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# Spontaneous Formation of a Chiral Structure in an Achiral Banana-Shaped Molecular System

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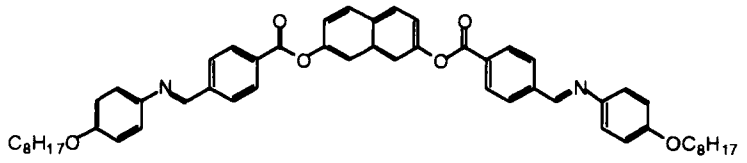
We have synthesized a new banana-shaped compound, having naphthalene as a center of molecule. This compound exhibited an unconventional smectic texture by optical microscopy where the growth of small-fractal domains was observed. Moreover, two different chiral domains were found to form in the smectic phase as well as in the Smblue phase which can be considered to possess a helical structure. The details will be discussed.

*Keywords:* banana-shaped molecule; fractal growth; anisotropy; helical structure

## INTRODUCTION

Helicity has generated much interest in the field of liquid crystal research and has been extensively studied over the past two decades. Many kinds of helical structure have been found and notably, chiral ferroelectric and anti-ferroelectric phases were shown to result from a helical arrangement of the molecules. Recently, Watanabe *et al.* have reported some liquid crystals, the so-called Banana-shaped molecules [**1, 2**]. They proposed the formation of a helical structure which was expected to appear in a high temperature smectic phase by means of electro-optical microscopy when a fringe pattern changed into a fan-shaped texture after applying an electric field. Link and his co-workers [**3**], however, suggested an alternative orientation of the molecules in the smectic layer of this phase in terms of antiferroeletric packing of the bent-core achiral molecules in each smectic layer. Both assumptions, however, allow the appearance of spontaneous polarization of a non-chiral compound. There is still no evidence to describe helical structures in a low temperature smectic phase or Smblue phase at present [**1, 2**]. This prompted us to extensively investigate the other type of banana-shaped molecular system with different mesogenic core as shown below.

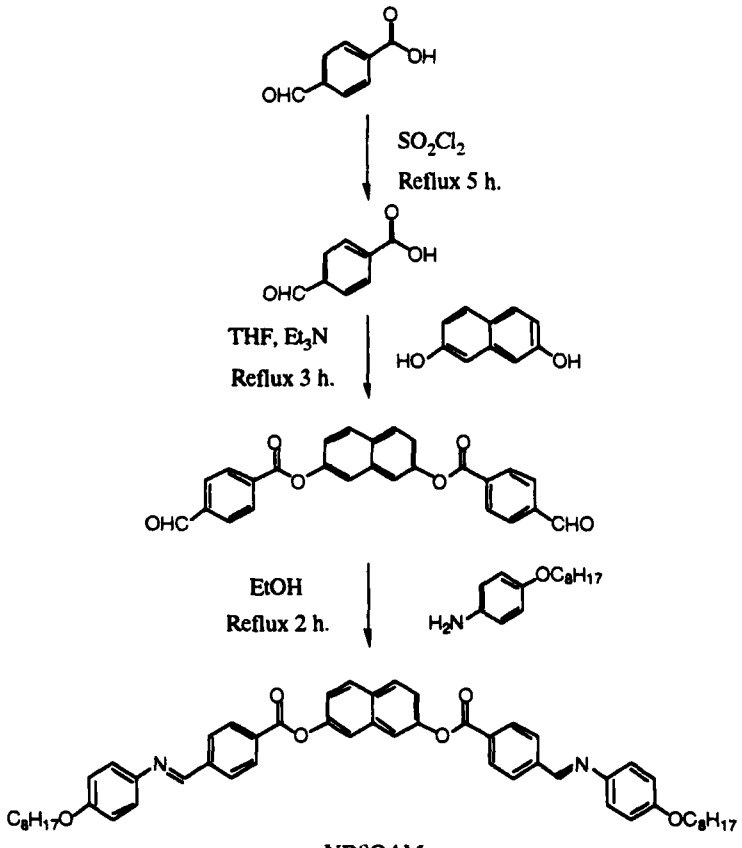


ND8OAM

For this material, we used naphthalene as the molecular core linked to two side wings. The molecules named 2,7-naphthalene bis[4-(4-n-octyloxyphenyliminomethyl) benzoate] (ND8OAM) exhibited an unidentify texture in the high temperature smectic phase as well as a lower temperature Smblue phase, although the structure of the phases could not be determined from these observations. In this report, we observed an appearance of two different chiral domains in both smectic phases by means of optical microscopy and circular dichroic measurement.

## EXPERIMENTAL SECTION

Synthesis of ND8OAM is shown in the following scheme.




ND8OAM

SCHEME Synthesis of ND8OAM

The optical microscopic texture of ND8OAM was examined using a polarizing microscope (Olympus, BH-2) equipped with a hot stage (Mettler FP 80 HT). DSC thermogram data was obtained using a Perkin Elmer DSC2 differential scanning calorimeter. X-ray diffraction

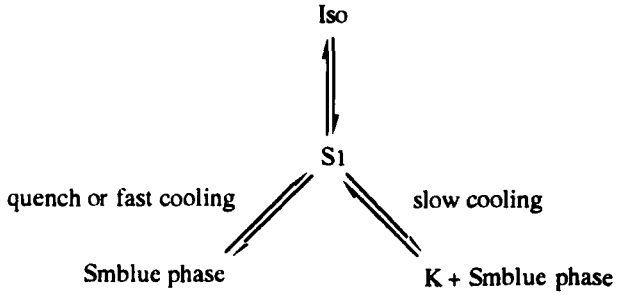
measurement was performed using a Rigaku-R-AXIS (CuKα, 40 kV, 100 mA) and circular dichroic data was obtained using a JASCO, J-720WI circular dichroic spectrometer.

## RESULTS AND DISCUSSION

Transition temperatures and enthalpies of ND8OAM are shown in the Table together with a diagram which shows the transitions of the material.

TABLE Transition temperatures for ND8OAM

| n | Phase transition °C (enthalpy, kJ/mol)<br>Heating<br>Cooling |
|---|---|
| 8 | S1 222 (17.8) I 237 (7.9)<br>S1 232 (8.3) BP & K 205 (14.6) |




Diagram

On cooling (10 °C/min.) from the isotropic state, we observed an occurrence of small-fractal domain at temperature 232 °C which gradually developed and finally coalesced to form an unconventional smectic texture at temperature 227 °C as can be seen in FIGURE 1. It should be noted that the texture displayed a weak birefringence in comparison with a general smectic phase. By rotating the hot stage we could not observe any change in birefringence which suggested the absence of anisotropic effects in the mesophase. Moreover, the texture was somewhat viscous after shearing between glass plates. These observations suggest the formation of a highly ordered mesophase which suggests a helical structure.

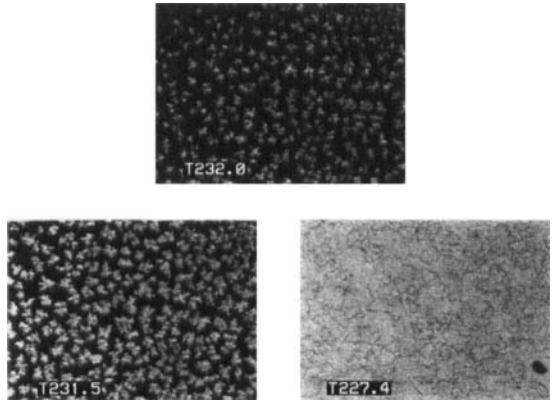



FIGURE 1 Optical microscopic textures of ND8OAM taken in the S1 phase

On further cooling (10 °C/min.) to 205 °C, a transparent Smblue phase appeared with no change of texture and birefringence and was accompanied by the growth of crystals in some regions of texture. On the other hand, crystallization did not occur and only Smblue phase was observed if the cooling rate was 20 °C/min. or faster. Interestingly, both the S1 and Smblue phases exhibited two different domains which can be distinguished by changing the degree of polarizer or analyzer (see FIGURE 2).

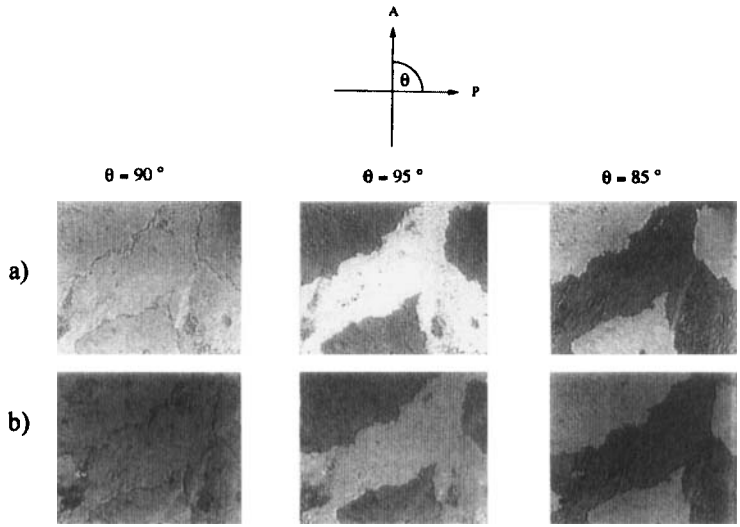



FIGURE 2 Optical microscopic textures of ND8OAM taken in a) S1 and b) Smblue phases, by changing the degree of polarizer

The contrasting colours of the two domains indicates the formation of different chiral domains, possibly helices of opposite handed sense. It should be noted that neither stripes nor finger-print pattern, characteristic of a helical structure, appeared in this texture as it was in the case of 8-P-OIMB [**1, 3**] and other chiral smectic textures. These results imply that the molecular orientation in a layer normal of both smectic phases should have the same macroscopic pattern. However, the X-ray data of S1 phase shows a typical smectic diffraction pattern with two inner sharp reflections corresponding to layer spacings of 40.9 Å and 19.4 Å as well as in the Smblue phase with layer spacings of 48.7 Å, 24.2 Å and 16.4 Å, respectively. A diffuse scattering in the wide angle region at about 4.5 Å was observed in the S1 phase, indicating a liquid-like order within the smectic layer and it intensified in the Smblue phase indicating the highly ordered nature of the phase. According to the proposed molecular orientation in the smectic layer of the banana-shaped molecule in reference [**3**], we would postulate an alignment of the molecules in the smectic layer of our case : 1) the constituent molecules are aligned and tilted with respect to the layer normals in the S1 phase and then the tilt angle decreases in order of decreasing temperature to the Smblue phase as an angle about 35 degree determined from the layer spacings of the S1 and Smblue phases. It should be noted that this value is almost equal to the angle between the highest temperature smectic phase and the Smblue phase in 8-O-PIMB [**2**]; 2) the molecules typically aligned

normal to the layers but the rotation of C-O ester bond caused the distortion and elongation of the length of molecule in the mesophases as proposed in our previous report [4].

To understand an occurrence of the chiral structure, a circular dichroic measurement was carried out in the Smblue phase (FIGURE 3A). The measurements were repeated after heating the sample into isotropic melt and then quenched into Smblue phase.

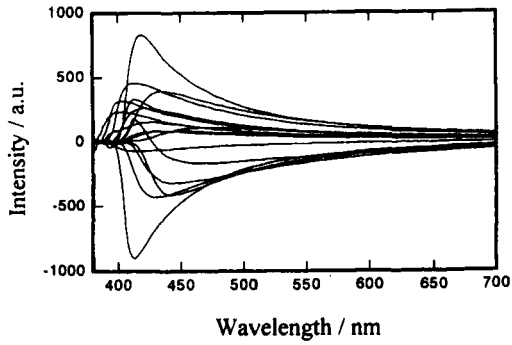



FIGURE 3A CD spectra taken in the Smblue phase, by repeating the experiments

As clearly seen that the peaks wavelength around 420 nm which correspond to the blue reflection colour were detected while an absorption spectrum of this material showed an absorbance at wavelength lower 400 nm. These observation may suggest the existence of a helical structure for this phase.

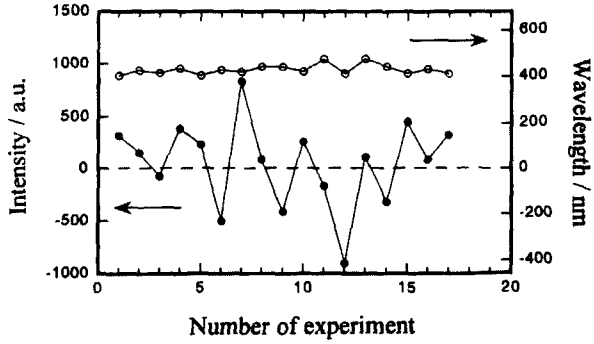



FIGURE 3B Peak wavelength and dichroic ratio obtained for repeated experiments

FIGURE 3B shows a plot of dichroic ratio, wavelength and experiment number and suggest the equal occurrence of right- and left-handed helices. However, to confirm the co-existence of two different domains, the sample was slowly cooled (1 °C/min) from isotropic melt into the S1 phase, to form two large domains, followed by quenching into Smblue phase. Again circular dichroic measurements were carried out. The results are shown in FIGURE 4.

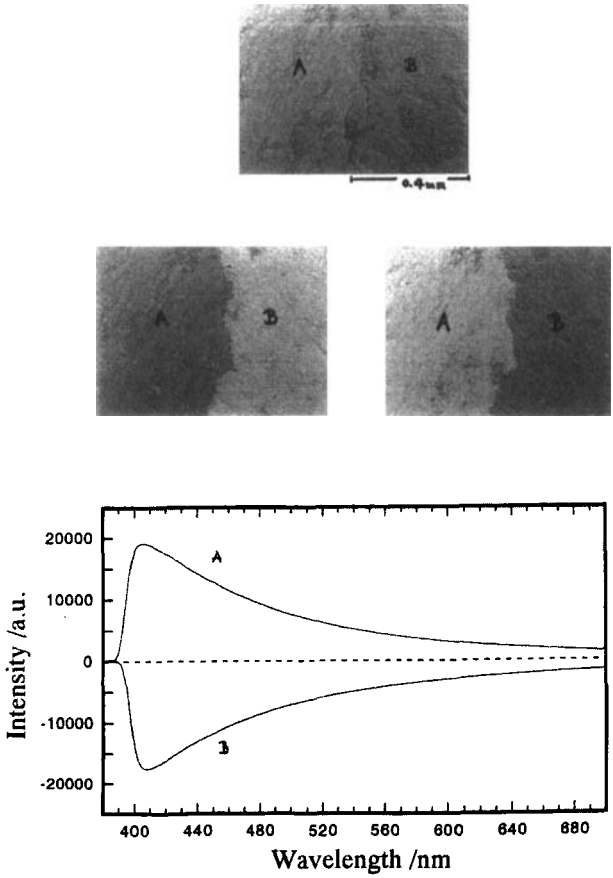



FIGURE 4 Optical microscopic texture and CD spectra taken in the two domains A and B of the Smblue phase

From this result, it is clear that the regions A and B gave opposite signs of dichroic ratio, indicating a difference in the sign of the orientation of a macroscopic structure in these domains. If this is a real occurrence of a helix, we would say that a helical structure is spontaneously formed and two domains of right- and left-handed helices are exhibited simultaneously. Two basic questions arise from this phenomena.

(1) What is the structure of the helix ?

(2) Why is a helical structure form in such molecule?

For the first question, the texture exhibited a very weak birefringence and no anisotropy as mentioned above. This may suggest the formation of a three-dimensional helical structure. For the second question, there are three possibilities which could be taken into account. (1) It maybe different as in case of hindered Naphthalene ketones which can adopt conformations by the rotation of the Ar-CO bond when the energy difference between the twisted ground state and the planar transition state is sufficiently high [5]. If the conformational ground state is maintained in the mesophase in this case, this maybe a driving force for the formation of a helical structure in this material. (2) The twisting power can be induced from the dipole-dipole interaction [6] as was mentioned in the first report about spontaneous formation of helix in achiral molecules [1, 2]. (3) As reported by Heppke [7], an ordering of bent shape molecule by tilting with respect to the layer normal can generate a mirror image so that it would build up an

enantiomorphic structure by chirality [8]. However, we do not have decisive data to clarify the results at the present.

In conclusion, we have synthesized a banana-shaped molecule which does not include a chiral moiety. The molecule exhibited an unconventional smectic texture as well as a Smblue phase. Interestingly, for these liquid crystals a chiral domain which may suggested the occurrence of a helical structure was found to appear in both SI and Smblue phases. Moreover, a distinct co-existence of two domains of right- and left-handed helices was detected under polarizing optical microscopy and circular dichroism. This is an alternative example of the formation of a chiral structure in an achiral molecular system. However, in order to fully understand this phenomena we need more significant data and experiments and our progress will be reported in due course.

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