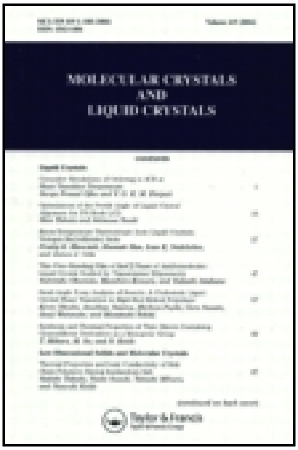

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Spectroscopic Study of a Disc-Like Liquid Crystal: Hexa-N-Nonanoyloxytriphenylene Structure and Dynamics of the Alkyl Chains

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SPECTROSCOPIC STUDY OF A DISC-LIKE LIQUID CRYSTAL: HEXA-N-NONANOYLOXYTRIPHENYLENE STRUCTURE AND DYNAMICS OF THE ALKYL CHAINS

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Abstract The structure of the alkyl chains bonded to the aromatic core in hexa-n-nonanoyloxytriphenylene is studied as a function of temperature. In the crystal phase, the spectra suggest a disorder of the chains due to angular fluctuations about the carbon-carbon bonds in the vicinity of trans states. Numerous conformational defects appear at the first phase transition.

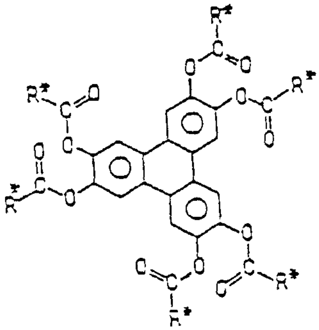
INTRODUCTION

The existence and nature of mesophases built up with disc-shaped molecules such as hexasubstituted benzene, triphenylene or truxene derivatives, is now definitely established[1-2]. These new mesogenic systems exhibit one or several D columnar phases (two dimensional array of liquid tubes) and/or a N_D nematic or N_D^* cholesteric phase[3].
Two simple crystallographic parameters are sufficient for the classification of columnar arrangements ; the two-dimensional lattice symmetry (hexagonal : D_h, rectangular : D_r or oblique : D_{ob}) and the order or disorder of the molecular stacking in the columns[1].

In spite of the small number of disc-like mesogens which have been synthesized up to now (<100) an extremely rich polymorphism has been discovered with several kinds of columnar-columnar transitions and "normal", "inverted" or "reentrant" columnar-nematic sequences[1]. Anyway, except for systematic X-ray studies[2], few physical investigations have been performed such as calorimetry[3], optical microscopy[4-5], and NMR investigations[6]. Some conformational calculations have also been performed, using semi-empirical methods, on triphenylene[7] and truxene[8] systems. However the molecular geometry (for instance relative position of the aliphatic chains and the central flat rigid core) remains unknown even in the crystalline phase[7] and the processes of the transitions are not elucidated. In particular no precise information exists on the behavior of the alkyl chains.

In this preliminary work, we present an investigation of the chain ordering of a triphenylene derivative (hexa-n-nonanoyloxytriphenylene, C8HAT[1]) by means of infrared and Raman spectroscopy, in the crystalline, columnar and isotropic phases. This triphenylene derivative presents the following phase transitions :

$R^* = C_8H_{17}$



$$K \underset{6.11}{\overset{62^{\circ}C}{\rightleftharpoons}} D_{rd} \underset{0.62}{\overset{129^{\circ}C}{\rightleftharpoons}} I \qquad \Delta H\ (\text{Kcal mole}^{-1})$$

K : crystalline phase, I : isotropic phase

D_{rd} : rectangular disordered columnar phase belonging to the pgg two dimensional space group[1] or to the $P2_{1}/_{a}$ symmetry in terms of the eighty plane space groups[2]. This phase corresponds to a tilted columnar arrangement with two different columnar directions in the lattice (Figure 1).

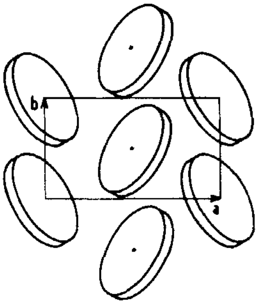


FIGURE 1. Rectangular lattice ($P2_{1}/_{a}$) of C8HAT columnar phase.

EXPERIMENTAL SECTION

Preparation of the material.

The C8HAT derivative was prepared starting from veratrole through the classical process published elsewhere[3]. Anyway an improvement was used in the last step, reaction of the hexahydroxytriphenylene (HHT) with the required acid chloride. Instead of using equimolecular proportions of the reacting materials in dry pyridine, the HHT (2g) was heated (160°C) with a large excess of nonanoylchloride (20g) for 2 hours. Then the mixture was cooled, poured over crushed ice and extracted into ether. After the classical workup, the crude triphenylene was crystallized from ethanol and then purified by chromatography on silicagel using benzene as eluant, then refluxed in dry ethanol with charcoal and filtered through a sintering funnel (G7) under a nitrogen atmosphere. At last, the sample was recrystallized from ethanol and dried under vacuum.

Experimental procedure

Infrared spectra were measured with an evacuatable Bruker model 113 FTIR spectrometer equiped with a MCT detector. The resolution was 2cm^{-1}. A film of the sample was prepared by heating the powder to few degrees above the melting point between CsI windows. Raman spectra were recorded with a Coderg T800 spectrometer and a Spectra-Physics model 171 argon ion laser. The 514.5 nm line was used with a power less than 500 mW. Spectral slit widths were 1 to 2.5 cm^{-1}. The sample temperature was regulated to ± 1°C with a Coderg CRN2 continuous nitrogen flow cryostat.

SPECTROSCOPIC STUDY OF THE CRYSTAL PHASE

An analysis of the spectra observed in the crystal phase is necessary in order to determine the structure of the chains in this phase and to obtain a good understanding of their dynamics in the disordered mesomorphic and isotropic phases. Raman and infrared spectra of C8HAT are complicated by the presence of bands due to the transitions of the aromatic core and of the ester function. However several spectral domains contain only bands of the alkyl chains which can be discussed with reference to the corresponding spectrum of n-alkanes and n-alkylammonium ions in long chain perovskites $(C_n H_{2n+1} NH_3)_2CdCl_4$. When the alkyl chains are in extended configurations, non localized modes give rise to progression bands which are mainly observed in the infrared spectrum[9-10-11-12]. Their number, their frequency and their intensity depend on both chain length and chain conformation.

The infrared spectrum of phase K shows well defined progression bands, in particular those associated with methylene wagging and rocking vibrations (Figure 2). A detailed analysis of the infrared spectrum using normal coordinate treatment will be reported later.

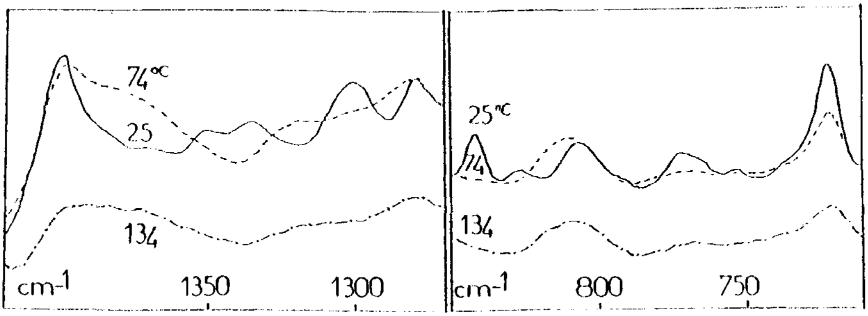


FIGURE 2. Infrared spectrum of two characteristic spectral domains.

—— K ; — — — D_{rd} ; · — · — I

In the Raman spectrum, the most intense bands in the region of the optical skeletal modes correspond to the limiting cases $\psi = 0$ or π of an infinite chain ; they are observed at 1063 and 1122 cm^{-1}. A very weak diffusion near 1080 cm^{-1} may be due to a small proportion of gauche forms (Figure 3).

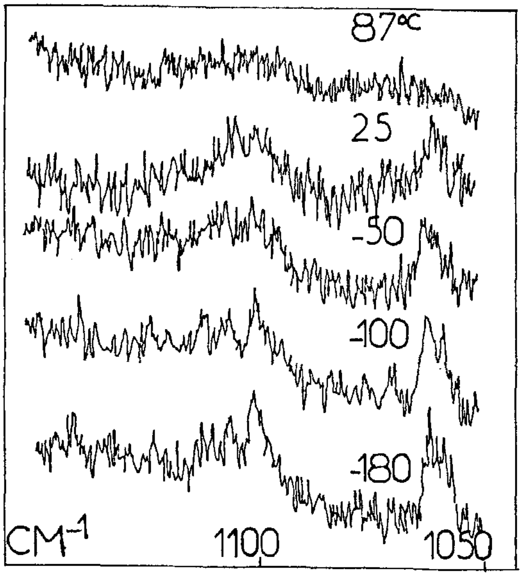


FIGURE 3. Temperature dependence of the Raman spectrum between 1050 and 1150 cm^{-1}.

A second type of vibrations involves motions which are localized in part of the chain. The frequency of the methyl rocking vibration is observed at 891 cm^{-1}, which corresponds to a conformer with trans structures in the vicinity of the methyl group in n-alkyl chains. All these features of the Raman spectrum are weak.

An examination of the diffusion spectrum in the CH stretching region reveals a disorder. The band corresponding to the antisymmetric CH_2 stretching mode $\nu_a(CH_2)$, at 2885 cm^{-1} is wide and scarcely emerges from a broad background, as is observed in the disordered phases of long chain compounds. This effect may be due to lateral packing, conformational disorder or dynamic factors.

However the high frequency wing does not show a strong intensity near 2940 cm^{-1}, which indicates that gauche forms are not very numerous. Analysis of the CH_2 bending region cannot give any information as these transitions are overlapped by strong lines of the triphenylene ring.

Figures 3 and 4 display the Raman spectra at different temperatures. When the temperature is lowered to about -180°C the peak height of the band at 2885 cm^{-1} strongly increases and its width decreases. The ratio of the peak height at 2940 and 2885 cm^{-1},

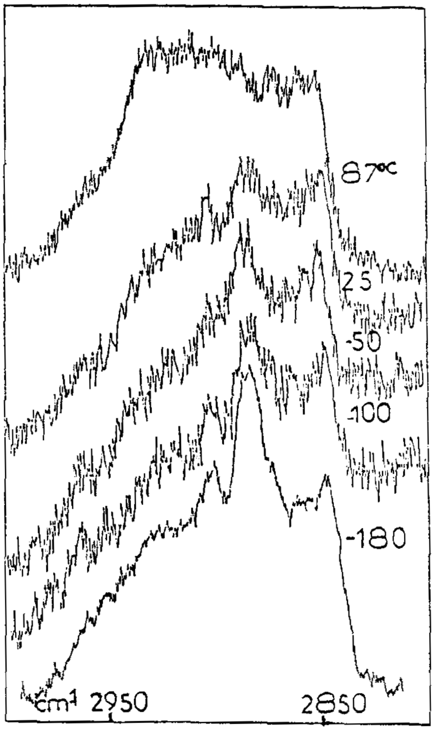


FIGURE 4. Temperature dependence of the Raman spectrum in the CH stretching domain.

related to the evolution of the proportion of gauche forms[13-14], remains nearly the same. The frequency of the ν_s(CH2) vibration does not shift. The intensity of the delocalized modes corresponding to an intramolecular coupling and that of the methyl rocking vibration increase at low temperature.

Thus, the disorder is less important at low temperature and the spectra do not show any conformational modification. The features of the CH stretching domain at room temperature can be explained by a motion which becomes less and less important with decrease of temperature. The Raman spectrum of C8HAT at 25°C shows similarities with that of the phase stable below the melting point of $C_{40}H_{82}$[15]. In the model proposed for this phase, the chains are nearly fully extended. There are significant angular fluctuations about the carbon-carbon single bonds. These fluctuations are loosely correlated. They are largely confined to the vicinity of the trans-states. So they maintain a fairly linear shape of the molecules , but a small probability exists for values in the vicinity of gauche state.

Such a model accounts for the features of our Raman and infrared spectra. It also explains why the authors who proposed a structure for the crystal of C3HAT from X-ray diffraction measurements were unable to locate the carbon atoms of the alkyl chains[16].

CHANGES IN THE SPECTRA OF THE DISORDERED PHASES

Mesophase

The vibrational spectra of the mesophase are far different from those of the crystal. In the infrared spectrum, the progression bands due to non localized modes are replaced by broad maxima due to the transitions of different chain conformations (Figure 2). Moreover, it has been shown that short sequences of bonds have localized vibrations which absorb at specific frequencies[11-17]. For example, GG sequences absorb at 1353 cm^{-1}, end gauche defects at 1342 cm^{-1}, kinks (GTG'sequences) at 1367 and near 1310 cm^{-1}. All these defects exist in the mesophase and are responsible of the strong wing on the low frequency side of $\delta_s(CH_3)$ (at 1377 cm^{-1}) and of the hump near 1310 cm^{-1}.

Raman bands corresponding to the transitions active in long transplanar chains, at 1063 and 1122 cm^{-1}, are no longer observed. The peak of the methyl rocking vibration at 891 cm^{-1} also disappears. In the CH stretching domain, the spectrum is thoroughly modified , the antisymmetric CH_2 stretching mode collapses into a broad background near 3000 cm^{-1}. The peak intensity near 2940 cm^{-1} strongly increases with respect to that of the symmetric CH_2 stretching vibration. In addition, the frequency of $\nu_s(CH_2)$ increases from 2850 to 2855 cm^{-1} which indicates decreasing trans-sequence length[18].

All these changes indicate a strong increase of gauche content at the first phase change, in agreement with the high value of the transition enthalpy[3].

Isotropic phase

In the infrared spectrum, the maxima which replaced the progression bands of the crystal overlap and form a continuous background. This phase is characterized by a great conformational disorder of the chains. The variety of defects is greater than in molten n-alkanes or in the most disordered phases of perovskites and the gauche structures are much more numerous.

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