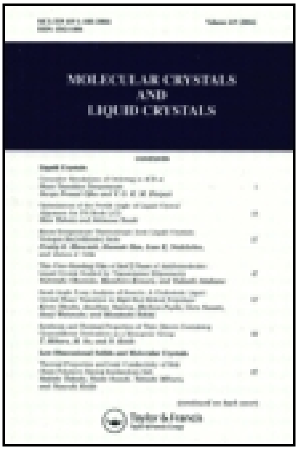

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Phase Transition Behaviour of Symmetric and Non-Symmetric Dimeric Liquid Crystals

Atsushi Yoshizawa [a] & Shinobu Hatai [a]

[a] Department of Materials Science and Technology, Hirosaki University, Hirosaki, Japan

To cite this article: Atsushi Yoshizawa & Shinobu Hatai (2004): Phase Transition Behaviour of Symmetric and Non-Symmetric Dimeric Liquid Crystals, Molecular Crystals and Liquid Crystals, 411:1, 169-176

To link to this article: http://dx.doi.org/10.1080/15421400490434991

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 169/[1211]–176/[1218], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490434991

PHASE TRANSITION BEHAVIOUR OF SYMMETRIC AND NON-SYMMETRIC DIMERIC LIQUID CRYSTALS

*Atsushi Yoshizawa** *and Shinobu Hatai*
Department of Materials Science and Technology,
Faculty of Science and Technology Hirosaki University,
3, Bunkyo-cho, Hirosaki 036-8561, Japan

We have prepared novel symmetric and non-symmetric dimeric liquid crystals possessing a phenylpyrimidine moiety and investigated the transition behaviour. We discuss effect of the spacer length and the core structure on the transition behaviour. The present system is thought to be a model to investigate molecular packing in SmA and SmC phases of 2-ring phenylpyrimidine liquid crystals. Results of binary mixture systems between the dimeric materials indicate that intermolecular interaction organized by antiparallel packing of the phenylpyrimidine group increases the stability of the SmC phase.

Keywords: dimer; liquid crystals; phase transition; smectic phase

1. INTRODUCTION

Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low-molecular mass mesogens [1–3]. For instance, the transition properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Furthermore smectic liquid-crystalline properties of dimeric liquid crystals are interesting [1,4]. Smectic phases of dimeric liquid crystals have the variation in the layer spacing. Furthermore non-symmetric dimeric liquid crystals can show two different SmA modifications [1,5]. On the other hand, we have investigated the microscopic organization of molecules in SmA, SmC* and SmCa* phases by means of C-13 NMR [6–8]. NMR results suggest that (1) cooperative motion for the core parts contributes to the orientational order of molecules in each layer and (2) inter-layer permeation of tails causes correlation between cores in adjacent layers. We have investigated the

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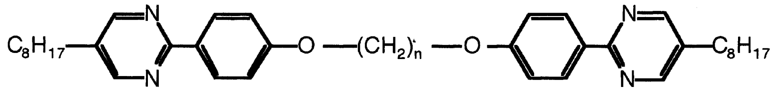
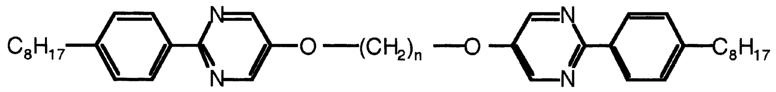
Corresponding author. Email: ayoshiza@cc.hirosaki-u.ac.jp structure-property relations in system consisting of chiral twin molecules and host molecules [9–11]. The matching of the core structures between a host and a chiral twin molecule was found to induce a stronger helical structure in the SmC phase [11,12].

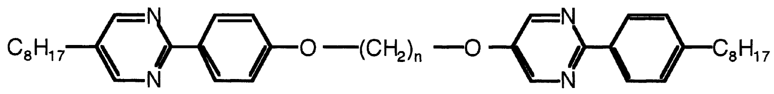
In the present study, we prepared the following symmetric and non-symmetric dimeric liquid-crystalline materials and investigated the structural effect on the transition behaviour. 2-ring phenylpyrimidine liquid crystals are useful SmC base materials for ferroelectric liquid crystals. The present dimeric system is thought to be a model to investigate molecular packing in SmA and SmC phases of the 2-ring phenylpyrimidine materials.



1-n



2-n



3-n

2. EXPERIMENTAL

2.1. Materials

***1,7-Bis [4-(5-octyl-2-pyrimidinyl)phenyloxy]heptane* 1–7**

To a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (710 mg, 2.5 mmol) and 1,7-dibromohexane (258 mg, 1.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (331 mg, 2.4 mmol). The reaction mixture was stirred at reflux for 4 h. After the filtration of participate, the solvent was removed by evaporation. Recrystallization from ethanol-ethylacetate (1:1) gave the desired product, yield 542 mg (82%).

^{1}HNMR (270 MHz, solvent $CDCl_3$, standard TMS) $^{\delta}$H: 8.56 (4 H, s), 8.35 (4 H, d, J = 8.9 Hz), 6.97 (4 H, d, J = 8.9 Hz), 4.03 (4 H, t, J = 6.5 Hz), 2.59 (4 H, t, J = 7.6 Hz), 1.1–1.9 (34 H, m), 0.88 (6 H, t, J = 6.6 Hz); IR (KBr, cm^{-1}) 2955, 2925, 1605, 1540, 1255 Compound **1–11** was obtained in a similar method to that for compound **1–7**.

1,7-Bis [2-(4-octylphenyl)pyrimidine-5-yloxy]hexane 2–6

To a solution of 5-hydroxy-2-(4-oxtylphenyl)pyrimidine (710 mg, 2.5 mmol) and 1,6-dibromohexane (244 mg, 1.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (331 mg, 2.4 mmol). The reaction mixture was stirred at reflux for 4 h. After the filtration of participate, the solvent was removed by evaporation. Recrystallization from ethanol-ethylacetate (1:1) gave the desired product, yield 488 mg (75%).

^{1}HNMR (270 MHz, solvent $CDCl_3$, standard TMS) $^{\delta}$H: 8.44 (4 H, s), 8.25 (4 H, d, J = 8.1 Hz), 7.27 (4 H, d, J = 8.1 Hz), 4.11 (4 H, t, J = 6.4 Hz), 2.65 (4 H, t, J = 7.8 Hz), 1.1–1.9 (32 H, m), 0.88 (6 H, t, J = 6.6 Hz); IR (KBr, cm^{-1}) 2955, 2925, 1610, 1545, 1275 Compounds **2–7, 2–8, 2–9** and **2–11** were obtained in a similar method to that for compound **2–6**.

1-[4-(5-octyl-2-pyrimidinyl)phenyloxy]-11-[2-(4-octylphenyl)pyrimidine-5-yloxy]undecane 3–11

To a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (568 mg, 2.0 mmol) and 1, 11-dibromoundecane (942 mg, 3.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (276 mg, 2.0 mmol). The reaction mixture was stirred at 80℃ for 5 h. After the filtration of participate, the solvent was removed by evaporation. The residue was washed with ethanol and purified by column chromatography on silica gel with dichloromethane. Recrystallization from ethanol gave 5-octyl-2-[4-(11-bromoundecyloxy) phenyl]pyrimidine, yield 470 mg (45%).

To a solution of 5-octyl-2-[4-(11-bromoundecyloxy)phenyl]pyrimidine (420 mg, 0.8 mmol) and 5-hydroxy-2-(4-oxtylphenyl)pyrimidine (284 mg, 1.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (138 mg, 1.0 mmol). The reaction mixture was stirred at reflux for 4 h. After the filtration of participate, the solvent was removed by evaporation. Recrystallization from ethanol-ethylacetate (1:1) gave the desired product, yield 470 mg (43%).

^{1}HNMR (270 MHz, solvent $CDCl_3$, standard TMS) $^{\delta}$H: 8.56 (2 H, s), 8.43 (2 H, s), 8.34 (2 H, d, J = 8.9 Hz), 8.24 (2 H, d, J = 8.2 Hz), 7.26 (2 H, d, J = 8.2 Hz), 6.97 (2 H, d, J = 8.9 Hz), 4.08 (2 H, t, J = 6.6 Hz), 4.02 (2 H, t, J = 6.6 Hz), 2.65 (2 H, t, J = 7.6 Hz), 2.59 (2 H, t, J = 7.6 Hz), 1.1–1.9 (42 H, m), 0.88 (6 H, t, J = 6.6 Hz); IR (KBr, cm^{-1}) 2955, 2920, 1610, 1545, 1275, 1250.

Compound **3–7** was obtained in a similar method to that for compound **3–11**.

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 Nikon

Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnance and FP80 control unit. The heating and cooling rates were 2℃ min^{-1}. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200.

3. RESULTS AND DISCUSSION

3.1. Liquid-crystalline Properties

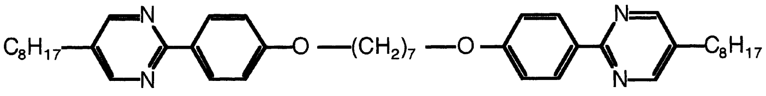
Molecular structures, transition temperatures and enthalpies for the novel dimeric materials are listed in Figure 1. Transition temperatures for the corresponding monomeric compounds are shown in Figure 2.

Symmetric dimeric compounds **2-n** except for **2–11** showed a phase transition of Iso Liq to SmA. Increasing the spacer length, the I-SmA transition temperature decreased. A marked odd-even effect in the transition temperatures depending on the parity of the spacer was observed. On the other hand, compounds **1–7** and **1–11** showed a phase transition of Iso Liq to N. The difference in the stability of smectic phases between **1-n** and **2-n** may be attributed to the difference in transition behaviour between the corresponding monomeric compounds **8-PYP-8O** and **8O-PYP-8**. 5-alkyloxy-pyrimidine group affects the stability of smectic phases. Non-symmetric dimeric compound **3–7** was found to have higher stability of the smectic phases in comparison with the symmetric dimeric compound **2–7**.

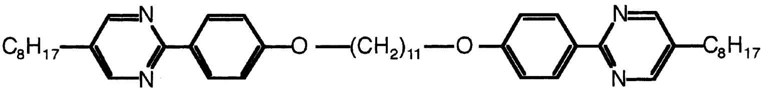
We discuss the difference in the stability of the smectic phases based on the molecular arrangement. For symmetrical dimers with the mesogenic units connected to the spacer through ether groups, smectic phase behaviour was found for terminal alkyl groups longer than half the spacer length. In these cases the smectic layer spacings were found to be about equal to the molecular length [3]. This behaviour was also found for some non-symmetric dimers [13]. Thus, we assume that the present system has this molecular arrangement in the SmA and SmC phases. Possible models of molecular arrangement for **1–7, 2–7** and **3–7** are shown in Figure 3. **1–7** did not show smectic phases, indicating that molecular packing shown in Figure 3(a) is unfavourable for **1–7**. Two models, i.e., parallel (Fig. 3(c)) and antiparallel (Fig. 3(d)) arrangements, are possible for **3–7**.

3.2. Binary Mixture Studies

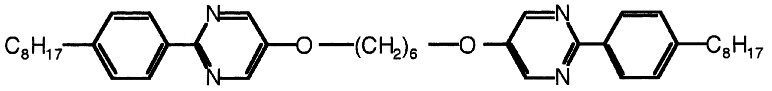
In order to understand intermolecular interaction responsible for SmA and SmC phases of the phenylpyrimidine system, we have investigated transition behaviour of a one to one binary mixture by weight between the dimeric liquid crystals. Transition temperatures of binary mixtures are shown in Table 1.



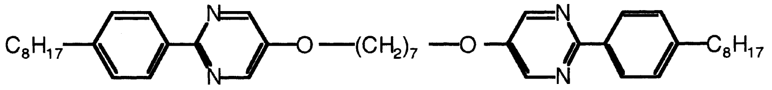
1-7: Iso Liq 109 (-2.1) N 106 recryst mp 111



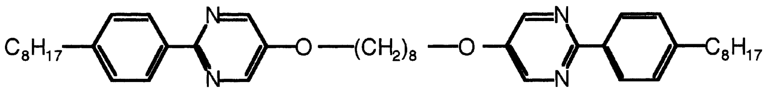
1-11: Iso Liq 103 (-2.8) N 92 recryst mp 101



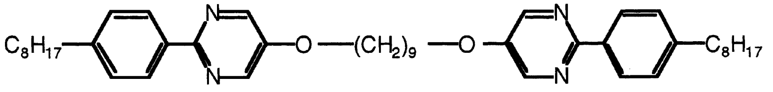
2-6: Iso Liq 168 (-13.5) SmA 147 SmC 138 SmX 120 recryst mp 168



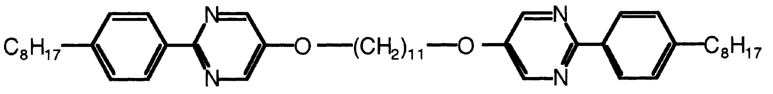
2-7: Iso Liq 120 (-10.2) SmA 83 SmC 80 recryst mp 96



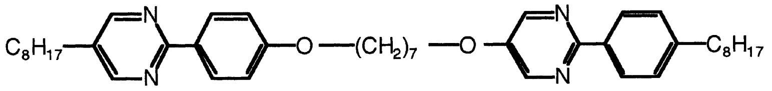
2-8: Iso Liq 139 (-14.5) SmA 92 recryst mp 134



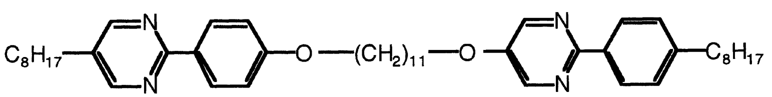
2-9: Iso Liq 106 (-5.8) SmA 92 recryst mp 106



2-11: Iso Liq 103 recryst mp 107

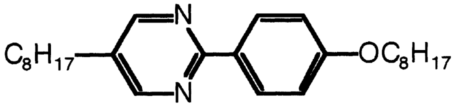


3-7: Iso Liq 132 (-15.2) SmA 123 SmC 120 recryst mp 130

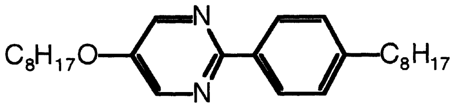


3-11: Iso Liq 121 recryst mp 125

FIGURE 1 Molecular structures, transition temperatures and transition enthalpies for the dimeric compounds.



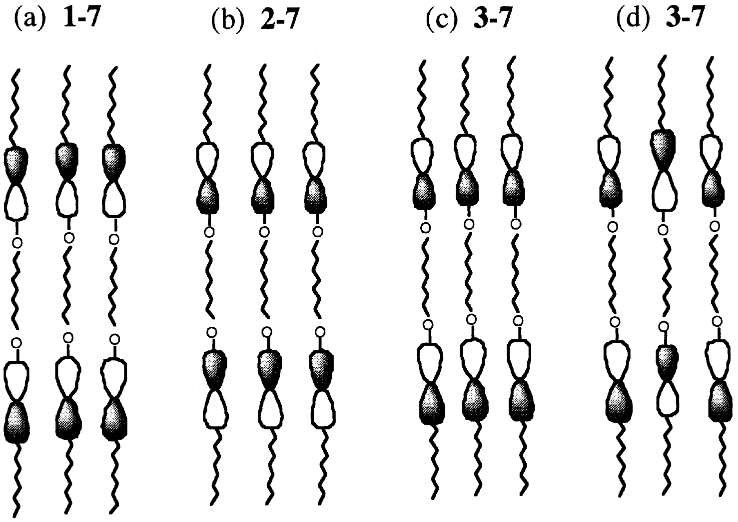
8-PYP-8O: Iso Liq 68 N 62 SmA 56 SmC



8O-PYP-8: Iso Liq 83 SmA 63 SmC

FIGURE 2 Molecular structures and transition temperatures for the corresponding monomeric compounds.

In the mixture of **1–7** and **2–7** the marked increase in the thermal stability of the SmC phase was observed. And a SmC phase was found to be induced in the mixture of **1–11** and **2–11**. The results indicate that the antiparallel arrangement is favourable for the SmC phase (Fig. 4(a)). With respect to the mixture of **2–7** and **3–7**. the I-SmA transition temperature of the mixture is slightly lower than that of **3–7** for 2℃, however, the SmA-SmC transition temperature of the mixture is markedly lower than that of **3–7** for 17℃. In the mixture parallel and antiparallel arrangements



(a) **1-7** (b) **2-7** (c) **3-7** (d) **3-7**

FIGURE 3 Possible models of molecular arrangements for **1–7**, **2–7** and **3–7**.

TABLE 1 Transition Temperatures (℃) for a One to One Binary Mixture by Weight Between Dimeric Liquid Crystals on Cooling

	Cryst		SmC		SmA		N		Iso
1–7 / **2–7**	●	98	●	111	●	124			●
1–11 / **2–11**	●	75	●	87	●	104			●
2–7 / **3–7**	●	95	●	106	●	130			●
1–11 / **2–7**	●	81	●	85	●	113			●
1–7 / **1–11**	●	79					●	105	●
2–7 / **2–9**	●	71			●	113			●
3–7 / **3–11**	●	96	●	99	●	116			●

can coexist (Fig. 4(b)). Thus, there is no significant difference in the stability of the SmA phase between parallel and antiparallel arrangements of the phenylpyrimidine moiety, on the other hand, the intermolecular

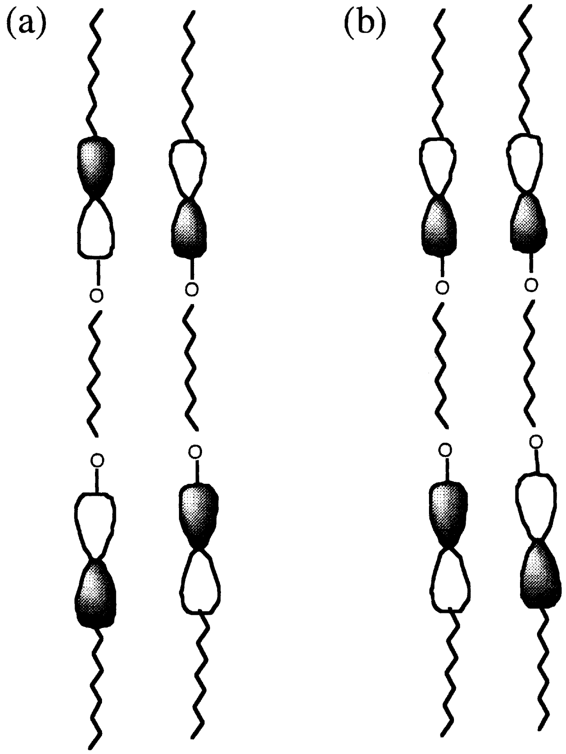


FIGURE 4 Effect of core-core interaction on stability of SmA and SmC phases of a one to one binary mixture. (a) **1–7** and **2–7**; (b) **2–7** and **3–7**.

interaction organized by the antiparallel arrangement is thought to be more favourable than that by the parallel one in the SmC phase. With respect to a binary mixture of **1–11** and **2–7**, the stability of the SmC phase of the mixture is compatible with that of **2–7**. The mismatch in the central spacer length between **1–11** and **2–7** is thought to suppress the favourable antiparallel packing. In a mixture of **1–7** and **1–11**, a wide temperature range of a N phase was observed, indicating that the mismatch in the spacer length between them does not affect the stability of the nematic phase. In a mixture of **2–7** and **2–9**, the stability of the SmA phase was slightly affected by mixing the two compounds, and the SmC phase of **2–7** disappeared in the mixture. With respect to a binary mixture of **3–7** and **3–11**, the SmA-SmC transition temperature of the mixture was markedly lower than that of **3–7**, indicating that core-core interaction between antiparallel phenylpyrimidine moieties contributes to formation of the SmC phase.

4. CONCLUSIONS

We have prepared novel symmetric and non-symmetric dimeric compounds and investigated the transition properties. The results of binary systems indicate that intermolecular interaction organized by antiparallel packing of the phenylpyrimidine group increases the stability of the SmC phase. However, there is no significant difference in packing effect between parallel and antiparallel arrangements on the stability of the SmA phase.

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