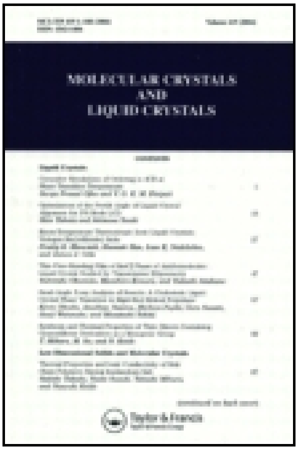

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Infrared Spectral Studies of Triphenylene Mesogens Possessing Terminal Functional Groups in the Peripheral Chains for Hydrogen-Bond Interaction

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INFRARED SPECTRAL STUDIES OF TRIPHENYLENE MESOGENS POSSESSING TERMINAL FUNCTIONAL GROUPS IN THE PERIPHERAL CHAINS FOR HYDROGEN-BOND INTERACTION

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Temperature dependence of infrared spectra for three homologues of the triphenylene mesogens with two terminal carboxylic acids was measured. These mesogens show Col_h mesophase. These results revealed the existence of some hydrogen bonding interactions in the isotropic, mesomorphic as well as solid phases. The increase of the dimeric C=O (ca. 1712 cm^{-1}) and the

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decrease of the monomeric C=O (ca. 1740 cm^{-1}*) were observed at the isotropic to Col*$_h$ *phase transition on cooling. The absorption intensity of the dimeric C=O stretching band in Col*$_h$ *phase is larger than that in the isotoropic phase. It was indicated that for the explanation of Col*$_h$ *thermal stability for these homologues molecular rotational fluctuation around the columnar axis in Col*$_h$ *is significantly suppressed by the hydrogen bonding interaction and the suppression depends on the spacer length in their homologues, considering that the thermal stability of Col*$_h$ *phase is related to both the rotational fluctuation and the instability of hexagonal packing of molecules and these could be operated by hydrogen bond interaction.*

Keywords: columnar mesophase; discotic; hydrogen bond; IR spectra; liquid crystal; triphenylene

INTRODUCTION

Rotational fluctuation around the columnar axis is an important factor for the occurrence of columnar mesophase. Some spectroscopic studies revealed that the rotational fluctuations are of msec to μsec in time scale and the allowance of rotation is strictly related to the intermolecular interaction through the peripheral chains. Indeed, a twin discotic mesogen in

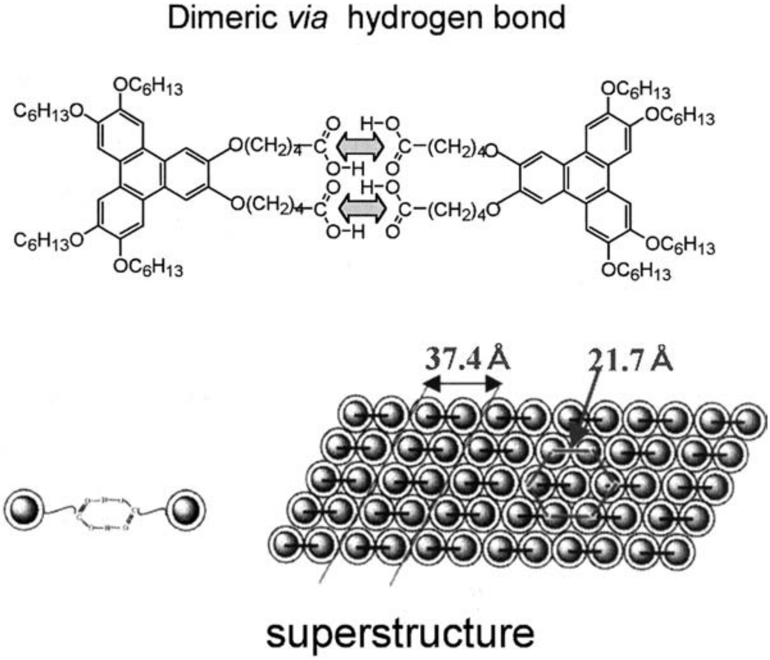


FIGURE 1 Possible model for the superstructure of hexagonal lattice of n = 4.

which two rigid cores are linked at the end of one peripheral chain shows narrower angle for the allowance and the thermal stability of columnar phase increases [1,2].

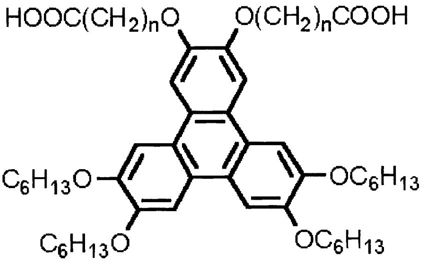
Recently, we reported that a homologous series of a triphenylene mesogen which has two carboxylic acids at the end of the adjacent two aliphatic tails show a columnar mesophase with a dimeric superstructure (Fig. 1) in addition to the hexagonal arrangement of columns caused by the intermolecular hydrogen bonding interaction [3]. Furthermore, it was found that the strength of the hydrogen bonding interaction is essentially important for the thermal stability of columnar phase as well as for the occurrence of columnar mesophase [4].

In this work, the temperature dependence of three homologous which have a different length of the spacer connecting a carboxylic acid and the mesogenic core were measured and the effect of the hydrogen bonding interaction on the mesomorphism is discussed.

EXPERIMENTAL

Synthesis

The compounds (1, 2 and 3) were synthesized according to the literature with slight modification [5,8].



1: n=3

2: n=4

3: n=5

SCHEME

Measurement

The phase transition temperatures and enthalpies were obtained using a Differential Scanning Calorimeter (TA Instrument, 2920 MDSC) and the textures of mesophases were observed by a polarizing microscope (Olympus, BH-2) equipped with a hot stage (Mettler, FP80HT).

The temperature dependent FT-IT spectra were measured using a FT-IT spectrometer (Bio-Red FTS 6000) with a hot stage (Mettler, FP90HT). The measurements were performed with temperature cooling at 5°C/min. The compound was sandwiched by two BaF_2 crystal plates for the measurement using silica beads with 2 μm-diameter for adjusting the sample thickness.

RESULTS AND DISCUSSION

Mesophase Behavior

The thermodynamic data of the homologues used in this study are summarized in Table 1. Two homologous **1** and **3** showed a monotropic mesophase with hexagonal columnar arrangements. Compound **2** gives an enantiotropic Col_h phase.

The comparison with the corresponding symmetrical triphenylene mesogen, 2,3,6,7,10,11-hexahexyloxytriphenylene (C6OTP), which shows Col_h phase between 70°C and 100°C [9], revealed that the clearing temperatures decrease in the following order, **1** > **2** > C6OTP > **3**.

IR Spectra

The hydrogen bonds interaction working among carboxylic groups in some organic compounds have been studied by IR spectroscopy to show that the

TABLE 1 Transition Temperatures and Enthalpies of Carboxylic Acid Derivatives

Compound	Phase transition	Temperature/(°C)	ΔH (kJ/mol)
1: n = 3	Cr → I	130	55.8
	$(Col_h \rightarrow I)^a$	(117.4)	4.8
2: n = 4	$Cr \rightarrow Col_h$	94.0	51.8
	$(Col_h \rightarrow I)$	105.3	6.1
3: n = 5	Cr → I	103.2	74.3
	$(Col_h \rightarrow I)^a$	(80.6)	^{b}
C6OTP	$Cr \rightarrow Col_h$	70^c	–
	$(Col_h \rightarrow I)$	100^c	–

[a]: Parenthesis indicate monotoropic phase transition.

[b]: The phase transition enthalpy was not determined because of the recrystalization on cooling.

[c]: Ref. [9].

cyclic dimer mainly exists in the pure liquid and solid states. An alternative structure of organic acids in the condensed states is a long polymeric chain of hydrogen-bonded carboxylic acids groups. In concentrated solutions, pure liquid and crystalline states, the existence of several associations of acetic acids are proposed, namely cyclic dimer, open dimer, "free" monomer and "sideways" acid dimer as shown in Figure 2 [10–14].

In these studies, it was reported that in the carbonyl stretching region (1600–1800 cm^{-1}), the signature of the open and cyclic dimer is an infrared band at *ca.* 1710 cm^{-1}. The C=O stretching band at *ca.*, 1740 cm^{-1} is characteristic of the free monomer.

The temperature dependence of infrared spectra was measured for the carbonyl stretching and O–H stretching regions for the homologues.

Figure 3 shows the temperature-dependent infrared spectra of **2** in the region of 1800 to 1650 cm^{-1} on cooling in the isotoropic, mesomorphic and crystal phases. The strong carbonyl stretching vibration around 1710 cm^{-1} is assigned to the carboxylic acid cyclic/open dimer, while the free carboxylic acids shows a weak band for the carbonyl stretching vibration at 1740 cm^{-1}.

A remarkable change could be observed at the phase transition from the isotropic to columnar mesophase and from the columnar mesophase to crystal.

As the temperature is decreased, the dimeric carboxylic acid (1712 cm^{-1}) group increases at the isotoropic-columnar phase transition on cooling. A large amount of hydrogen-bonded pairs of the acid groups is formed in the $\mathrm{Col_h}$ phases.

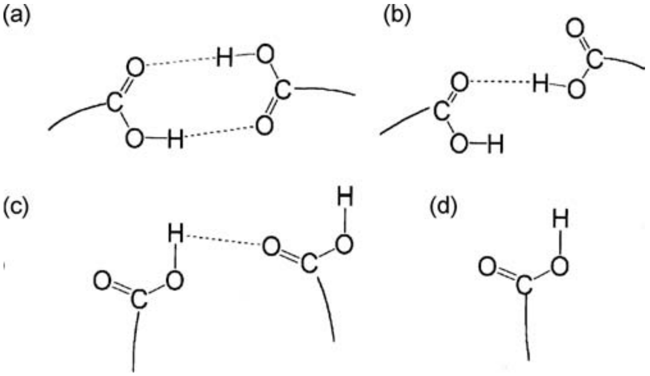


FIGURE 2 Four possible forms of carboxylicacids groups in the condensed phase (a) cyclic dimer, (b) open dimer, (c) "sideways" acid dimer, (d) free monomer.

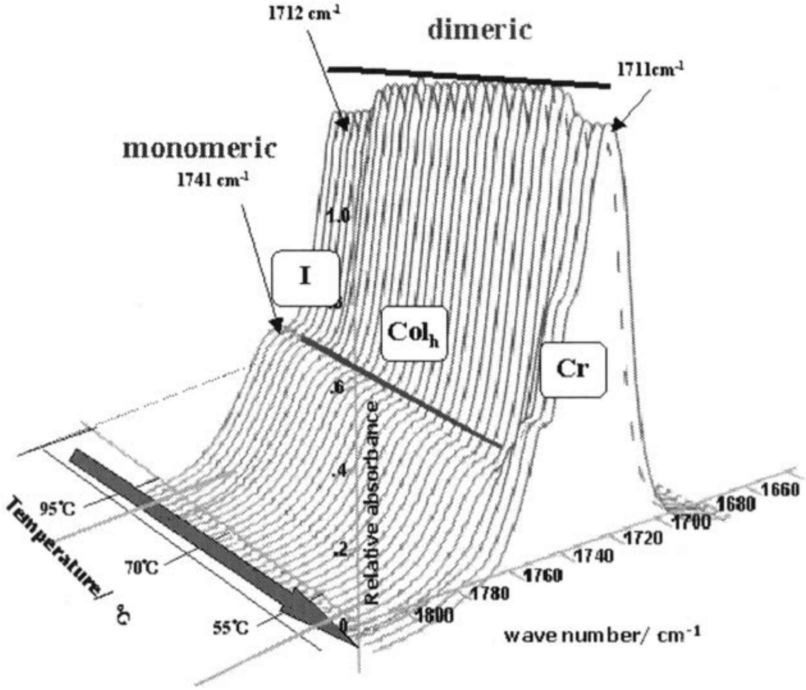


FIGURE 3 Temperature dependence of IR absorption of C=O stretching mode on cooling for n = 4.

The absorption at $1740\,\mathrm{cm}^{-1}$ derived from the monomeric carboxylic acids can be seen only in the isotropic and $\mathrm{Col_h}$ phases and decreases in magnitude with decreasing temperature. This behavior is the same as for the O−H stretching band at *ca.* $3550\,\mathrm{cm}^{-1}$. This band at $3550\,\mathrm{cm}^{-1}$ is assigned to the O−H stretching vibration of the "free" monomer. The intensity of this band decreases at the isotoropic-columnar phase transition on cooling.

In the spectra a very broad band centered at *ca.* $3300\,\mathrm{cm}^{-1}$ is observed and this is assigned to the O−H stretching vibration in a hydrogen bonding cyclic dimer. In the spectra of the columnar phase, a broad shoulder at $3300\,\mathrm{cm}^{-1}$ is enhanced and it is probably due to the formation of an open dimer of the acids.

The temperature dependence of infrared spectra on cooling for **1** and **3** shows the similar behavior to that of **2**. These are shown in Figures 4 and 5.

The intensities of the dimeric C=O stretching band are larger than those in the isotoropic phase for these homologues. This may indicates the forma-

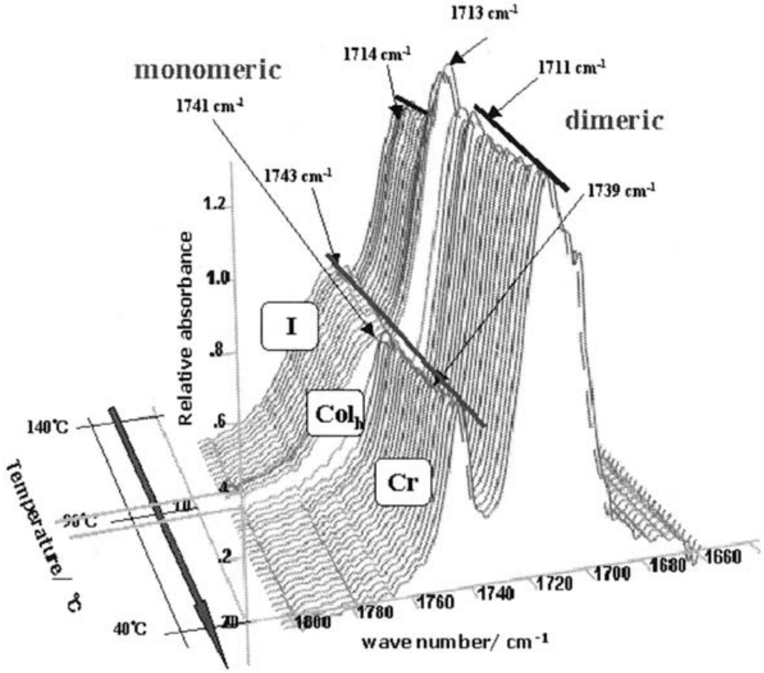


FIGURE 4 Temperature dependence of IR absorption of C=O stretching mode on cooling for n = 3.

tion of mesophase is initiated by hydrogen bonding interaction. Indeed, the phase transition behavior of the homologue **2** shows strong dependence of the cooling rate from the isotoropic phase.

A large amount of hydrogen-bond pairs of the acids group is formed in the $\mathrm{Col_h}$ phase. It could be reasonably thought that hydrogen bond interaction leads to the increase of the thermal stability of $\mathrm{Col_h}$ phase due to the less rotational fluctuation, which causes the increase of intermolecular interactions.

The fact that the thermal stability of $\mathrm{Col_h}$ phase for **2** (n = 4) is higher than that for C6OTP is probably due to the less rotational fluctuation in a normal hexagonal packing of $\mathrm{Col_h}$ phase by hydrogen bond interaction as schematically are shown in Figure 6(b).

However, the shorter and longer spacer lengths are thought to cause the instability of hexagonal packing of columns and these correspond to the cases of **1** (n = 3) and **3** (n = 5). These are also shown in Figure 6(a) and (c). Thus, it is thought that hydrogen bond interaction among

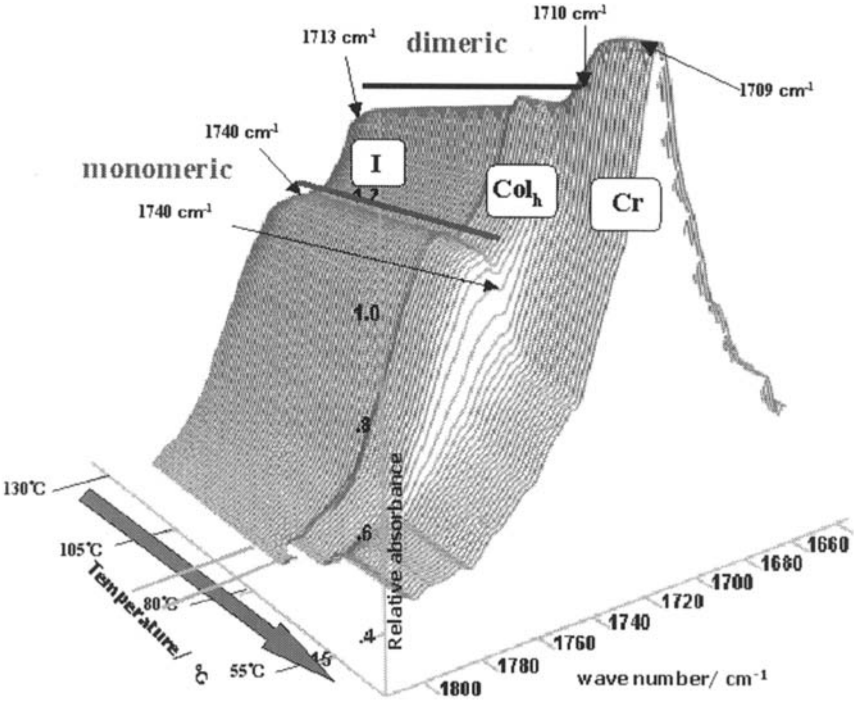


FIGURE 5 Temperature dependence of IR absorption of C=O stretching mode on cooling for n = 5.

carboxylic acid groups causes less fluctuation around columnar axis to elevate the thermal stability of $\mathrm{Col_h}$ phase and on the other hand, the instability of packing decreases the thermal stability of columnar arrangement. In the case of **1**, the shorter spacer provides more rigid situation, that is, far less fluctuations which is disadvantageous for the thermal stability of mesophase.

CONCLUSION

Considering the hydrogen boding interaction among discotic molecules relates to the rotational fluctuation and columnar packing in the mesophase, it is reasonable to think that the molecular rotational fluctuation around the columnar axis is significantly suppressed by the hydrogen bonding interaction to make the intermolecular interaction stronger and the spacer length relates to the instability of columnar packing in a hexagonal

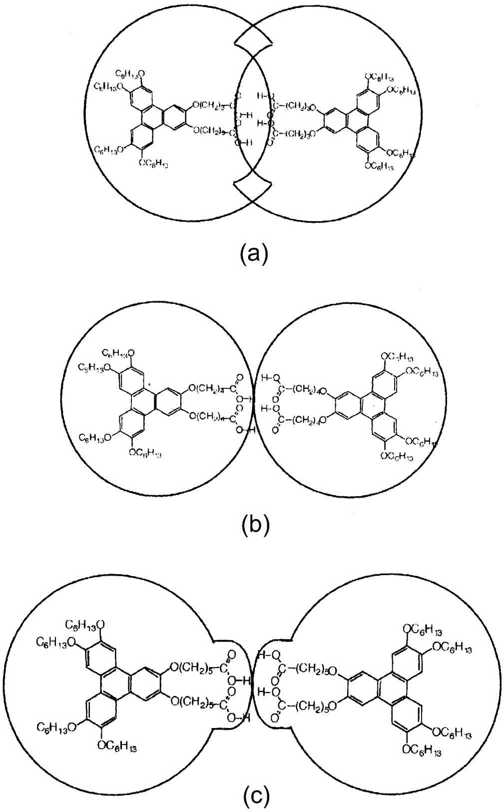


FIGURE 6 Packing of triphenylenes in the Col_h mesophase. (a) 1 (b) 2 (c) 3.

way. Therefore, it was indicated in this work that these factors affect the stability of columnar mesophase.

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