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Mesomorphic behaviour in bent-shaped molecules with side wings at different positions of a central naphthalene core

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Six bent-shaped molecules were prepared with central bent cores based on 2,7-, 1,7-, 1,6-, 1,3-, 1,2- and 2,3-dihydroxynaphthalene groups with side wings containing a Schiff's base moiety and dodecyloxy tail, N(2,7), N(1,7), N(1,6), N(1,3), N(1,2) and N(2,3). All of the compounds form fluid smectic mesophases and their mesomorphic behaviour and properties are discussed in terms of their molecular structure. The compounds are categorized into two groups; in one of them, N(2,7), N(1,6) and N(1,3), the bent cores have a bent angle of 120° between the side wings, whereas in the other, N(1,7), N(1,2) and N(2,3), the bent angle is 60°. The typical banana molecule, N(2,7), in the first group, forms a chiral blue phase that shows two distinguishable domains with opposite optical rotations and circular dichroism. Under an electric field, the chiral blue phase is transformed to strongly birefringent B2 phase which possesses a basically homochiral SmC_AP_A structure. N(1,3) also forms a chiral blue phase, but, in contrast, N(1,6), where the side wings are asymmetrically substituted, forms a typical antiferroelectric B2 phase with the racemic SmC_SP_A structure. N(1,2) and N(2,3) of the other group assume a U-like shape to form a conventional SmA phase. Of interest is the fact that N(1,7) forms a chiral blue phase irrespective of having a small bent angle of 60°. This indicates that the distance between side wings as well as the bent angle plays an important role for the formation of banana-shaped smectic phases.

1. Introduction

Since Niori *et al*. [1] discovered that achiral bent-shaped molecules (so-called banana molecules) can form banana phases with a unique polarity and chirality, their mesomorphic properties have been extensively studied in relationship to their chemical structure by preparing numerous series of banana molecules [2–5]. The banana molecules form unusual smectic mesophases differing from the conventional smectic phases so far observed in classical rod-like molecular system. Thus, banana liquid crystals have become a new field in liquid crystal science.

The banana smectic phases have been designated B1–B7 phases. Among these phases, the most widely investigated phase is the B2 phase. Since the molecules in the B2 phase are tilted to the layer, four types of structure differing in chirality and polarity are formed. These are distinguished using the nomenclature $SmC_{S\text{ or }A}P_{F\text{ or }A}$. Here, the first two subscripts, S and A, specify syn- or anticlinicity, respectively, which mean the correlation of molecular tilt to the layer. The second pair of subscripts, F and A, specify ferro- or antiferroelectricity, respectively, depending on polar correlation between adjacent layers. According to the switching current and optical microscopic measurements, most of them exhibit antiferroelectric switching in the ground state [6–9], and their switching properties have been exploited for potential use in device applications.

The B4 phase has been extensively studied as well from the viewpoint of system chirality. The remarkable feature of the B4 phase is that it exhibits very low birefringent domain textures that are composed of the two distinguishable domains with opposite optical rotations (ORD). In addition, these two domains exhibit distinct circular dichroism (CD) with opposite sign [10–14].

From the viewpoint of chemical structure, the structure–property relationship in bent-core molecules is a very important factor for the system of the mesophase and development of polar order and chirality [15]. Thus, the variation of the central bent cores as well as the diversity of the terminal alkyl chains and linking groups can cause a considerable change of the molecular shape [16–22], which decides whether a banana phase or conventional smectic phase

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is constituted. For this reason, many approaches have been performed by introducing substituents into the central core. For example, halogen, nitro, methoxy and methyl functional groups have been attached to different positions of the central core [23–27]. However, most of the central cores used for a long time for preparation of banana-shaped molecules are resorcinol derivatives substituted at the 1,3-positions, and a large number of studies are still considering resorcinol derivatives. On the other hand, Matsuzaki *et al.* [28, 29] reported the mesomorphic behaviour of 1,2-phenylene and 2,3-naphthylene compounds, but these compounds only form the classical nematic and/or smectic phases. Recently, several attempts to introduce new central core units have been reported [30, 31]. Watanabe and co-workers [13, 32] reported a novel series of banana molecules with a central core based on a 2,7-dihydroxynaphthalene unit, N(2,7)-*n*-O-PIMB, and demonstrated the appearance of distinct formation of helical or chiral banana phases [13, 14]. Subsequently, dihydroxynaphthalene-2,7- was introduced as a new type of central core unit, preserving the bent angle at 120° [15, 33, 34].

In this paper, we report the preparation of six molecules with central naphthalene cores where typical Schiff's based side wings are substituted on 2,7- 1,7-, 1,6-, 1,3-, 1,2- and 2,3-positions. The effects of the substituent positions on the mesomorphic behaviour and structures are discussed.

2. Experimental

2.1. *Measurements*

Texture observations were made under crossed polarization using polarizing optical microscopy (POM) on an Olympus BX50 equipped with a temperature-controlled Mettler Toledo FP 82 hot stage. Transition temperatures were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 calorimeter. Electro-optical switching behaviour was observed using a high-speed voltage amplifier (FLC Electronics, F20A) connected to function generator (NF Electronic Instruments, WF 1945A). The sample was sandwiched between glass substrates with ITO electrodes and the thickness was 5.5 μm. The polarization reversal current was measured by applying a triangular wave voltage. Circular dichroism (CD) data were collected using a JASCO J-720WI CD spectrometer. X-ray diffraction measurements were performed using a Rigaku-Rint-2000 diffraction with Cu K_α radiation.

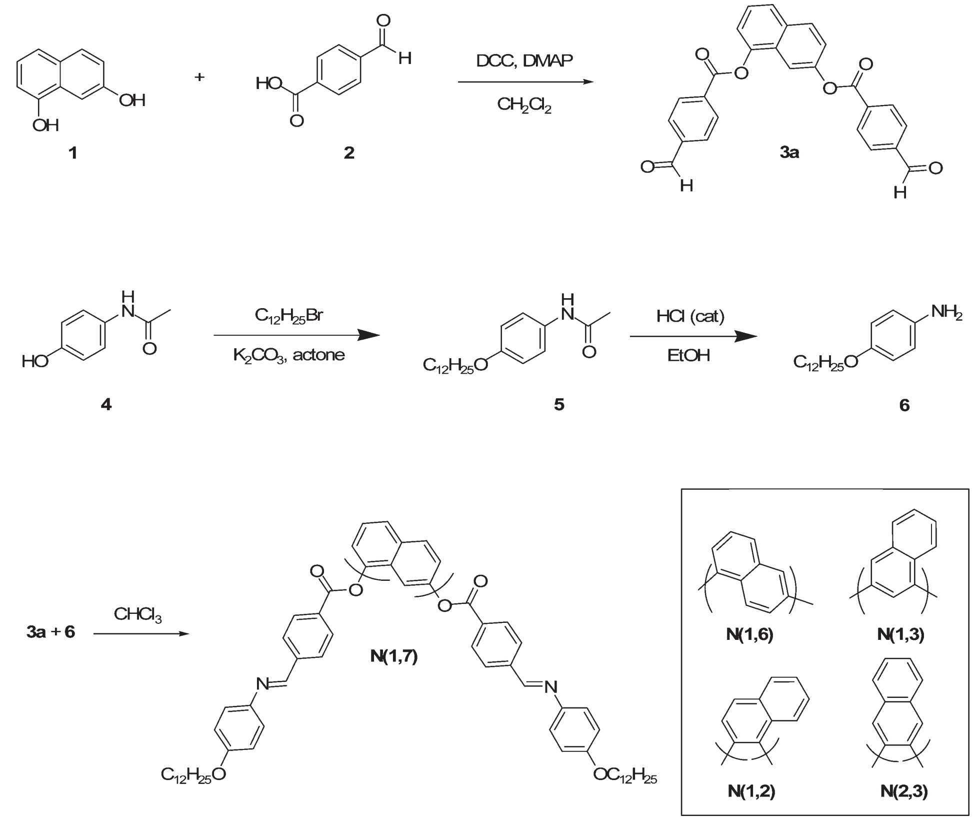
2.2. *Synthesis*

Scheme 1 outlines a typical synthetic route leading to the banana-shaped liquid crystals. The synthetic routes to the target compounds are as follows. Dialdehyde **3** was prepared from commercially available dihydroxynaphthalene **1** and the final product from **4** was obtained using procedures described by Thisayukta *et al.* [13]. All reagents were purchased from TCI (Tokyo Kasei Kogyo Co, Ltd) and used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, 230–400 mesh). ^{1}H NMR spectra were recorded on a JEOL FT-NMR AL 400 (400 MHz) spectrometer using chloroform as an internal standard. Elemental analysis was determined by CHNS-932 and VTF-900.

2.2.1. Synthesis of dialdehydes, 3. To a solution of 1,7-dihydroxynaphthalene **1** (0.50 g, 3.12 mmol) in CH_2Cl_2 (20 ml) was added 1,3-dicyclohexylcarbodiimide (1.61 g, 7.80 mmol), 4-dimethylaminopyridine (0.95 g, 7.80 mmol) and 4-formylbenzoic acid **2** (1.03 g, 6.86 mmol). The mixture was stirred at room temperature two days. After filtration to remove precipitated materials, the filtrate was separated by chromatography on silica gel (CH_2Cl_2) and then recrystallized from dichloromethane/ethanol to give **3a** (0.95 g, 72%) as a white solid. **3b**, **3c**, **3d**, and **3e** were similarly prepared in 65%, 48%, 32% and 60% yield, respectively. For **3a**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–8.07 (m, 6H), 8.36 (d, J=8.4 Hz, 4H), 8.48 (d, J=8.4 Hz, 4H), 10.13 (s, 1H), 10.15 (s, 1H). For **3b**, ^{1}H NMR δ 7.39–8.10 (m, 6H), 8.41 (d, J=8.4 Hz, 4H), 8.50 (d, J=8.4 Hz, 4H), 10.16 (s, 1H), 10.18 (s, 1H). For **3c**, ^{1}H NMR δ 7.43–8.09 (m, 6H), 8.40 (d, J=8.4 Hz, 4H), 8.48 (d, J=8.4 Hz, 4H), 10.15 (s, 1H), 10.17 (s, 1H). For **3d**, ^{1}H NMR δ 7.53–7.99 (m, 6H), 8.25 (d, J=8.4 Hz, 4H), 8.50 (d, J=8.4 Hz, 4H), 10.16 (s, 1H), 10.18 (s, 1H). For **3e**, ^{1}H NMR δ 7.55–7.57 (m, 2H), 7.88–7.91 (m, 4H), 8.25 (d, J=8.0 Hz, 8H), 10.0 (s, 2H).

2.2.2. Synthesis of *N*-(4-dodecyloxyphenyl)acetoamide, 5. A mixture of 4-acetoamidophenol **4** (2.00 g, 13.2 mmol), 1-bromododecane (3.95 g, 15.8 mmol) and potassium carbonate (5.09 g, 36.9 mmol) in acetone (40 ml) was heated under reflux 12 h. To this solution was added water (50 ml) and the product was extracted with diethyl ether (30 ml × 3). The combined organic layers were dried (Na_2SO_4), concentrated and recrystallized from ethanol to give **5** (2.62 g, 62%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=7.2 Hz, 3H), 1.26–1.79 (m, 20H), 2.14 (s, 3H), 3.91 (t, J=6.4 Hz, 2H), 6,83 (d, J=8.8 Hz, 2H), 7.15 (br s, NH), 7.36 (d, J=8.8 Hz, 2H).

2.2.3. Synthesis of 4-dodecylphenylamine, 6. An ethanol (35 ml) solution of **5** (2.60 g, 8.13 mmol) and a



Scheme 1. Typical synthetic route leading to banana-shaped liquid crystals. N(2,7) was synthesized using procedures described previously [13].

catalytic amount of concentrated HCl was stirred at 70°C. After one day, the solvent was evaporated *in vacuo*; saturated $NaHCO_3$ (30 ml) was added to the residue. The mixture was extracted with diethyl ether (30 ml × 3); the combined ether extract was dried (Na_2SO_4) and concentrated to give **6** (2.18 g, 97%). ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=7.2 Hz, 3H), 1.26–1.76 (m, 20H), 3.39 (br s, NH_2), 3.86 (t, J=6.4 Hz, 2H), 6,62 (d, J=8.8 Hz, 2H), 6.73 (d, J=8.8 Hz, 2H).

2.2.4. Synthesis of 1,7-naphthalenebis[4-(4-dodecyloxyphenyliminomethyl)]benzoates. A solution of **6** (0.72 g, 2.59 mmol) and dialdehyde **3a** (0.50 g, 1.17 mmol) in chloroform (25 ml) was heated under reflux for 3 h. The reaction mixture was concentrated and recrystallized from chloroform/ethanol to give a yellow crystal of N(1,7) (0.90 g, 81%). Target compounds N(1,6), N(1,3), N(1,2) and N(2,3) were similarly prepared in 92%, 67%, 87% and 63% yield, respectively.

For N(1,7), ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.6 Hz, 6H), 1.26–1.81 (m, 40H), 3.98 (t, J=6.4 Hz, 4H), 6.93–8.01 (m, 18H), 8.29 (d, J=8.4 Hz, 2H), 8.40 (d, J=8.4 Hz, 2H), 8.56 (s, 1H), 8.58 (s, 1H). Elemental analysis: calculated for $C_{62}H_{74}N_2O_6$, C 78.95, H 7.91, N 2.97, O 10.18; found, C 79.21, H 8.02, N 3.11, O 10.26%.

For N(1,6), ^1H NMR δ 0.80 (t, J=6.8 Hz, 6H), 1.19–1.75 (m, 40H), 3.90 (t, J=6.4 Hz, 2H), 3.91 (t, J=6.4 Hz, 2H), 6.85–8.01 (m, 18H), 8.24 (d, J=8.4 Hz, 2H), 8.33 (d, J=8.4 Hz, 2H), 8.49 (s, 1H), 8.52 (s, 1H). Elemental analysis: calculated for $C_{62}H_{74}N_2O_6$, C 78.95, H 7.91, N 2.97, O 10.18; found, C 78.30, H 8.04, N 3.06, O 9.78%.

For N(1,3), ^1H NMR δ 0.88 (t, J=7.2 Hz, 6H), 1.24–1.80 (m, 40H), 3.992 (t, J=6.4 Hz, 2H), 3.997 (t, J=6.4 Hz, 2H), 6.94–8.10 (m, 18H), 8.33 (d, J=8.4 Hz, 2H), 8.41 (d, J=8.4 Hz, 2H), 8.59 (s, 1H), 8.61 (s, 1H). Elemental analysis: calculated for $C_{62}H_{74}N_2O_6$, C 78.95, H 7.91, N 2.97, O 10.18; found, C 78.71, H 7.71, N 3.11, O 10.18%.

For N(1,2), ^1H NMR δ 0.88 (t, J=6.8 Hz, 6H), 1.26–1.80 (m, 40H), 3.96 (t, J=6.4 Hz, 2H), 3.97 (t, J=6.4 Hz, 2H), 6.89–7.94 (m, 18H), 8.16 (d, J=8.4 Hz, 2H), 8.48 (d, J=8.4 Hz, 2H), 8.53 (s, 1H), 8.61 (s, 1H). Elemental analysis: calculated for $C_{62}H_{74}N_2O_6$, C 78.95, H 7.91, N 2.97, O 10.18; found, C 78.73, H 8.13, N 2.95, O 10.20%.

For N(2,3), ^1H NMR δ 0.88 (t, J=7.2 Hz, 6H), 1.26–1.82 (m, 40H), 3.96 (t, J=6.4 Hz, 4H), 6.90 (d, J=8.8 Hz, 4H), 7.23 (d, $J=8.8$ Hz, 4H), 7.52–7.89 (m, 10H), 8.16 (d, $J=8.4$ Hz, 4H), 8.48 (s, 2H). Elemental analysis: calculated for $C_{62}H_{74}N_2O_6$, C 78.95, H 7.91, N 2.97, O 10.18; found, C 78.57, H 7.93, N 2.96, O 10.16%.

3. Results

The banana-shaped molecules with central bent cores based on 2,7- 1,7-, 1,6-, 1,3-, 1,2- and 2,3-dihydroxynaphthalene units and side wings containing a Schiff's base moiety (see scheme 1) are denoted by N(2,7), N(1,7), N(1,6), N(1,3), N(1,2), and N(2,3), respectively. All the compounds exhibited enantiotropic transitions. Table 1 summarizes the transition temperatures and associated enthalpy changes for these compounds, which were determined using DSC in conjunction with POM.

N(2,7) is one of the typical symmetrical banana molecules. As reported previously, it shows three mesophases on cooling [13]. The highest temperature B2* phase exhibits a broad outer reflection so that the layer is constructed by liquid-like packing of molecules as in the well-known B2 phase. N(1,6) possesses a similar bent angle to N(2,7), but has asymmetric side wings. It forms a typical B2 phase on cooling from an isotropic liquid, which is accompanied by a transition with high transition enthalpy and a second transition with low transition enthalpy. The latter two phases may be crystalline. N(1,7) and N(1,3) exhibit a transition from isotropic liquid to the B2*-like phase that is not followed by crystallization under any conditions. N(1,2) and N(2,3) form the typical smectic A (SmA) phase on cooling from an isotropic liquid and then transform to a crystalline phase. Thus, all the compounds form a well-defined fluid mesophase at a temperature region just below the isotropic melt, although the types of mesophase depend on the structure of central core. A more detailed structural description of the mesophases in each compound will be given below.

We first refer to the highest temperature B2* phase of symmetrical N(2,7). This B2* phase is interesting since it shows an unconventional texture. Several small fractal nuclei initially appear from the isotropic melt on cooling, and gradually associate into large domains. The texture of each domain exhibits a very weak birefringence and no anisotropy, as shown in figure 1a. The neighbouring domains of the B2* phase separated by a clear boundary show opposite ORD and CD. The maximum peak of CD is observed at around 400 nm and simultaneously the blue colour is observed by naked eyes. For these reasons, this phase is called a chiral blue phase. X-ray patterns show an outer broad reflection at around 4.5 Å and an inner layer reflection with a spacing of 44.8 Å. Thus, the molecules are packed into a layer with a liquid-like nature. From the layer spacing, the tilt angle is estimated to be about 40° [13]. The B2* phase hence is considered to have the same packing nature as the B2 phase, and to possess the helical structure induced in each layer like the twisted grain boundary phase [35]. These weakly birefringent chiral domains are altered to the strongly birefringent fan-shaped domains on application of external electric field, as shown in figure 1b. This indicates the transformation of the chiral blue phase to the well-known B2 phase. In this fan-shaped texture, the light extinction directions are along the polarizer in the field-off state, whereas in the field-on state the extinction directions are inclined from the polarizer. Moreover, the switching current behaviour on applying a triangular wave electric field reveals two switching current peaks in a half cycle, meaning that this phase is antiferroelectric. Thus, the field-induced B2 phase was found to possess a homochiral SmC_AP_A structure from its electro-optical behaviour, the details of which will be reported elsewhere [36], together with related studies [37–39]. In the B4 phase two chiral domain textures are retained completely.

In N(1,6), the typical B2 phase appears as strongly birefringent domains in a circular shape on cooling from the isotropic liquid phase (figure 2a). This phase exhibits distinct switching behaviour in an applied electric field. By applying a rectangular-wave field, the

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in brackets) of bent-shaped compounds with a naphthalene core (based on cooling data).

	Cr_1	Cr_2	B4	$B4^f$	B2*	B2	SmA	I
N(2,7)	–	–	• 170.0 (8.11)	• 196.9 (27.7)	• 224.0 (18.9)	–	–	•
N(1,6)	• 95.8 (2.79)	• 130.1 (9.91)	–		–	• 193.5 (25.4)	–	•
N(1,3)	–	–	• 121.9 (22.0)	–	–	–	–	•
N(1,7)	–	–	• 145.7 (27.4)	–	–	–	–	•
N(1,2)	• 84.4 (11.3)	–	–		–	–	• 151.6 (5.34)	•
N(2,3)	• 72.2 (8.99)	–	–		–	–	• 244.3 (6.52)	•

$B4^f$ is a B4 phase with a frustrated structure. In B2* the superscript * indicates a mesophase with domains of opposite chirality sense whereby the molecules themselves have achiral configurations [15].

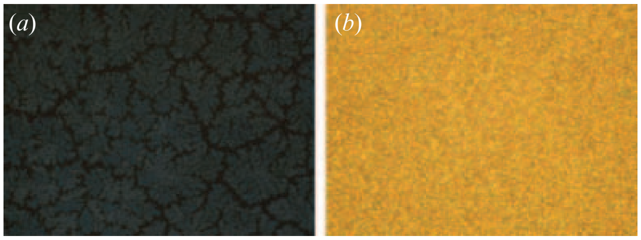


Figure 1. (a) Photomicrograph of the characteristic domain textures observed for the chiral blue phase of N(2,7). Textures show very weak birefringence, but a clear boundary under crossed polarizer. As can be detected by the rotation of the polarizer or analyser from the perfect cross position, each domain possesses chirality, the sign of which is opposite between the neighbouring domains. (b) By applying an external electric field above a threshold, an antiferroelectric switching behaviour is observed and, simultaneously, texture transformation occurs in the entire area. The resulting texture is grainy, but highly birefringent.

fan-shaped textures are well developed to a relatively large size, as shown in figure 2b. For this developed texture, we can recognize that extinction brushes appear parallel to the polarizers upon application of a field and that the characteristic stripe domains appear in the field-off state. By applying a triangular wave electric field, two switching current peaks are observed in a half cycle, as shown in figure 3, meaning that this phase is also antiferroelectric. Thus, the B2 phase in N(1,6) has the racemic SmC_SP_A structure as its ground state, and electro-optical switching takes place between SmC_SP_A and SmC_AP_F.

The layer spacing of the B2 phase is 44.8 Å, which is the same as that of the B2* phase of N(2,7). Hence, the tilting of the molecules is significant. On cooling the B2 phase to the lower temperature phase, only a change of birefringence is observed without significant change of texture. It does not switch in an applied electric field. There is no apparent difference between this intermediate phase and the lowest temperature crystal phase by texture observation, although an obvious transition peak is observed by DSC measurements. Moreover, a layer spacing of 50 Å was observed for both phases. Thus, we conclude that the two phases existing at the lower temperature region below the B2 phase are crystalline.

It is interesting that compounds N(1,7) and N(1,3) exhibit a chiral blue phase, as in N(2,7). This can be observed from the microscopic textures in figure 4. To confirm the generation of chiral domains, a CD measurement was carried out. Figure 5 shows the CD spectra observed for N(1,7) (solid curves) and N(1,3) (dashed curves). Here, large domains are formed by gradual development of a few nuclei due to very slow cooling from the isotropic liquid at 0.5°C $\min^{-1}$ and the focused light was irradiated on each domain. The distinct CD peaks from the adjacent domains are

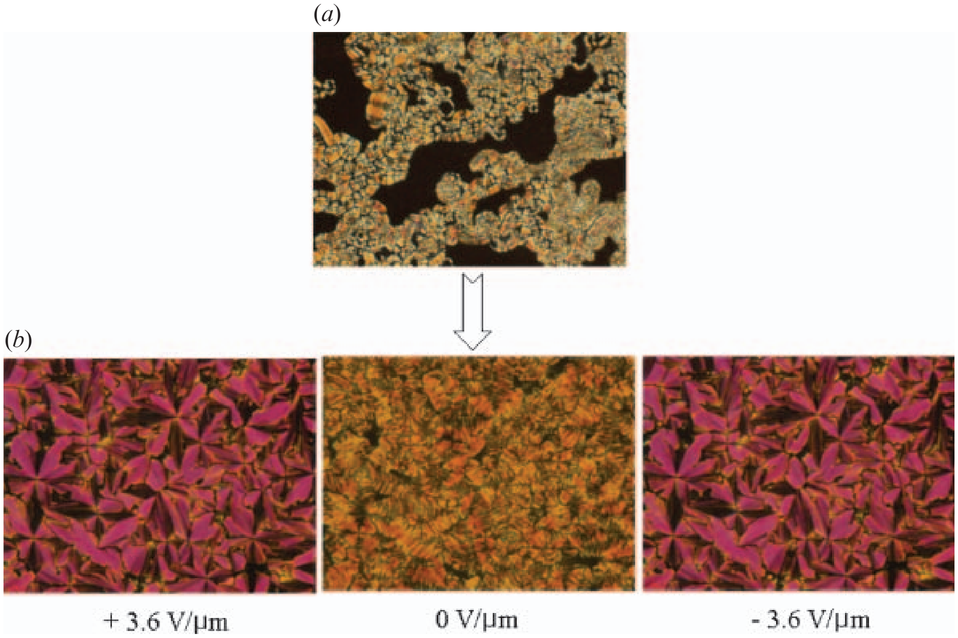


Figure 2. (a) Photomicrograph of the typical B2 phase of N(1,6) with strong birefringent domains in a circular shape, which appears from the isotropic melt on cooling. (b) Switching behaviour under the application of an electric field. It is found that circular domains of SmC_SP_A ($E=0\,V\,\mu m^{-1}$) switch to SmC_AP_F under a field of $\pm 3.6\,V\,\mu m^{-1}$ (5.5 μm thick cell).

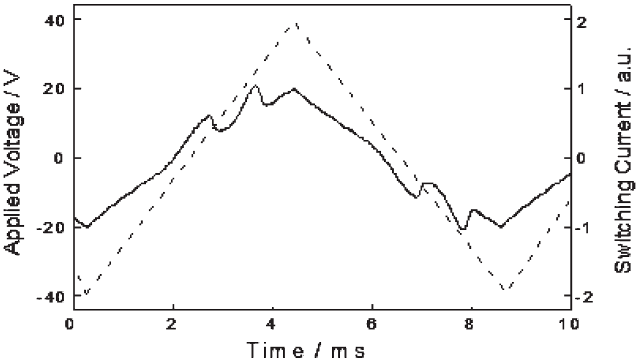
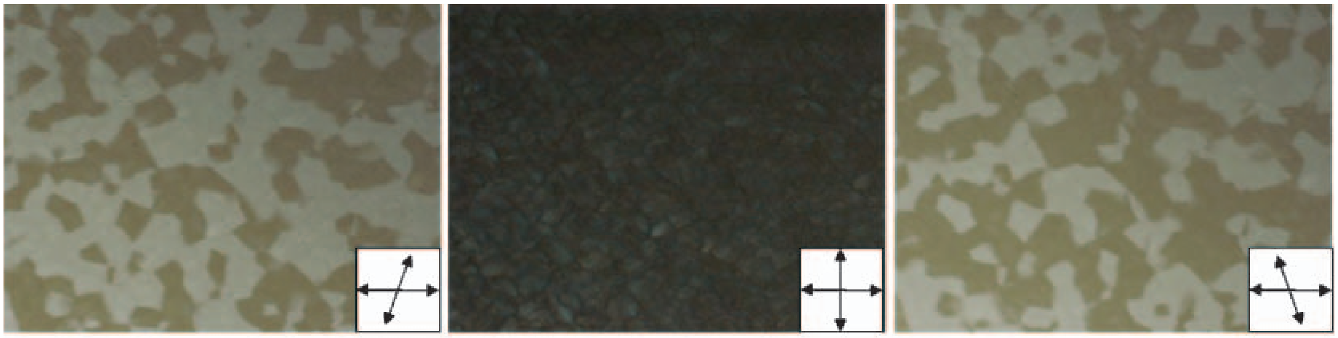


Figure 3. Polarization reversal current in the B2 phase of N(1,6) at 160°C under the application of 78 V_{pp} triangular wave voltage of 24 Hz (5.5 μm thick cell).

observed with opposite signs with a maximum peak around 440 nm. These results are obviously the same as those observed in the chiral blue phase of N(2,7).

The X-ray pattern indicates a broad outer hallow at around 4.5 Å, showing the liquid-like packing within a layer. The layer spacings for N(1,7) and N(1,3) are 33.2 Å and 39.1 Å, respectively. The fairly small layer spacing for N(1,7) is reasonable because the bent angle between the side wings is 60°, whereas it is 120° for N(1,3). Both of the chiral blue phases do not switch by applying an electric field, probably because of their high viscosity.

N(1,2) and N(2,3) form a SmA phase, as for conventional rod-like molecules. When N(1,2) is slowly cooled down from the isotropic liquid phase, the batonnets texture first appears and then grows up to the focal-conic fan texture of the SmA phase, as shown in figure 6a. In a homeotropic sample aligned by shearing, the texture becomes completely dark (figure 6b). On further cooling, the SmA phase directly transforms to a crystalline phase. The symmetric compound, N(2,3), also shows the same phase sequence, i.e. isotropic–SmA–crystal. The temperature range of the SmA phase in N(2,3) is wider than that of N(1,2) because of better packing efficiency. The SmA layer spacings of N(1,2) and N(2,3) are 32.9 Å and 35.7 Å, respectively. These spacings are as expected for these molecules of U-like shape. In other words, the SmA liquid crystals in these compounds are formed with the bent direction of molecules aligned perpendicular to the layer.



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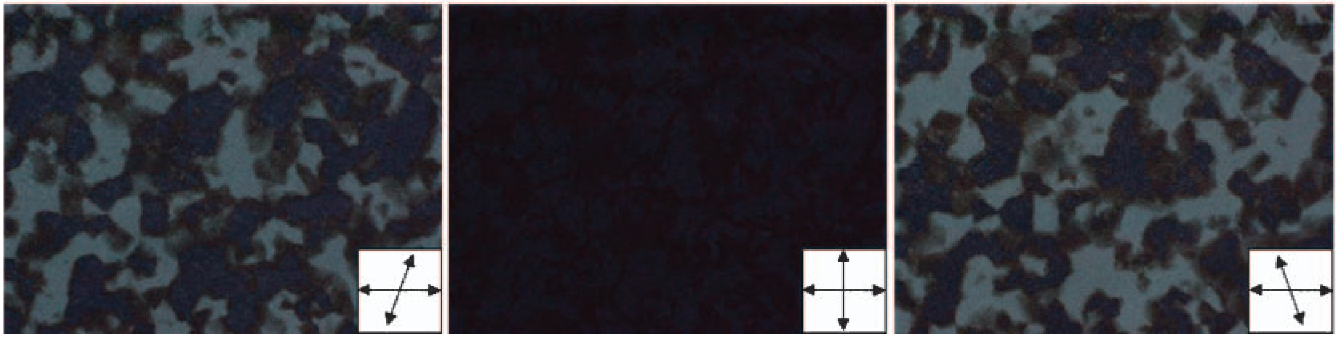

(*b*)

Figure 4. Microphotographs of chiral blue phases observed for (a) N(1,7) and (b) N(1,3). Under the cross polarization, weakly birefringent textures are observed, but two different domains with opposite sign of optical rotation can be detected by the clockwise and anticlockwise rotation of the analyser.

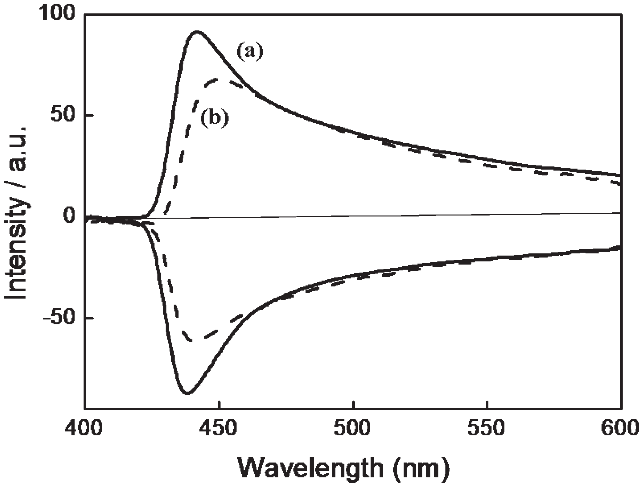

Figure 5. CD spectra taken by focusing the light on each chiral domain of (a) N(1,7) (solid curves) and (b) N(1,3) (dash curves). The different sign of the CD can be clearly observed between two domains with opposite optical rotations (see figure 4).

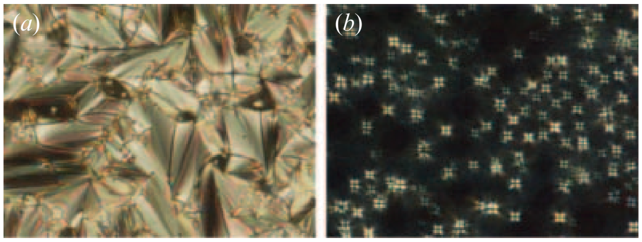

Figure 6. Photomicrographs of the textures of the SmA phase in N(1,2) at 140°C: (a) the focal conic fan texture and (b) homeotropic texture prepared by shearing between glass plates.

4. Discussion

Most banana-shaped molecules have been synthesized by using resorcinol derivatives as a bent core. These resorcinol based compounds have the bent angle of about 120°, which has been considered to be a very important factor for the preparation of banana phases.

Figure 7 shows the chemical geometries of the six compounds studied here. Calculations were performed using the program, Gaussian 03. Rev D. 02. The bent angles of the central bent core of N(2,7), N(1,6) and N(1,3) are 119.6°, 119.6° and 119.9°, respectively, whereas for N(1,7), N(1,2) and N(2,3) they are 60.1°, 60.4° and 59.4°, respectively. Thus, the first three compounds are candidates for banana molecules. As mentioned above, in fact these compounds exhibit the banana smectic phase. Among these three compounds, the transition temperatures are interestingly compared. The highest isotropization temperature (T_i=229°C) for the banana phase is observed for the symmetrical banana molecule, N(2,7). N(1,6) with the same bent angle and distance between side wings as N(2,7), shows the relatively lower T_i of 194°C, indicating that the asymmetric attachment of side wings destabilizes the banana phase because of the random head–tail alignment in molecular packing into a layer. N(1,3)

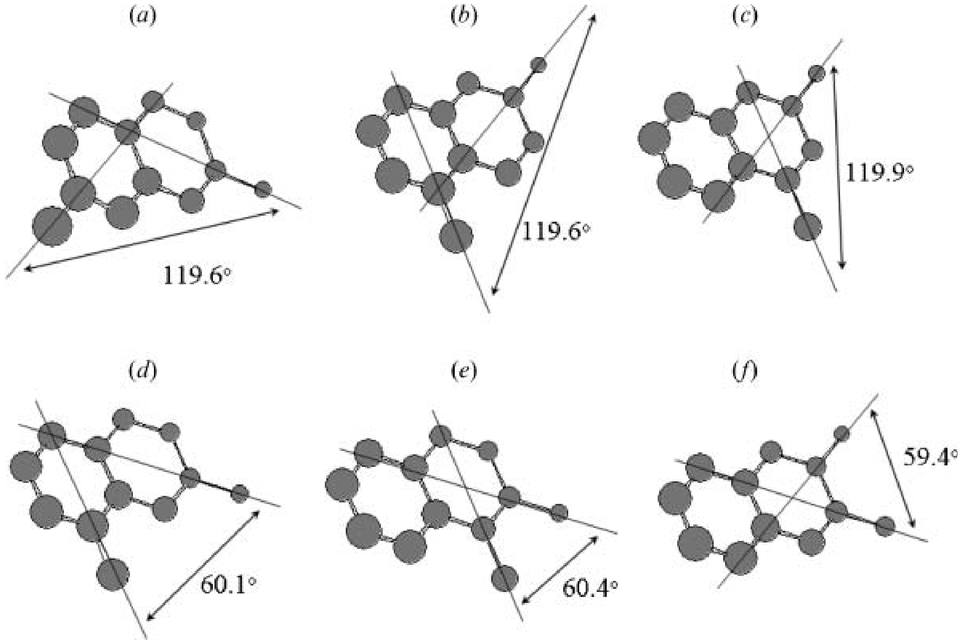

Figure 7. Molecular modelling of (a) N(2,7), (b) N(1,6), (c) N(1,3), (d) N(1,7) (e) N(1,2), and (f) N(2,3) by the Gaussian 03. Rev D. 02 program, and their bent angles.

should be compared with the classical banana molecule, 1,3-phenylenebis[4-(4-dodecyloxyphenyliminomethyl)] benzoate [P(1,3)-12-O-PIMB]. The T_i of 122°C for N(1,3) is remarkably lower than the T_i of 170°C for P(1,3)-12-O-PIMB. This is a reasonable trend since the laterally attached phenyl ring on the central core decreases the packing efficiency within a layer. More interesting is the phase structure formed by these three compounds. N(2,7) and N(1,3) form a chiral blue phase with basically homochiral B2 structure, whereas N(1,6) forms a racemic B2 phase. Comparing the phase structure between symmetric N(2,7) and asymmetric N(1,6), we know that the racemic state of the B2 phase becomes preferable by the asymmetric introduction of side wings to the central core. The reason, however, is not clear.

Matsuzaki *et al.* [28, 29] studied the mesomorphic behaviours of the 1,2-phenylene and 2,3-naphthalene compounds with the bent angle of about 60°, instead of resorcinol derivatives. They found that these compounds only form the classical nematic and/or smectic phases, but not banana phases. The reason is simply because the molecules assume a U-like shape and behave like a calamitic molecule. In accord with this result, our compounds N(1,2) and N(2,3), with a bent angle of 60°, also form the calamitic SmA phase. However, it is surprising to find that N(1,7) exhibits a typical banana phase irrespective of having a bent angle of 60°. This unconventional formation of a banana phase may be attributed to the long distance between the positions of two sticking side wings. The distance in N(1,7) is three times longer than those of N(1,2) and N(2,3), so that the central bent core has a highly anisotropic shape. Efficient accommodation of such a long central core may be achieved in the banana phase rather than in the conventional SmA phase, as illustrated in figure 8.

5. Conclusions

In this study, we prepared six bent-shaped molecules based on naphthalene bent cores, N(2,7), N(1,7), N(1,6), N(1,3), N(1,2) and N(2,3). All of the compounds form fluid smectic mesophases and their mesomorphic behaviours and properties have been considered in terms of their molecular structure. These compounds are categorized into two groups; in one of them, N(2,7), N(1,6) and N(1,3), the side wings are attached to the central core with a bent angle of 120°, whereas in the other, N(1,7), N(1,2) and N(2,3), the bent angle is 60°. The typical banana molecule, N(2,7), in the first group forms a chiral blue phase that is characterized by two distinguishable domains showing opposite optical rotations and distinct circular dichroism with opposite sign.

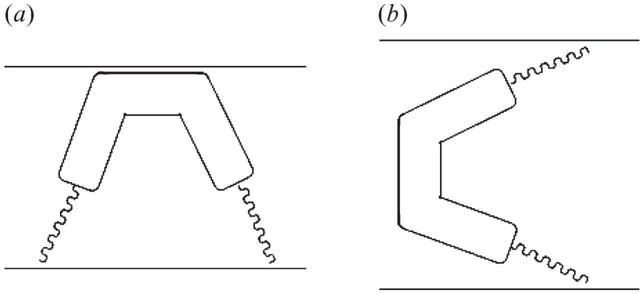

Figure 8. Illustration of two possible types of packing into (a) the calamitic smectic phase and (b) the banana smectic phase in N(1,7).

Under an electric field, this phase is altered to the birefringent B2 phase that exhibits antiferroelectric switching with a ground-state homochiral $\mathrm{SmC_AP_A}$ structure. N(1,3) also forms the chiral blue phase, but in contrast, N(1,6) with side wings attached asymmetrically, forms the typical B2 phase with the racemic $\mathrm{SmC_SP_A}$ structure. The result indicates that the chirality of the B2 phase strongly depends on the symmetry of side wings. N(1,2) and N(2,3), belonging to the other group, form the conventional SmA phase. Of interest is the fact that N(1,7) forms the blue banana phase irrespective of having a small bent angle of 60°, showing that the length between side wings as well as the bent angle plays an important role for the formation of banana phases.

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