322 K as established from DSC and the polarising microscopy. As has already been shown for low molar mass LC molecules³ there is no significant change in the order parameter during the phase transition from the crystalline to the smectic phase, however, this seems to be a new and interesting result and it will be investigated in greater detail at a later stage.

The result could be connected with the orientations of the ester groups. As shown in the previous section, the third band corresponding to one of the three C=O conformations disappeared exactly at this temperature. Possibly the presence of such oriented molecules in the crystalline phase is energetically more stable and cause the better alignment. This interesting behaviour has also been reflected in the dependence of the order parameter on temperature with direct bias voltage of 20 V.

3.3. Effect of an electric field

The studies on the dependence of the IR dichroism ratio for some vibrational bands on the applied direct bias field across the cell are important for the understanding of the re-orientations of molecules during the electric switching. Now, we present a study of the order parameter for the various vibrations and the molecular tilt angle as functions of temperature and applied direct bias voltage.

The molecular tilt angle obtained from the IR spectra for the benzene ring stretching vibrations (1608 cm^{-1}) and from electro-optical measurements by using polarizing microscopy is shown in Fig. 9. We find a close agreement between the molecular and optical tilt angles in temperature range 320 - 328 K. As is seen from Fig. 9 the dependence of molecular tilt angle on temperature is almost independent of the direct bias voltage in the range 5-20 V. This is confirmed by the results of the dependence of the tilt angle on direct bias voltage (Fig. 10) for $\nu=1608\text{ cm}^{-1}$. The results imply that the helix is unwound at a threshold voltage of less than 2 V and tilt angle does not change with a direct bias voltage greater than 5 V.

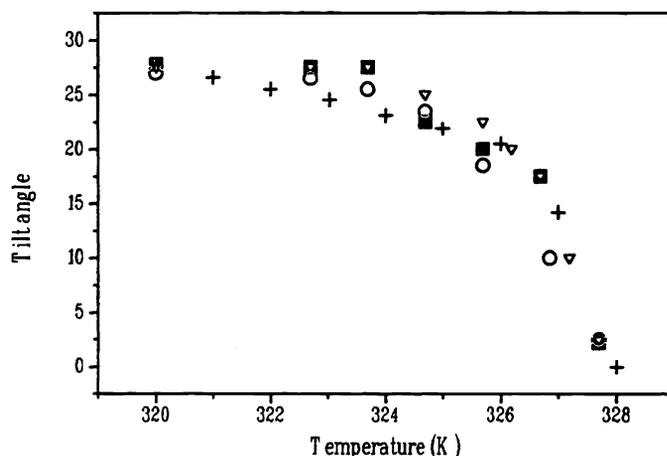


Fig. 9. The dependence of tilt angle on temperature for electro-optic measurements (+) and IR ($\nu=1608\text{ cm}^{-1}$) measurements at different applied voltage (o - 5 V; v - 15 V; square - 20 V).

The order parameter of the smectic C^* phase is found to be independent of direct bias voltage in the range 5-15 V as seen from Fig.10.

The dependence of the order parameter on temperature (in region 320-325 K) for various applied direct bias voltage is shown in Figs. 11. We can see from this Figure that the peculiarity at around 324.5 K still exist.

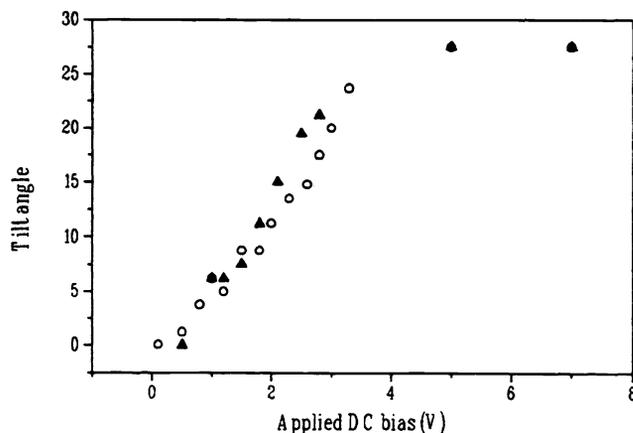


Fig. 10. The dependence of the tilt angle on DC bias for IR (o) and electro-optic measurements.

Fig. 12 shows the plot of the order parameter vs direct bias voltage for $T=323$ K. The order parameter is found to increase significantly (quite noticeable for 1608 cm^{-1}) when the helix is unwound by the bias voltage and then does not change very much for voltages greater than 5 V. We conclude that the book-shelf layer structure is formed in the cell for applied bias voltage more than 5 V (see our paper⁹).

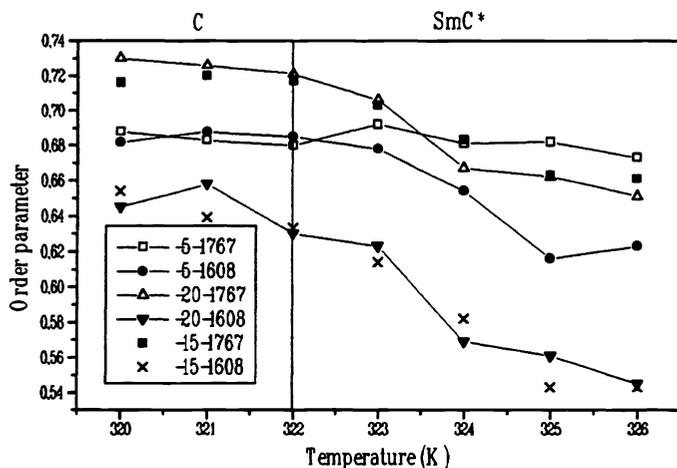


Fig. 11. The dependence of order parameter for different IR bands on temperatures at different applied voltage.

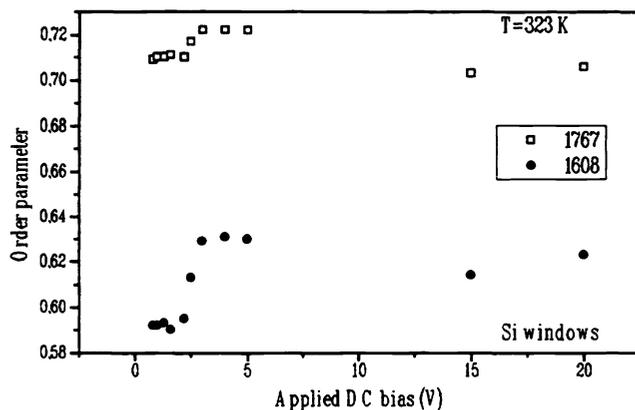


Fig. 12. Order parameter on applied DC bias for two different IR bands.

4. CONCLUSIONS

An interesting results has been found for a FLC material 4-(3)-(S)-methyl-2-(S)-chloropentanoyloxy-4'-octyloxybiphenyl (ZT). The molecular structure given in Fig. 1 shows that one of the ends of this molecule has a short alkyl chain and two chiral carbon atoms. Such a structure produces molecular packing which does not allow the alkyl chain rotate

freely. These rigid alkyl chain structures cause a higher orientation of the carbonyl and CH₃ groups with respect to mesogenic group.

5. REFERENCES

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* Permanent address: Vavilov State Optical Institute, St.-Petersburg, Russia.