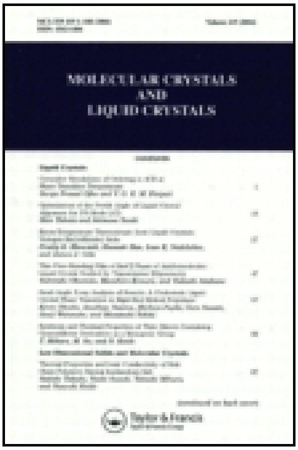

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Observation of the Orientational Transition in Hexa(hexylthio)Triphenylene using Polarized FTIR Study

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Observation of the Orientational Transition in Hexa(hexylthio)Triphenylene using Polarized FTIR Study

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The results of polarised FTIR study of hexa-(hexylthio)-triphenylene (HHTT), contained between ZnSe and CaF_2 windows, are being presented.This gives some supplementary information on orientation of molecules in different phases. An orientational transition of HHTT contained between two CaF_2 windows in D_{hd} phase is being reported.

Keywords: discotic liquid crystal; infrared absorption; orientational transition

INTRODUCTION

The study of the influence of the surface structure on the orientation of discotic liquid crystals in the mesophase is extremely important from the scientific and applicational points of view [1]. Recently we observed the orientational transition in hexapentyloxy-triphenylene contained between different substrates under certain experimental conditions (temperature and time variations) [2,3]. Here we present the results of the polarised FTIR study of hexa(hexylthio)-triphenylene contained between ZnSe and CaF_2 windows. Hexa(hexylthio)-triphenylene (HHTT) is one of the few known discotic mesogen systems with both short-range intracolumnar stacking in a conventional discotic hexagonal liquid crystalline phase (D_{hd}) and long-range intracolumnar order in the helical columnar phase D_{ho}. As it was shown [1] the helical columnar phase of this discotic material is very suitable for a fast transport of photogenerated charge carriers. Previously this material was studied using different techniques including X-ray [4-6] and FTIR spectroscopy [6]. Authors of Ref. [6] based on the analysis of changes in the frequency maxima for different vibrations (alkyl chain CH_3 and core C-C stretch) drew conclusions about the structure change at the phase transitions. We obtained in this work some supplementary information about the orientation of molecules in different phases as well as the orientational transition of HHTT contained between two CaF_2 windows in the D_{hd} phase.

R=SC_6H_{13}

(C – 335°K D_{ho} – 343°K D_{hd} – 366°K I)

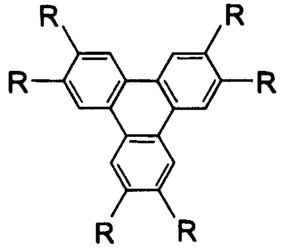

FIGURE 1 Structure and phase sequences of hexa(hexylthio)-triphenylene (HHTT).

EXPERIMENTAL

The synthesis of hexa(hexylthio)-substituted of triphenylene has been described in Refs. [7,8]. The structure formula and the phase sequences are shown in Fig. 1. This compound exhibits two mesophases in between crystalline (C) and the isotropic (I) phases: helical columnar phase D_{ho} with the long intracolumnar order, and a conventional discotic hexagonal disordered phase (D_{hd}) with the short-range intracolumnar order. Two different cells with HHTT were prepared for FTIR study. For one of the cells a ZnSe windows were used without any surface treatment. Windows were washed in acetone and methanol and dried using a tissue. A 11 μm mylar spacer was used in order to control the cell thickness. HHTT was filled at a temperature of 383° K (in the isotropic phase) using capillary effect. After that the cell was cooled slowly down to the crystalline phase at a rate 0.1° K per minute. For the second cell the CaF_2 windows coated by GeO at oblique evaporation (at angle of 85° and thickness ~ 1000 Å) were used. This cell was prepared in the same manner as previously described using a ZnSe cell.

The IR spectra in the wavenumber range 600 - 4000 cm^{-1} for ZnSe cell and in the wavenumber range 1000-4000 cm^{-1} for CaF_2 cell are recorded using a Fourier transform infrared spectrometer FTS-Digilab 60 A within a temperature range of 300-420 K. The IR cell, containing the sample sandwiched in between windows, was thermostated to within ± 0.1 K.

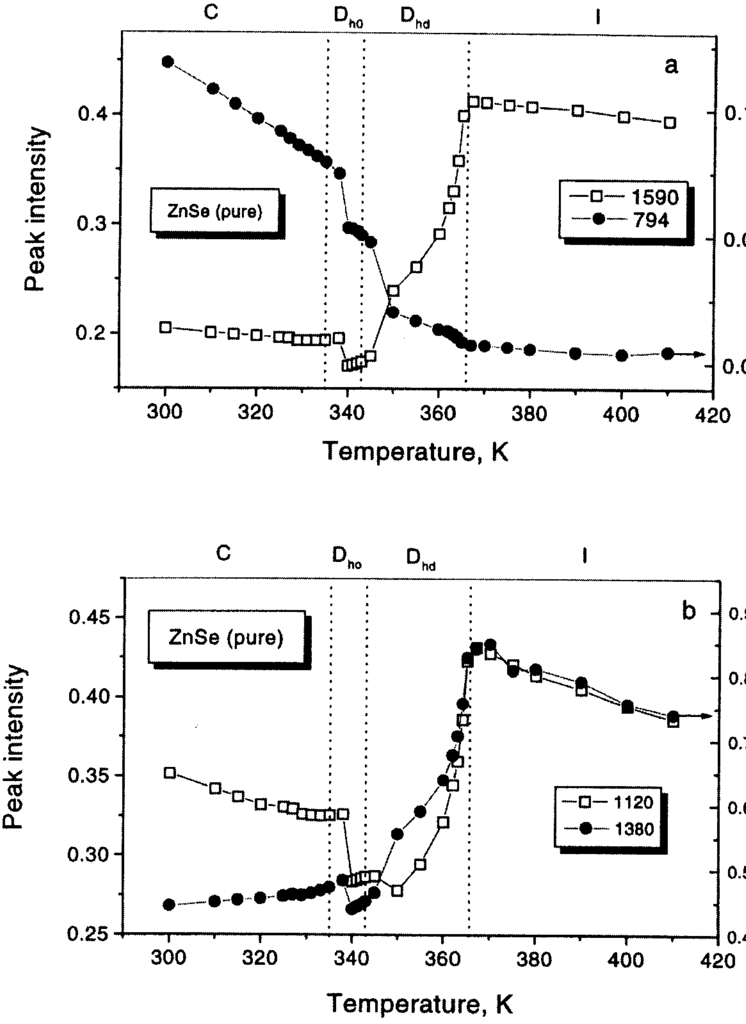

FIGURE 2 The dependence of the peak intensity of aromatic (in plane - 1590 cm^{-1} and out of plane -794 cm^{-1}) and alkyl chain (1120 and 1380 cm^{-1}) vibrations on temperature for HHTT contained in between pure ZnSe windows. The thickness of the cell is ~ 11 μm.

The measurements have been performed with an increase in temperature from the crystalline to the isotropic phase. Data were taken in 5°K increments at temperatures quite far from the phase transitions and in 1° K increments around the phase transition. In order to check the possible leakage of the sample from the FTIR cell, after the measurements the sample was cooled slowly down to crystalline phase and measured again at temperature of 300° K. In the case of ZnSe cell the measurements were repeated twice. The results obtained were found to be similar.

RESULTS AND DISCUSSIONS

We focus our attention here mainly on the amplitude changes although the frequencies changes were also analysed and compared with the results obtained in Ref. [6]. We shall mention about this analysis at a latter stage.

Figs. 2 and 3 show the temperature dependence of the intensity of a few chosen vibrational bands. Those are: C-C aromatic stretching vibrations at ~1590 and 1550 cm^{-1}, CH bending modes near 1380 cm^{-1}, C-H out of plane deformation around 700-800 cm^{-1}, CH_2 and CH_3 symmetric and asymmetric stretching vibrations in the frequency range 2820-3000 cm^{-1}.

For our case of the alignment of HHTT, a dramatic changes in the amplitude have been observed at $C \rightarrow D_{ho}$ and $D_{ho} \rightarrow D_{hd}$ phase transition as seen from Figs. 2 and 3. For the $D_{hd} \rightarrow I$ phase transition a different behaviour for different cells have been found. We can see from Fig. 2 (ZnSe cell) continuous transition and for the CaF_2 cell (Fig. 3) quite a dramatic phase transition. This difference will be discussed below. It should be noted here that $D_{hd} \rightarrow I$ phase transition is also quite noticeable on the diagram of the peak intensity *vs* temperature (not shown). At the same time the amplitude and frequency maxima are quite stable in D_{ho} phase. This shows that there are no large changes in the intracolumnar order in between those phases except that intracolumnar distance changes due to the conformational changes of alkyl chains (see [6] for details).

However, as was shown using X-ray studies [6], the intercolumnar distance decreases rapidly and linearly with increase in temperature. This will affect the intermolecular interactions and cause the change of the intensity of bands as seen for a majority of vibrational bands observed.

As seen from Figs. 2 and 3 the intensity of the in-plane vibrations continuously increases in the D_{hd} phase. However this behaviour is

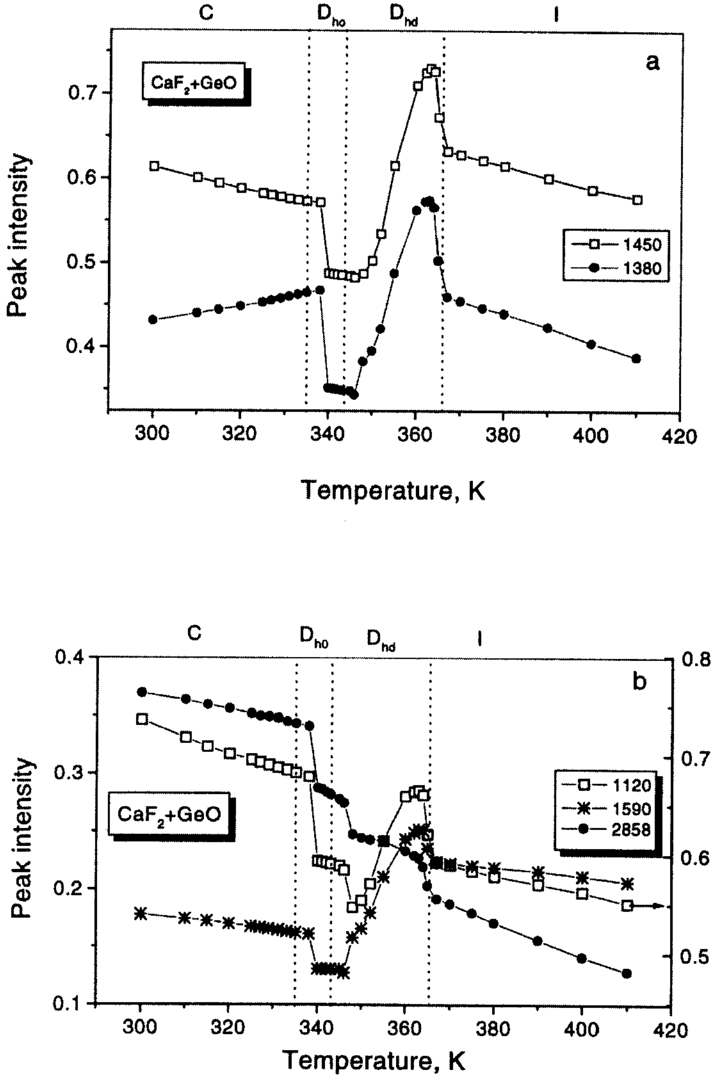

FIGURE 3 The same as in Fig. 2 for HHTT contained in between CaF_2 windows coated by GeO at oblique evaporation.

different for HHTT contained between ZnSe and CaF_2 windows. We can see that the intensity of in-plane vibrations (C-C aromatic stretching vibration near 1590 cm^{-1}) in the D_{hd} phase (I_{hd}) changes with respect to the intensity of this band in the isotropic phase (I_l) from $I_{hd}<I_i$ to the $I_{hd}>I_i$. Usually by comparison of these intensities we can draw conclusion about the orientation of the columns axis with respect to the windows [2,3,9]. Mainly two kind of the orientation of discotics are known - side-on (homeotropic) if intensity of the in-plane vibration in discotic phase is higher than in the isotropic phase and reverse for the edge-on (planar) orientation. So, it is quite obvious that for HHTT contained between CaF_2 windows we observed the orientational transition from the edge-on orientation to the side-on orientation. The behaviour of the frequency maxima of CH_3 bands (symmetric at ~ 2960 cm^{-1} and asymmetric at ~ 2870 cm^{-1} stretching vibration) shows that the frequency increases for the D_{ho} phase, then drops down slightly in D_{hd} phase. However when temperature increases up to the 360°K (where a different type of orientation is observed) the frequency maxima is of the same value as for D_{ho} phase. We pressume that this behaviour is due to the conformational change of the alkyl chain. As was shown in [6] the $C\rightarrow D_{ho}$ transition primarily involves motion of the end methyl groups. (It is probable that the amplitude of the thermal vibrations increases, the distribution of enviroments become wider, and that the static *gauche* bonds found in the C phase may dissapear). Microscopically, the $D_{ho}\rightarrow D_{hd}$ transition primarily involves a change in the core-core interactions, with no dramatic change in configurations of the tail.

In order to check why such a large difference is observed for CaF_2 and ZnSe cells, we carry out the polarised IR transmission measurements at the oblique and normal incidence of light at a temperature of 343°K (in helical D_{ho} phase). Figs. 4 *a* and *b* show the results of the polarised measurements for both cells together with theoretical prediction using the following expression for the absorbance as a function of the angle of polarisation, θ [9,10]:

$$A(\theta) = -\log(10^{-A_\perp} + (10^{-A_\parallel} - 10^{-A_\perp})\sin^2(\theta), \qquad (1)$$

From figures 2 and 3 one can see quite a large difference between these two cases. For CaF_2 windows a dichroism is small, whereas quite noticeable dichroism is observed for the ZnSe windows. The same effect has been observed for hexapentyloxytriphenylene sandwiched between ZnSe and CaF_2 windows. The easy orientation direction of the surface of the windows is presumably responsible for these effects. For ZnSe

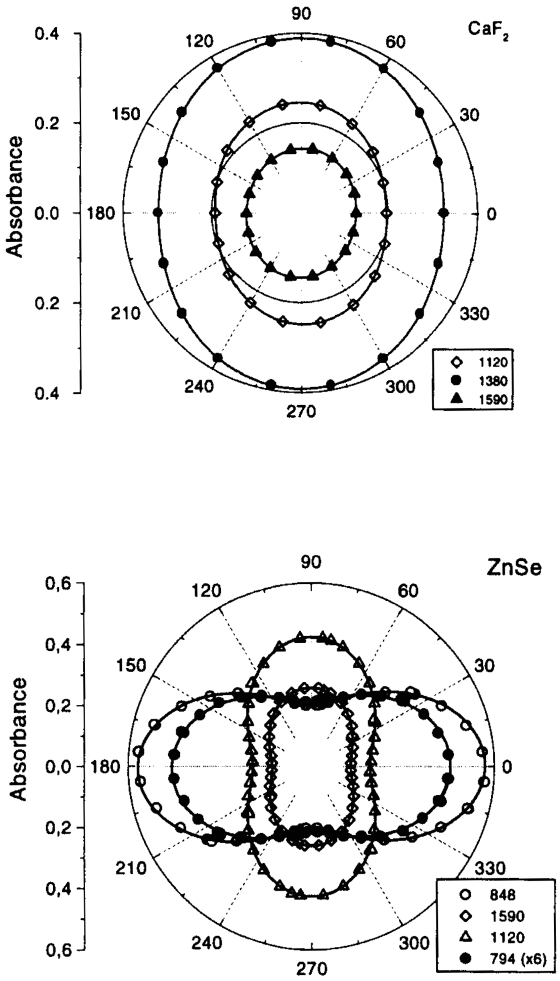

FIGURE 4 The intensity distribution for in-plane and out-of-plane vibrations in the window plane (Y-Z plane) for (*a*) CaF_2+GeO cell and (*b*) for ZnS cell. Solid lines on the plots show the calculated functions using Eq. (1).

windows there is a preferable easy direction orientation on the surface of these cuts [11]. This cause the homogeneous-planar orientation in D_{ho} phase for HHTT contained between ZnSe windows. For CaF_2 there are at least three easy axes of orientation on the surface of these cuts. These cause heterogeneous-planar orientation of HHTT. The later orientation is not stable and with temperature it can be converted to the side-on alignment (see [2] for details). The side-on alignment is more homogeneous, thus again a long-range order appears in the D_{hd} phase. Thus we can find more dramatic changes in between D_{hd}→I phase both in the amplitude and in the frequencies of vibrational bands.

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