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Synthesis and physical properties of novel liquid crystal trimers containing resorcinol as a linking unit

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A homologous series of novel liquid crystal trimers in which cyanobiphenyl and phenylpyrimidine moieties are connected via resorcinol was prepared and their physical properties investigated. 3-{6-[4-(4-Cyanophenyl)phenyl]hexyloxy}-1-{6-[4-(5-octylpyrimidine-2-yl)phenyl]hexyloxy}benzene, compound **I-(6,6)**, was found to show monotropic nematic, smectic A and anticlinic smectic C (SmCanti) phases. We investigated the effects of the spacer length and the linking group on the phase transition behaviour. In addition, trimers with identical mesogenic units were prepared and their physical properties compared with those containing two different mesogens. Only the *meta*-substituted trimers showed the SmCanti phase despite its reduced tendency to exhibit liquid crystallinity than the *ortho*- and *para*-substituted trimers.

1. Introduction

Supramolecular assemblies composed of oligomeric liquid crystals are of current interest in the design of new liquid crystalline materials [1]. Dimeric liquid crystals are attractive because they exhibit different properties from those of conventional low molar mass mesogens. For example, the transitional 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 transitional properties of linear liquid crystal trimers on varying the spacer lengths [4]. U-shaped liquid crystals have been investigated by several research groups [5–8]. Attard and Douglass reported property–structure correlations of the dimeric compounds derived from phthalic acid, providing important insights about U-shaped liquid crystal systems [8]. More recently, in 1,3-benzene derivatives, examples of which were first synthesized by Matsunaga *et al.* [9], antiferroelectric and ferroelectric properties have been found in these banana-shaped molecules by Watanabe *et al.* [10, 11]. The banana-shaped system has opened new design possibilities for chirality and phase structures in liquid crystals [12, 13].

We have reported novel pre-organized systems, as illustrated in figure 1, e.g. U-shaped molecules [14], binaphthyl derivatives [15] and λ–shaped molecules [16]; the pre-organized supermolecules were found to induce unusual ordering in the supramolecular liquid crystalline phase. Then, we prepared a homologous series of dimeric liquid crystals, α-(4-cyanobiphenyl-4′-yloxy)-ω-[4-(5-alkylpyrimidine-2-yl)phenyl-4″-oxy]alkanes (*m*PY*n*OCB) where cyanobiphenyl and phenylpyrimidine moieties are connected via a flexible central spacer [17]. 8PY11OCB was found to show a phase sequence of I–N–SmA–SmCanti. Furthermore, a novel frustrated liquid crystalline phase was obtained in some binary mixtures between 6PY9OCB and 8PY11OCB, which appeared below a nematic or smectic A phase and was found not to possess a clear layered structure [18].

We report here the synthesis and physical properties of a homologous series of novel liquid crystal trimers in which cyanobiphenyl and phenylpyrimidine groups are connected via resorcinol.

2. Experimental

2.1. *Preparation of materials*

5-Octyl-2-(4-hydroxyphenyl)pyrimidine was obtained from Midori Chemical Corporation. Purification of final products was carried out using column chromatography over silica gel (63–210 μm) (Kanto Chemical Co., Inc.) using dichloromethane or a dichloromethane/

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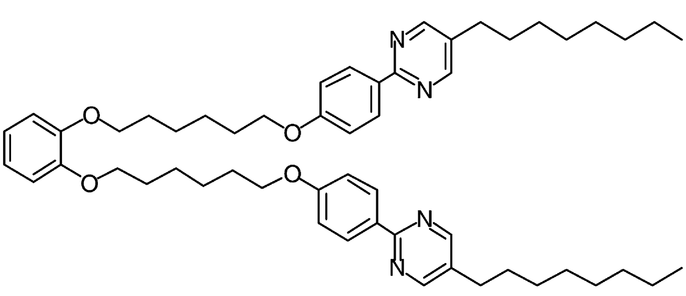
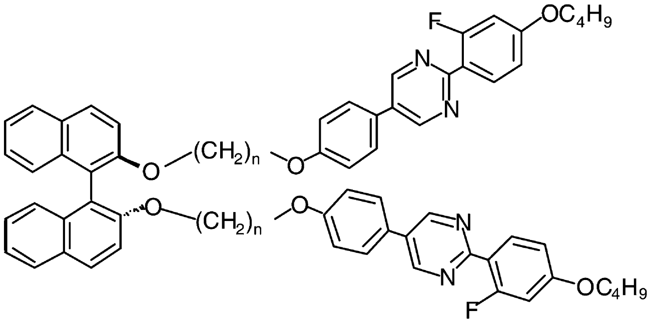
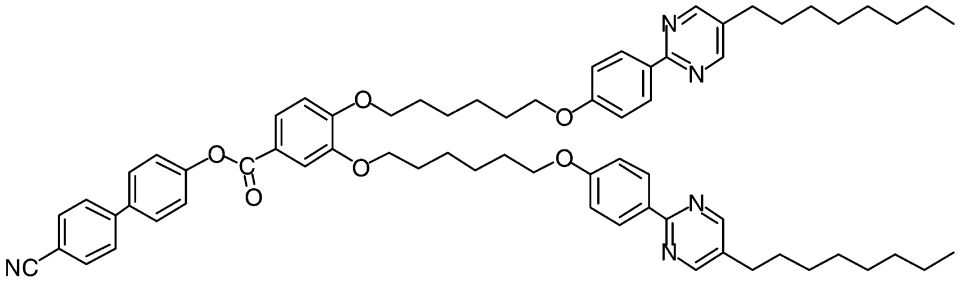


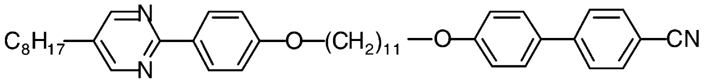
BOPPHB



Binaphthyl mesogenic derivative



λ-shaped mesogenic molecule



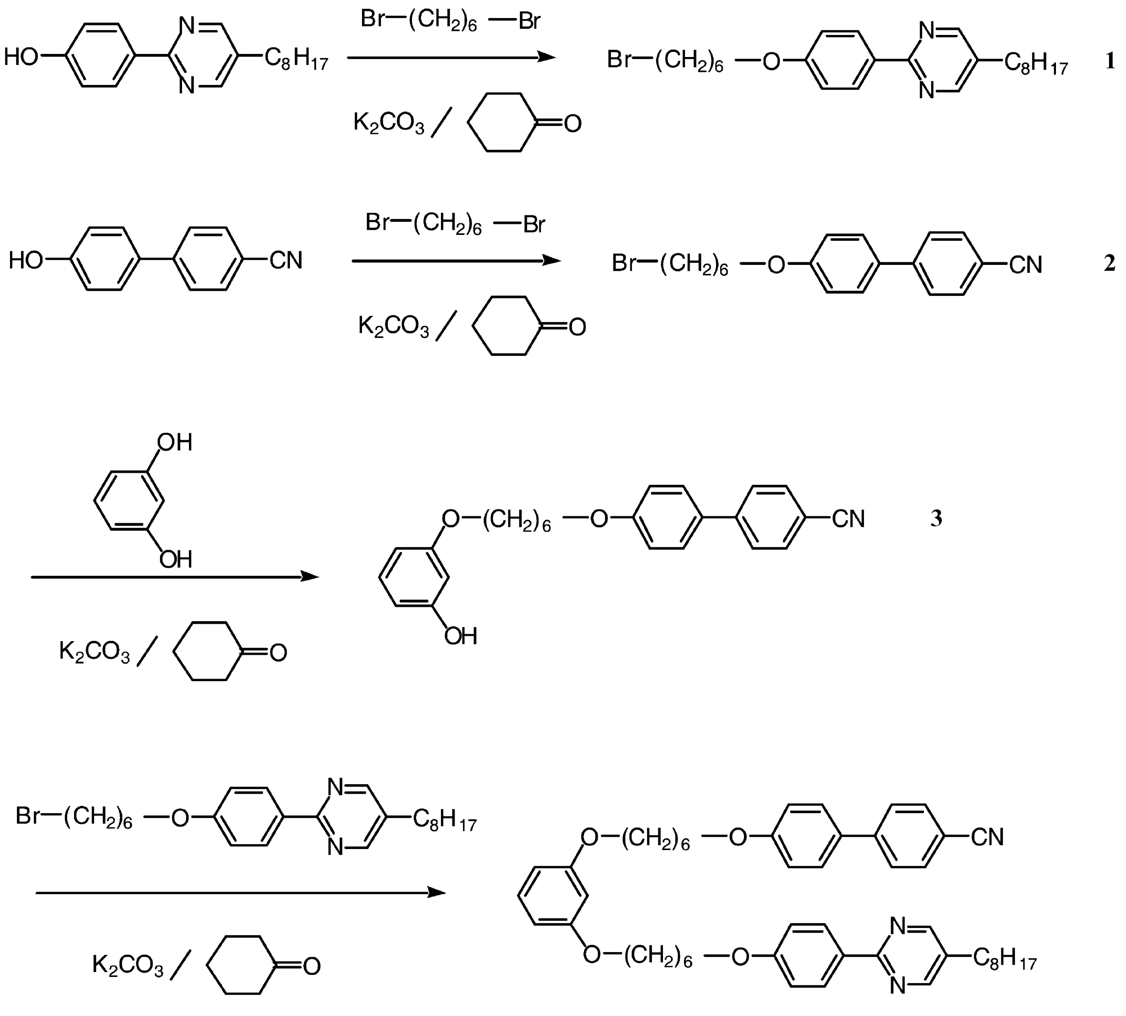
8PY11OCB

Figure 1. Oligomeric liquid crystals with unusual liquid crystalline phases.

ethyl acetate mixture as the eluent. The structure of final products was elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (Jeol JNM-GX270). The synthetic route for a typical compound, 3-{6-[4-(4-cyanophenyl)phenyl]hexyloxy}-1-{6-[4-(5-octylpyrimidine-2-yl)phenyl]hexyloxy}benzene I-(6,6), is shown in scheme 1.

To a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (1.15 g, 4.0 mmol) and 1,6-dibromohexane (1.95 g, 8.0 mmol) in cyclohexanone (5 ml) was added potassium carbonate (0.55 g, 4.0 mmol). The reaction mixture was stirred at 80°C for 8 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane. 5-Octyl-2-[4′-(6-bromohexyloxy)phenyl]pyrimidine (**1**) was obtained; yield 1.38 g (3.1 mmol, 76%).

To a solution of 4-cyano-4′-hydroxybiphenyl (0.80 g, 4.0 mmol) and 1,6-dibromohexane (1.46 g, 6.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (0.55 g, 4.0 mmol). The reaction mixture was stirred at



I-(6,6)

Scheme 1. Synthetic route for compound **I-(6,6)**.

80°C for 6 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with (8/2) dichloromethane/hexane. 4-Cyano-4′-(6-bromohexyloxy)biphenyl (**2**) was obtained; yield 0.90 g (2.5 mmol, 63%).

To a solution of compound **2** (0.80 g, 2.3 mmol) and 1,3-dihydroxybenzene (0.26 g, 2.3 mmol) in cyclohexanone (5 ml) was added potassium carbonate (0.32 g, 2.3 mmol). The reaction mixture was stirred at 90°C for 5 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with (19/1) dichloromethane/ethylacetate. The intermediate product, 3-{6-[4-(4-cyanophenyl)phenyl]hexyloxy}-1-hydroxybenzene, compound **3**, was obtained; yield 1.06 g (2.7 mmol, 57%).

To a solution of compound **1** (0.26 g, 0.6 mmol) and compound **3** (0.23 g, 0.6 mmol) in cyclohexanone (5 ml) was added potassium carbonate (0.08 g, 0.6 mmol). The reaction mixture was stirred at 130°C for 6 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with (19/1) dichloromethane/ethylacetate. The desired product, 3-{6-[4-(4-cyanophenyl)phenyl]hexyloxy}-1-{6-[4-(5-octylpyrimidine-2-yl)phenyl]hexyloxy}benzene, **I-(6,6)**, was obtained; yield 0.23 g (0.30 mmol, 52%). ^{1}H NMR(270 MHz, solvent $CDCl_3$, standard TMS): δ_H/ppm: 8.58(s, 2H,Ar–**H**), 8.37(d, 2H,Ar–**H**, J=8.9 Hz), 7.70–7.61(m, 4H, Ar–**H**), 7.51(d, 2H, Ar–**H**, J=8.9 Hz), 7.14(t, 1H, Ar–**H**, J=8.4 Hz) 6.98(d, 2H, Ar–**H**, J=8.9 Hz), 6.97(d, 2H, Ar–**H**, J=8.9 Hz), 6.48(d, 2H, Ar–**H**, J=8.4 Hz), 6.47(s, 1H, Ar–**H**), 4.04(t, 2H, –OC**H**$_2$–, J=6.2 Hz), 4.02(t, 2H, –OC**H**$_2$–, J=6.5 Hz), 3.96(t, 4H, –OC**H**$_2$–, J=6.5 Hz), 2.60(t, 2H, J=5.4 Hz), 1.87–1.53(m, 28H, aliphatic–**H**), 0.88(t, 3H, –C**H**$_3$, J=6.5 Hz). IR (KBr) ν_{max}/cm^{-1}: 2944, 2923, 2852, 2223, 1603, 1583.

The other compounds reported here were prepared in by similar methods to that for compound **I-(6,6)**.

2.2. *Liquid crystalline and physical properties*

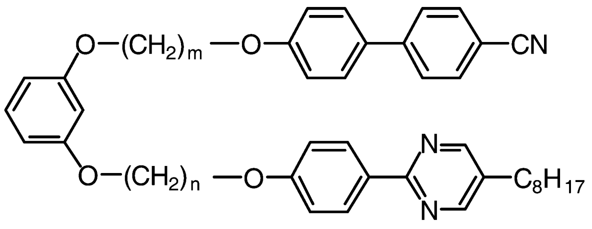
The initial assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikkon Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were 5°C min^{-1}, unless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

3. Results and discussion

3.1. *Trimers with differing mesogenic groups*

3.1.1. Effect of the spacer length. Molecular structure, temperatures and enthalpies of transition for compounds **I-(*m,n*)** determined by optical microscopy and DSC are shown in table 1. Compounds **I-(4,4)** and **I-(5,5)** showed no liquid crystalline behaviour. On the other hand, compounds **I-(6,6)**, **I-(7,7)** and **I-(8,8)** exhibited monotropic liquid crystalline phases. Furthermore, compounds **I-(6,6)** **I-(8,8)** and **I-(8,6)** exhibited an anticlinic SmC phase. Compound **I-(6,6)** was found to show the phase sequence: I–N–SmA–SmCanti. The anticlinic SmC 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. All transitions from isotropic liquid to liquid crystal are very close together and no odd–even effect is observed. For the mesogenic compounds with a resorcinol central unit and symmetrical spacers, both spacers are varied and, due to the geometry of the 1,3-substituted resorcinol group, the overall parity of the spacer including the middle group remains the same, i.e. odd. Only compound **I-(8,7)** has an overall even parity of the spacer. However, the I to SmA transition temperature and enthalpy are only marginally higher than those of compounds **I-(7,7)** and **I-(8,8)**. On the other hand, there is a clear alternation in crystallization temperature except for **I-(4,4)**. An explanation why SmCanti is found for compounds **I-(6,6)**, **I-(8,8)** and **I-(8,6)** may be that these compounds can be supercooled sufficiently to observe the phase.

Table 1. Molecular structure, transition temperatures (°C) on cooling and enthalpies (kJ mol^{-1}) of transition (in brackets) for compounds **I-(*m,n*)**.



I-(m, n)

I-(*m,n*)	Recryst	SmCanti	SmA	N	I	m.p.
I-(4,4)	• 119				•	136
I-(5,5)	• 98				•	122
I-(6,6)	• 35	• 75 (0.5)	• 88 (2.3)	• 91 (2.2)	•	100
I-(7,7)	• 75		• 90 (8.6)		•	99
I-(8,8)	• 44	• 54[a]	• 92 (9.8)		•	74
I-(8,6)	• 55	• 71[a]	• 93 (9.3)		•	94
I-(8,7)	• 58		• 94 (11.7)		•	100

[a] Enthalpies too small to be detected.

3.1.2. Effect of the linking group. We have prepared the corresponding 1, 2- and 1, 4-benzene derivatives and compared the transition behaviour with that of compound **I-(6,6)** (see figure 2). The 1, 2-benzene derivative, **II-(6,6)**, exhibited enantiotropic N and SmA phases. The 1, 4-benzene derivative, **III-(6,6)**, shows the highest T_{IN}. Only the 1, 3-disubstituted trimer showed the SmCanti phase despite its reduced tendency to exhibit liquid crystalinity over the 1, 2- and 1, 4-disubstituted trimers.

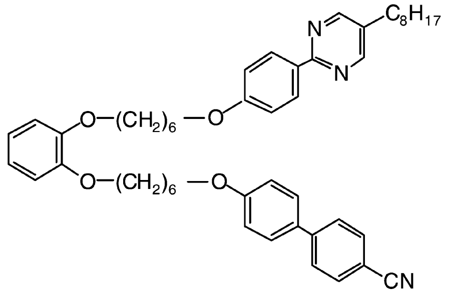
3.2. *Trimers with identical mesogenic groups*

3.2.1. Cyanobiphenyl as the mesogen. Molecular structures, transition temperatures and enthalpies of transition for trimers in which two cyanobiphenyl mesogenic moieties are connected via resorcinol are shown in table 2. Compounds **IV-(4,4)**, **IV-(6,6)** and **IV-(8,8)** exhibited a N phase, whereas compounds **IV-(5,5)** and **IV-(7,7)** did not show a N phase owing to the high recrystallization temperature. Compound **IV-(6,7)** was found to show the N phase. On the other hand, the phase transition temperatures of 1,2-bis{6-[4-(4-cyanophenyl)phenyl]hexyloxy}benzene were I 124°C (3.2 kJ mol^{-1}) N 117°C recryst, and the melting point was 128°C. Although liquid crystallinity for the 1,3-benzene derivative is lower than the 1, 2-benzene derivative, the phase sequence did not depend on the substituted positions. The synthesis and transition properties for 1,2-bis{ω-[4-(4-cyanophenyl)phenyl] alkyloxy}benzene have also been reported by Jackson *et al.* [19].

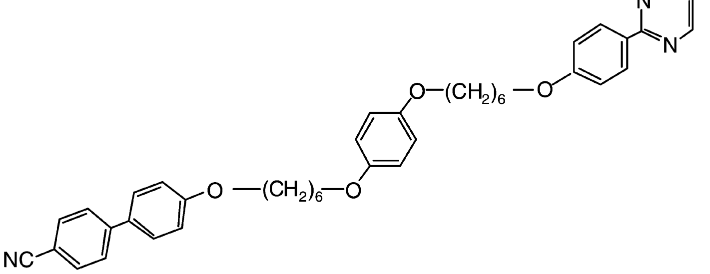
3.2.2. Phenylpyrimidine as the mesogen. Molecular structures, transition temperatures and enthalpies of transition for trimers in which two phenylpyrimidine mesogenic moieties are connected via resorcinol are shown in table 3. None of the compounds showed liquid crystalline behaviour. On the other hand, 1, 2-bis{6-[4-(5-octylpyrimidine-2-yl)phenyl]hexyloxy}benzene showed N and SmC phases [14].

3.3. *Molecular organization models*

Let us now discuss the phase transition sequence I–N–SmA–SmCanti seen for **I-(6,6)**. Favourable relative orientations of the cyanobiphenyl and phenylpyrimidine moieties in **I-(*m*,*n*)** is thought to contribute to the appearance of the SmCanti phase. Intermolecular interactions between such mesogenic moieties were



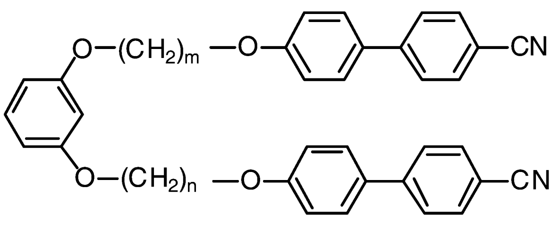
II-(6, 6): recryst 51 SmA 109 (3.8) N 113 (2.5) I mp 99



III-(6, 6): recryst 153 N 158 (9.7) I mp 166

Figure 2. Molecular structures, transition temperatures (°C) on cooling and enthalpies (kJ mol^{-1}) of transition (in brackets) for compounds **II-(6,6)** and **III-(6,6)**.

Table 2. Molecular structure, transition temperatures (°C) on cooling and enthalpies (kJ mol^{-1}) of transition (in brackets) for compounds **IV-(*m,n*)**.



IV-(m, n)

IV-(*m,n*)	Recryst	N	I	m.p.
IV-(4,4)	• 80	• 123 (1.2)	•	122
IV-(5,5)	• 113		•	137
IV-(6,6)	• 96	• 112 (2.0)	•	112
IV-(7,7)	• 104[a]	• 104[a]	•	123
IV-(8,8)	• 66	• 106 (3.0)	•	107
IV-(6,7)	• 93	• 112 (4.0)	•	145

[a] The I–N transition and recrystallization occurred simultaneously.

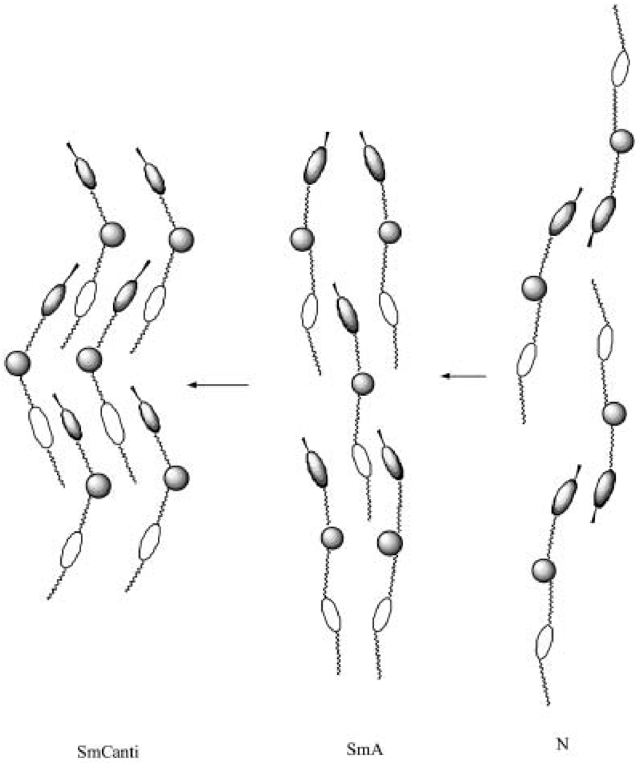
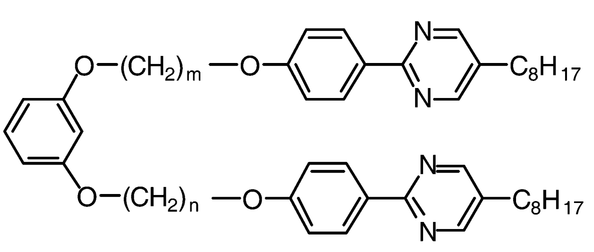


Figure 3. A schematic molecular organization model for the N–SmA–SmCanti phase transitions of compound **I-(6,6)**.

known to have significant effects on the molecular assemblies in liquid crystalline phases: (a) antiparallel interaction between cyanobiphenyl groups promotes the formation of N and SmA phases; (b) interaction between phenylpyrimidine groups stabilizes smectic phases, especially a SmC phase; and (c) interaction between cyanobiphenyl and phenylpyrimidine groups induces a SmA phase. Only a few compounds have so far been reported to show the nematic phase and anticlinic SmC phase [17, 20, 21]. Aoki and Nohira reported that the racemic modification of TFMB shows the anticlinic phase with the presence of a narrow temperature range nematic phase [20]. Nishiyama *et al.* reported that ferrielectric and anriferroelectric chiral liquid crystal dimers show a stable chiral nematic phase [21]. Furthermore, Nishiyama *et al.* found that the introduction of a thioether linkage instead of the ether group into the twin molecular configuration stabilizes the antiferroelectric phase [22]. They noted that the strong polarity and high mobility of the central spacer allows the thiaalkyl twin to produce a conformational transition in the SmA phase. We give the following explanations for the unusual phase sequence of I–N–SmA–SmCanti for compound **I-(6,6)**: (1) intermolecular antiparallel interaction between cyanobiphenyl groups produces the N phase; (2) interaction between cyanobiphenyl and phenylpyrimidine induces the intercalated SmA phase; and then (3) reorganization to the bent shaped structure for effective molecular packing can give the SmCanti phase. Models for molecular organization in the N, SmA and SmCanti phases are shown in figure 3. We note that X-ray data are now necessary to confirm the intercalated SmA phase.

Table 3. Molecular structure and transition temperatures (°C) on cooling for compounds **V-(*m,n*)**.



V-(m, n)

V-(*m,n*)	Recryst	I	m.p.
V-(6,6)	• 111	•	115
V-(7,7)	• 86	•	99
V-(6,7)	• 107	•	114

4. Conclusions

We have designed a homologous series of novel liquid crystal trimers in which cyanobiphenyl and phenylpyrimidine moieties are connected via resorcinol. Only the *meta*-substituted trimers with differing mesogenic units showed the SmCanti phase. The property–structure correlations suggest that core–core interactions between cyanobiphenyl and phenylpyrimidine moieties organized by the flexible bent structure can induce the SmCanti phase.

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