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Molecular structure and chiral liquid crystalline phases

B K SADASHIVA
Raman Research Institute, C.V. Raman Avenue, Bangalore 560 080, India

Abstract. We describe briefly some results obtained on both chiral and achiral compounds exhibiting chiral mesophases. We report the first example of a single component system exhibiting the undulated twist grain boundary C^* or UTGB$_{C^*}$ phase. Preliminary results concerning a few achiral compounds composed of banana-shaped molecules exhibiting a mesophase is reported. They have been investigated by polarized light optical microscopy, differential scanning calorimetry and x-ray diffraction studies.

Keywords. Chiral; achiral; banana-shaped molecules; undulating twist grain boundary phase.

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1. Introduction

As is well known, cholesteryl benzoate, the first thermotropic liquid crystal to be discovered is chiral in nature. However, chiral compounds and the mesophases exhibited by them were not examined in detail for a long time. The discovery of ferroelectricity in 1975 by Meyer *et al* [1] gave an impetus to the study and growth of chiral liquid crystals. Since then, a large number of new compounds have been synthesized and studied systematically [2]. Later, as a result of careful investigations on chiral smectic liquid crystals, the antiferroelectric phase was discovered [3]. In the meantime, the twist grain boundary *A* phase was discovered serendipitously [4]. A number of new materials were synthesized exhibiting the antiferroelectric [5] as well as twist grain boundary phases [6] which helped in assessing the molecular structural requirements for obtaining such phases.

The discovery of novel ferroelectric smectic phase formed by achiral banana-shaped molecules in 1996 by Niori *et al* [7] has opened new vistas for generating chiral phases from achiral systems. In addition, very recently a new mesophase viz. undulated twist grain boundary C^* (UTGB$_{C^*}$) phase was discovered in our laboratory [8] in a binary mixture.

In this paper, we report some results obtained from both chiral and achiral systems. This concerns the twist grain boundary *A* phase, a pure single component system exhibiting the undulated twist grain boundary phase and the preliminary results on the mesophase exhibited by compounds composed of achiral banana-shaped molecules.

2. Experimental

The intermediate and final compounds were purified by column chromatography on silica gel using chloroform or chloroform/ethyl acetate mixtures. They were further purified by crystallization from suitable solvents. The purity of all the compounds was checked by thin layer chromatography (Merck Kieselgel 60 F_{254} pre-coated plates) and by normal phase

high performance liquid chromatography using μ-porasil column (3.9 mm$\times$300 mm, Waters Associates Inc.) and 2% ethyl acetate in dichloromethane as the eluent. The purity was found to be greater than 99% for all the final compounds. The chemical structures of all the compounds were confirmed by using a combination ^{1}HNMR spectroscopy (Bruker WP80SY spectrometer or Bruker AMX 400 MHz spectrometer) with tetramethyl silane as an internal standard, infrared spectroscopy (Shimadzu IR 435 spectrophotometer) and elemental analysis (Carlo-Erba 1106 analyser). Specific optical rotations were measured using chloroform as the solvent (Optical Activity AA 1000 polarimeter).

The phase assignments and transition temperatures were determined by thermal polarized light microscopy using a polarizing microscope (Leitz Laborlux 12 P0L) equipped with a heating stage and a controller (Mettler FP 52 and FP 5, respectively), as also from thermograms recorded on a differential scanning calorimeter (Perkin-Elmer Model Pyris-1D). The calorimeter was calibrated using pure indium as a standard.

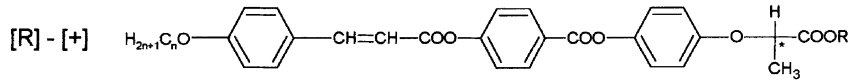
3. Results and discussion

3.1 *Twist grain boundary phases*

In 1972, de Gennes [1] predicted that twist or bend distortions can be incorporated into a layered smectic *A* structure by the presence of an array of screw or edge dislocations. A theoretical model for such an array of distortions for smectic liquid crystals made of chiral molecules was proposed by Renn and Lubensky [2]. Such a phase was discovered by Goodby *et al* [4] in some phenyl propiolate derivatives. In this phase, blocks of smectic *A* layers rotate with respect to one another thereby forming a helical structure. The axis of the helix is perpendicular to the long axes of the molecules. The blocks are separated from one another by screw dislocations. It was also predicted that rows of screw dislocations will form grain boundaries in the phase. This phase was termed as the twist grain boundary *A* or TGB_A phase. In the last ten years or so, a large number of compounds exhibiting the TGB_A phase have been synthesized [11–17]. One of the main characteristics of the TGB_A phase is the filamentary texture that it exhibits and this has been used to identify the mesophase. In addition, corresponding to the smectic *C* and smectic C^* phases, TGB_C and TGB_{C^*} phases have also been predicted [18, 19].

The molecular structural requirements for the appearance of TGB phase have been reviewed [20]. Two of the most important requirements for the occurrence of the TGB phase are the high optical purity and the strong chirality associated with the molecules. We report here briefly some of the results obtained on 4-*n*-alkoxycinnamic acid derivatives using lactic acid as the chiral moiety.

The compounds chosen have the general structure shown below:



n = 10, 11, 12

R = -CH $(CH_3)_2$ Series I

= -CH_2 CH $(CH_3)_2$ Series II

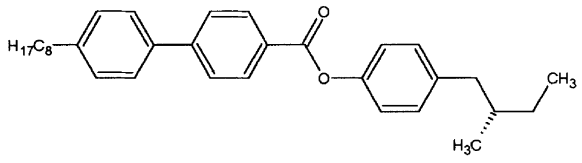
= -$(CH_2)_3$ CH_3 Series III

Figure 1. Photomicrograph of the filamentary texture of the TGB_A phase of compound $n = 12$, series I at 132.8°C.

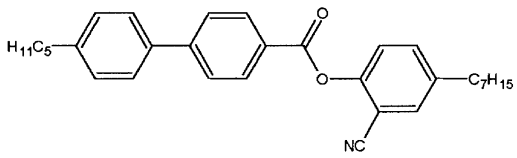
In order to investigate the effect of molecular chirality on the stabilisation of TGB_A phase, three series of compounds using lactic acid as the chiral moiety were synthesized. These have the same basic molecular structure but differ in the type of alcohol used. It was found that only homologues of series I exhibited the TGB_A phase. A photomicrograph of the filamentary texture shown by the dodecyl homologue of series I is shown in figure 1. The absence of this phase in the other two series of compounds suggests that the TGB_A is very sensitive to small changes in the molecular structure particularly close to the chiral centre. A detailed paper concerning the results of the above investigations will be published elsewhere [21].

3.2 *Undulated twist grain boundary phase*

Pramod *et al* [8] reported the discovery of a new twist grain boundary phase having a modulated structure. The new phase was found in binary mixtures of the following two compounds.



K 67.0 SmI^* 70.0 SmC^* 85.0 SmA 134.6 N^* 140.5 I

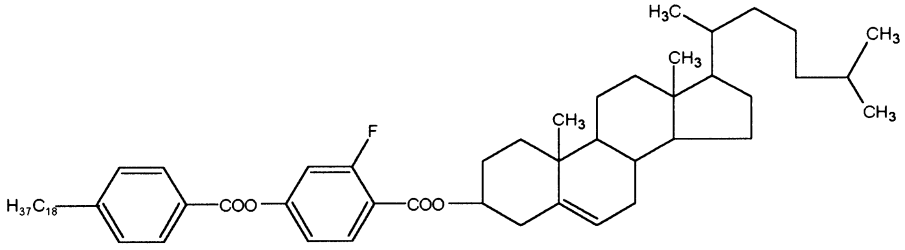


K 45.0 N 102.0 I

The physical studies which were carried out with about 36 wt % of the non-chiral cyano substituted compound showed the following sequence of transitions on cooling as observed under a polarizing microscope: I 121.7N 76.8 TGB_A. Further cooling of the sample to 63°C showed a distinct transition from the TGB_A phase to another phase which developed a square grid pattern. Based on careful optical observations, x-ray scattering studies and the effect of an external AC electric field in different geometries, they concluded that this is a new mesophase in which there is a helical arrangement of tilted molecules within each SmC^* like block. In addition, these TGB_{C^*} blocks have a two-dimensionally undulating structure such that it forms a square grid. Since the grain boundaries also undulate along the entire structure the new phase was called the undulated TGB_{C^*} or $UTGB_{C^*}$ phase.

Since this $UTGB_{C^*}$ phase was observed not only in the above mixture but in a couple of other systems, we decided to explore the possibility of obtaining such a phase in a pure, single component system.

We synthesized several compounds and report here the observations made on the following compound.



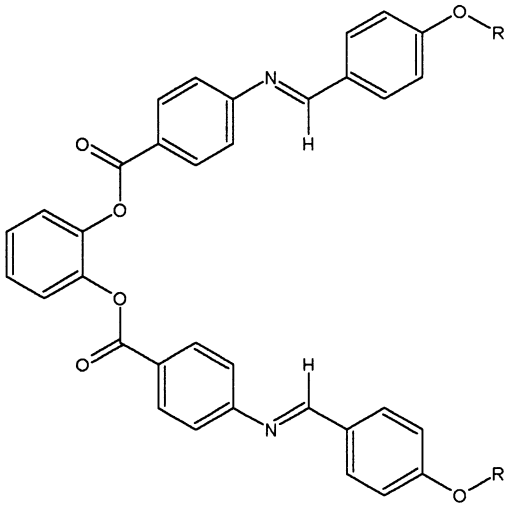
The compound was sandwiched between a glass slide and a cover slip and heated to about 200°C at which temperature, a thin film of the sample is obtained. Heating the sample to >240°C induces thermal decomposition. Hence, the sample is cooled from about 200°C. When the temperature reaches 164°C, a texture as shown in figure 2 appears. This is characterized by filaments which look like beaded chains and the ends of which seem to spiral. Similarly when a homogeneously aligned sample is cooled slowly a square grid pattern as shown in figure 3 is clearly obtained. Further cooling of the sample results in a ferroelectric phase. Based on these observations, we believe that this mesophase is $UTGB_{C^*}$ and this compound represents the first example of a pure material exhibiting such a phase. We have synthesized a number of other compounds exhibiting this phase and the physical measurements are in progress. The results of these investigations will be reported elsewhere [22].

Figure 2. Photomicrograph of the texture observed at 163.8°C on cooling from the cholesteric phase of the *n*-octadecyl compound ($UTGB_{C^*}$ phase).

Figure 3. Photomicrograph of the square grid pattern of the $UTGB_{C^*}$ phase at 150°C, homogeneous alignment.

3.3 *Mesophases formed by banana-shaped molecules*

A belief existed for a long time that mesophases are obtained by compounds which are rod-like or lath-like in shape. However, mesophases exhibited by compounds whose constituent molecules are not rod-like are also not new. Vorlander had reported [23] long back that certain compounds which are non-linear in shape showed mesogenic properties. For example, he had reported that an isophthalic acid derivative viz. bis (4-methoxyphenylazophenyl) isophthalate exhibited a mesophase which was shown to be nematic between 164° and 213°C [24]. Similarly, 1,2-phenylene bis (4-ethoxyphenylazoxybenzoate) is reported [24] to exhibit a nematic phase between 184° and 218°C. It was Kuboshita *et al* [25] who recently investigated in detail the mesomorphic behaviour of compounds with non-linear molecular structure as shown below:



Interestingly these compounds exhibited the classical nematic and smectic *A* phases. In addition some of the middle homologues also showed a monotropic smectic *B* phase. This work on the mesomorphic behaviour of bent core molecules was further extended by Matsunaga and co-workers [26–28].

However, it was Niori *et al* [29] who showed very recently that compounds composed of banana-shaped molecules exhibit a smectic mesophase which has spontaneous polarization and hence show ferroelectric properties. These compounds represent the first examples of achiral molecules exhibiting ferroelectricity. Since then, there has been great enthusiasm not only to synthesize new materials but to examine their interesting properties [30–33].

As part of a programme to synthesize and study the properties of compounds composed of banana-shaped molecules, we report here the preliminary results obtained on three of the compounds. The bent core compounds were synthesized according to the pathway shown in figure 4. The detailed synthetic procedure will be reported elsewhere. The transition temperatures and the associated enthalpies for the three compounds are summarized in table 1. As can be seen, all the three derivatives are enantiotropic mesomorphic and the

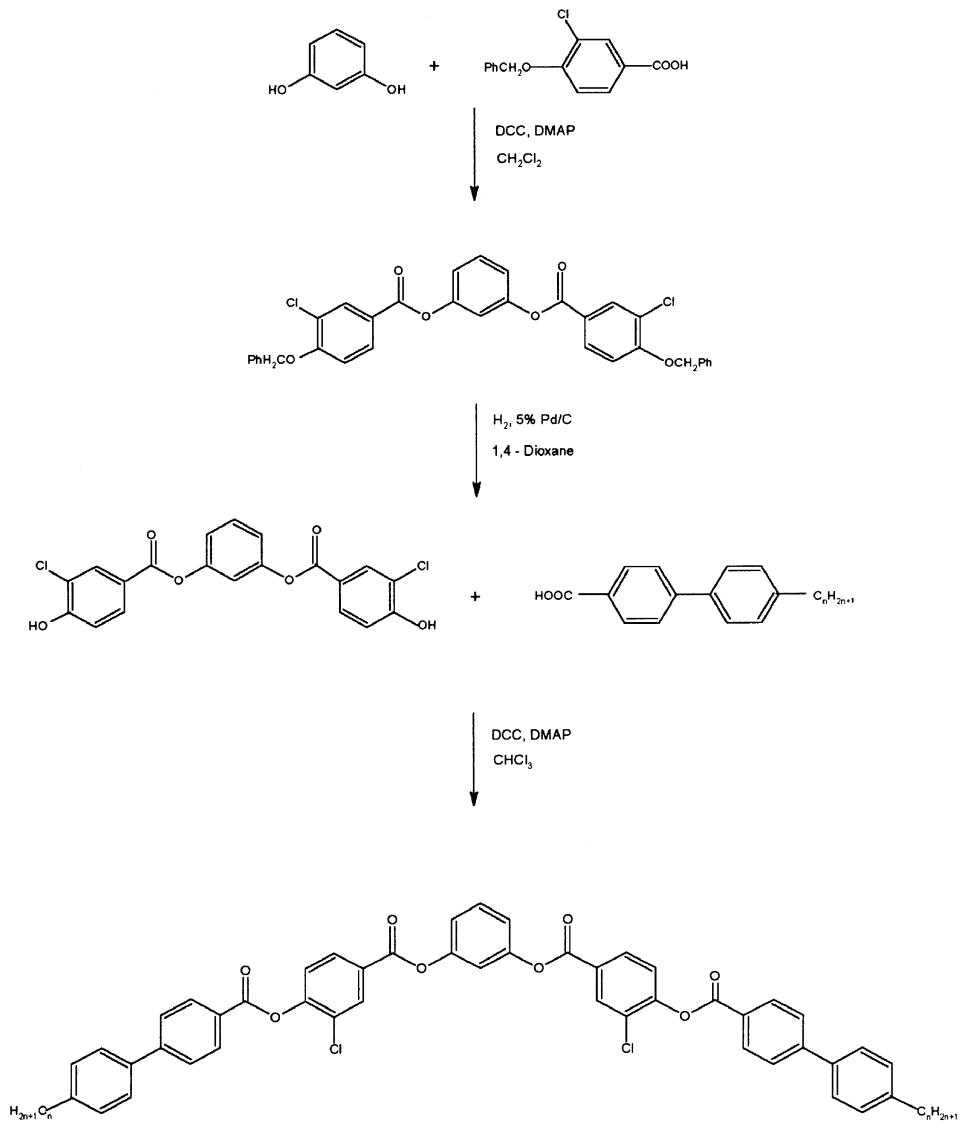


Figure 4. Synthetic pathway used for the preparation of the banana-shaped compounds.

compounds with *n*-decyl and *n*-undecyl chains have a mesophase range of about 25°. On cooling the isotropic liquid, a highly birefringent mesophase appears which eventually leads to fan-like texture. Sometimes large platelets appear. The texture of the mesophase obtained for compound 3 is shown in figure 5. This texture is very similar to that exhibited by some truxenes [34] which have been characterized as Col_{rd}. The differential calorimetric thermograms of compounds 2 and 3 are shown in figure 6. It is seen that the clearing enthalpy of the three compounds are not only quite high but are also comparable

Table 1. Transition temperatures (°C) and (in italics) enthalpies ($kJ\,mol^{-1}$) for the banana-shaped compounds. K = crystalline phase; M = mesophase; I = isotropic phase.

Compound number	n	K	M	I
1	10	·	132.0	156.50
			20.2	*16.05*
2	11	·	128.00	153.00
			15.91	*15.36*
3	12	·	131.0	148.00
			15.15	*14.34*

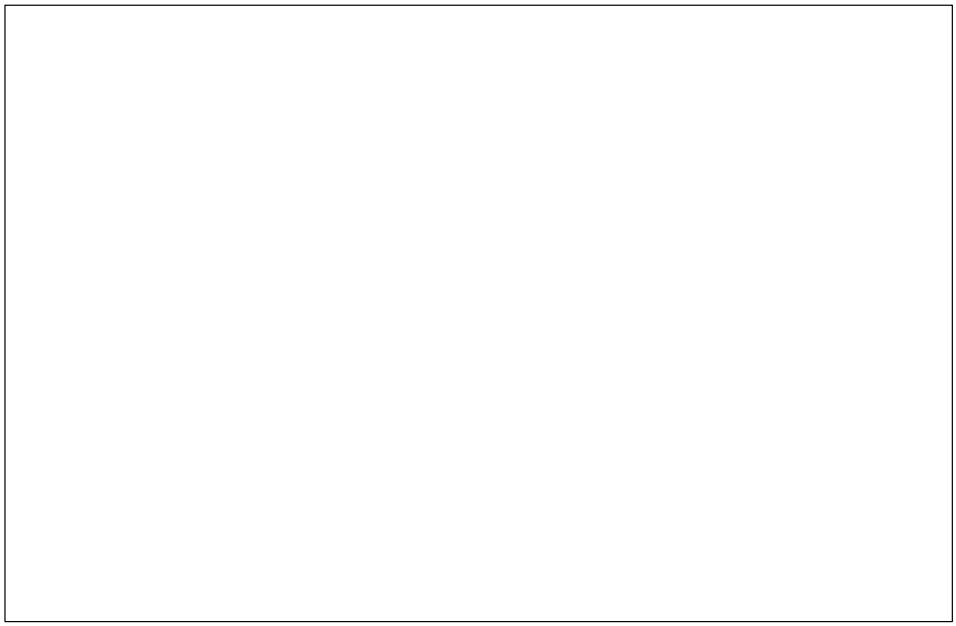


Figure 5. Photomicrograph of the texture obtained on cooling from the isotropic liquid, banana-shaped compound, $n = 12$, 147.5°C.

to the melting enthalpy. For example, the dodecyl homologue has a melting enthalpy of $15.15\,kJ\,mol^{-1}$ while the clearing enthalpy is $14.34\,kJ\,mol^{-1}$. This indicates that the mesophase is highly ordered. Though the mesophase is ordered, the displacement of the cover slip of a sandwiched sample between a glass slide and a cover slip is rather easy.

The mesophases exhibited by banana-shaped molecules so far reported appear to be lamellar in nature. However, preliminary x-ray data obtained on compound 3 indicate that the mesophase is not layered.

It also suggests a columnar structure which is probably tetragonal in nature. Coupled with the thermodynamic data and textural observation we believe that the mesophase is

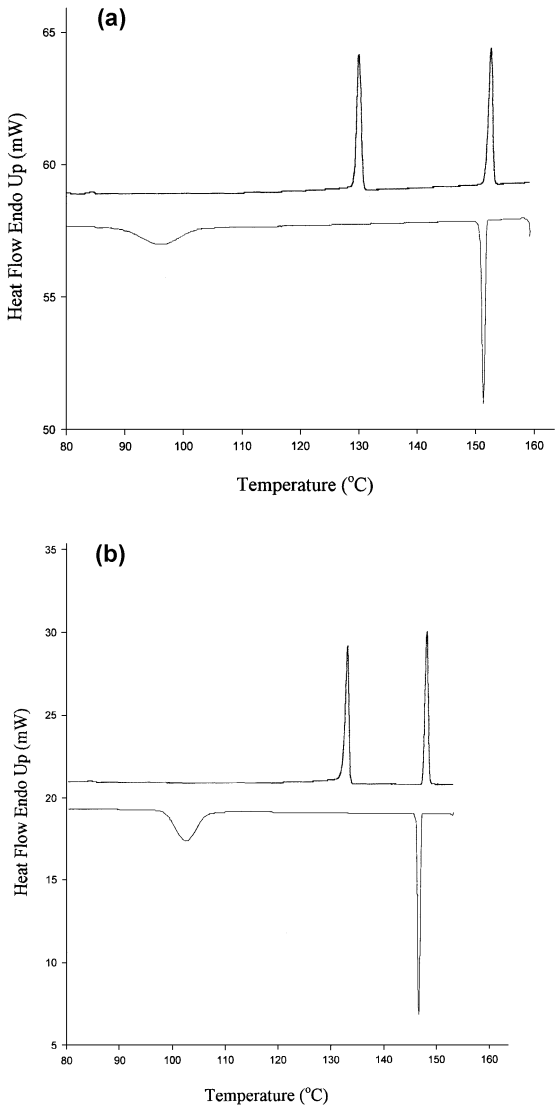


Figure 6. Differential scanning calorimetric thermograms (both heating and cooling cycles) of the banana-shaped compounds; (**a**) compound 2, $n = 11$; (**b**) compound 3, $n = 12$.

indeed columnar. Of course other physical measurements are necessary to identify the structure of the mesophase and we plan to carry out the same.

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