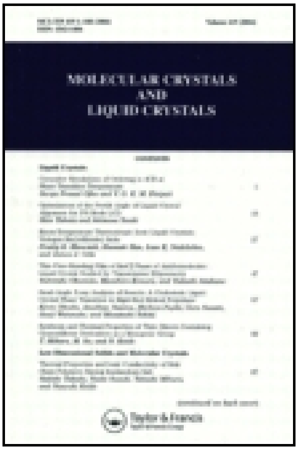


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Vibrational Study of the Phase Transitions in Three Triphenylene Hexa n-Alkanoates

M. Rey-Lafon [a] & A. Tazi Hemida [a]

[a] Laboratoire de Spectroscopie Moléculaire et Cristalline, U.R.A.124-C.N.R.S.-Université de Bordeaux I, 351, Cours de la Libération, 33405, TALENCE Cedex, FRANCE

Version of record first published: 04 Oct 2006.

To cite this article: M. Rey-Lafon & A. Tazi Hemida (1990): Vibrational Study of the Phase Transitions in Three Triphenylene Hexa n-Alkanoates, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 178:1, 33-51

To link to this article: http://dx.doi.org/10.1080/00268949008042707

Mol. Cryst. Liq. Cryst., 1990, Vol. 178, pp. 33–51
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Vibrational Study of the Phase Transitions in Three Triphenylene Hexa *n*-Alkanoates

M. REY-LAFON and A. TAZI HEMIDA

Laboratoire de Spectroscopie Moléculaire et Cristalline, U.R.A.124-C.N.R.S.-Université de Bordeaux I, 351, Cours de la Libération 33405 TALENCE Cedex (FRANCE)

(*Received May 15, 1989; in final form June 15, 1989*)

Triphenylene hexa-*n*-alkanoates (C_mHAT) present thermotropic structural phase transitions in the solid state, before giving rise to columnar mesophases and to the isotropic state. A temperature-dependence study of the infrared and Raman spectra of C_8HAT, C_{10}HAT and C_{12}HAT provides a description of the molecular conformations in the ordered phases and shows that the disordering process begins in the crystalline state. It implies angular deformations about the aliphatic carbon skeleton in the disorderd solid phases, while a very important conformational disorder appears at the crystal-mesophase transition, together with a change in the position of the ester plane with respect to the aromatic core. Dynamics of the alkanoates chains thus play an important part in the mechanism of the phase transitions.

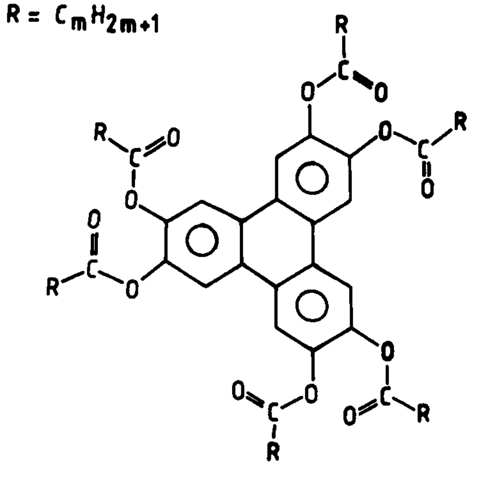
INTRODUCTION

The nature of mesophases formed by compounds containing disc-shaped molecules, such as hexasubstituted derivatives of benzene, triphenylene or truxene, is well established and a considerable effort has been made for several years to characterize the structural differences of their various phases.[1-7] Several mesomorphic phases have been identified including columnar, nematic and cholesteric.

Our work concerns three triphenylene hexa-*n*-alkanoates (C_mHAT)(m = 8, 10, 12), the polymorphism of which is relatively simple.

Calorimetric[3] and X-ray diffraction[2] studies have shown that these compounds present one or two columnar mesophases between the crystal and the isotropic state. The stable phase above the crystal-liquid crystal transition has been described as D_{rd}[2,6,8]: D refers to discoid, r to a rectangular bidimensional array of the columns, d to a disordered stacking of the molecules in the column. Another mesomorphic phase, observed in C_{10}HAT and C_{12}HAT when raising the temperature, is denoted D_{hd} (h indicates an hexagonal bidimensional lattice)[2] (Figure 1). Within a column, the distance between the aromatic cores of two molecules is about 4 Å. The unit cell parameters and the space group of the planar lattice have been determined in the case of C_{11}HAT; the space group is $P2_1/a(pgg)$ in the D_{rd} phase and $P6/m2/m2/m$ in the D_{hd} phase.[2]

As the molecular arrangements in the crystal and in the mesophase are related,



[9–11] X-ray diffraction measurements have been performed on the solid phases of C_3HAT, C_4HAT and C_5HAT; they have allowed determination of the structure of C_3HAT which could be obtained as a single crystal.[12] The space group is $R\bar{3}c$, the columns are located at the nodes of a hexagonal lattice. Within a column, the molecules are associated in pairs with their triphenylene cores parallel (Figure 2). But X-ray experiments were unable to provide any information on the conformation of the ester chains. If the latter are assumed to be in an all-*trans*-conformation and coplanar with the aromatic core, the mean diameter of a molecule is about 22 Å and the molecules have to be partly inserted in the free space of the neighbouring columns, between the pairs. The ester chains can be located on the same side of the plane of the aromatic core (form 1) or alternatively on both sides (form 2). After a CNDO/2 calculation, form 2 is more stable than form 1 by 8.8 KJ mole^{-1}.

A semi-empirical calculation carried out on C_mHAT ($m = 3$–7) has established the preferential conformation for the isolated molecule, a pair of molecules and a set of molecules.[13,14] They correspond to the dihedral angles θ_1 ($C_{IV}-C_I-O_1-C_0$)

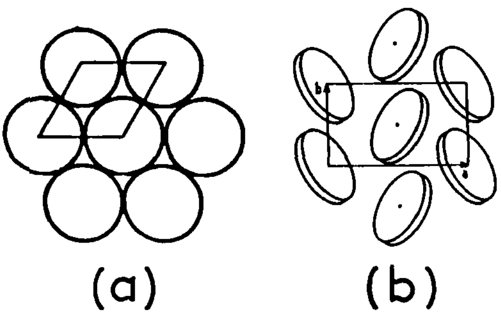


FIGURE 1 Structure of the mesophases D_{hd} (*a*) and D_{rd} (*b*).

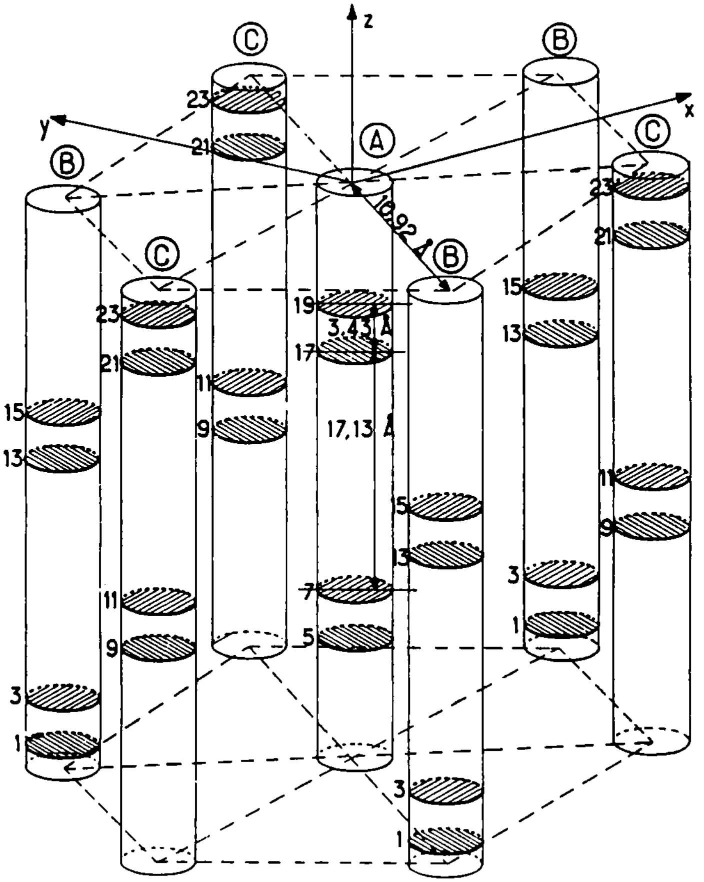


FIGURE 2 Schematic drawing of molecular arrangement in the crystal of C_3HAT^{12}. Triphenylene cores are represented as shaded discs. Alkyl chains are not represented.

$= \theta_1' (C_{III}-C_{II}-O_1'-C_0') = 55°$ and $\theta_2(O_1-C_0-C_1-C_2) = \theta_2' (O_1'-C_0'-C_1'-C_2') = 75°$ (Figure 3) for the molecule, the chains I and II being respectively situated above and under the triphenylene core. The molecules are associated in pairs in which the O_2 oxygen atoms of a molecule lie opposite to two hydrogen atoms of the other molecule (Figure 4). The molecular stacking in a column is irregular if $m \geqq 5$. The interactions within a column or between the columns are of van der Waals type.

A dynamical disorder of the chains in the D_{hd} mesophases of three triphenylene hexaesters, $C_{10}HAT$, $C_{11}HAT$, $C_{12}HAT$ and in the room temperature crystal phase of C_8HAT has been proposed from ^{2}HNMR[6] and vibrational spectroscopy,[7] respectively.

The studies reported so far provide therefore very little information on the molecular geometry, in particular on the hydrocarbon chain conformation and on the relative position of the aliphatic skeleton and the central flat core, even in the

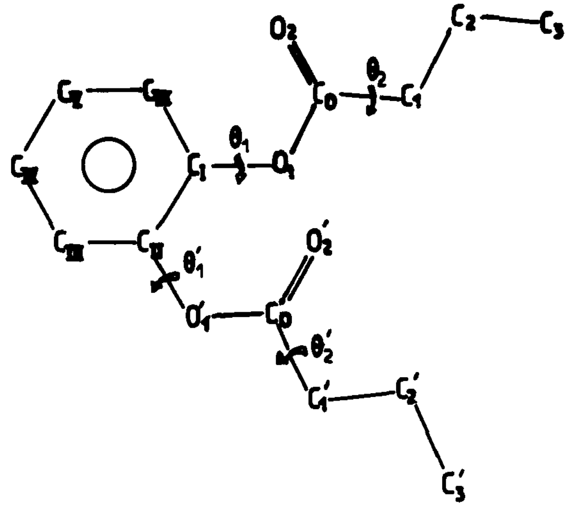


FIGURE 3 Schematic representation of one third of C_3HAT molecule.[13,14] Hydrogen atoms are not represented.

solid state. Neither do they elucidate the mechanism of the transitions. The aim of this work is to analyse the molecular structural properties and to obtain a view of the processes which induce the phase transitions and the existence of liquid crystalline states. With this purpose, we have applied two complementary techniques, Raman scattering spectroscopy and infrared absorption spectroscopy, to C_8HAT, $C_{10}HAT$, $C_{12}HAT$ and to a derivative of C_8HAT bideuterated on a methylene group. Indeed, when the dynamics are long enough, vibrational spectroscopy gives information on the structure of the different isomers. The spectra present specific bands associated with the ester groups and characteristic of their geometry or packing; they also provide indications of the conformation of the methylene chains and their changes as a function of temperature, by means of an analysis based on the earlier studies of n-paraffins. Furthermore, bideuteration of a methylene group allows us to be precise about the local conformation, as the CD_2 rocking mode, $r(CD_2)$, infrared frequency depends on the conformation of the C–C bonds on either side of the CD_2 group.[15–18]

As the disordering process seems very complex and probably begins in the crystalline state, we performed preliminary calorimetric and X-ray diffraction measurements on the solid state.

EXPERIMENTAL SECTION

Compounds C_mHAT were prepared starting from veratrole through the classical procedure[3] with the improvement described elsewhere.[7] In this procedure, the alkyl chains are grafted onto hexahydroxytriphenylene by action of the acid chloride. The preparation of C_8HAT bideuterated on the methylene adjacent to the carbonyl

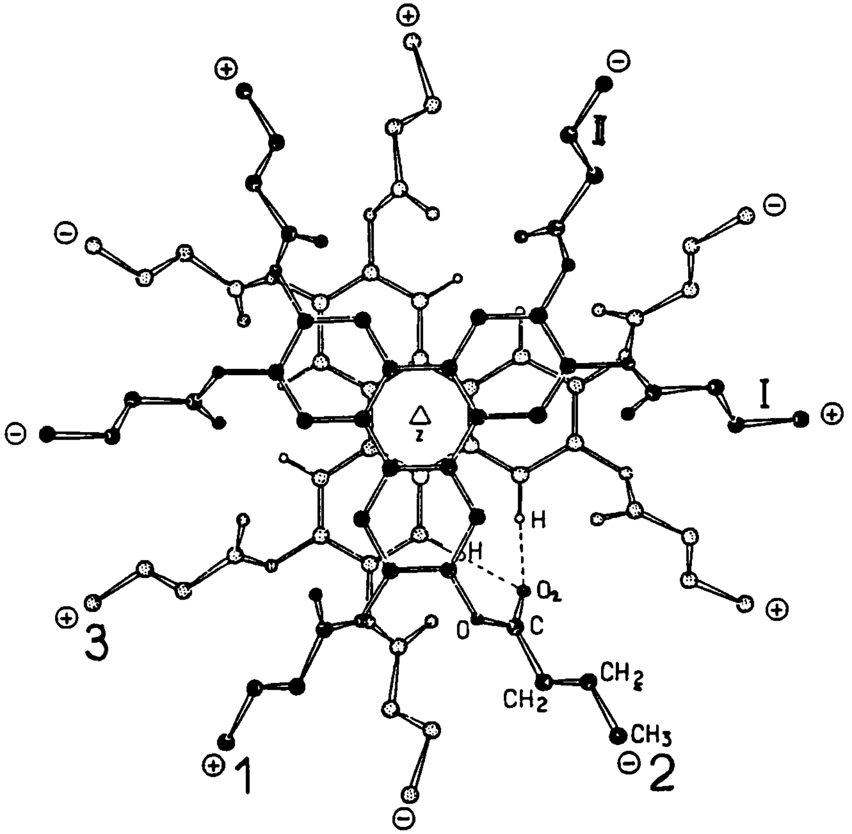


FIGURE 4 The most stable arrangement of a pair of molecules of C_3HAT^{13}.

group (C_8HAT-1, 1d_2) required the synthesis of the corresponding bideuterated acid chloride.[19]

Raman spectra of the powdered samples were recorded with a Coderg T800 spectrometer using argon ion laser models 165 and 171. The line at 514.5 nm was used as exciting line with a power less than 200 mW. The spectral slit width varied from 1 to 3 cm^{-1}. The spectra were accumulated on a computer Minc 1103. The temperature of the cell was regulated within one degree with a Coderg CRN2 continuous nitrogen flow cryostat between 90 and 370 K and with a Cryodyne model 20 helium cryostat for temperatures down to 20 K.

The polycrystalline films used for the infrared study were prepared by melting the powder on a CsI window followed by slow cooling or by evaporation from an ethanolic solution. The spectra were recorded with a grating spectrometer Perkin-Elmer 983 G (resolution 3 cm^{-1}) or with a Bruker 113 V interferometer (resolution 1 cm^{-1}); the latter was equipped with a cooled MCT detector. Low temperatures, obtained by means of a continuous nitrogen flow or using the liquid helium Cryodyne model 20, were controlled to ± 1K.

TABLE I

Transition temperatures and enthalpies for C_mHAT.[a]

	T(K)	Phase	ΔH (KJ mol^{-1})
C_8HAT		K_1	
	281		1.19
		K_2	
	335^b		25.539^b
		D_{rd}	
	398^b		2.599^b
		I	
$C_{10}HAT$		K_1	
	254		2.33
		K_2	
	302		0.27
		K_3	
	340^b		50.16^b
		D_{rd}	
	381^b		0.0
		D_{hd}	
	394.5^b		1.254^b
		I	
$C_{12}HAT$		K_1	
	255		0.39
		K_2	
	356^b		71.060^b
		D_{rd}	
	371^b		0.125^b
		D_{hd}	
	391^b		1.024^b
		I	

[a] The measurements have been performed using a Dupont de Nemours apparatus model DSC 910/990.
[b] Values published in Reference 1b.

EVIDENCE OF SOLID-SOLID PHASE TRANSITIONS BY CALORIMETRIC AND DIFFRACTION MEASUREMENTS[20]

Guinier-Lenné or Guinier-Simon recordings and enthalpic diagrams of C_8HAT, $C_{10}HAT$ and $C_{12}HAT$ show the existence of one or two solid-solid phase transitions depending on the compound. Transition temperatures and enthalpies are reported in Table I together with the notation of the phases. One notices that the enthalpy change at the crystal-mesophase transition for each compound is by far the most important.

SPECTROSCOPIC STUDY OF THE ORDERED PHASES.

A detailed analysis of the spectra obtained for the most ordered crystalline phases stable at low temperature is necessary to determine the structure of the molecules and to understand their behaviour when raising the temperature. The vibrations of the aromatic core have been identified from the spectrum of triphenylene.[21-23] As, during our study, we have not found any noticeable change in a well identified triphenylene band, we have limited our analysis to the aliphatic part and the ester function. Spectral domains that we could analyse are 500–800, 1275–1400, 1445–1485, 1700–1850 and 2800–3000 cm^{-1} in the infrared spectra and 800–900, 1000–1200 and 2800–3000 cm^{-1} in the Raman spectra.

In order to facilitate the interpretation of the spectra and to obtain an assignment

TABLE II

Calculated and observed frequencies for $CH_3(CH_2)_7COOC_6H_5$ and $CH_3(CH_2)_6CD_2COOC_6H_5$ between 705 and 450 cm^{-1}.

	Assignment	ν_{calc} cm^{-1}	ν_{obs} cm^{-1}	PED 100 $L_{ik}^2 F_{ii}/\lambda_k$
C_8HAT	$\gamma(C{=}O)$	703	696	$0{,}62\ r(CH_2) + 0{,}19\ \gamma(C{=}O)$
	$\delta(C{=}O)$	642	655	$0{,}24\ \delta(C{=}O) + 0{,}16\ \nu(CC)_\alpha + 0{,}16\ \delta(CCC)_{al} + 0{,}15\ \delta(CCC)_{ar}$
	$\delta(CCC)_{ar}$	610	623	$0{,}83\ \delta(CCC)_{ar} + 0{,}15\ \delta(CH)$
	$\delta(CCC)_{ar}$	546	553	$0{,}3\ \delta(CCC)_{ar} + 0{,}13\ \delta(OCC)_{al} + 0{,}11\ \delta(C{=}O)$
	$\iota(CC)_{ar}$	541	529	$0{,}89\ \iota(CC)_{ar} + 0{,}26\ \gamma(CH)$
	$\delta(CCC)_{al}$	501	503	$0{,}6\ \delta(CCC)_{al}$
$C_8HAT\text{-}1{,}1d_2$	$r(CD_2)$	655	690	$0{,}36\ r(CD_2) + 0{,}22\ r(CH_2)$
	$\delta(C{=}O)$	615	650	$0{,}27\ \delta(CCC)_{ar} + 0{,}17\ \nu(CC)_\alpha + 0{,}13\ \delta(C{=}O) + 0{,}11\ \delta(CCC)_{al}$
	$\delta(CCC)_{ar}$	609	615	$0{,}72\ \delta(CCC)_{ar} + 0{,}15\ \delta(CH)$
	$\iota(CC)_{ar}$	542	579	$\iota(CC)_{ar}$
	$\delta(CCC)_{ar}$	521	509	$0{,}3\ \delta(CCC)_{ar} + 0{,}24\ \delta(CCC)_{al} + 0{,}1\ r(CD_2)$
	$\delta(CCC)_{al}$	497	469	$0{,}49\ \delta(CCC)_{al} + 0{,}1\ \delta(C{=}O)$

$\gamma(C{=}O)$ of $C_8HAT\text{-}1{,}1d_2$ is coupled with the $r(CH_2)$ vibrations and calculated at frequencies higher than 720 cm^{-1}.

of the ester group vibrations, we performed a normal coordinate calculation on a model molecule, namely phenyl nonanoate $CH_3(CH_2)_7COOC_6H_5$ and its α-bideuterated derivative $CH_3(CH_2)_6CD_2COOC_6H_5$. As the molecular geometry is not known, we used the geometrical parameters of the preferential structure proposed for C_7HAT[13,14] in which the dihedral angles θ_1 and θ_2 are respectively equal to 55 and 75° (Figure 3); the chains are assumed to be in the standard tetrahedral geometry (C—C = 1.54 Å, C—H = 1.093 Å). For the hydrocarbon chain, the force field used is that derived by Snyder *et al.* for the *n*-paraffins,[24] and for the ester group that obtained by Kim *et al.* for phenyl acetate[25]; for the benzene ring, we used the force constants proposed by La Lau and Snyder.[26] As the force field obtained does not contain any interaction constant between the vibrations of the ester group and those of the neighbouring methylene groups, we introduced $f[\delta(C{=}O), w(CH_2)]$ and $f[\gamma(C{=}O), r(CH_2)]$ which exist in the force fields of acetone[27] and cyclohexanone[28]; we adjusted them to the values −0.16 and −0.09 mdyn Å rad^{-2} in order to account for the spectral domain 700–450 cm^{-1}. Obviously, this calculation only gives approximate results; however it accounts for the experimental spectra for both C_8HAT and $C_8HAT\text{-}1{,}1d_2$, with the above structural hypothesis (Table II). We think that the approximate calculated frequencies allow a correct assignment of the ester group vibrations.

Band splittings due to coupling of the molecular motions in the unit cell are observed in the infrared spectrum, for the methylene rocking $[r(CH_2)]$ and bending $[\delta(CH_2)]$ vibrations (Figure 5). They indicate that the chains are roughly immobile and that the intermolecular interactions are rather strong.

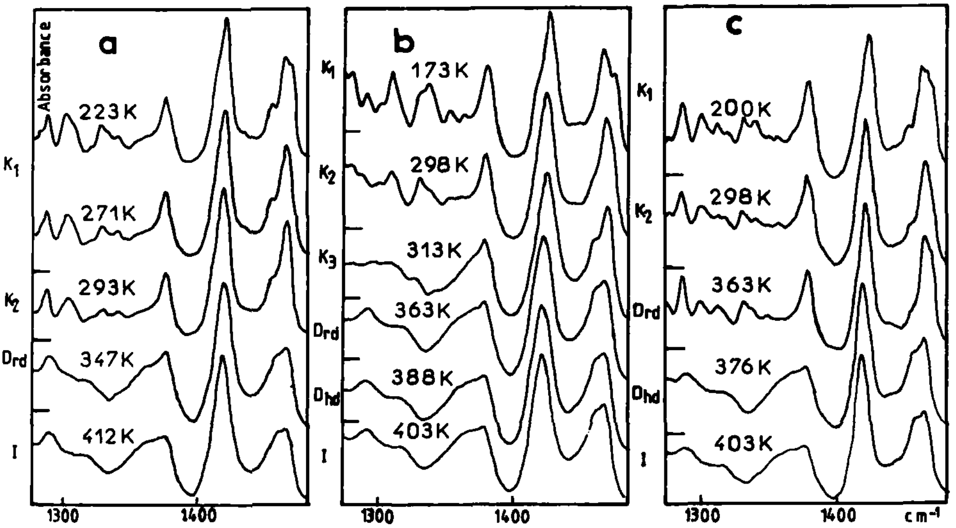


FIGURE 5 Temperature dependence of the infrared spectra between 1275 and 1485 cm^{-1} (*a*) C_8HAT; (*b*) C_{10}HAT; (*c*) C_{12}HAT.

Conformation of the alkylchains

The spectral features of the methylene chains in the most ordered crystalline phases show analogies with those of solid *n*-paraffins; they can thus be analysed by comparison with the spectra of the corresponding *n*-alkanes.

Several vibrations correspond to non localized modes; their number, their frequency and their intensity depend on chain length and conformation. They give rise to progression bands which are characteristic of extended chains and are mainly observed in the infrared spectra, especially in the spectral domains corresponding to the rocking and wagging deformations of the methylene groups[17,18] (Figure 5). In the Raman spectra, the most intense bands due to the methylene chains correspond to the limit modes $\varphi_k = 0$ or π of an infinite chain (φ_k is the phase difference between the movements of adjacent oscillators[29]); characteristic bands of *trans*-chains are observed, for instance the carbon-carbon elongations near 1130 and 1065 cm^{-1}. However, a weak hump near 1080 cm^{-1}, which has been assigned to *gauche* bonds in the *n*-paraffins,[17] shows the existence of some conformational defects. The spectrum is displayed in Figure 6 in the case of C_{10}HAT.

Localized modes correspond to movements of a limited part of the chains; their frequency depends on the local conformation only and is independent of the chain length. For instance, the frequency of the methyl rocking, r(CH_3), at 891 cm^{-1} in the Raman spectrum corresponds to a *trans*-conformation near the methyl group. In the infrared spectrum, the frequency of the methyl bending mode $\delta_s(CH_3)$, near 1379 cm^{-1} in the three compounds, is higher than in the *n*-alkanes, which indicates that the interactions at the chains ends are weaker.[17]

The CD_2 rocking of C_8HAT–1,1d_2 also is a localized mode. With the assumed geometry, its frequency is calculated at 655 cm^{-1}, so it can be assigned to the 690

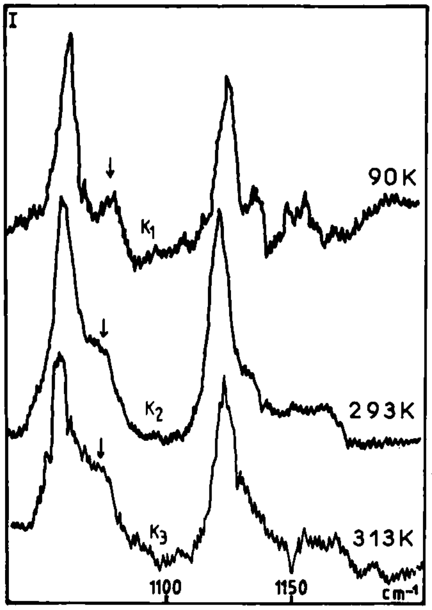


FIGURE 6 Temperature dependence of the Raman spectrum of $C_{10}HAT$ between 1035 and 1200 cm^{-1}.

cm^{-1} infrared band (Table II, Figure 7b). If the CH_2–CD_2 bond is in the *gauche* conformation, the calculation shows that $r(CD_2)$ is coupled to $r(CH_2)$ vibrations in modes which appear above 720 cm^{-1}. Thus only a *trans*-geometry allows interpretation of the experimental results.

In the CH stretching domain, 2800–3000 cm^{-1}, the Raman spectra of the three

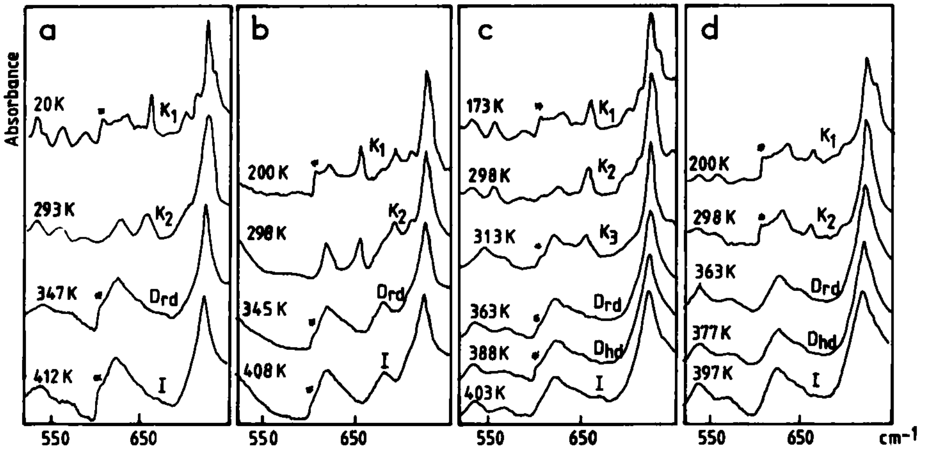


FIGURE 7 Temperature dependence of the infrared spectra between 520 and 750 cm^{-1}. (*a*) C_8HAT; (*b*) C_8HAT-1,1d_2; (*c*) $C_{10}HAT$; (*d*) $C_{12}HAT$. *Artefact due to a change of grating in the spectrometer.

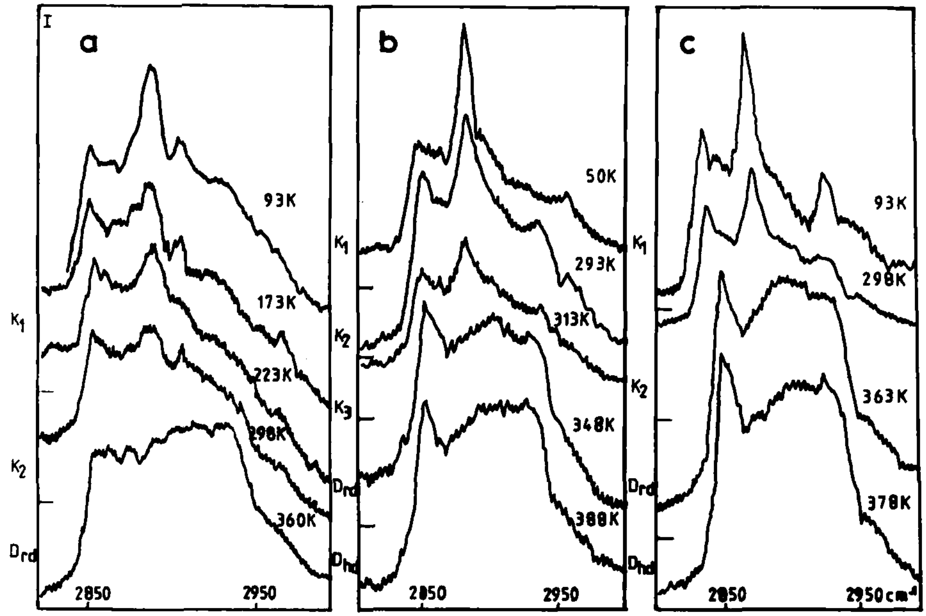


FIGURE 8 Temperature dependence of the Raman spectra between 2880 and 3000 cm^{-1}. (*a*) C_8HAT; (*b*) C_{10}HAT; (*c*) C_{12}HAT.

compounds present the fundamental characteristics of the polyethylene spectrum (Figure 8). The peaks near 2850 and 2880 cm^{-1} correspond to the symmetrical and antisymmetrical elongations of the methylenes. The more or less visible maxima at about 2870, 2952 and 2964 cm^{-1} have been assigned to the methyl stretching vibrations. The other ones and the broad signal between 2850 and 3000 cm^{-1} are characteristic of extended chains and due to Fermi resonances between the $\nu_s(CH_2)$ fundamental and the quasi continuum of the bending progression band overtones.[30,31,32]

It must be noted that our measurements are unable to prove that extended chains are strictly *trans*-planar or that the conformational defects correspond to rotation angles of exactly 120°; there could be slight angular distorsions of the *trans*- or *gauche* states which would not be large enough to perturb in a detectable way the coupling between adjacent oscillators and the vibrational frequencies. We shall use the words "*trans*" (T) and "*gauche*" (G) with this reservation.

Conformation of the ester groups

Characteristic vibrations of the ester functions are observed in the infrared spectra. The band which corresponds to the carbonyl stretching mode is complex. It possesses two maxima in the spectra of C_8HAT and C_{12}HAT (Figure 9). The shape of the peak at about 1770 cm^{-1} depends on the temperature and the compound. For C_8HAT, it is broad at 20 K and narrows when the temperature rises, while it is narrow at low temperature and broadens as the temperature is raised in the spectrum of C_{12}HAT. The frequency of the other peak is 1756 cm^{-1} for C_8HAT and 1760 cm^{-1} for C_{12}HAT. Three components, at 1771, 1762 and 1753 cm^{-1} are observed in the spectrum of C_{10}HAT between 13 and 193 K (Figure 9). The shoulder at 1762 cm^{-1} has vanished above this temperature, but the band at 1771 cm^{-1} presents a wing on the low frequency side.

The splitting into two components near 1770 and 1756 cm^{-1} cannot be due to the crystalline field effect as it is still observed when this effect has disappeared after the other transitions. It cannot be explained either by a Fermi resonance with the overtone of a vibration near 880 cm^{-1}; indeed the splitting and the relative intensities of the bands are insensitive to the temperature variation. This analysis suggests the existence of two different carbonyl groups which can be more or less engaged in some type of interaction. Two types have been considered:

—dipolar interaction between neighbouring carbonyls

—interaction between oxygen 2 of one carbonyl group and two aromatic hydrogens of the other molecule in a pair.

The dipolar splitting can be evaluated using a simple model of dipole-dipole interaction.[33,34] The wavenumbers of the symmetrical and antisymmetrical vibrations of two coupled oscillators are given by:

$$\bar{\nu}^2_{sym} = \frac{1}{4\pi^2c^2\mu^*}(F + f_{12})$$

$$\bar{\nu}^2_{asym} = \frac{1}{4\pi^2c^2\mu^*}(F - f_{12})$$

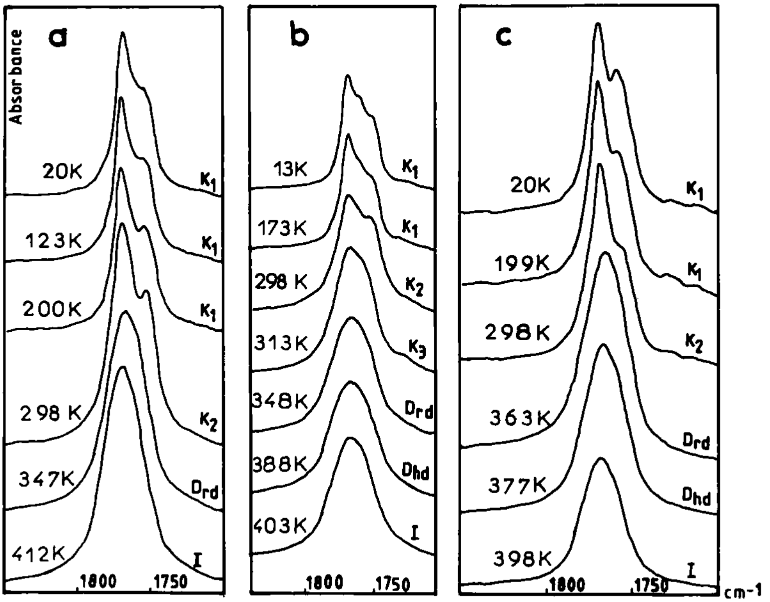


FIGURE 9 Temperature dependence of the carbonyl stretching domain. (*a*) C_8HAT; (*b*) C_{10}HAT; (*c*) C_{12}HAT.

where F is the force constant of the isolated oscillator and μ^* its reduced mass; f: interaction constant; c: sound velocity.

With this model, and assuming the geometry proposed by Pesquer *et al.*,[13,14] the calculated splitting due to an interaction between two C═O of two neighbouring chains (1 and 2) is 1 cm^{-1}; it is 6 cm^{-1} for an interaction between two C═O of two neighbouring molecules (1 and 3) (Figure 4). Obviously this type of interaction cannot explain the 14, 18 and 11 cm^{-1} splittings observed in the spectra of C_8HAT, C_{10}HAT and C_{12}HAT respectively. But it can account for the low frequency wing of the 1770 cm^{-1} band in C_8HAT and for the shoulder near 1762 cm^{-1} in C_{10}HAT which decrease when the temperature rises and vanish at about 298 K. The lowest frequency component is then assigned to a CO in relatively strong interaction with two aromatic hydrogens of another molecule, forming stable pairs in agreement with the results of conformational calculations on C_mHAT (m = 3–7).[13,14]

Assignment of the carbonyl deformations, δ(C═O) and γ(C═O) is based on the normal coordinate treatment of the model molecule (Table II, Figure 7). An intense infrared band near 1163 cm^{-1} and an absorption near 1195 cm^{-1}, the frequency of which does not vary with temperature, are respectively attributed to ν(Cal–O) and ν(Car–O), in agreement with the results of the calculation.

The low temperature crystal phase is thus characterized by a rather important degree of order in the lattice. The aliphatic parts mainly are in an extended conformation, though a few *gauche* forms are present. The structure of the ester group is the same for the three compounds. Spectroscopic results are compatible with the molecular geometry proposed from a conformational calculation on shorter homologues. The existence of pairs of molecules is supported by the presence of two kinds of interactions between vibrators of neighbouring molecules: a strong one between a CO group and two hydrogens of the aromatic core and a weaker one of a dipole-dipole type between two carbonyls.

SPECTROSCOPIC STUDY OF THE DISORDERED SOLID PHASES

As analysis of the enthalpic diagrams and of the X-ray diffraction patterns indicates that C_8HAT, C_{10}HAT and C_{12}HAT present a different polymorphism in the solid state, we separately consider each of them.

Triphenylene hexa-*n*-nonanoate

Comparison of the spectra of phases K_1 and K_2 shows the following features:

1) intermolecular interactions decrease;
2) the intensity of the bands characteristic of extended chains diminishes;
3) the structure of the ester group is not modified.

1—The absorption at 1770 cm^{-1} narrows and becomes nearly symmetrical: the dipolar interaction between neighbouring molecules is too weak to be detected. Splittings due to the crystalline field are not observed in phase K_2 which indicates a strong diminution of the intermolecular interactions.

It is interesting to note that the factor group splitting starts diminishing when the temperature is raised within the K_1 phase and disappears at the transition (Figure 5).

2—Intensity of the infrared progression bands due to the CH_2 wagging and rocking vibrations diminishes, but their frequency is not modified and no new band is observed. In the Raman spectrum, the lines corresponding to the skeleton vibrations of the extended molecules and that of r(CH_3) at 891 cm^{-1} are also weaker.

The most important modifications concern the CH stretching domain in the scattering spectrum (Figure 8). The band corresponding to the antisymmetrical valence mode $v_a(CH_2)$, at 2885 cm^{-1}, scarcely emerges from a broad scattering background, as observed in the disordered phases of compounds containing long aklyl chains. This effect appears near 263 K and progressively increases. It can be related to the lateral packing, the conformational disorder or to dynamical factors. The high frequency maxima characteristic of intra-chain coupling of *trans*-structures are not observed. However, the peak intensity ratio I_{2940}/I_{2850}, which has been related to the evolution of a proportion of *gauche* forms, is about the same as in phase K_1.

The previous features show that, in phase K_2, the alkyl chains present a rather important disorder which is not due to an appreciable quantity of conformational defects. They can be accounted for by the onset of angular fluctuations about the carbon-carbon single bonds; these fluctuations are confined in the vicinity of the *trans*-states and maintain the linear shape of the chains, though a weak probability exists for values in the vicinity of the *gauche* state. This hypothesis also explains the evolution of the factor group splittings within phase K_1 and their progressive vanishing.

3—In the 700–450 cm^{-1} frequency domains, all the bands are broadened but the frequencies are not modified as well for C_8HAT as for C_8HAT−1,1d_2 (Figure 7). The two farthest maxima of the CO stretching absorption remain at the same frequency (Figure 9).

In conclusion, the $K_1 \Rightarrow K_2$ transition of C_8HAT is accompanied neither by the appearance of a noticeable conformational disorder nor by a modification of the structure of the ester group. The main phenomenon seems to be the onset of angular fluctuations about the carbon-carbon skeleton of the alkyl parts. Coupling of molecular motions in the unit cell becomes weaker but the interaction between a carbonyl and two nitrogens within a pair of molecules is not modified.

Triphenylene hexa-*n*-undecanoate

C_{10}HAT presents two solid-solid phase transitions, at 254 and 302 K, leading to phases K_2 and K_3 respectively (Table I).

Phase K_2. The changes in the spectra when going from the K_1 to the K_2 phase are of two types:

1) the crystalline field effect is weaker
2) the intensity of the progression bands diminishes

1—Factor group splittings are still observed in the infrared spectrum on the CH_2

rocking fundamental and on the out-of phase CH_2 bending; but the magnitude of the splittings decreases when the temperature is raised and becomes equal to zero at 273 K. Dipole-dipole interactions are not detectable. This behaviour could be explained by the occurrence of deformation fluctuations along the carbon-carbon skeleton. The strong interaction between a carbonyl and two hydrogens remains unchanged (Figure 9).

2—The intensity of the CH_2 rocking and wagging progression bands observed in the infrared spectrum diminishes but the frequencies are not modified; no new band appears in the spectral range 1275–1400 cm^{-1} where vibrations characteristic of peculiar sequences of bond structures are expected (Figure 5).

In Raman spectrum, the most intense lines remain those which correspond to extended chains, at 1066 and 1127 cm^{-1}, and the $r(CH_3)$ peak at 891 cm^{-1}; however, the hump near 1080 cm^{-1} has increased (Figure 6). In the CH stretching domain, the peak intensity at 2884 cm^{-1} decreases and the ratio I_{2940}/I_{2850} increases by about 10%. These modifications indicate a weak augmentation of the number of *gauche* forms.

Phase K_3. Spectral modifications, in phase K_3, are important. They affect the bands characteristic of extended chains and those of the ester function.

1—Several infrared progression bands completely disappear and new absorptions occur in the CH_2 wagging domain. Indeed, the wing on the low frequency side of the $\delta_s(CH_3)$ band, at 1379 cm^{-1}, can be deconvoluted into two maxima near 1365 and 1354 cm^{-1}; in addition, a shoulder near 1340 cm^{-1} and a broad absorption near 1310 cm^{-1} appear (Figure 5). These features have been observed in the spectra of the disordered phases of *n*-alkanes and other compounds containing long hydrocarbon chains[24,35]; they have been assigned to conformational defects of the type GTG or GTG′ (near 1310 and 1365 cm^{-1}), GG sequences (near 1354 cm^{-1}) and end gauche forms (1340 cm^{-1}).[24,36]

In the Raman spectrum, the CH stretching domain resembles that of phase K_2. Though the peak height at 2884 cm^{-1} is weaker, the ratio I_{2940}/I_{2850} is about the same (Figure 8). So, the number of *gauche* forms is nearly the same in phases K_2 and K_3, which is consistent with the low value of the $K_2 \Rightarrow K_3$ transition enthalpy.

2—The evolution of the carbonyl absorption bands suggests a modification of the local structure; the band assigned to $\nu(\mathrm{Cal{-}O})$ is no longer observed and the out-of-plane deformation $\gamma(C{=}O)$ line is shifted from 696 to 690 cm^{-1} and is scarcely visible. However, the carbonyl stretching absorption is still split into two components at the same frequencies as in phase K_2. Thus, the interaction responsible for the low component is not perturbed and the dihedral angle θ_1 remains the same. This suggests that the modification involves the dihedral angle θ_2 which represents the inclination of the aliphatic skeleton plane with respect to that of the ester group (Figure 3).

The high temperature solid state of $C_{10}HAT$ is thus more disordered than the K_2 phase of C_8HAT; it presents some conformational defects in addition to angular fluctuations along the methylene chains; the structure of the ester function also is modified.

Triphenylene hexa *n*-tridecanoate

At first glance, the spectra of phases K_1 and K_2 are not very different. The Raman spectrum is still typical of a solid containing extended chains and no band characteristic of different conformers is observed. The geometry of the ester group is not modified since the CO group frequencies are the same.

The changes in the spectra are of two types:

1) the crystalline field effects decrease
2) the intensity of the bands assigned to CH_2 waggings and rockings weakens.

1—Factor group splittings are progressively reduced when the temperature rises and are still present at room temperature; this can be observed for instance on the CH_2 bending infrared bands and indicates a lessening of the intermolecular coupling.

2—The second feature which characterizes the K_2 phase is the weakening of the intensities of the progression bands. In the Raman spectrum, the peak intensity at 2884 cm^{-1} diminishes but the ratio I_{2940}/I_{2850} is practically the same as in phase K_1. These modifications can be explained by the onset of angular deformation movements about the C—C bonds of the chains, as in phase K_2 of C_8HAT. The motions are less important in C_{12}HAT, since the crystalline field effects are observed until 298 K.

SPECTROSCOPIC STUDY OF THE MESOMORPHIC AND ISOTROPIC PHASES

The solid-liquid crystal transition leads to a D_{rd} mesophase for the three compounds. In addition, C_{10}HAT and C_{12}HAT present a D_{hd} mesophase between the D_{rd} phase and the isotropic state (Table I).

Phase D_{rd}

Vibrational spectra of the D_{rd} phases are very similar in the three C_mHAT. They are quite different from the spectra of the disordered solids. Both the features assigned to the methylene chains and those due to the ester function are strongly modified.

1—Conformational evolution of the hydrocarbon part.

In infrared, the progression bands are replaced by broad maximums due to the transitions of different conformers; the frequency of the $r(CH_2)$ fundamental, near 720 cm^{-1}, indicates the presence of trans sequences of at least three or four bonds.[24] The scattering lines characteristic of extended chains are no longer observed and the maximum at about 1080 cm^{-1}, assigned to gauche forms, is important. In the CH stretching domain, the peak intensity near 2940 cm^{-1} increases with respect to that of $\nu_s(CH_2)$ (near 2850 cm^{-1}). The $\nu_s(CH_2)$ frequency increases by 6 cm^{-1} which indicates a shortening of the trans sequences.[37] The $\nu_a(CH_2)$ band collapses into a broad scattering near 2900 cm^{-1}.

The previous features reveal an important conformational disorder. The presence of some specific sequences of bond structures is deduced from the analysis of the infrared spectrum between 1275 and 1400 cm^{-1}. The low frequency wing of the $\delta_s(CH_3)$ band near 1379 cm^{-1} can be deconvoluted into three maximums at 1344, 1353 and 1366 cm^{-1}; the first two respectively indicate the presence of gauche bonds near the methyl and of GG sequences; the third one and a broad absorption near 1316 cm^{-1} are characteristic of defects of the type GTG or GTG′.

2—Modification of the structure of the ester groups.

The absorptions corresponding to ν(Cal—O) and to γ(C═O) are not observed and the δ(C═O) deformation is perhaps responsible for the shoulder at 640 cm^{-1}. Moreover, the C═O stretching band is single, its frequency being that of the high frequency component in the solid phases; this band is broad, its width at half intensity maximum being 41 cm^{-1} in the spectrum of C_{10}HAT; this suggests the existence of a non-resolved splitting due to a weak interaction on one carbonyl. X-ray diffraction studies have shown that the molecules are associated in pairs in the mesomorphic phases; the distance between two cores within a pair is increased by about 5% with respect to the solid phase structure. Such a weak increase is not sufficient to explain the evolution of the ν(C═O) absorption domain. The latter suggests a variation of the angle between the planes of the aromatic part and of the ester group (dihedral angle θ_1) which is expected to decrease. But, after the conformational calculation performed on C_mHAT (m = 3–7[13,14]), $\theta_1 < 50°$ corresponds to a considerable energy and is not likely. The same calculation indicates an energy minimum for $\theta_1 = 83°$, with the hypothesis of molecules in form 1 (all the chains situated on the same side of the central core); the energy difference with respect to the more stable form 2 ($\theta_1 = 55°$; $\theta_2 = 75°$) is about 1.7 KJ.mole^{-1}. With such a structure, the strong interaction between a carbonyl and two hydrogens of the aromatic part of the other molecule, which is responsible of the high stability of the pairs in the solid state, is lost. Interactions of the dipolar type are possible between two neighbouring chains.

Assuming $\theta_2 = 75°$ and varying θ_1, we have calculated the distance between the oxygens of two chains attached on the same phenyl ring and the splitting due to their interaction, using the dipole-dipole model. The results are reported in the following table:

θ_1	D (Å)	$\Delta\nu$ (cm^{-1})
90°	2.76	13
80°	3.43	7
70°	4.09	4
60°	4.7	2

They show that a θ_1 dihedral angle of about 70° should be a physically reasonable solution. However, some contribution of a slow dynamical effect cannot be ruled out.

In both hypotheses, the cohesion of the pairs in the mesomorphic D_{rd} phases should be due to the interactions between the aromatic cores.

Phases D_{hd}

The only modifications observed in the spectra when going from the D_{rd} to the D_{hd} phase is a slight increase (3 cm^{-1}) in the $\nu_s(CH_2)$ frequency; it indicates a shortening of the *trans*-sequences.[37] So, the lattice deformation at this transition is not accompanied by an increase in the conformational disorder, which explains the very weak transition enthalpies.

Isotropic phases

The conformational disorder is still more important in the isotropic phses, as shown by the broadening of the absorption near 1460 cm^{-1}, due to the CH_2 bending motion of a number of conformers, and the increased intensity of the maxima characteristic of defects. No modification is observed in the spectrum of the carbonyl group.

CONCLUSION

This vibrational study shows the existence of a polymorphism in the solid state of the discoid compounds C_8HAT, C_{10}HAT and C_{12}HAT and provides new information on the structures of the various solid and mesomorphic phases.

In the most ordered solid phases, the aliphatic chains are mainly in an extended conformation; they are located alternately on either side of the triphenylene core and tilted with respect to its plane. The molecules are stacked in columns and two molecules are associated to form a pair through a strong interaction between an oxygen and two aromatic hydrogens and a weaker one, of dipolar type, between two carbonyls. The degree of order in the lattice is important.

Thermotropic phase transitions first lead to disordered solid phases. Except in the case of C_{10}HAT, the disorder does not imply a noticeable quantity of conformational defects which explains the low transition emthalpies. The spectra suggest the onset of angular fluctuations around the aliphatic carbon skeleton. Intermolecular interactions progressively weaken when raising the temperature, but the strong interaction between two molecules in a pair is maintained.

The solid-mesophase transitions imply the occurrence of a very important conformational disorder. The spectra show the existence of all the types of conformational defects which have been evidenced in molten *n*-paraffins, such as GTG or GTG′ structure, GG sequences and gauche bonds near the methyl. In addition, the inclination of the ester group with respect to the triphenylene plane seems to be modified. The interaction between two molecules in a pair is different in nature and weaker than in the solid states.

The microscopic structure is about the same in all the mesophases of these three triphenylene hexa-*n*-alkanoates. In the isotropic phases, the number of *gauche* bonds is slightly higher.

We thus conclude that the disordering process in C_8HAT, C_{10}HAT and C_{12}HAT is strongly related to the dynamics of the aliphatic parts of the molecules. The onset of angular fluctuations along the carbon-carbon skeleton and the appearance of a few *gauche* bonds induce solid-solid phase transitions. The loss of the tridimensional lattice is related to a very important "melting" of the alkyl chains, which shows that the chains play an essential part in the correlation between the columns in the solid state. At the same time, a modification of the inclination of the COO group with respect to the triphenylene core causes a strong diminution in the stability of the pairs.

Acknowledgments

The authors are very grateful to Prof. C. DESTRADE, to Drs. M. PESQUER and B. DESBAT for fruitful discussions and to Dr. J. DEVAURE for critically reading the manuscript. Drs. N. B. CHANH and J. R. HOUSTY are thanked for their help during the calorimetric and X-ray diffraction study. Sincere thanks are due also to A. ROUBINEAU, R. CAVAGNAT and J. C. CORNUT for their competent technical assistance.

References

1. (a) C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984). (b) C. Mondon-Bernaud, Thesis, Bordeaux 1980.
2. A. M. Levelut, *J. Chim. Phys.*, **80**, 149, (1983) and *Proc. Intern. Conf. on Liquid Crystals, Bangalore* (Heyden and Son, 1980).
3. C. Destrade, M. C. Mondon and J. Malthete, *J. Phys. (Paris)*, **40**, C3-17 (1979).
4. Y. Bouligand, *J. Phys. (Paris)*, **41**, 1307 (1980).
5. P. Ostwald, *J. Phys. (Paris) Lett.*, **42**, L-171 (1981).
6. D. Goldfarb, E. Lifshitz, H. Zimmermann and Z. Luz, *J. Chem. Phys.*, **82**, 5155 (1985).
7. M. Rey-Lafon, C. Destrade and A. Tazi Hemida, *Mol. Cryst. Liq. Cryst.*, **137**, 381 (1986).
8. C. R. Safinya, K. S. Liang, W. A. Varady, N. A. Clar and G. Andersson, *Phys. Rev. Lett.*, **53**, 1172 (1984).
9. W. R. Krigbaum, Y. Chatani and G. Barber, *Acta Cryst.*, **B26**, 97 (1977).
10. W. R. Krigbaum and G. Barber, *Acta Cryst.*, **B27**, 1884 (1971).
11. R. F. Bryan and L. Fallon, *J. Chem. Soc., Perkin II Trans*, 1175 (1975).
12. M. Cotrait, P. Marsau, C. Destrade and J. Malthete, *J. Phys. (Paris) Lett.*, **40**, L-519 (1979).
13. M. Cotrait, P. Marsau, M. Pesquer and V. Volpilhac, *J. Phys. (Paris)*, **43**, 355 (1982).
14. M. Pesquer, M. Cotrait, P. Marsau and V. Volpilhac, *J. Phys. (Paris)*, **41**, 1039 (1980).
15. G. Zerbi and M. Gussoni, *Chem. Phys. Lett.*, **74**, 24, (1980).
16. R. G. Snyder and M. W. Poore, *Macromolecules*, **6**, 709 (1960).
17. G. Zerbi, R. Magni, M. Gussoni, K. H. Moritz, A. Bigotto and S. Dirlikov, *J. Chem. Phys.*, **75**, 3175 (1981).
18. R. G. Snyder, M. Maroncelli, H. L. Strauss, L. A. Elliger, D. G. Cameron, H. L. Casal and H. H. Mantsch, *J. Am. Chem. Soc.*, **105**, 133 (1983).
19. The chemical syntheses have been performed in the Centre de Recherches Paul Pascal, Bordeaux, under the direction of Professor C. Destrade who is gratefully acknowledged.
20. These measurements have been performed in the Laboratoire de Cristallographie de l'Université de Bordeaux I.
21. V. Schettino, *J. Mol. Spectros.*, **34**, 76 (1970).
22. R. Mecke and K. Witt, *Z. Naturforsch.*, **21A**, 1899 (1966).
23. G. Neerland, B. N. Cyvin, J. Burnwell and S. J. Cyvin, *Spectroscopy Lett.*, **15**, 137 (1982).
24. R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).
25. Y. Kim, H. Noma and K. Machida, *Spectrochim. Acta*, **42A**, 891 (1986).
26. C. La Lau and R. G. Snyder, *Spectrochim. Acta*, **27A**, 2073 (1971).
27. M. T. Forel and M. Fouassier, *J. Chim. Phys.*, **67**, 1132 (1970).
28. M. Rey-Lafon and M. T. Forel, *J. Chim. Phys.*, **68**, 384 (1971).
29. R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85, 117 (1963).
30. R. G. Snyder, S. L. Hsu and S. Krimm, *Spectrochim. Acta*, **34A**, 395 (1978).

31. S. Abbate, G. Zerbi and S. L. Wunder, *J. Phys. Chem.*, **86**, 3140 (1982).
32. R. G. Snyder and J. R. Sherer, *J. Chem. Phys.*, **71**, 3221 (1979).
33. R. M. Moravie and J. Corset, *J. Chim. Phys.*, **74**, 707 (1977).
34. C. J. F. Bottcher, "*Theory of Electric Polarization*", 2nd ed., Vol. 1, Elsevier, Amsterdam (1973).
35. L. Ricard, M. Rey-Lafon and C. Biran, *J. Phys. Chem.*, **88**, 5614 (1984).
36. M. Maroncelli, S. P. Qi, H. L. Strauss and R. G. Snyder, *J. Am. Chem. Soc.*, **104**, 6237 (1982).
37. L. Ricard, S. Abbate and G. Zerbi, *J. Phys. Chem.*, **89**, 4793 (1985).