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Odd–even effects in the phase transition behaviour of novel U-shaped liquid crystals

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A homologous series of U-shaped dimeric liquid crystals in which two mesogenic groups are connected via catechol has been prepared and the effects of terminal alkyl chains, alkyl spacers and core structures on the transition properties investigated by means of optical microscopy and differential scanning calorimetry. The phase sequence exhibits a pronounced odd–even effect as the length and parity of the spacers is varied, in which the even members favour the nematic and smectic C phases, whereas the odd members favour the nematic and smectic A phases. We discuss the transition behaviour of the U-shaped compounds in terms of molecular shape.

1. Introduction

Supramolecular assemblies composed of oligomeric liquid crystals (LCs) are of current interest in the design of new liquid crystalline materials [1]. Liquid crystal oligomers consist of semi-rigid mesogenic units connected via flexible spacers [2–4]. Dimeric LCs are attractive because they exhibit different properties from those of conventional low molar mass LCs and serve as model compounds for main chain LC polymers. For example, the transition properties of dimeric LCs are known to depend on the length and parity of the flexible spacer. Furthermore, LC trimers [5] and tetramers [6] have been reported. Pronounced odd–even effects were observed for the transition properties of linear LC oligomers on varying the spacer length. The transition behaviour is interpreted in terms of the average molecular shape of those oligomers. U-shaped LCs have been investigated by several research groups [7–11]. Attard and Douglass reported property–structure correlations of dimeric compounds derived from phthalic acid, providing important insights about U-shaped LC systems [10]. Jackson *et al.* reported that cyanobiphenyl-based LC dimers containing catechol as a linking group showed odd–even effects on varying the parity of the spacer for the melting and clearing points, in which the even members have the higher values [11].

We have reported novel pre-organized U-shaped systems as shown in figure 1, i.e. a U-shaped molecule containing catechol as a linking group [12], and binaphthyl derivatives [13, 14]; the pre-organized supermolecules were found to induce unusual ordering in the supramolecular LC phase. For example, the U-shaped dimeric molecule BOPPHB, in which two phenylpyrimidine moieties are connected via catechol, was found to have a localized layered structure in the nematic (N) phase, and unusual enthalpy changes were observed in the N phase on heating from the monotoropic smectic C (SmC) phase. Furthermore, conoscopic observations suggested that the N phase was biaxiality [12]. We designed a coupling between axial chirality and the U-shaped system. The binaphthyl derivatives with an even number of atoms in the spacers showed a chiral nematic phase, and those with an odd number of atoms showed a blue phase. The remarkable odd–even effect of the chirality-dependent phase transition is thought to be attributable to the different configuration of the binaphthyl derivatives from MM2 models; the mesogenic groups of the odd dimer are more twisted than those of the even dimer [14].

We report here the effects of structural modifications of the U-shaped dimeric molecule (BOPPHB) on phase transition properties. In this article BOPPHB is referred to as I(6, 8). Effects of the terminal chain lengths, spacer lengths and mesogenic core structures on the LC phase transition behaviour were investigated. Figure 2 shows the molecular structures of the newly prepared U-shaped mesogenic compounds and the corresponding monomeric compounds.

2. Experimental

2.1. *Preparation of materials*

Purification of final products was carried out using column chromatography over silica gel (63–210 μm)

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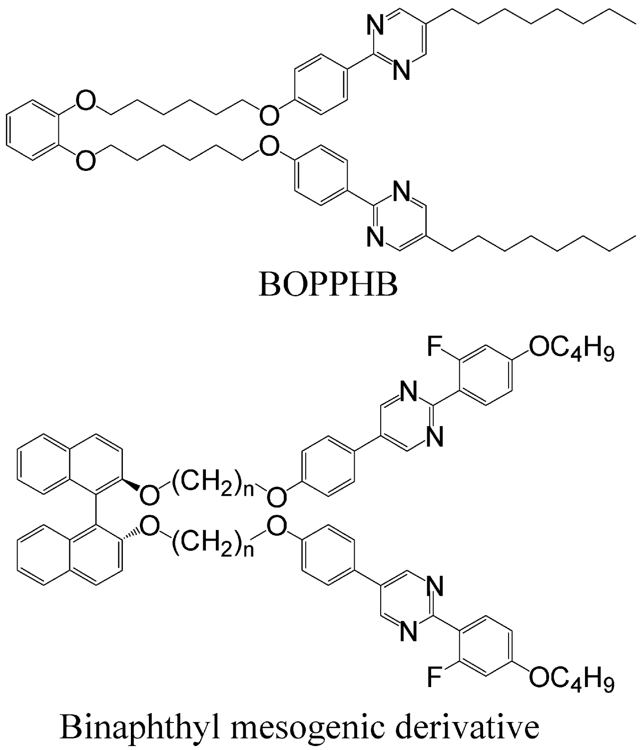


Figure 1. Pre-organized U-shaped mesogenic systems.

(Kanto Chemical Co., Inc.) using dichloromethane or a dichloromethane/ethyl acetate mixture as eluant, followed by recrystallization from ethanol or an ethanol/chloroform mixture. The purity of the final compound was checked by thin layer chromatography (TLC, aluminum sheets, silica gel 60 F254 from Merck); dichloromethane was used as the solvent. Detection of products was achieved by UV irradiation (λ=254 and 365 nm). The structure of the final product was elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270). The analyses of the structures of the products by spectroscopic methods were found to be consistent with the predicted structures.

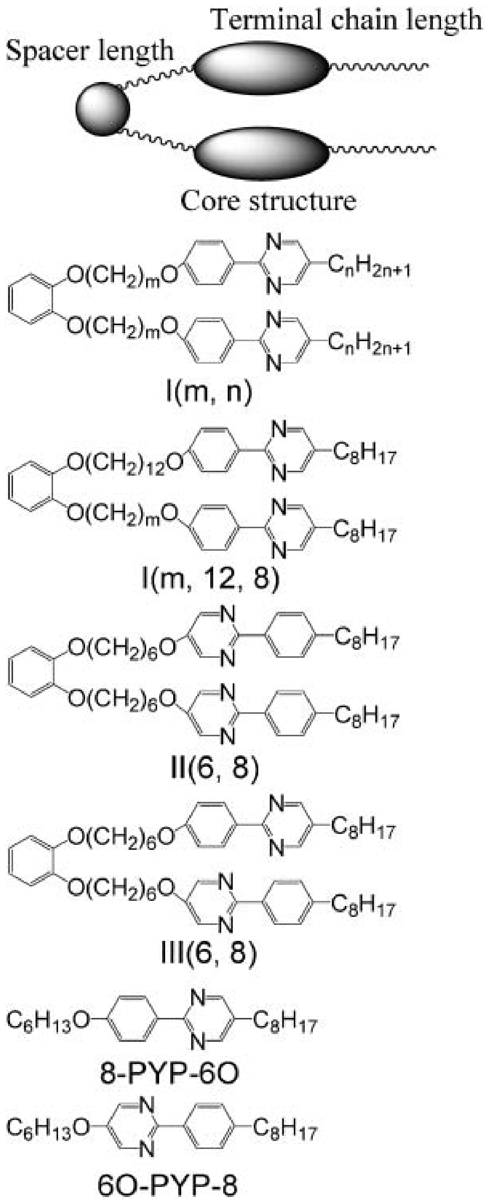


Figure 2. Schematic representation of the molecular structural modifications investigated.

2.1.1. 1, 2-Bis{4-[4-(5-octylpyrimidin-2-yl)phenyloxy]-butyloxy}benzene, I(4, 8). 5-Octyl-2-(4-hydroxyphenyl) pyrimidine (Midori Chemical Corp.) (0.57 g, 2.0 mmol) and 1, 4-dibromobutane (0.65 g, 3.0 mmol) were dissolved in cyclohexanone (10 ml). Potassium carbonate (0.28 g, 2.0 mmol) was added and the resulting mixture stirred at 80°C for 6 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product, 2-[4-(4-bromobutyloxy)phenyl]-5-octylpyrimidine (**1**), was purified by column chromatography using dichloromethane as eluant; yield 0.58 g (68%).

Compound **1** (0.42 g, 1.0 mmol) and catechol (0.049 g, 0.45 mmol) were dissolved in cyclohexanone (10 ml). K_2CO_3 (0.14 g, 1.0 mmol) was then added and the resulting mixture stirred at 140°C for 14 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using a dichloromethane/ethyl acetate (29/1) mixture as eluant, and recrystallized from a chloroform/ethanol (1/4) mixture (5 ml); yield 0.25 g (69%). δ_H (270 MHz, $CDCl_3$, TMS):

8.55 (s, 4H, Ar–H), 8.33 (d, 4H, Ar–H, J=8.9 Hz), 6.96 (d, 4H, Ar–H, J=9.2 Hz), 6.90 (s, 4H, Ar–H), 4.12–4.06 (m, 8H, –OCH_2–), 2.58 (t, 4H, Ar–CH_2–, J=7.7 Hz), 2.03–1.27 (m, 32H, aliphatic–H), 0.88 (t, 6H, –CH_3, J=6.6 Hz). IR: ν/cm^{-1}(KBr) 2925, 2853 (C–H str.), 1608, 1587 (C=C str.), 1252 (C–O str.).

2.1.2. 1-{12-[4-(5-Octylpyrimidin-2-yl)phenoxy]dodecyloxy}-2-{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}-benzene, I(6, 12, 8). 4-(12-Bromododecyloxy)phenyl]-5-octylpyrimidine (0.96 g, 1.8 mmol) and catechol (0.40 g, 3.6 mmol) were dissolved in cyclohexanone (5 ml). Potassium carbonate (0.25 g, 1.8 mmol) was then added and the resulting mixture stirred at 70°C for 9 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using dichloromethane as eluant, and recrystallized from a chloroform/ethanol (1/6) mixture (7 ml). 2-{12-[4-(5-Octylpyrimidin-2-yl)phenyloxy]dodecyloxy}phenol (**2**) was obtained; yield 0.20 g (20%). δ_H (270 MHz, $CDCl_3$, TMS): 8.56 (s, 2H, Ar–H), 8.34 (d, 2H, Ar–H, J=8.9 Hz), 6.96 (d, 2H, Ar–H, J=8.6 Hz), 6.95–6.81 (m, 4H, Ar–H), 5.64 (s, 1H, Ar–OH), 4.08–4.02 (m, 4H, –OCH_2–), 2.59 (t, 2H, Ar–CH_2–, J=7.4 Hz), 1.85–1.28 (m, 26H, aliphatic–H), 0.88 (t, 3H, –CH_3, J=6.5 Hz). IR: ν/cm^{-1}(KBr) 3518 (O–H str.), 2927, 2856 (C–H str.), 1608, 1582 (C=C str.).

Compound **2** (0.16 g, 0.29 mmol) and 2-[4-(6-bromohexyloxy)phenyl]-5-octylpyrimidine (0.18 g, 0.40 mmol) were dissolved in cyclohexanone (5 ml). K_2CO_3 (0.040 g, 0.30 mmol) was then added and the resulting mixture stirred at 120°C for 6 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using a dichloromethane/ethyl acetate (40/1) mixture as eluant, and recrystallized from a chloroform/ethanol (1/6) mixture (4 ml); yield 0.15 g (57%). δ_H (270 MHz, $CDCl_3$, TMS): 8.56 (s, 4H, Ar–H), 8.34 (d, 4H, Ar–H, J=8.9 Hz), 6.96 (d, 4H, Ar–H, J=8.6 Hz), 6.88 (s, 4H, Ar–H), 3.96–4.06 (m, 8H, –OCH_2–), 2.58 (t, 4H, Ar–CH_2–, J=7.4 Hz), 1.85–1.28 (m, 52H, aliphatic–H), 0.88 (t, 6H, –CH_3, J=6.5 Hz). IR: ν/cm^{-1}(KBr) 2925, 2853 (C–H str.), 1609, 1586 (C=C str.).

2.1.3. 1, 2-Bis{6-[2-(4-octyphenyl)pyrimidin-5-yloxy]-hexyloxy}benzene, II(6, 8). 1, 2-Bis(6-bromohexyloxy)benzene (0.44 g, 1.0 mmol) and 2-(4-octylphenyl)-pyrimidin-5-ol (0.71 g, 2.5 mmol) were dissolved in cyclohexanone (5 ml). K_2CO_3 (0.41 g, 3.0 mmol) was then added and the resulting mixture stirred at 150°C for 8 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using a dichloromethane/ethyl acetate (50/1) mixture as eluant; yield 0.51 g (61%). δ_H (270 MHz, $CDCl_3$, TMS): 8.41 (s, 4H, Ar–H), 8.24 (d, 4H, Ar–H, J=8.6 Hz), 7.26 (d, 4H, Ar–H, J=8.4 Hz), 6.89 (s, 4H, Ar–H), 4.07 (t, 8H, –OCH_2–, J=6.5 Hz), 2.65 (t, 4H, Ar–CH_2–, J=7.6 Hz), 1.90–1,27 (m, 40H, aliphatic–H), 0.88 (t, 6H, –CH_3, J=6.8 Hz). IR: ν/cm^{-1}(KBr) 2923, 2852 (C–H str.), 1609, 1582 (C=C str.), 1253 (C–O str.).

2.1.4. 2-(4-{6-[2-(6-Bromohexyloxy)phenyloxy]hexyloxy} phenyl)-5-octylpyrimidine, III(6, 8). 1, 2-Bis(6-bromohexyloxy)benzene (0.40 g, 0.92 mmol) and 5-octyl-2-(4-hydroxyphenyl)pyrimidine (0.13 g, 0.45 mmol) were dissolved in cyclohexanone (5 ml). Potassium carbonate (0.062 g, 0.45 mmol) was then added and the resulting mixture stirred at 80°C for 6 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using a dichloromethane/ethyl acetate (40/1) mixture as eluant. 2-(4-{6-[2-(6-bromohexyloxy)phenyloxy]hexyloxy}phenyl)-5-octylpyrimidine (**3**) was obtained; yield 0.18 g (31%).

Compound **3** (0.18 g, 0.28 mmol) and 2-(4-octylphenyl)pyrimidin-5-ol (0.043 g, 0.15 mmol) were dissolved in cyclohexanone (5 ml). K_2CO_3 (0.020 g, 0.28 mmol) was then added and the resulting mixture stirred at 100°C for 8 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using a dichloromethane/ethyl acetate (40/1) mixture as eluant and was then recystallized from a chloroform/ethanol (1/4) mixture (5 ml); yield 0.18 g (78%). δ_H (270 MHz, $CDCl_3$, TMS): 8.55 (s, 2H, Ar–H), 8.41 (s, 2H, Ar–H), 8.34 (d, 2H, Ar–H, J=8.9 Hz), 8.24 (d, 2H, Ar–H, J=8.4 Hz), 7.26 (d, 2H, Ar–H, J=8.4 Hz), 6.96 (d, 2H, Ar–H, J=8.9 Hz), 6.89 (s, 4H, Ar–H), 4.06 (t, 2H, –OCH_2–, J=6.8 Hz), 4.02 (t, 2H, –OCH_2–, J=6.5 Hz), 4.01 (t, 4H, –OCH_2–, J=6.5 Hz), 2.69 (t, 2H, Ar–CH_2–, J=7.8 Hz), 2.57 (t, 2H, Ar–CH_2–, J=7.8 Hz), 1.87–1.26 (m, 40H, aliphatic–H), 0.88 (t, 6H, –CH_3, J=6.6 Hz). IR: ν/cm^{-1}(KBr) 2923, 2854 (C–H str.), 1584 (C=C str.), 1254 (C–O str.).

2.2. *Liquid crystalline and physical properties*

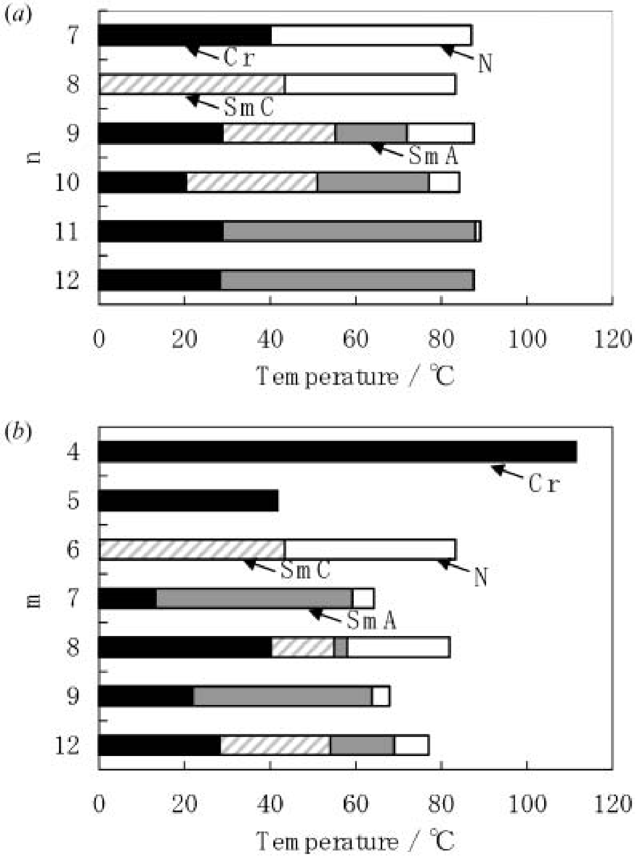
The initial assignments and corresponding transition temperatures for the final product were determined by thermal optical microscopy using a Nikkon Optiphoto POL polarizing microscope equipped with a Mettler FP82 hot stage and FP80 control unit. The heating and cooling rates were 5°C min^{-1}, unless otherwise indicated. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The materials were studied at a scanning rate of 5°C min^{-1}, for both heating and cooling cycles, after encapsulating in aluminum pans.

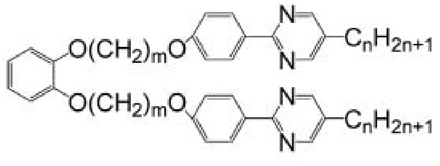
3. Results and discussion

3.1. *Effect of the terminal chain length and spacer length*

Transition temperatures and associated entropies ($\Delta S/R$) of the dimeric molecules I(m, n) are listed in table 1.

Figure 3 (*a*) shows the effect of the terminal alkyl chain length n on the transition properties. In the series I(6, n), the length of the terminal alkyl chains n is varied from 7 to 12 methylene units, while that of the spacers m is held at 6 methylene units. The clearing temperatures exhibit a small alternation on varying parity of n, in which the odd members have the higher values than the even members. This can be explained by the alternation of the length-to-breadth ratio. The same alternation upon changing the terminal chain lengths is observed in the corresponding monomeric series n-PYP-6O, see figure 4 (*a*). Compound I(6, 7), possessing the shorter terminal alkyl chains, shows only the N phase. The SmA and/or SmC phases additionally appear on increasing the length of the terminal alkyl chains. The SmC phase disappears with increasing the length of the terminal alkyl chains. No odd–even effect is seen for the phase sequence of I(6, n) on varying the terminal chain length. Figure 3 (*b*) shows effect of spacer length m on the transition properties. In series I(m, 8), the length of the spacers m is varied from 4 to 9 and 12 methylene units, while that of the terminal chains n is held at 8 methylene units. The clearing temperatures show a pronounced alternation in which the even





I(m,n)

Figure 3. Transition temperatures (°C) for (*a*) I(6, n) and (*b*) I(m, 8) on cooling.

Table 1. Transition temperatures (°C) and $\Delta S/R$ (in parentheses) for I(m, n). Square brackets indicate a monotropic transition.

m	n	I		N		SmA		SmC	m.p.
4	8	•							111.4
5	8	•							41.7
6	7	•	87.0 (0.9)	•					83.1
6	8	•	83.3 (1.2)	•			[43.4 (0.1)	•]	76.0
6	9	•	[87.6 (1.4)	•	72.0 (0.1)	•	55.2 (–^{a})	•]	87.8
6	10	•	84.2 (1.2)	•	[77.1 (0.7)	•	51.0 (–^{a})	•]	80.5
6	11	•	[89.1 (1.9)	•	87.9 (2.6)	•]			92.5
6	12	•			87.0 (5.5)	•			80.5
7	8	•	64.3 (0.9)	•	[59.2 (1.4)	•]			62.4
8	8	•	[81.9 (1.2)	•	58.0 (–^{a})	•	55.0 (–^{a})	•]	91.6
9	8	•	[67.9 (1.1)	•	63.8 (1.4)	•]			72.0
12	8	•	[77.0 (1.6)	•	69.0 (0.4)	•	54.0 (0.2)	•]	78.0

[a] Too small to be detected

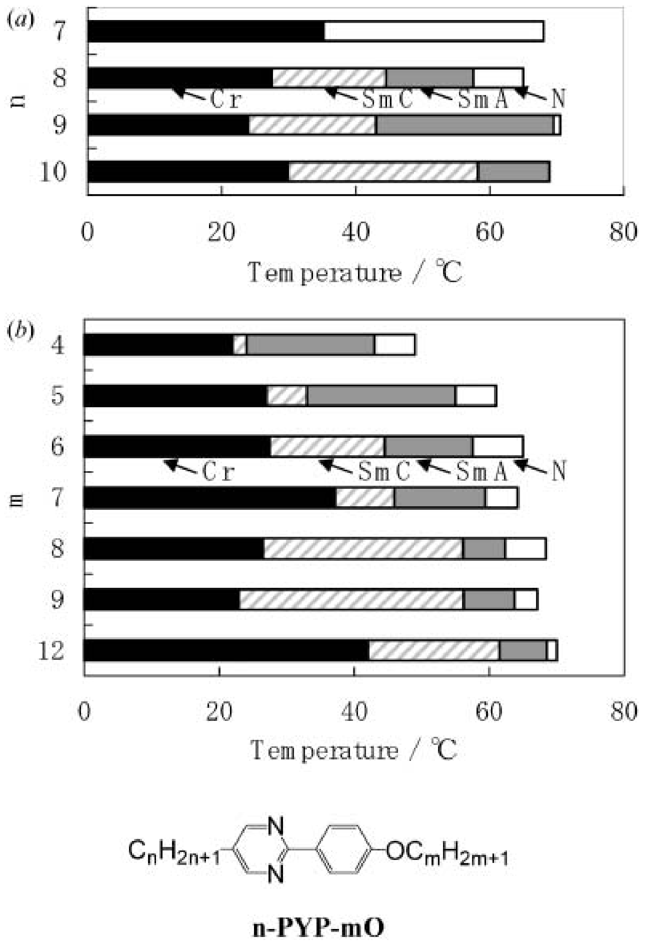


Figure 4. Transition temperatures for (*a*) *n*-PYP-6O and (*b*) 8-PYP-*m*O on cooling [16].

members have higher values than the odd members. The compounds having the shorter spacers (n=4, 5) exhibit no mesophase. A marked odd–even effect is seen for a phase sequence of compounds having the intermediate alkyl spacers (n=6–9); the even members favour the N and SmC phases, whereas the odd members favour the N and SmA phases. The compound having the longest spacers (n=12) shows the phase sequence I–N–SmA–SmC. In contrast, all compounds of the corresponding monomeric series 8-PYP-*m*O show the phase sequence I–N–SmA–SmC, see figure 4 (*b*). It is noteworthy that the parity of the spacers has a large influence on the LC properties for dimeric systems; that is, the even members have a tendency to form a tilted smectic phase (SmC), whereas the odd members have a tendency to form an orthogonal smectic phase (SmA).

We now discuss the effects of the terminal chain length and the spacer length on phase transition behaviour of I(*m*, *n*). In our previous study [12], X-Ray diffraction of I(6, 8) suggested that the layer spacing is about the same as the length of the molecule in a U-shape. Our C-13 NMR studies of smectic liquid crystals revealed that (1) cooperative motion of the core parts contributes to the orientational order of the molecules in each layer, (2) interlayer penetration of tails causes correlation between cores in adjacent layers, and (3) an excluded volume effect of the core parts plays an important role in the SmA to SmC (or SmC*) transition [15]. With respect to the present U-shaped compound I(*m*, *n*), the parity of the spacers is thought to affect the configuration of its two mesogenic parts as discussed later. Difference in the configuration between the dimer with odd-numbered spacers and the dimer with even-numbered spacers can produce significant difference in the cooperative motion of the core parts. Therefore, the phase sequence of the U-shaped compound depends on the parity of the spacers. On the other hand, the parity of the terminal chain is not thought to affect the cooperative motion.

Turning to the disappearance of the SmC phase for I(6, 11) and I(6, 12), we assume a monolayer structure in which the molecules exist in a U-shape. Increasing the tail length in compounds I(6, *n*), the molecular organization in each layer is thought to change from figure 5 (*a*) to figure 5 (*b*). The excluded volume effect producing the SmA to SmC transition is not effective for the molecular packing shown in figure 5 (*b*). Thus, the SmC phase disappears in compounds I(6, 11) and I(6, 12). To understand the odd–even effects of the spacers on the configuration of the mesogenic parts of the U-shaped compounds, we estimated the molecular conformations for I(6, 8) and I(6, 7) using MM2 calculations (see figure 6). In I(6, 8) the mesogenic cores are coparallel, whereas in I(6, 7) they cross. This difference in configuration of the mesogenic parts between I(6, 8) and I(6, 7) may cause different intralayer interactions, resulting in different types of smectic phases (SmA or SmC). We note that the molecular shape obtained from MM2 calculations does not reflect

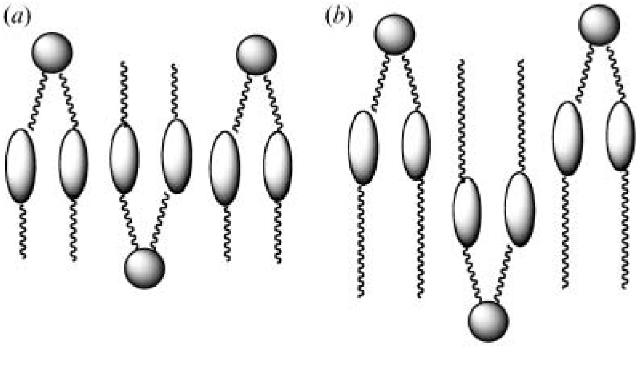


Figure 5. Possible models for molecular organization in the smectic phase of (*a*) I(6, 8) and (*b*) I(6, 12).

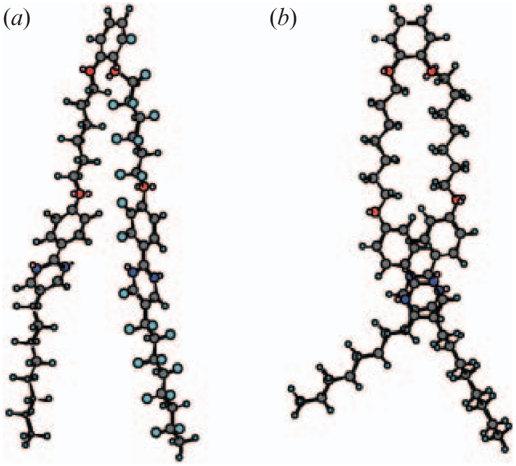


Figure 6. Expected molecular conformations for (*a*) I(6, 8) and (*b*) I(7, 8) calculated by the MM2 method.

a real structure of the dimeric molecule in the LC phase. X-ray diffraction is a useful tool to give some insight about molecular packing of the present dimeric compound in the smectic phases. However, we cannot perform a systematic XRD measurement for the different phases of the different compounds. Thus we have insufficient enough information to discuss how the molecules pack in the smectic phases.

Phase transition temperatures and entropies determined for the U-shaped dimeric molecules possessing two different alkyl chain spacers I(*m*, 12, 8) are listed in table 2. The even member I(6, 12, 8) exhibits the phase sequence I–N–SmA–SmC, whereas the odd member I(7, 12, 8) exhibits I–N–SmA. Although I(6, 12, 8) shows a SmC phase, these compounds with different spacer lengths do not show a pronounced alternation. An XRD measurement at 61.7°C in the SmA phase of I(6, 12, 8) gives a layer spacing of d=32.7 Å, whereas the molecular length of I(6, 12, 8) is estimated to be 39.3 Å. One possible molecular organization is shown in figure 7. The XRD result suggests that the smectic phase is a monolayer structure in which molecules can exist in a U-shape. As shown in figure 7, the parity of the spacer is not thought to cause significant difference in the intralayer core–core interaction between I(6, 12, 8) and I(7, 12, 8).

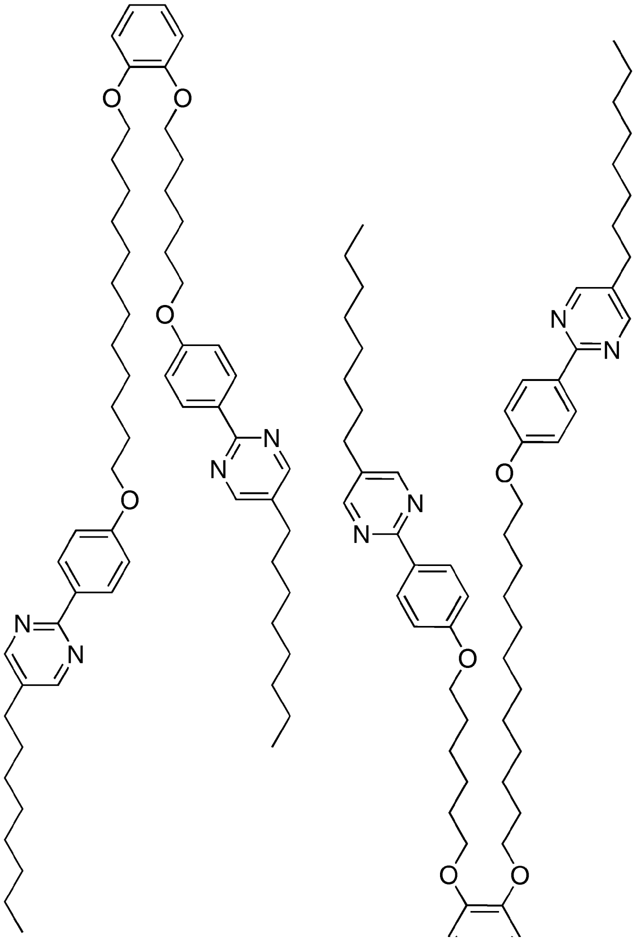


Figure 7. A possible model for molecular organization in the SmA phase of I(6, 12, 8).

3.2. *Effect of the mesogenic core structure*

We prepared compound II(6, 8) possessing the opposite orientation of phenylpyrimidine cores to those of compounds I(6, 8) and III(6, 8) possessing the antiparallel orientation of phenylpyrimidine cores, and investigated the effect of modifications of the mesogenic cores of compound I(6, 8) on the phase transition behaviour. Transition temperatures of dimeric molecules I(6, 8)–III(6, 8) and the corresponding monomeric molecules 8-PYP-6O and 6O-PYP-8 are listed in table 3.

Table 2. Transition temperatures (°C) and $\Delta S/R$ (in parentheses) for I(*m*, 12, 8). Square brackets indicate a monotropic transition.

m	*m*'	*n*	I		N		SmA		SmC	m.p.
6	12	8	•	84 (1.6)	•	[64 (0.2)	•	54 (–[a])	•]	83
7	12	8	•	73 (1.0)	•	63 (0.6)	•			62

[a] Too small to be detected.

Table 3. Transition temperatures (°C) and $\Delta S/R$ (in parenthesis) for I(6, 8)–III(6, 8). Square brackets indicate a monotropic transition.

	I		N		SmA		SmC	mp
I(6,8)	•	83.3 (1.2)	•			[43.4 (0.1)	•]	76.0
II(6,8)	•			124 (7.8)	•			76.0
III(6,8)	•			102.5 (6.2)	•			83.2
8-PYP-6O	•	65	•	57.5	•	44.5	•	27.5
6O-PYP-8	•			83	•	61.5	•	46

In contrast to compound I(6, 8) showing the N and SmC phases, compounds II(6, 8) and III(6, 8) show only the SmA phase. The orientation of phenylpyrimidine cores was, therefore, found significantly to affect the phase transition behaviour. The clearing temperatures of the dimeric compounds reflect those of the corresponding monomeric molecules: 8-PYP-6O has a lower value than 6O-PYP-8. The 5-alkoxypyrimidine unit induces a higher clearing temperature than the 5-alkylpyrimidine unit and stabilizes the SmA phase. Therefore, electrostatic core–core interactions can contribute to the stability of the SmA phase.

4. Conclusion

A homologous series of U-shaped dimeric compounds in which two mesogenic groups are connected via catechol showed a pronounced odd–even effect of the spacers on the phase sequences; the even members favour the SmC phase, whereas the odd members favour the SmA phase.

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