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Infrared absorption study of hexapentyloxytriphenylene
A discotic liquid crystal

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Fourier transform infrared absorption (FTIR) spectroscopy has been used to study a discotic liquid crystal. IR spectra are reported as a function of temperature for hexapentyloxytriphenylene (H5T). The order parameter *S* has been determined using unpolarized radiation and by comparing the spectra of the discotic phase with that of the isotropic phase. Variations in frequency for some of the most significant bands are presented as a function of temperature.

1. Introduction

Chandrasekhar *et al.* discovered the discotic mesophase in 1977 [1] while investigating the optical and X-ray properties of hexa-substituted esters of benzene. Since then several hundred papers have appeared on the synthesis and characterization of discotic liquid crystals. Several new discotic liquid crystals have since been discovered.

Discotic liquid crystals are composed of flat or nearly flat cores with semi-flexible tails. Deuterium NMR studies have shown that liquid crystals cannot be idealized by rigid rods or discs [2]. Many types of discotic liquid crystals [3–12] and discotic liquid crystal polymers [13] have been synthesized where the structure of the core and of the semi-flexible tails have been altered. A classification of the disc-like mesogens has recently been attempted by Destrade *et al.* [14].

In the discotic phase, molecular cores form long range ordered columns. The structure of discotic liquid crystals is similar to the hexagonal phase of soap–water and other lyotropic systems. The centres of the cores form a rectangular or hexagonal lattice [3] in the plane normal to the column's axis. The aromatic cores are usually inclined at an angle of about 55–60° to the column's axis. The inclination depends on the lengths of the tails and strengths of the polar groups. Such inclination translates the centres of the cores and consequently the lattice becomes pseudo-hexagonal [15].

Discotic liquid crystals are interesting materials since they form highly ordered structures in discotic phases. The two main possibilities for alignment in discotic liquid crystals are: *side on*, where the aromatic cores are parallel to the plates of the cell (see figure 1 (*a*)), and the second possibility is *edge on*, where the central discs are perpendicular to the windows of the cell (figure 1 (*b*)). Long wing CH groups and strong

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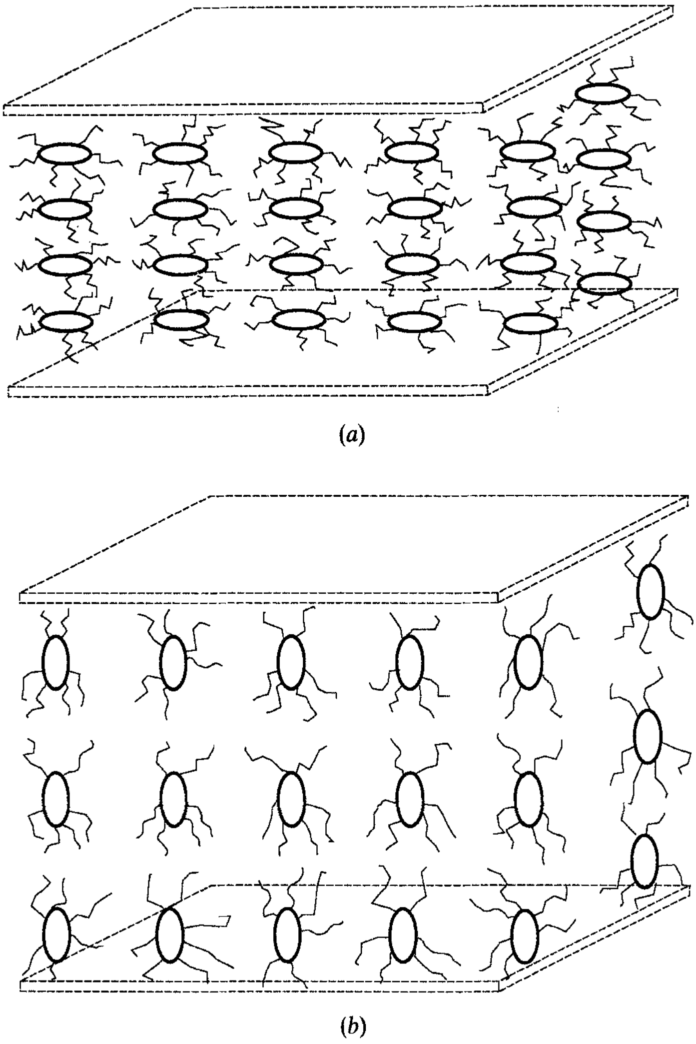
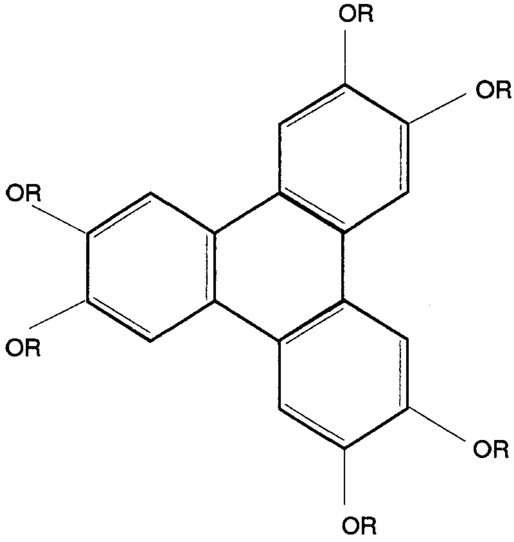


Figure 1. Two main possibilities of ordering in discotic liquid crystals: (*a*) 'side on', (*b*) 'edge on'.

polar groups are responsible for *side on* alignment. On the other hand, the short wing CH groups and weak polar groups are responsible for *edge on* alignment [12]. Some papers have appeared on theoretical models [16, 17] and experimental studies [18–20] concerning the alignment in discotic liquid crystals.

In this paper we investigate changes of the order parameter and of the frequency with temperature for some bands of a discotic liquid crystal (H5T) using FTIR spectroscopy. We have also studied the IR spectra of hexapropyloxytriphenylene (H3T), similar in structure to H5T but having shorter alkyl tails. Consequently, the latter does not form a discotic mesophase. This is done to be able to compare the spectra of two similar compounds. The chemical formulae for both H3T and H5T are given in figure 2.

This seems to be the first attempt where an investigation of the order parameter *S* of a discotic liquid crystal using IR spectroscopy has been made.



For H3T: R= C_3H_7

For H5T: R= C_5H_{11}

Figure 2. Chemical formulae of H3T and H5T.

2. Experimental

H3T and H5T have been synthesized by Karthaus and Ringsdorf [21]. The polarized microscopy study shows the following phase transitions:

H3T: C 445 K I

H5T: C 342 K D_{ho} 395 K I.

D_{ho} is a discotic hexagonal ordered phase as it exhibits a helical order and a three-column superlattice. Consequently the distances between the planes of the cores are approximately the same. However a different situation is observed for a discotic hexagonal disordered phase (D_{hd}), where the molecules form a hexagonal array of columns; both helical and superlattice orders are lost.

A Digilab FTS-60A IR spectrometer with a MCT detector has been used. A total of 64 scans were co-added to compute an absorbance spectra with a resolution of 0·25 cm^{-1} in the wavenumber range of 700–4000 cm^{-1}. Spectra were collected for different temperatures in the range 300 K (a crystalline phase, C) to 405 K (an isotropic phase, I). The temperature increment was kept at about 5 K, except near the transition from C to D_{ho}. Here the temperature increment used was 1 K. An Oxford Intelligent Programmable Temperature Controller ITC4 was used to stabilize the temperature to within 0·1 K.

The sample, weighing approximately 3 mg, was placed between two silicon windows in the isotropic phase. Then the sample was cooled to room temperature and placed in the measuring compartment of the IR spectrometer. The H3T spectrum has been recorded at room temperature only to compare it with the spectrum of H5T. H5T while contained in the cell was heated to the isotropic phase and then was cooled slowly to room temperature. The procedure of repeated heating and cooling was adopted to obtain a better sample alignment.

The spectra of the silicon windows for different temperatures have been subtracted from the measured sample spectra. Spectra were smoothed and base corrections were made. Programs were used to find the peak positions, to fit the complex peaks to the sum of the lorenzian and gaussian functions and to determine the areas under the peaks. All these programs were supplied with the spectrometer by Bio-Rad Digilab.

3. Results and discussion

3.1. *Band assignment*

The spectra of H3T and H5T at 300 K are shown in figure 3. Using the published IR data [20, 22–30] we make the following band assignments:

CH_3 asymmetric stretching vibration, near 2950 cm^{-1};
CH_2 asymmetric stretching vibration, near 2930 cm^{-1};
CH_3 symmetric stretching vibration, near 2870 cm^{-1};
CH_2 symmetric stretching vibration, near 2860 cm^{-1};
C–C aromatic stretching vibration, near 1617 cm^{-1};
C–C aromatic in-plane deformation, near 1518 cm^{-1};
CH_2 scissoring vibration, near 1468 cm^{-1};
C–C aromatic in-plane deformation, near 1439 cm^{-1};
CH bending mode, near 1389 cm^{-1};
CH_2 out-of-plane wagging vibration, near 1300 cm^{-1};
benzene–O stretching vibration, near 1263 cm^{-1};
C–O–C stretching asymmetric vibration, near 1174 cm^{-1};
C–O–C stretching symmetric vibration, near 1000–1100 cm^{-1};
CH aromatic out-of-plane vibration, near 836 cm^{-1}.

Differences in the bands between H5T and H3T are observed for CH_2 asymmetric stretching and CH_2 symmetric stretching vibrations near 2800–3000 cm^{-1}. This is due to a smaller number of C atoms in the alkyl tails in H3T. The C–O–C symmetric bands in the range 1000–1100 cm^{-1} also show some differences in the absorbance. For CH out-of-plane vibration near 837 cm^{-1}, the value of absorbance is found to be higher for

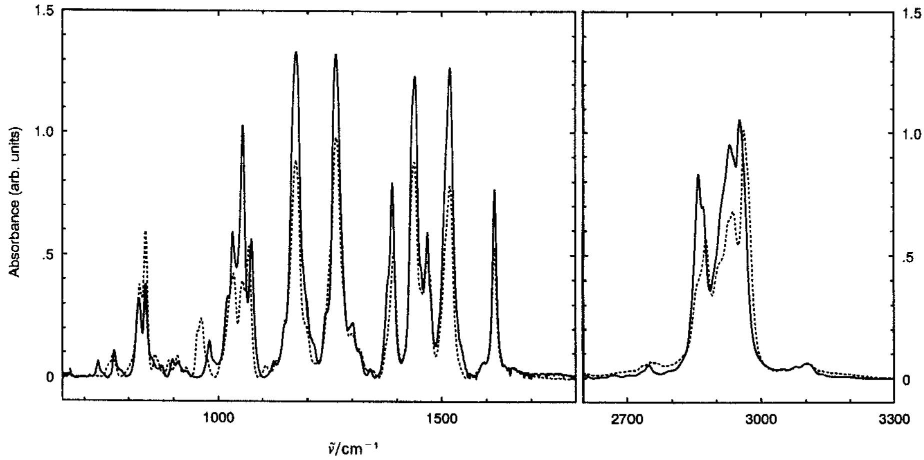


Figure 3. The IR spectra of H3T and H5T——, H5T; ····, H3T.

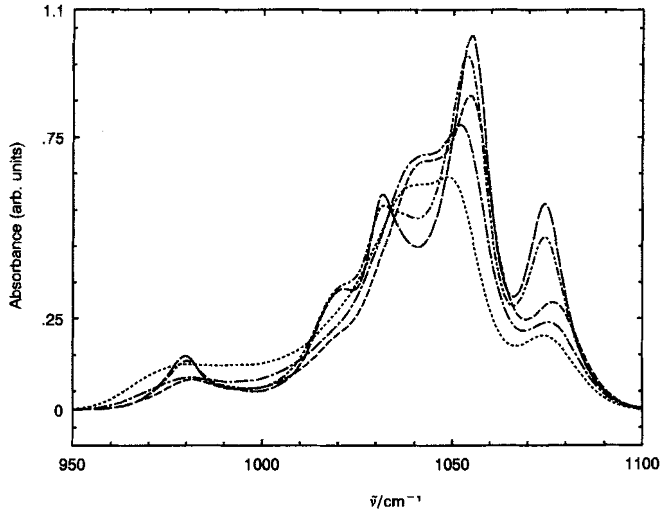


Figure 4. The IR spectra of C–O–C vibration of H5T at different temperatures. – –, 300 K (C); –··–, 338 K (C); - - - -, 340 K(D_{ho}), –·–, 390 K (D_{ho}); . . . , 400 K (I).

H3T than for H5T. During the heating stage, significant changes in the shape of the C–O–C symmetrical bands in the range of 1000–1100 cm^{-1} are observed (figure 4). The most significant changes in the shape of these bands occurred near the phase transition temperatures. However changes in the magnitude of absorbance for the discotic material with temperature are very weak for CH_2 and CH_3 stretching vibrations. The latter observation suggests that the tails are highly disordered even in the discotic phase. Comparing the spectra of the discotic phase to that in the isotropic phase we find that the order in H5T is the side on type. The type of order has been deduced from the observation that absorption is higher in the discotic than in the isotropic phase for vibrations parallel to the core.

3.2. *The order parameter*

In order to investigate the alignment in H5T, we use Neff's method of analysis [31]. In figure 5 we present the schematic diagram showing an interaction of an unpolarized IR beam with a discotic material. Θ is the angle between the normal to the plane of the aromatic core and the direction of an incident IR beam.

Ψ is the angle between the normal to the plane of the core and direction of the transition dipole moment vector—$\mathbf{p}_i$, where

$$\mathbf{p}_i=\frac{d\mathbf{m}_i}{dq_i} \tag{1}$$

and $\mathbf{m}_i$ is the dipole moment vector and q_i is the normal coordinate of the ith mode. Ψ depends on the conformation of the alkyl tails for the CH_2 and CH_3 vibrations and is approximately the same for vibrations of the cores that correspond to different molecules. The angle Θ is different for different molecules and its average value determines the order parameter for the central part of the molecule.

R_i is the dichroism ratio which for an unpolarized beam is defined as follows:

$$R_i=\frac{I_D}{I_I}. \tag{2}$$

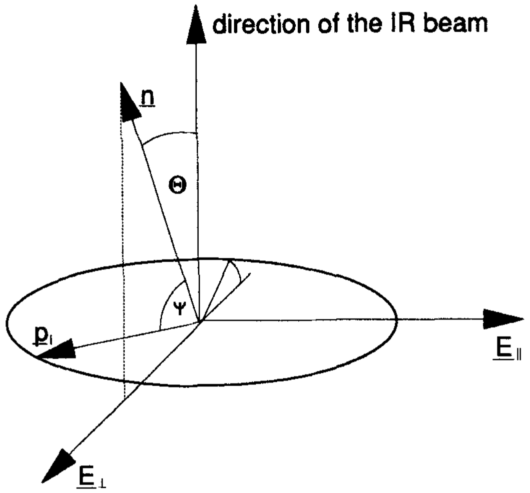


Figure 5. Schematic diagram showing the interaction of an unpolarized IR beam with a discotic material.

R_i can be obtained from calculated values of the integrated absorbance (I_D) for the discotic phase and integrated absorbance (I_I) for the isotropic phase. Using Neff's calculations for unpolarized radiation, I_D is given as

$$I_D = \cos^2 \Psi \langle \sin^2 \Theta \rangle + \tfrac{1}{2} \sin^2 \Psi \langle 1 + \cos^2 \Theta \rangle. \tag{3}$$

This is well known that in the isotropic phase

$$\langle \sin^2 \Theta \rangle_I = \tfrac{2}{3} \tag{4}$$

$$\langle \cos^2 \Theta \rangle_I = \tfrac{1}{3} \tag{5}$$

for unpolarized radiation I_I is given as

$$I_I = \cos^2 \Psi \langle \sin^2 \Theta \rangle_I + \tfrac{1}{2} \sin^2 \Psi \langle 1 + \cos^2 \Theta \rangle_I. \tag{6}$$

substituting equations (4) and (5) into (6) we obtain

$$I_I = \tfrac{2}{3}(\cos^2 \Psi + \sin^2 \Psi) = \tfrac{2}{3}. \tag{7}$$

The order parameter S is defined as

$$S = 1 - \tfrac{3}{2} \langle \sin^2 \Theta \rangle \tag{8}$$

then

$$\langle \sin^2 \Theta \rangle = \tfrac{2}{3}(1 - S). \tag{9}$$

Substituting equations (3), (7) and (9) into (2) and assuming $\Psi = 90°$ we obtain

$$R_i = 1 + \tfrac{1}{2} S \tag{10}$$

then the equation for the order parameter becomes

$$S = 2(R_i - 1). \tag{11}$$

Such a situation appears for the C–C in-plane vibrations of a benzene ring and for the C–O–C stretching vibrations.

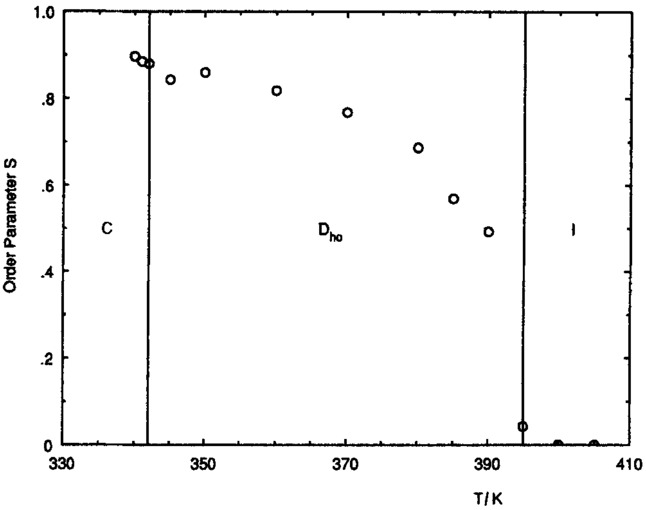


Figure 6. Order parameter S for the C–C aromatic stretching vibration near 1617 cm^{-1}.

On repeating the calculations for $\Psi = 0°$ we obtain

$$S = 1 - R_i. \qquad (12)$$

The above result can reasonably be applied to CH out-of-plane vibrations of the benzene ring.

A plot of S versus temperature for the C–C aromatic stretching vibration which occurs at 1617 cm^{-1} is shown in figure 6. We have found $S \cong 0{\cdot}85$ for this vibration. The value of S is so large as to conclude that the cores of the discotic material are almost perfectly aligned. The H5T material seems to be aligned by self-organization of the cores of the molecules. The reason for S being large can be attributed to the cause that central triphenylene discs may almost be normal to the column's axis [3]. Deuterium NMR spectroscopy study of hexa-*n* hexyloxy triphenylene (a discotic liquid crystal) provided the value of the order parameter $S = 0{\cdot}95$ for the core [3]. Previous liquid crystal measurements have shown that this band near 1600 cm^{-1} as well as the CH aromatic out-of-plane vibration near 800–850 cm^{-1} are the most sensitive indicators of ordering in liquid crystals, liquid crystal polymers and discotic liquid crystals [3, 33, 34]. The plot for the order parameter for CH aromatic out-of-plane vibration as a function of temperature is presented in figure 7 and its maximum value in the D_{ho} phase is $S \cong 0{\cdot}8$. A plot of S for C–O–C asymmetric stretching vibration near 1175 cm^{-1} is shown in figure 8. The maximum value of S is found to be $\cong 0{\cdot}38$. Though C–O–C bonds are directly connected to central cores, yet the directions of the dipole moments for these vibrations are not exactly parallel to the plane of the core and these vary with the conformation. Therefore S for the C–O–C bands is almost three times less than that for the C–C aromatic stretching vibration near 1617 cm^{-1}. From our measurements we have found the maximum calculated value of $S \cong 0{\cdot}6$ for C–O–C symmetric stretching vibration. The plot of S as a function of temperature for this vibration is shown in figure 9. This value is greater than the value for the C–O–C asymmetric vibration but is still less than the value for the C–C aromatic stretching vibration near 1617 cm^{-1}.

A quite opposite situation has been found for CH_2 and CH_3 stretching vibrations near 2900 cm^{-1}. The order parameter for the entire band 2780–3050 cm^{-1} has been

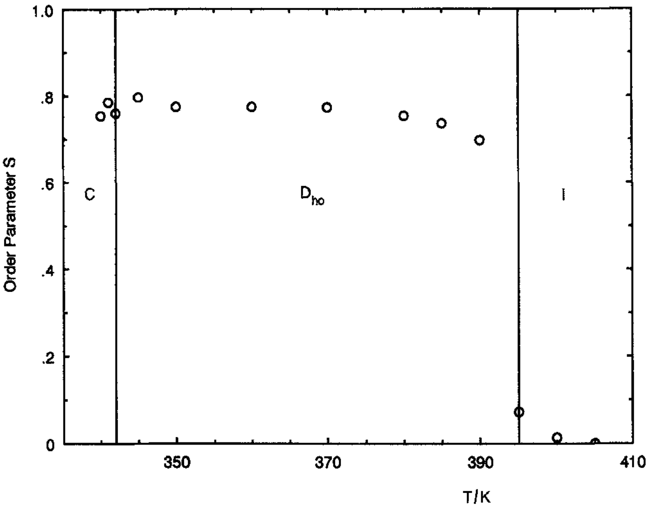


Figure 7. Order parameter S for the CH aromatic out-of-plane vibration near 837 cm^{-1}.

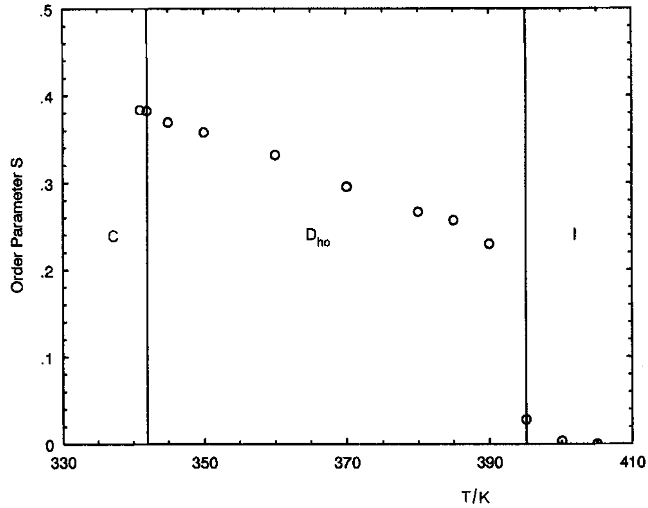


Figure 8. Order parameter S for the C–O–C stretching asymmetric vibration near 1174 cm^{-1}.

calculated and is found to be extremly small; $S \cong 0{\cdot}015$. The calculations for each of the CH_2 and CH_3 asymmetric vibrations have confirmed this value of S for these bands which is close to zero within experimental error. This follows from the hypothesis that CH_2 and CH_3 stretching vibrations of the alkyl tails have many possible directions for the transition dipole moment vectors due to flexibility of the tails and due to the presence of different conformations. All the presented plots for the order parameter as a function of temperature show that S decreases with an increase in temperature; $S \rightarrow 0$ at temperatures some 5 K before the phase transition to the isotropic phase.

3.3. *Frequency changes*

We have observed frequency changes for all bands of H5T with temperature. Frequency changes for a few bands of H5T are shown in figures 10–14. The strong

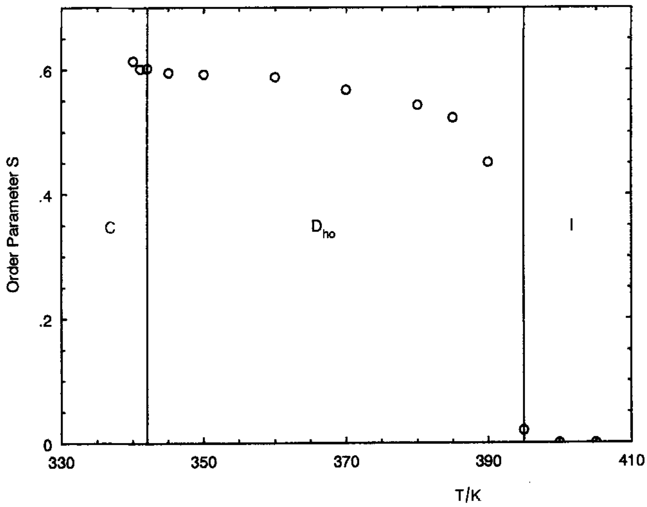


Figure 9. Order parameter *S* for the C–O–C stretching symmetric vibration near 1000–1100 cm^{-1}.

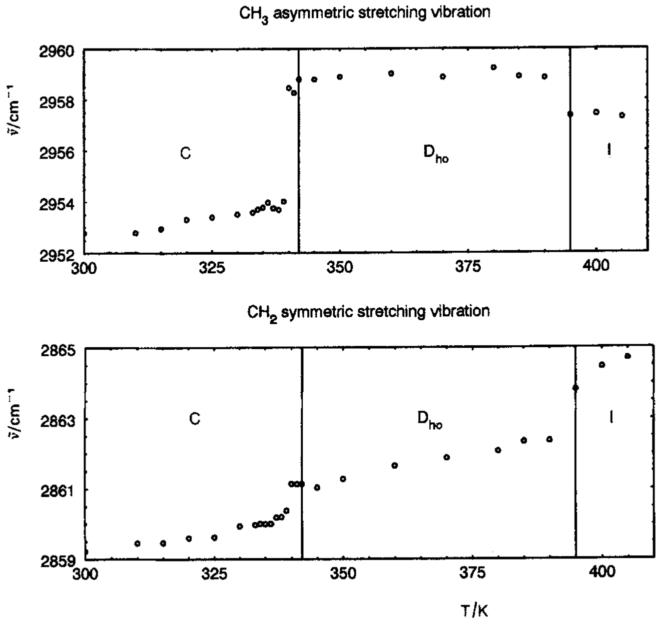


Figure 10. Frequency changes for the CH_2 and CH_3 stretching vibrations near 2900 cm^{-1}.

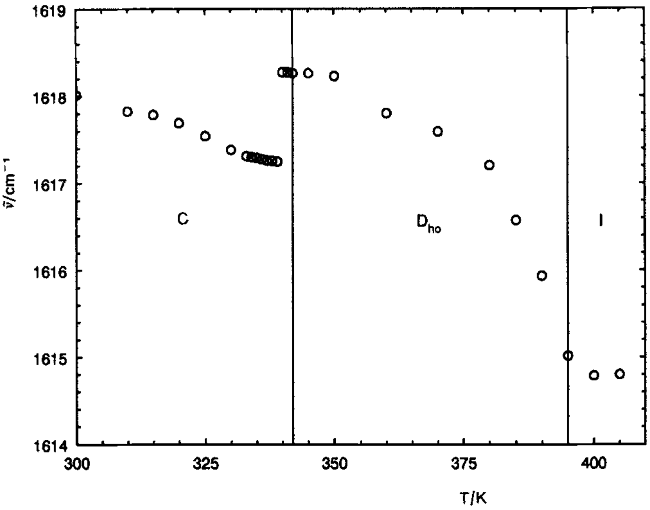


Figure 11. Frequency changes for the C–C aromatic stretching vibration near 1617 cm^{-1}.

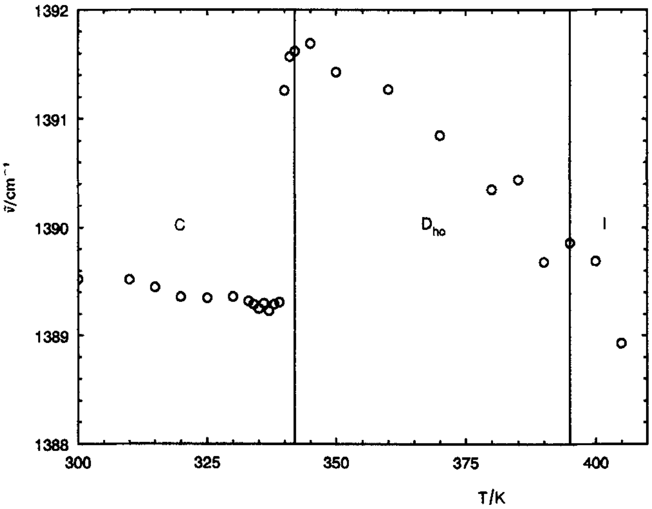


Figure 12. Frequency changes for the CH bending mode near 1389 cm^{-1}.

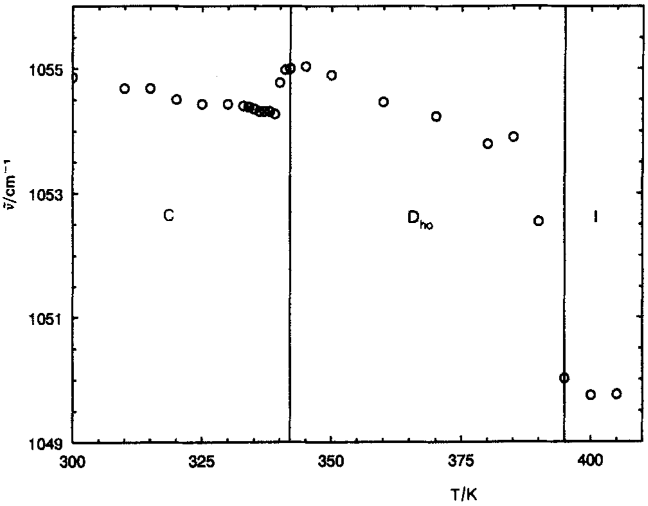


Figure 13. Frequency changes for the C–O–C stretching symmetric vibration near 1052 cm^{-1}.

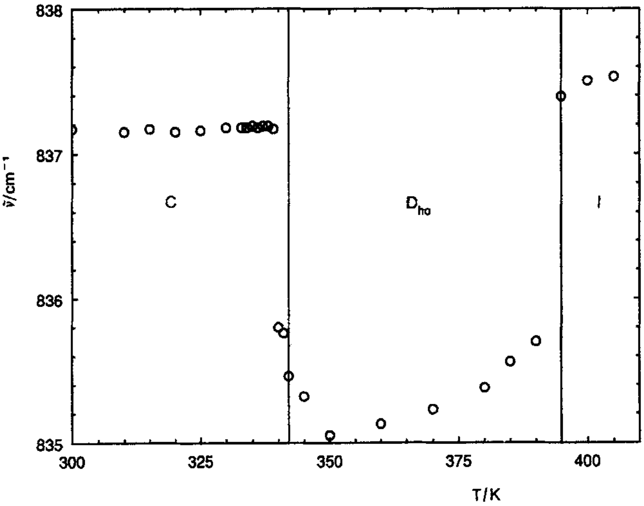


Figure 14. Frequency changes for the CH aromatic out-of-plane vibration near 837 cm^{-1}.

discontinuity in the frequency (1–4 cm^{-1}) occurred some 2–3 K below the C–D$_{ho}$ phase transition for all the bands that were investigated. The wavenumber is related to the force constant *k* and the effective mass by a well-known expression

$$\bar{\nu} \sim \sqrt{\left(\frac{\langle k \rangle}{m_r}\right)}, \qquad (13)$$

where $\langle k \rangle$ is an average value over the molecular interactions of a vibration and m_r is the reduced mass of a vibration. Since repulsive forces become much greater than the attractive ones at short interatomic distances, a significant increase in the wavenumber can be expected. Such an increase was observed for all the investigated bands, except the CH out-of-plane vibration near 837 cm^{-1}, before the C to D$_{ho}$ transition. For the

CH out-of-plane vibration the frequency decreased by about 1·2 cm^{-1} 3 K below the C to D_{ho} transition temperature.

At the D_{ho} to I phase transition, the frequency decreased abruptly for the CH_3 asymmetric stretching vibration near 2958 cm^{-1}, the C–C aromatic stretching vibration near 1617 cm^{-1}, the CH bending mode near 1389 cm^{-1} and for the C–O–C symmetric stretching vibrations. The increase in frequency for this phase transition occurred for the CH aromatic out-of-plane vibration near 836 cm^{-1}and the CH_2 symmetric stretching vibration near 2863 cm^{-1}. Different changes in frequency for these two bands appeared during the first (C to D_{ho}) phase transition (see figures 10 and 14). The frequency increased for the CH_2 symmetric stretching vibration and decreased for CH aromatic out-of-plane vibration. Nevertheless, in all the cases we have observed large changes in frequency versus temperature some few degrees below the phase transition temperature. This means that the short range order in the discotic H5T material changes about 2–3 K below the phase transition temperatures. The CH bending modes are sensitive to alkyl chain conformation and to chain packing [34]. A frequency change by about 2 cm^{-1} for the CH bending mode near 1390 cm^{-1} suggests that during the C to D_{ho} phase transition changes occur in the conformation and chain packing.

4. Summary

The order parameter and frequency changes for H5T (a discotic liquid crystal) have been investigated using FTIR spectroscopy. It has been found that this technique is capable of providing extremely useful results. Changes in the frequency of the bond vibrations have been interpreted to occur in terms of the changes in the short range order in H5T. These abrupt frequency changes have been found to occur approximately 3 K below the C to D_{ho} phase transition at 342 K. This phase transition temperature was determined using polarizing microscopy. We believe that the polarizing microscopy allows the observation of long range order in liquid crystals, whereas infrared spectroscopy is also capable of providing quantitative information about the short range order. Our results show that changes in the long range order are initiated by changes in the short range order some 10 K below the actual transition temperature. An abrupt change in the short range order, however, occurs some 3 K below the actual phase transition temperature and this is believed to be caused by changes in the intermolecular interactions.

Calculations of the order parameter help us also to assign vibrations to the different bands, since the structure of the compound and the type of alignment is known. This is possible because vibrations of the core are more indicative of the order parameter than other parts of the molecule.

FTIR spectroscopy is useful in determining not only the order of entire molecules, but also that of their parts. From our measurements we have concluded that molecules of H5T have organised themselves side-on. The central cores of the discotic molecules of H5T are highly ordered and the alkyl tails are completely disordered.

The vibration near 1054 cm^{-1} is found to be highly sensitive to the phase transition (see figure 4). A further investigation to study the behaviour of this band for similar compounds could be interesting.

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