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Phase transition behaviour of novel Y-shaped liquid crystal oligomers

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We have designed novel liquid crystal oligomers in which three mesogenic units are connected via 3,5-dihydroxybenzoic acid. 4-Cyanobiphenyl-4′-yl 3,5-bis{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}benzoate and 4-(5-octylpyrimidine-2-yl)phenyl 3,5-bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxy}benzoate have been prepared, and their physical properties investigated by optical microscopy and differential scanning calorimetry. The Y-shaped liquid crystal oligomers were found to show a direct phase transition from isotropic liquid to anticlinic SmC (SmCanti) phase.

1. Introduction

Supramolecular assemblies composed of supermolecules, i.e. oligomeric and dendritic liquid crystals, are current topics in the field of liquid crystalline chemistry [1]. Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low-molecular mass mesogens. For example, the transition properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Many kinds of dimeric and trimeric mesogenic molecules have been reported [2, 3]. Pronounced odd–even effects were observed for the transition properties of linear liquid crystal trimers on varying the spacer length [4]. Recently, dendritic liquid crystals have been investigated intensively, because functional dendrimers have rich supramolecular chemistry and self-assembling properties [5–7]. The introduction of a bent-shape in a molecular structure is another important strategy in the design of supermolecules. Recently in 1, 3-benzene derivatives first synthesized by Matsunaga *et al*. [8], antiferroelectric and ferroelectric properties have been found by Watanabe *et al*. [9, 10]. The rigid banana-shaped system has given new concepts for chirality and phase structures in liquid crystals [11, 12]. Furthermore, Samulski *et al*. [13] and Kumar *et al*. [14] discovered the biaxial nematic phase in a family of substituted oxadiazoles that have a bent-shape structure.

As shown in these examples, pre-organization [15] or a 'bottom-up' approach, is an important concept in the design of mesogenic molecules [1, 16, 17]. We have reported novel pre-organized systems, e.g. U-shaped molecules [18], binaphthyl derivatives [19] and λ–shaped molecules [20]; the pre-organized compounds were found to induce unusual ordering in the supramolecular liquid crystalline phase. The λ–shaped molecule, 4-cyanobiphenyl-4′-yl 3,4-bis{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}benzoate (figure 1, compound **1a**), showed a phase sequence of isotropic – nematic – smectic A– incommensurate smectic A [20]. Recently we found that a liquid crystal oligomer in which cyanobiphenyl and phenylpyrimidine groups are connected via 1,3-dihydroxybenzene exhibits a phase sequence of isotropic – nematic – smectic A –anticlinic SmC (figure 1, compound **2a**) [21]. In this article we report novel Y-shaped liquid crystal oligomers in which three mesogenic units are connected via 3, 5-dihydroxybenzoic acid. We discuss the effect of the relative configuration of the mesogenic moieties in liquid crystal oligomers on their phase transition.

2. Experimental

2.1. *Preparation of materials*

2.1.1. 3, 5-Bis{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}benzoic acid. 5-Octyl-2-(4-hydroxyphenyl)pyrimidine (1.14 g, 4.0 mmol) purchased from Midori Kagaku Co., Ltd. and 1,6-dibromohexane (1.95 g, 8.0 mmol) were dissolved in cyclohexanone (15 ml). Potassium carbonate (0.55 g, 4.0 mmol) was added and the resulting mixture stirred at 75°C for 5 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product

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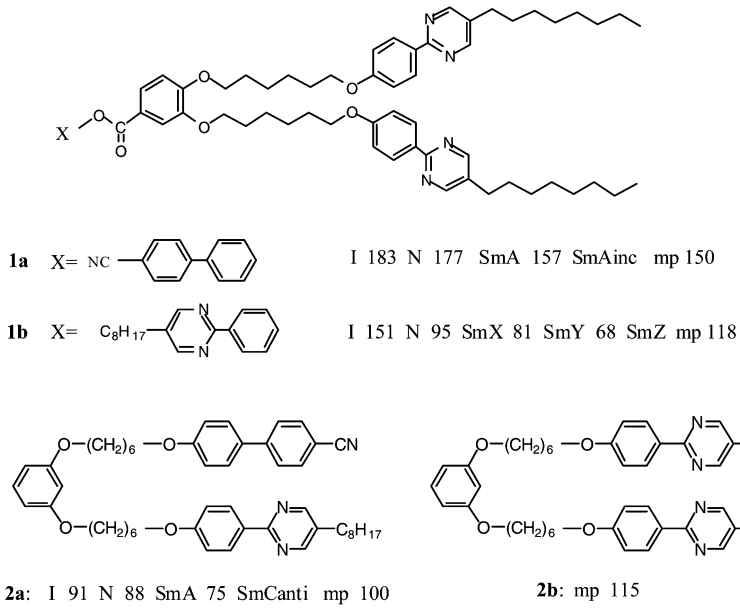


Figure 1. Molecular structures and transition temperatures (°C) of the λ–shaped molecules and the bent shaped trimers.

was purified by column chromatography using dichloromethane as eluant, yielding 0.95 g (53%) of 2-[4-(6-bromohexyloxy)phenyl]-5-octylpyrimidine. A portion of this intermediate (0.30 g, 0.67 mmol) and methyl 3,5-dihydroxybenzoate (57 mg, 0.34 mmol) were dissolved in cyclohexanone (5 ml). K_2CO_3 (93 mg, 0.67 mmol) and KI (11 mg, 0.067 mmol) were then added and the resulting mixture stirred at 140°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 toluen/ethyl acetate (15/1) mixture as eluant, and recrystallized from ethanol; yield 179 mg (59%).

The methyl 3,5-bis{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}benzoate thus obtained (150 mg, 0.17 mmol) was added to a solution of KOH (170 mg, 3 mmol) in ethanol (95%, 15 ml). The resulting mixture was stirred under reflux for 1 h, then acidified with HCl (conc. 1.0 ml). Water (25 ml) was added to the mixture and the aqueous phase extracted with dichloromethane (3×30 ml). The organic extracts were combined, dried over Na_2SO_4, filtered and the solvent removed by evaporation under reduced pressure; yield 146 mg (98%) of the target compound.

2.1.2. 4-Cyanobiphenyl-4′-yl 3,5-bis{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}benzoate, 3. To a solution of 3,5-bis{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}benzoic acid (140 mg, 0.16 mmol) and 4-cyano-4′-hydroxybiphenyl (60 mg, 0.16 mmol) in dichloromethane (10 ml), *N*,*N*′-dicyclohexylcarbodiimide (33 mg, 0.16 mmol) and 4-(*N*,*N*-dimethylamino) pyridine (2 mg, 0.02 mmol) were added. The resulting solution was stirred at room temperature overnight, and precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel (using a toluene/ethyl acetate (15/1) mixture as eluant). Recrystallization from an ethanol/chloroform mixture gave the desired product; yield 81 mg (48%). NMR: δ_H (270 MHz, $CDCl_3$, TMS): 8.60 (s, 4H, Ar–H), 8.40 (d, 4H, Ar–H, J=8.9 Hz), 7.75–7.66 (m, 4H, Ar–H), 7.63 (d, 2H, Ar–H, J=8.9 Hz), 7.39–7.31 (m, 4H, Ar–H), 6.99 (d, 4H, Ar–H, J=8.9 Hz), 6.74 (t, 1H, Ar–H, J=2.3 Hz), 4.06 (t, 4H, –OCH_2–, J=6.2 Hz), 4.04 (t, 4H, –OCH_2–, J=6.2 Hz), 2.61 (t, 4H, Ar–CH_2–, J=7.6 Hz), 1.90–1.25 (m, 40H, aliphatic–H), 0.88 (t, 6H, –CH_3, J=6.6 Hz). ν/cm^{-1}(KBr):2927, 2855, 2226, 1740, 1607, 1587, 1432, 1168.

2.1.3. 4-(5-Octylpyrimidine-2-yl)phenyl 3, 5-bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxy}benzoate, 4. To a solution of 3,5-bis{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}benzoic acid (151 mg, 0.17 mmol) and 4-(5-octylpyrimidine-2-yl)phenol (48 mg, 0.17 mmol) in dichloromethane (10 ml), *N*,*N*′-dicyclohexylcarbodiimide (35 mg, 0.17 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (2 mg, 0.02 mmol) were added. The resulting solution was stirred at room temperature overnight, and precipitated materials were removed by filtration. After removal of the solvent by

evaporation, the residue was purified by column chromatography on silica gel (using a toluene/ethyl acetate (15/1) mixture as eluant). Recrystallization from an ethanol/chloroform mixture gave the desired product; yield 65 mg (33%). NMR: δ_H (270 MHz, $CDCl_3$, TMS): 8.62 (s, 2H, Ar–H), 8.59 (s, 4H, Ar–H), 8.50 (d, 2H, Ar–H, J=8.6 Hz), 8.38 (d, 4H, Ar–H, J=8.9 Hz), 7.39–7.31 (m, 4H, Ar–H), 6.98 (d, 4H, Ar–H, J=8.9 Hz), 6.72 (t, 1H, Ar–H, J=2.3 Hz), 4.05 (t, 4H, $-OCH_2-$, J=6.2 Hz), 4.04 (t, 4H, $-OCH_2-$, J=6.2 Hz), 2.63 (t, 2H, Ar–CH_2-, J=7.6 Hz), 2.60 (t, 4H, Ar–CH_2-, J=7.6 Hz), 1.90–1.25 (m, 52H, aliphatic–H), 0.88 (t, 9H, $-CH_3$, J=6.6 Hz). ν/cm^{-1}(KBr):2927, 2855, 1742, 1607, 1587, 1432.

The other compounds presented in this paper were obtained by similar methods to that for compound **3**. Analytical data for the compounds are listed.

2.1.4. 4-Cyanobiphenyl-4′-yl 4-{6-[4-(5-octylpyrimidine-2-yl) phenyloxy]hexyloxy}benzoate, 5. NMR: δ_H (270 MHz, $CDCl_3$, TMS): 8.58 (s, 2H, Ar–H), 8.37 (d, 2H, Ar–H, J=8.9 Hz), 8.15 (d, 2H, Ar–H, J=8.9 Hz),7.75–7.66 (m, 4H, Ar–H), 7.63 (d, 2H, Ar–H, J=8.4 Hz), 7.33 (d, 2H, Ar–H, J=8.6 Hz), 6.98 (d, 4H, Ar–H, J=8.9 Hz), 4.08 (t, 2H, $-OCH_2-$, J=6.2 Hz), 4.06 (t, 2H, $-OCH_2-$, J=6.2 Hz), 2.60 (t, 2H, Ar–CH_2-, J=7.6 Hz), 1.89–1.27 (m, 20H, aliphatic–H), 0.88 (t, 3H, $-CH_3$, J=6.6 Hz). ν/cm^{-1}(KBr):2925, 2855, 2227, 1729, 1607, 1430, 1255, 1166.

2.1.5. 4-Cyanobiphenyl-4′-yl 3-{6-[4-(5-octylpyrimidine-2-yl) phenyloxy]hexyloxy}benzoate, 6. NMR: δ_H (270 MHz, $CDCl_3$, TMS): 8.66 (s, 2H, Ar–H), 8.45 (d, 2H, Ar–H, J=8.9 Hz), 7.80 (d, 1H, Ar–H, J=7.8 Hz), 7.75–7.67 (m, 4H, Ar–H), 7.67 (s, 1H, Ar–H), 7.64 (d, 2H, Ar–H, J=8.9 Hz), 7.42 (t, 1H, Ar–H, J=8.0 Hz), 7.34 (d, 2H, Ar–H, J=8.9 Hz), 7.19 (d, 1H, Ar–H, J=8.4 Hz), 7.01 (d, 2H, Ar–H, J=8.9Hz), 4.072 (t, 2H, $-OCH_2-$, J=6.2 Hz), 4.067 (t, 2H, $-OCH_2-$, J=6.2 Hz), 2.64 (t, 2H, Ar–CH_2-, J=7.6 Hz), 1.89–1.28 (m, 20H, aliphatic–H), 0.88 (t, 3H, $-CH_3$, J=6.8 Hz). ν/cm^{-1}(KBr):2925, 2855, 2227, 1739, 1427, 1270, 1174.

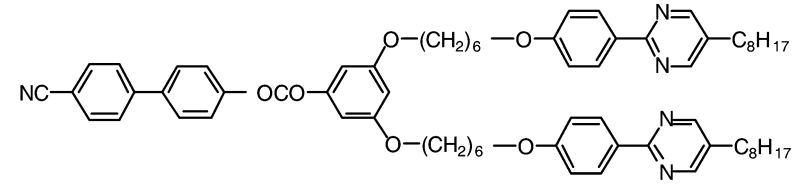
2.2. *Liquid crystalline and physical properties*

The initial phase assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikkon Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter.

3. Results and discussion

Molecular structures of the novel Y-shaped liquid crystal oligomers are shown in figure 2. Transition temperatures and enthalpies of transition for the novel trimers, compounds **3** and **4**, are shown in table 1. The compounds were studied at a scanning rate of 5°C min^{-1}, for both heating and cooling cycles.

The Y-shaped compounds **3** and **4** were found to exhibit a direct phase transition from isotropic liquid to anticlinic SmC (SmCanti). The SmCanti phase was identified by optical microscopy, i.e. the texture of the homeotropically aligned sample showed a schlieren texture which possessed singularities with both two (s=1/2) and four (s=1/4) brushes (see figure 3). Many bent core compounds with a SmCanti phase are known to show ferroelectric and antiferroelectric properties [9,



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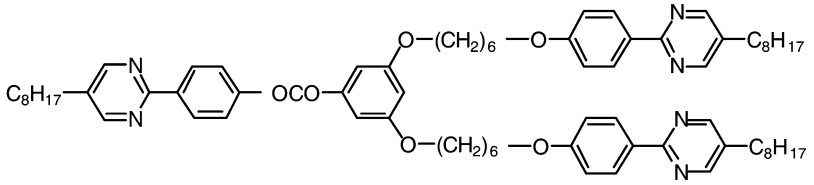

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Figure 2. Molecular structures of the novel Y-shaped compounds.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of transition, in parentheses, for compounds **3** and **4**. Square brackets indicate a monotropic transition.

Compound	SmCanti	I	m.p.
3	[• 95(12)]	•	106(68)
4	[• 71(14)]	•	87(82)

10, 22]. However, those electric properties were not detected in compounds **3** and **4**.

There is a marked difference in phase transition behaviour between the Y-shaped molecules and previously reported λ–shaped molecules (see figure 1). The λ–shaped molecule **1a**, possessing a cyanobiphenyl moiety as *X*, showed uniaxial phases, i.e. N, SmA and incommensurate SmA phases [20]. The other λ–shaped molecule **1b**, possessing a phenylpyrimidine moiety as *X*, showed three unusual smectic phases: uniaxial SmX, biaxial SmY and biaxial SmZ phases [20]. The mesogenic structure of *X* affects the phase transition of the λ–shaped molecules. On the other hand, both Y-shaped molecules showed only a biaxial SmCanti phase. The bent structure is thought to play an important role in the appearance of the anticlinic structure. The bent molecule **2b** did not show a liquid crystalline phase. Thus the introduction of the third mesogenic moiety as *X* group to the bent molecule plays an important role in the appearance of the SmCanti phase. The mesophase stability for compound **3**, possessing a cyanobiphenyl moiety as *X* group, is higher than that for compound **4** possessing a phenylpyrimidine derivative.

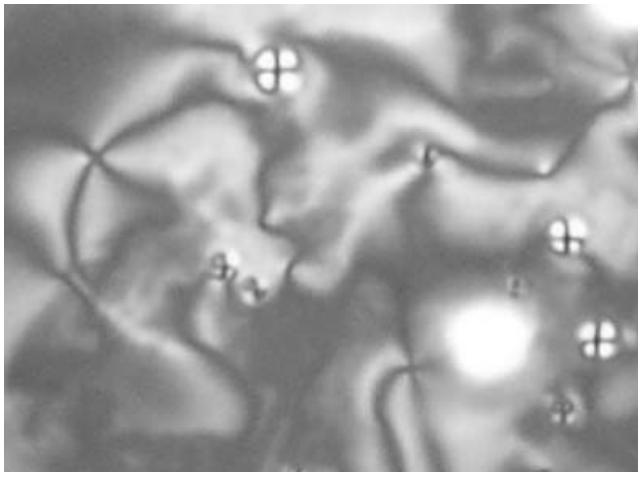
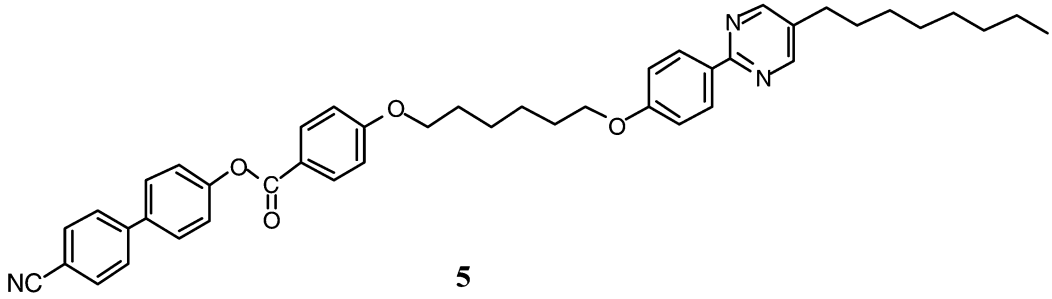


Figure 3. Photomicrograph of the homeotropically aligned SmCanti phase of compound **3** at 92°C.

We have also prepared the corresponding bimesogenic compounds **5** and **6**, and compared the phase transition properties with those of the Y-shaped compounds. The molecular structures of compounds **5** and **6** are shown in figure 4. Their transition temperatures and enthalpies of transition are shown in table 2.

Both compounds **5** and **6** were found to show uniaxial N and SmA phases. The I–N transition temperature of compound **5** is markedly higher than that of compound **6**. Based on the assumption that the alkyl chain adopts an all-*trans* configuration, the two mesogenic moieties



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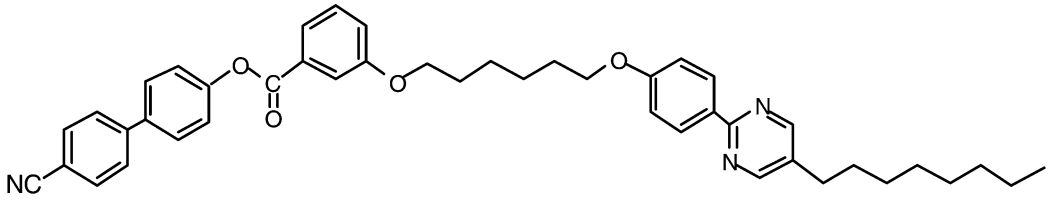

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Figure 4. Molecular structures of the bimesogenic compounds **5** and **6**.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of transition, in parenthesis, for compounds **5** and **6**. Square brackets indicate a monotropic transition.

Compound	SmA	N	I	m.p.
5	[• 104[a]]	• 275(3.2)	•	133(43)
6	[• 117(4.5)]	[• 121(1.3)]	•	125(69)

[a]The N-SmA and SmA-Cryst transitions occurred simultaneously. The total value of both transition enthalpies was 19.9 kJ mol^{-1}.

in compound **5** are almost parallel, whereas those of compound **6** are bent as show in figure 4. The higher I–N transition temperature of compound **5** can be explained by the parallel configuration of the two mesogenic moieties. Although it is unrealistic to consider only a single conformation for a dimer molecule, it should be noted that compound **6** does not show a SmCanti phase. Thus the appearance of the SmCanti phase of compounds **3** and **4** is attributed to the bent structure of the 1, 3-benzene derivative, and the third mesogenic unit plays an important role in stabilizing the anticlinic structure.

4. Conclusion

Novel Y-shaped molecules were prepared and were found to exhibit only a SmCanti phase. The transition behaviour of the Y-shaped compounds is quite different from that of the corresponding λ-shaped compounds. Strong anticlinicity observed for the Y-shaped compounds can result from coupling between the 1, 3-benzene derivative and the third mesogenic unit.

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