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Liquid Crystals

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Synthesis and phase transition behaviour of novel liquid crystal trimers

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Novel oligomeric compounds in which three mesogenic moieties are connected via 3,4-dihydroxybenzoic acid or 3,5-dihydroxybenzoic acid were prepared and the physical properties investigated. Some of the compounds were found to have a tendency to form glassy states. With respect to 4-cyanobiphenyl-4′-yl 4-octyloxy-2-(3,4-bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxybenzoyloxy)benzoate, it is possible to obtain a supercooled nematic phase despite it deviating from a strongly rod-like structure. We discuss intermolecular interactions between neighbouring mesogenic parts for the appearance of the nematic phase.

1. Introduction

Supramolecular assemblies composed of oligomeric liquid crystals are currently attracting much attention topics in the design of liquid-crystalline materials [1]. Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low-molar mass mesogens. For instance, 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 transition properties of linear liquid crystal trimers on varying the spacer length [4]. U-shaped liquid crystals have been investigated by several research groups [5–8]. Attard and Douglass reported property–structure correlations of the bimesogenic compounds derived from phthalic acid, providing important insights into the behaviour of U-shaped liquid crystal systems [8]. In 1,3-benzene derivatives first synthesized by Akutagawa *et al.* [9], antiferroelectric and ferroelectric properties have recently been found in such banana-shaped molecules by Watanabe and co-workers [10, 11]. Banana-shaped systems have revealed new concepts for chirality and phase structures in liquid crystals [12, 13].

We have reported liquid crystal oligomers in which cyanobiphenyl and phenylpyrimidine moieties are connected via a flexible spacer [14, 15, 16], 1,3-dihydroxybenzene [17], 3,4-dihydroxybenzoic acid [18, 19] or 3,5-dihydroxybenzoic acid [20], as shown in figure 1. **8PY11OCB** [14] and the V-shaped compound [17] exhibited the phase sequence I – N – SmA – SmCanti. The λ–shaped compound [18] was found to show a stable incommensurate SmA phase, however,

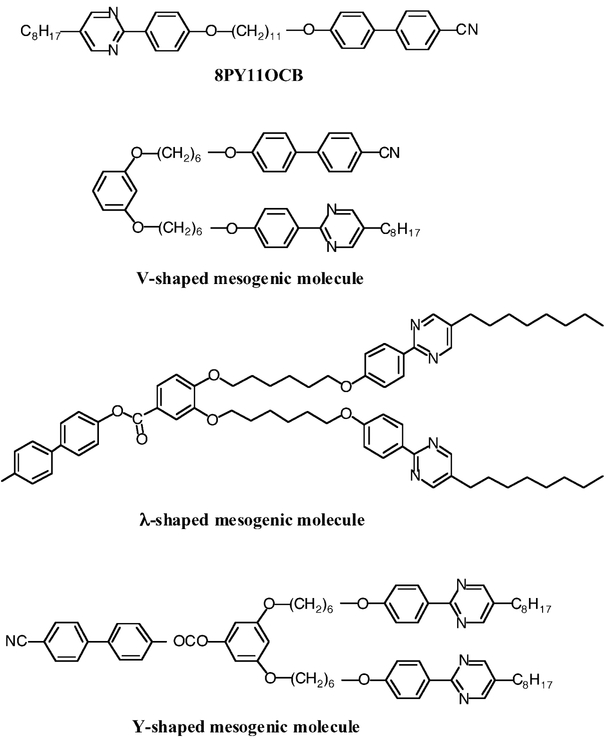

Figure 1. Liquid crystal oligomers possessing cyanobiphenyl and phenylpyrimidine units.

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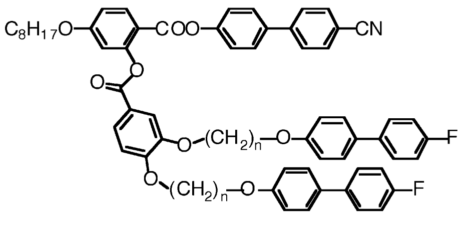
the Y-shaped compound [20] exhibited a direct transition from isotropic liquid to SmCanti phase.

We report here the synthesis and phase transition behaviour of a homologues series of novel oligomeric compounds in which three mesogenic moieties are connected via 3,4-dihydroxybenzoic acid or 3,5-dihydroxybenzoic acid, as shown in figure 2.

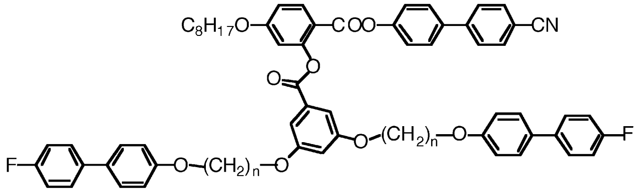
2. Experimental

2.1. *Spectroscopic analysis*

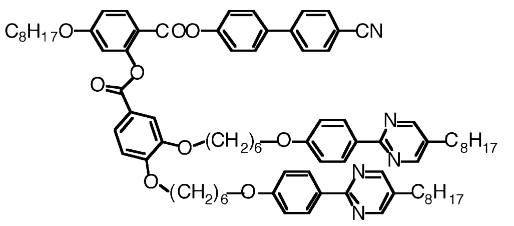
Purification of final product was carried out using column chromatography over silica gel (63–210 µm) (Kanto Chemical Co., Inc.) using toluene or a toluene–hexane mixture as the eluent, followed by recrystallization from ethanol. The structure of final product was elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270).



I-n



II-n



III-6

Figure 2. Molecular structures of novel oligomeric mesogenic compounds.

2.2. *Preparation of compounds*

2.2.1. 4-Cyanobiphenyl-4′-yl 4-octyloxy-2-(3,4-bis{[6-(4-fluorobiphenyl-4′-yloxy)hexyloxy]benzoyloxy})benzoate, I-6. For 4-fluoro-4′-(6-bromohexyloxy)biphenyl, potassium carbonate (0.69 g, 5.0 mmol) was added to a solution of 4-fluoro-4′-hydroxybiphenyl (0.94 g, 5.0 mmol) and 1,6-dibromohexane (1.71 g, 7.0 mmol) in cyclohexanone (15 ml). The reaction mixture was stirred at 90°C for 4 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography using a toluene/hexane (6/4) mixture as the eluent; yield 0.72 g (2.1 mmol, 41%); mp 78°C.

For 3,4-bis[6-(4-fluorobipheny-4′-yloxy)hexyloxy]-benzoic acid ethyl ester, 4-fluoro-4′-(6-bromohexyloxy)biphenyl (0.68 g, 1.9 mmol) and 3,4-dihydroxybezoic acid ethyl ester (0.16 g, 0.9 mmol) were dissolved in cyclohexanone (15 ml). Potassium carbonate (0.27 g, 1.9 mmol) and potassium iodine (0.033 g, 0.2 mmol) were then added and the resulting mixture was stirred at 130°C for 6 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography using a toluene as the eluent; yield 0.53 g (0.7 mmol, 81%); mp 115°C.

For 3,4-bis[6-(4-fluorobipheny-4′-yloxy)hexyloxy]-benzoic acid, 3,4-bis[6-(4-fluorobipheny-4′-yloxy)hexyloxy]benzoic acid ethyl ester (0.59 g, 0.8 mmol) was added to a solution of potassium hydroxide (0.18 g, 3.3 mmol) in ethanol (95%, 20 ml). The resulting mixture was stirred under reflux for 2 h. The solution was acidified with hydrochloric acid (concentrated, 1.0 ml). Water (20 ml) was added and aqueous phase was extracted with dichloromethane (3 × 20 ml). The organic layers were combined, dried over magnesium sulfate, filtered and evaporated; yield 0.27 g (0.4 mmol, 48%); mp 172°C.

For 2-hydroxy-4-octyloxybenzoic acid, 2,4-dihydroxy benzoic acid (7.70 g, 50 mmol) and 1-bromooctane (10.23 g, 53 mmol) were dissolved in ethanol (95%, 70 ml). A solution of potassium carbonate (10.36 g, 185 mmol) in water (40 ml) was then added and the resulting mixture was stirred at 95°C for 10 h. The solution was acidified with hydrochloric acid (2M, 80 ml). The solution was extracted with diethyl ether (3 × 50 ml). The organic extracts were combined, dried over magnesium sulfate, filtered and evaporated. Recrystallization from ethanol gave the compound; yield 0.89 g (3.4 mmol, 6.7%); mp 105°C.

For 4-cyanobiphenyl-4′-yl 4-octyloxy-2-hydroxybenzoate, 2-hydroxy-4-octyloxybenzoic acid (0.86 g, 3.2 mmol), 4-cyano-4′-hydroxybiphenyl (0.79 g, 4.0 mmol) and *N,N′*-dicyclohexylcarbodiimide (0.83 g, 4.0 mmol), were dissolved in dichloromethane. To this 4-dimethylaminopyridine (0.05 g, 0.4 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. Precipitated material was removed by filtration and the solvent was evaporated. Recrystallization from an ethanol/dichloromethane (1/1) mixture (2 × 6 ml) gave the compound; yield 0.55 g (1.2 mmol, 38%); mp 106°C.

For the target compound, 3,4-bis[6-(4-fluorobiphenyl-4′-yloxy)hexyloxy]benzoic acid (0.17 g, 0.4 mmol), 4-cyanobiphenyl-4′-yl 4-octyloxy-2-hydroxybenzoate (0.27 g, 0.4 mmol) and *N,N′*-dicyclohexylcarbodiimide (0.10 g, 0.5 mmol), were dissolved in dichloromethane. To this 4-dimethylaminopyridine (0.01 g, 0.05 mmol) was added and the reaction was stirred at room temperature for 20 h. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography using a toluene/ethyl acetate (20/1) mixture as the eluent. Recrystallization from an ethanol/dichloromethane (1/1) mixture (6 ml) gave the compound; yield 0.13 g (0.1 mmol, 30%); mp 100°C. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.20 (d, 1H, Ar-**H**, ^{3}J=8.9 Hz), 7.83(dd, 1H, Ar-**H**, ^{3}J=8.6 Hz, ^{4}J=1.9 Hz,), 7.69–7.38 (m, 15H, Ar-**H**), 7.18 (d, 2H, Ar-**H**, ^{3}J=8.9 Hz), 7.08 (d, 2H, Ar-**H**, ^{3}J=8.9 Hz), 7.05 (d, 2H, Ar-**H**, ^{3}J=8.6 Hz), 6.91 (d, 2H, Ar-**H**, ^{3}J=8.9 Hz), 6.90 (d, 2H, Ar-**H**, ^{3}J=8.9 Hz), 6.89 (d, 2H, Ar-**H**, ^{3}J=8.1 Hz), 6.80 (d, 1H, Ar-**H**, ^{4}J=2.7 Hz), 4.08–3.94 (m, 10H, -OC**H**$_2$-), 1.87–1.21 (m, 28H, aliphatic-**H**), 0.89 (t, 3H, -C**H**$_3$, ^{3}J=6.8 Hz). IR (KBr) ν_{max}/cm^{-1}: 2936, 2857 (C-H str.), 2227 ($C\equiv N$), 1605, 1588 (Ar).

The other compounds presented in this paper were obtained by a similar method to that for **I-6**. Analytical data for the other compounds are listed below.

2.2.2. 4-Cyanobiphenyl-4′-yl 4-octyloxy-2-(3,4-bis{[6-(4-fluorobiphenyl-4′-yloxy)heptyloxy]benzoyloxy})benzoate, I-7. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.20 (d, 1H, Ar-**H**, ^{3}J=8.9 Hz), 7.82 (dd, 1H, Ar-**H**, ^{3}J=8.2 Hz, ^{4}J=2.0 Hz), 7.69–7.40 (m, 15H, Ar-**H**), 7.18 (d, 2H, Ar-**H**, ^{3}J=8.6 Hz), 7.08 (d, 2H, Ar-**H**, ^{3}J=8.4 Hz), 7.05 (d, 2H, Ar-**H**, ^{3}J=8.6 Hz), 6.92 (d, 2H, Ar-**H**, ^{3}J=8.4 Hz), 6.91 (d, 2H, Ar-**H**, ^{3}J=8.91 Hz), 6.88 (d, 2H, Ar-**H**, ^{3}J=9.5 Hz), 6.79 (d, 1H, Ar-**H**, ^{4}J=2.4 Hz), 4.07–3.93 (m, 10H, -OC**H**$_2$-), 1.84–1.30 (m, 32H, aliphatic-**H**), 0.89 (t, 3H, -C**H**$_3$, ^{3}J=6.8 Hz). IR (KBr) ν_{max}/cm^{-1}: 2932, 2856 (C-H str.), 2226($C\equiv N$).

2.2.3. 4-Cyanobiphenyl-4′-yl 4-octyloxy-2-(3,5-bis{[6-(4-fluorobiphenyl-4′-yloxy)hexyloxy]benzoyloxy})benzoate, II-6. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.25 (d, 1H, Ar-**H**, ^{3}J=8.8 Hz), 7.71–7.45 (m, 14H, Ar-**H**), 7.35 (d, 2H, Ar-**H**, ^{4}J=2.4 Hz), 7.23 (s, 1H, Ar-**H**), 7.20 (s, 1H, Ar-**H**), 7.12 (d, 2H, Ar-**H**, ^{3}J=8.8 Hz), 7.10 (d, 2H, Ar-**H**, ^{3}J=8.8 Hz), 6.96 (d, 4H, Ar-**H**, ^{3}J=8.3 Hz), 6.94 (d, 1H, Ar-**H**, ^{4}J=2.9 Hz), 6.81 (d, 1H, Ar-**H**, ^{4}J=2.4 Hz), 6.68 (s, 1H, Ar-**H**), 4.07 (t, 2H, -OC**H**$_2$-, ^{3}J=6.4 Hz), 4.01 (t, 4H, -OC**H**$_2$-, ^{3}J=6.4 Hz), 3.99 (t, 4H, -OC**H**$_2$-, ^{3}J=6.4 Hz), 1.86–1.32 (m, 28H, aliphatic-**H**), 0.92 (t, 3H, -C**H**$_3$, ^{3}J=6.8 Hz). IR (KBr) ν_{max}/cm^{-1}: 2934, 2858 (C-H str.), 2226 ($C\equiv N$).

2.2.4. 4-Cyanobiphenyl-4′-yl 4-octyloxy-2-(3, 5-bis{[6-(4-fluorobiphenyl-4′-yloxy)heptyloxy]benzoyloxy})benzoate, II-7. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.21 (d, 1H, Ar-**H**, ^{3}J=8.9 Hz), 7.71–7.41 (m, 14H, Ar-**H**), 7.31 (d, 2H, Ar-**H**, ^{4}J=2.2 Hz), 7.21 (s, 1H, Ar-**H**), 7.18 (s, 1H, Ar-**H**), 7.09 (d, 2H, Ar-**H**, ^{3}J=8.6 Hz), 7.06 (d, 2H, Ar-**H**, ^{3}J=8.6 Hz), 6.93 (d, 4H, Ar-**H**, ^{3}J=8.4 Hz), 6.90 (d, 1H, Ar-**H**, ^{4}J=2.4 Hz), 6.78 (d, 1H, Ar-**H**, ^{4}J=2.4 Hz), 6.65 (s, 1H, Ar-**H**), 4.06 (t, 2H, -OC**H**$_2$-, ^{3}J=6.5 Hz), 3.98 (t, 4H, -OC**H**$_2$-, ^{3}J=6.5 Hz), 3.95 (t, 4H, -OC**H**$_2$-, ^{3}J=6.5 Hz), 1.87–1.30 (m, 32H, aliphatic-**H**), 0.89 (t, 3H, -C**H**$_3$, ^{3}J=6.6 Hz). IR (KBr) ν_{max}/cm^{-1}: 2942, 2856 (C-H str.), 2226 ($C\equiv N$).

2.2.5. 4-Cyanobiphenyl-4′-yl 4-octyloxy-2-(3,4-bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxy}benzoyloxy)-benzoate, III-6. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.58 (s, 4H, Ar-**H**), 8.35 (d, 1H, Ar-**H**, ^{3}J=8.8 Hz), 8.34 (d, 1H, Ar-**H**, ^{3}J=8.8 Hz), 8.23 (d, 1H, Ar-**H**, ^{3}J=8.8 Hz), 7.85 (dd, 1H, Ar-**H**, ^{3}J=8.8 Hz, ^{4}J=2.0 Hz), 7.72–7.69 (m, 3H, Ar-**H**), 7.62 (d, 2H, Ar-**H**, ^{3}J=8.3 Hz), 7.62 (d, 2H, Ar-**H**, ^{3}J=8.3 Hz), 7.54 (d, 2H, Ar-**H**, ^{3}J=8.3 Hz), 7.21 (d, 2H, Ar-**H**, ^{3}J=8.8 Hz), 6.99∼6.90 (m, 6H, Ar-**H**), 6.82 (d, 1H, Ar-**H**, ^{4}J=2.4 Hz), 4.10–4.00 (m, 10H, -OC**H**$_2$-), 2.61 (t, 4H, Ar-C**H**$_2$, ^{3}J=7.6 Hz), 1.86–1.29 (m, 52H, aliphatic-**H**), 0.90 (t, 9H, -C**H**$_3$, ^{3}J=6.6 Hz). IR (KBr) ν_{max}/cm^{-1}: 2926, 2854 (C-H str.), 2226 ($C\equiv N$).

2.3. *Liquid-crystalline and physical properties*

The initial assignments and corresponding transition temperatures for the products were determined by thermal optical microscopy using a Nikon Optiphoto POL polarizing microscope equipped with a Mettler FP82 hot stage and FP90 control processor. The heating and cooling rates were 5°C min^{-1}. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200. The materials were studied at a scanning rate of 2–10°C min^{-1}, for both heating and cooling cycles, after being encapsulated in aluminium pans.

3. Results and discussion

We have prepared three types of oligomeric compounds, i.e. compound **I-n**, in which a 4-cyanobiphenyl moiety and two 4-fluorobiphenyl moieties are connected via 3,4-dihydroxybenzoic acid, compound **II-n**, in which a 4-cyanobiphenyl moiety and two 4-fluorobiphenyl moieties are connected via 3,5-dihydroxybenzoic acid, and compound **III-6**, in which a 4-cyanobiphenyl moiety and two phenylpyrimidine moieties are connected via 3,4-dihydroxybenzoic acid. Temperatures and enthalpies of transition for compounds **I-n**, **II-n** and **III-6** determined by optical microscopy and DSC are shown in table 1.

Compound **I-6** exhibited a monotropic nematic phase. Recrystallization followed the I–N transition. The I–N and I–recryst transitions occurred simultaneously at a cooling rate of 1°C min^{-1}. Compounds **I-7**, **II-6** and **II-7** did not show any liquid-crystalline phase. A tendency for mesophase formation of compound **I-6** possessing a 3,4-benzene unit is stronger than that of compound **II-6** possessing a 3,5-benzene unit. With respect to compound **III-6**, it was possible to supercool the nematic phase of the material. Optical textures of compounds **I-6** and **III-6** in the homeotropic alignment N phase were completely dark, indicating that the N phase for both compounds is a uniaxial nematic phase. On the other hand, we previously reported that intermolecular interactions between cyanobiphenyl and phenylpyrimidine moieties can induce a smectic A phase [21]. The appearance of the N phase instead of an induced SmA phase for compound **III-6** indicates that the compound prefers antiparallel interactions between the cyanobiphenyl moieties than those between the cyanobiphenyl and phenylpyrimidine moieties in the N phase.

In order to investigate interactions between mesogenic parts, we performed miscibility studies. Figure 3 shows a binary phase diagram on cooling between compound **III-6** and 4-cyano-4′-hexyloxybiphenyl (**6OCB**). The N phase of both compounds proved to be miscible across the full composition range. Thus, the antiparallel interaction between cyanobiphenyl moieties is thought to be a driving force for the mesophase formation. Furthermore, a SmA phase was not induced in the binary phase diagram, indicating that the interaction between cyanobiphenyl and phenylpyrimidine units does not occur in the system.

Table 1. Phase transition temperatures (°C) and transition enthalpies (kJ mol^{-1}) (in brackets) for the novel oligomeric compounds. The cooling rate was 5°C min^{-1}.

Compound	recryst	glass	N	I	mp
I-6[a]	•		• 62 (0.9)	•	100 (53.0)
I-7	• 82			•	118 (75.4)
II-6		• 20		•	108 (54.1)
II-7		• 18		•	117 (112.3)
III-6		• 13	• 78 (2.5)	•	100 (85.5)

[a] Recrystallization occurred slowly. The nematic and crystalline phases coexisted in a wide temperature range.

Figure 4 shows a binary phase diagram on cooling between compound **III-6** and 5-octyl-2-(4-hexyloxyphenyl)pyrimidine (**8-PYP-6O**). The N phase of both compounds proved to be miscible across the full composition range. However, SmA and SmC phases of **8-PYP-6O** disappeared in a mixture of **8-PYP-6O** (75 wt%) and **III-6** (25 wt%). A SmA phase was not induced in the binary phase diagram.

We have also observed liquid-crystalline properties of intermediates of compound **III-6**. The molecular structures and the transition temperatures are shown in figure 5. 4-Cyanobiphenyl-4′-yl 4-octyloxy-2-hydroxybenzoate (**A**) showed only a N phase; however, 3, 4-bis(6-(4-(5-octylpyrimidine-2-yl)phenyloxy)hexyloxy)-benzoic acid ethyl ester (**B**) [18] showed N and SmA phases.

We now turn our attention to the molecular organization in the N phase of compound **III-6**. Although X-ray crystallography would provide valuable evidence for the geometrical structures, it is difficult to get a good sample of compound **III-6** and we do not have such information at present. Recently we have determined a crystal structure of a T-shaped compound and found that it forms a λ–shaped structure due to the flexible spacer [22]. Thus, it is realistic to assume a λ–shaped structure for the present oligomers.

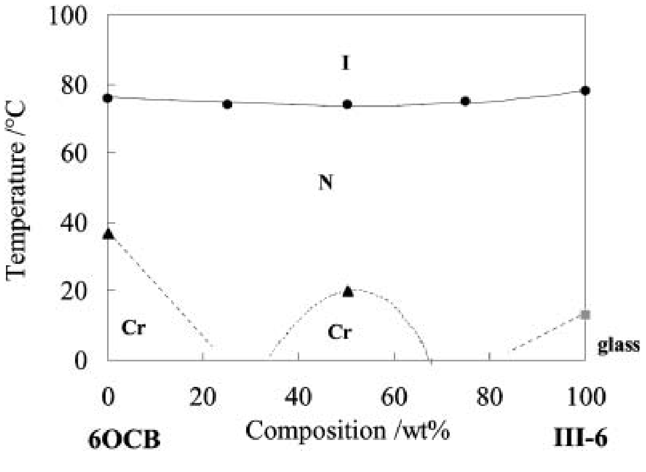


Figure 3. Phase diagram on cooling between compound **III-6** and 4-cyano-4′-hexyloxybiphenyl (**6OCB**).

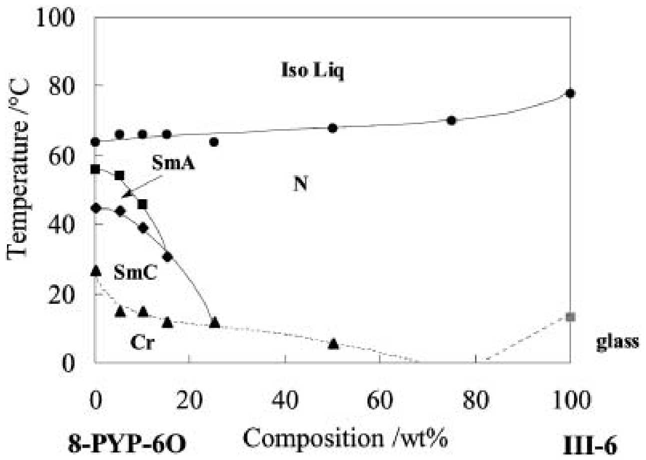
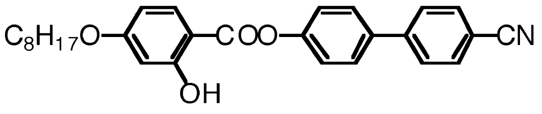
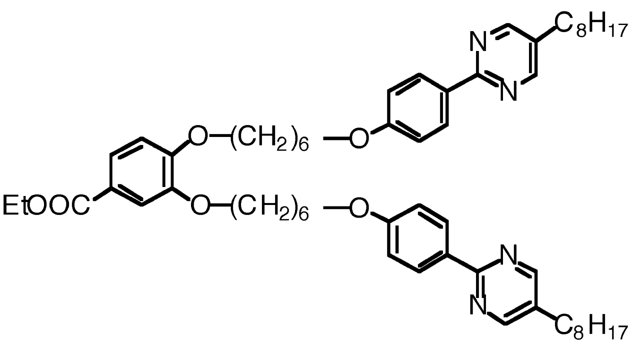


Figure 4. Phase diagram on cooling between compound **III-6** and 5-octyl-2-(4-hexyloxyphenyl)pyrimidine (**8-PYP-6O**).

The miscibility studies suggest that the driving force for appearance of the N phase is the antiparallel interaction between the cyanobiphenyl moieties. The interaction between the cyanobiphenyl and phenylpyrimidine moieties is thought to be hard to occur. Transition properties of intermediates of compound **III-6** indicate that: (i) interactions between cyanobiphenyl units of compound A induce a N phase and (ii) those between phenylpyrimidine units of compound B induce N and SmA phases. Compound **III-6** showed only a N phase, which is in contrast with a strong tendency to form smectic phases for our reported liquid crystal oligomers possessing cyanobiphenyl and phenylpyrimidine units [14–20]. Therefore, interactions between the cyanobiphenyl units are more favourable than those between the phenylpyrimidine units or those between the phenylpyrimidine and cyanobiphenyl units in the mesophase formation of compound **III-6**. Figure 6 shows a possible model for the molecular organization. The characteristic points are that: (i) the molecular shape is assumed to be a λ–shaped structure, (ii) dimerization via antiparallel interactions between the cyanobiphenyl moieties occurs, and (iii) the phenylpyrimidine moieties are thought to align along the director.



A: Iso liq 190 N 74 Cryst mp 106



B: Iso liq 92 N[85 SmA] 86 Cr mp 86

Figure 5. Molecular structures and phase transition temperatures (°C) of intermediates of compound **III-6**. 3,4-Bis(6-(4-fluorobipheny-4′-yloxy)hexyloxy)benzoic acid ethyl ester, which is an intermediate of compound **I-6**, showed a monotropic N phase. The transition temperatures were I 92°C N 90°C Cr on cooling and the melting point was 115°C.

4. Conclusion

Novel liquid crystal oligomers in which three mesogenic units are connected via 3,4-dihydroxybenzoic acid or 3,5-dihydroxybenzoic acid have been prepared. Compound **III-6** showed a monotropic nematic phase in spite of being far form the rod like structure. The appearance of the N phase can result from dimerization via antiparallel intermolecular interactions between the neighbouring cyanobiphenyl moieties.

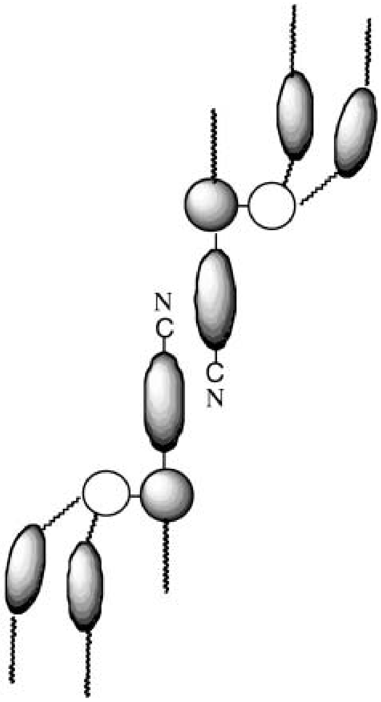


Figure 6. A possible model for the molecular organization of compound **III-6** in the N phase.

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