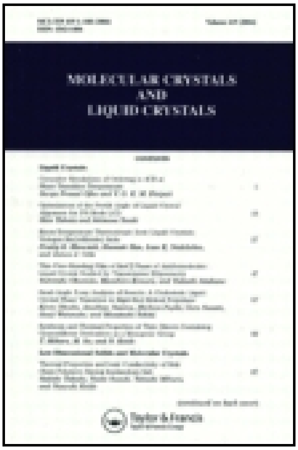

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Dynamics of the Nematic Phase Formed by Achiral Banana-shaped Materials

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DYNAMICS OF THE NEMATIC PHASE FORMED BY ACHIRAL BANANA-SHAPED MATERIALS

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We synthesized a series of achiral non-symmetric banana-shaped compounds. Some of them were found to exhibit a nematic phase. We are strongly interested in this nematic phase composed of the bent molecule. On the basis of the assumption that the dynamics of the nematic phase of the banana-shaped molecules could be much different from the conventional thermotropic nematic phase of the rod-like molecules, we carried out the dynamic light scattering measurement. And we will present the unique phase behaviour of newly synthesised non-symmetric banana-shaped material with dichloro-substituted mesogen.

Keywords: achiral system; biaxial; cholesteric phase; nematic phase; non-symmetric banana-shaped material

INTRODUCTION

We synthesized new series of non-symmetric banana-shaped materials almost which were found to form the B phase as usually expected for the bent shape molecules (this result is reported in another proceedings entitled “Search for the B Phase in an Achiral Non-symmetric Banana-shaped Materials”). Interestingly some of these materials exhibited a nematic phase that was confirmed by the polarised optical microscopy and the X-ray measurement. In the X-ray investigations, no sharp reflection associated with the periodically packing of the molecules was detected. We are strongly interested in the followings.

1. The molecular shape in a nematic state is bent or linear?
2. How are the molecules being packed in the orientational order?

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3. Possibility of the biaxial nematic phase.
4. Dynamics of the banana-shaped molecules are different from the conventional nematic phase?

Its molecular shape sterically hinders both translational motion along the molecular axis and rotational motion, which are most relevant microscopic motion of the fluctuation of the rod-like molecules. Thus, the dynamics of the nematic phase of banana-shaped molecules could be much different from those of the conventional thermotropic nematic phases. These are strongly related to the basic mechanism of interactions in the B phases (B1 – B7). Up to date, some banana-shaped compounds showing nematic phase have been reported [1–3]. However dynamics of the nematic phase of bent molecules have not yet been investigated actually. Therefore it is significantly important to get such information in order to discuss the whole banana-shaped molecular system.

RESULTS

All materials prepared are listed in Figure 1 their transition temperatures are summarized in Table 1. Compound 13 exhibited an interesting mesophase character and it will be presented later. In Figure 2 typical textures of nematic phase formed by an achiral banana-shaped compound are shown. As can be seen in Figure 2(a), $s = \pm 1/2$ defects are dominant over $s = \pm 1$ disclinations. In general, defects of $s = \pm 1$ are preferred in a uniaxial nematic phase due to the energetically low formation. On the contrary, defects of $s = \pm 1/2$ are favoured in a biaxial on since the $s = \pm 1$ defects are not able to relax the defect energy. Therefore the textual observation suggests that the nematic phase of compound 15 is possibly a biaxial phase. On the other hand, Figure 2(b) shows the texture of the nematic phase for compound 18 which exhibits additional B2 phase just below the nematic state. It seems to be very similar to that of the nematic phase of conventional rod-like molecules. From the textural point of view, we could not get exact information about the axiality. The EPR and ^{13}C NMR measurements are now in progress in order to confirm this problem. In the X-ray investigation of the nematic phase, two broad peaks are clearly observed and the outer broad peak originates from the liquid like packing of the molecules perpendicular to the n-director, whereas the inner one reflects the average molecular length. Therefore the molecular shape in the nematic state can be roughly imaged by estimating the X-ray inner broad peak. In Table 2, 1 (estimated from the inner broad peak) and L (calculated from the *all-trans* molecular length) are listed. The values of the all L are somehow about 1.3 times larger than those of l. This result

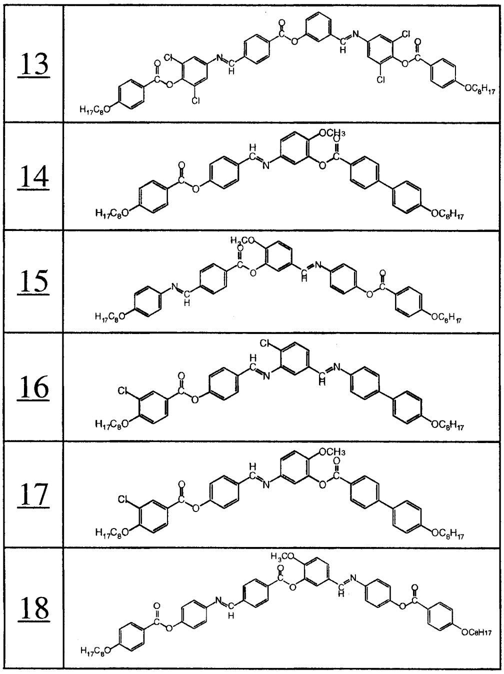


FIGURE 1 Chemical structures of non-symmetric banana-shaped materials exhibiting a nematic phase.

may indicate that the molecular shapes in the nematic state are not linear but still bent. The detailed X-ray investigations using an oriented sample are strongly needed. Then we carried out the dynamic light scattering (DLS) measurement which gives us the information about the microscopic molecular motion. Although the DLS investigation is the powerful method to explore the dynamics of the mesophase, the measurement is significantly dependent on the equipment. For example, the high temperature (over 200°C) is not allowed so that compound 16 could not be investigated. In addition to this problem, the sample which strongly disperses the light is

TABLE 1 Transition Temperatures of this Series

13	Iso. – 143°C – Unique phase – 71°C – K
14	Iso. – 116°C – N – 79°C – K
15	Iso. – 100°C – N – 83°C – SmA – 41°C – K
16	Iso. – 284°C – N – 250°C – SmC – 108°C – K
17	Iso. – 95°C – N – 79°C – B4
18	Iso. – 201°C – N – 162°C – B1 – 56°C – K

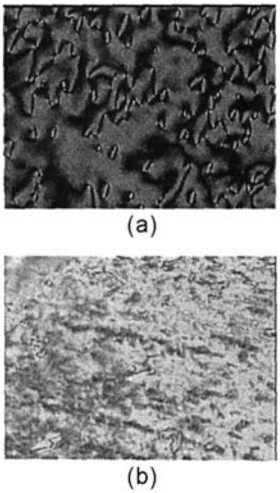
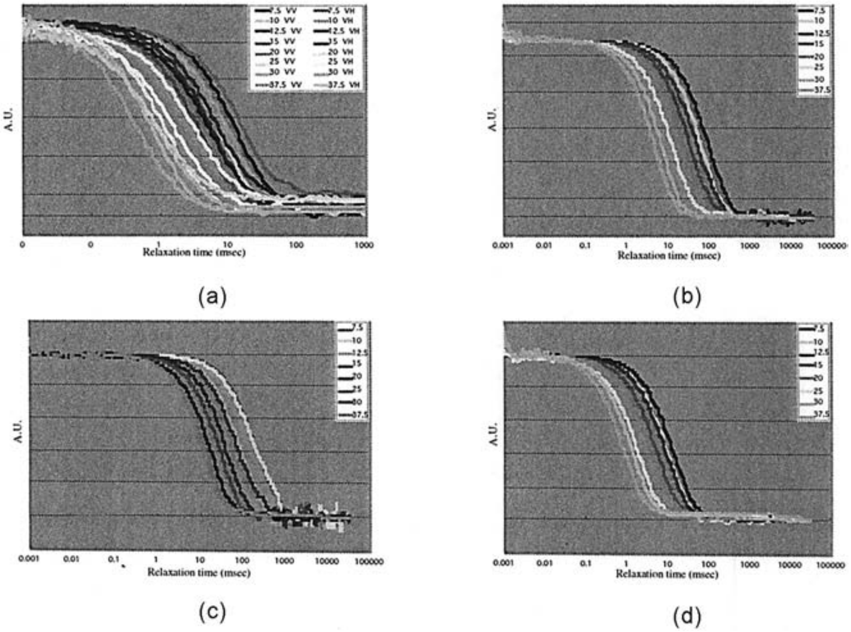


FIGURE 2 Typical textures of nematic phase observed for (a) 15 and (b) 18.

not suitable for the DLS measurement (compound 17). Figures 3 and 4 are the results of the DLS measurements. The former is the auto correlation function which is the plot of the normalized spectra against the relaxation time and the later dispersion relation which is the plot of the relaxation time against the wave number. We collected the DLS data with changing the angle of the incident beam. It is the general trend that the relaxation time decreases with increasing the angle between the incident beam and the sample. As can be seen in Figure 4, the relaxation time is proportional to the wave number and the slope of the line is almost -2 for all samples. This result indicates that the microscopic motion of molecules is the diffusive mode similar to the conventional rod-like molecule such as 5CB. It is noticeable that for compounds 14 and 15 the values of the extrapolation for the relaxation time are very large (380 and 810 msec, respectively) in

TABLE 2 Estimated (l) and *all-trans* (L) Molecular Length

Compound	l (Å)	L (Å)
14	33	45.8
15	36.6	47.7
17	34.5	45.8
18	41.6	52.4



(a) (b)

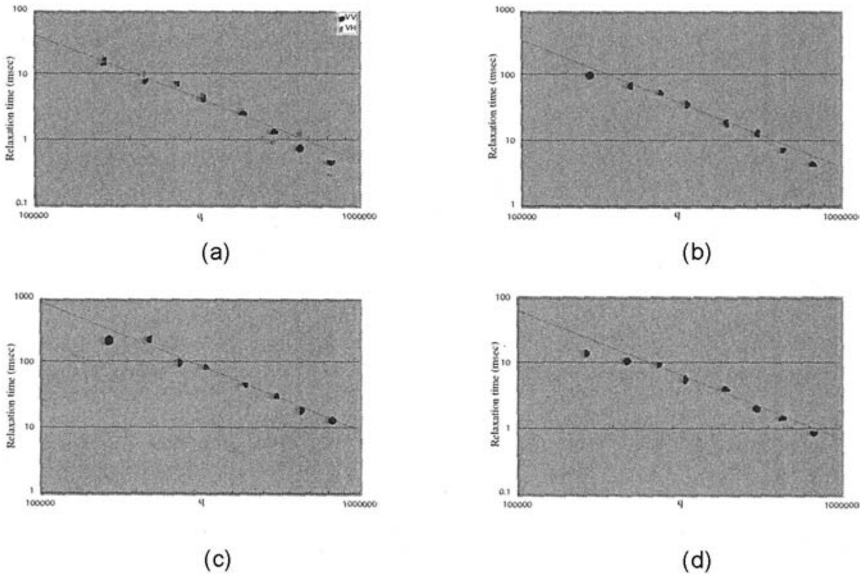
(c) (d)

FIGURE 3 Auto correlation function measured for (a) 13, (b) 14, (c) 15 and (d) 18.

comparison with the 5CB (∼10 msec). This indicates that the nematic phase of compound 14 and 15 shows a low elasticity or a high viscosity. Therefore the individual measurement is strongly needed in order to dissolve this problem. While on the other hand those of compound 13 and 18 are comparable to the conventional nematic phase, although they are still 4 or 6 times slower than that of 5CB.

INTERESTING TOPIC——COMPOUND 13

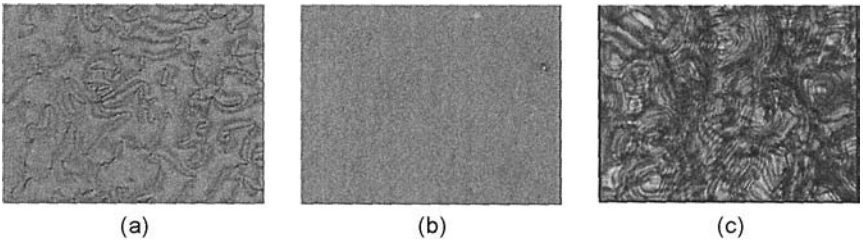
We would like to report here the interesting mesophase behaviour observed for compound 13. Strangely this compound exhibited a cholesteric-like character in spite of an achiral system. In Figure 5, the typical textures of this phase are shown. Interstingly the polarised optical textures are strongly dependent on the sample preparation. In non-treated glass cell, the schlieren texture was observed as usually can be seen in nematic state (Fig. 5(a)). However in the case of the surface treated cell the situation was much different from the case of non-treated glass. Figure 5(b) and (c) show the textures observed in homogeneous and homeotropic



(a) (b) (c) (d)

FIGURE 4 Dispersion relation observed for (a) 13, (b) 14, (c) 15 and (d) 18.

alignment cell, respectively. In the homogeneous geometry, the coloured monodomain was exclusively obtained (green in Fig. 5(b)) and this colour was sensitively dependent on the temperature (see Fig. 6(a)). Figure 6(b) shows the dependence of the spectra of the transmitted light on the sample rotation. As can be seen this graph, the spectra are independent of the rotation angle. This result strongly confirms that the colour does never result from the retardation of light but originates from some kind of macro structure such as helix. Figure 5(c) shows the droplet on the homeotropically aligned glass and it looks like very much a fingerprint of a cholesteric phase. The pitch could be estimated as about 14–15 μm from this



(a) (b) (c)

FIGURE 5 Textures of compound 13 observed in (a) non-treated glass plates, (b) homogeneously aligned cell and (c) droplet on the homeotropically aligned cell.

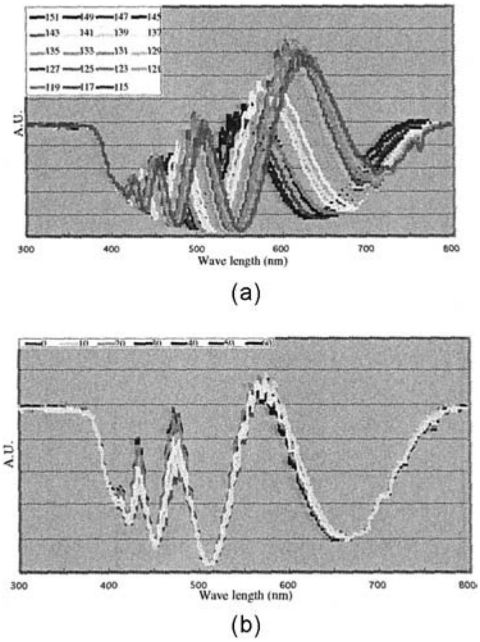


FIGURE 6 The spectra of the transmitted light of (a) temperature dependence and (b) sample rotation.

texture. Therfore the situation is very much similar to the TN cell in which the pitch is larger than the cell gap. Then on the basis of the assuption that cell geometry is the same as the TN cell (Fig. 7), we calculated the pitch (P) from the following formula,

$$P = (360/\theta) \bullet d.$$

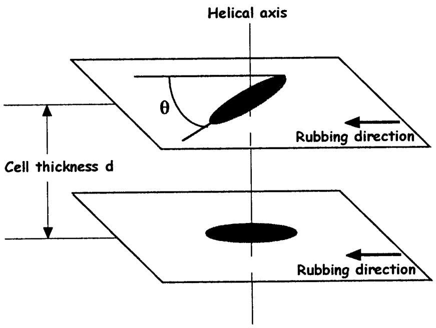


FIGURE 7 Representation of the twist angle.

TABLE 3 List of the Observed Twist Angle (θ) and the Calculated Pitch (P)

Cell thickness (μm)	θ (°)	P (μm)
3	80	13.5
4	105	13.7
5	110	16.3
10	265	13.6

Here θ is the optical rotation angle, d is the cell thickness. The calculated pitch (P) is listed in Table 3. These values are comparable to the experimental result obtained from the texture, although for the 5 μm cell it is slightly larger. It is emphasised that the spontaneous twisting along the molecular normal appears in an achiral system. Now we are planning to detect the helical sense and to consider the origin of the twisted macro structure. We observed the helical structure in an achiral nematic phase and this phenomena is the strong evidence that the origin of the chirality in the banana-shaped molecular system, such as ferro/antiferroelectricity and twisted structure in B4/B7 phases, is deeply related to the twist conformation of the molecule proposed by Watanabe group [4–8] as well as the spontaneous symmetry breaking by tilting [9].

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