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Topological Effect in Dimeric Liquid Crystals

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*We have prepared some new dimeric liquid crystals in which two phenylpyrimidine moieties are connected via (±)-trans-1,2-cyclohexanediol or p-toluenesulfon amide and investigated the transition behaviour. (±)-trans-1,2-Bis{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}cyclohexane **1** was found to show enantiotropic nematic (N) and smectic A (SmA) phases with a low melting point. On the other hand, N-p-toluensulfonyl-bis{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy}amine **2** showed only a monotropic SmA phase. We discuss topological effect of the connecting group on the phase transition behaviour.*

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

1. INTRODUCTION

The driving force of mesophase formation is a fundamental topic in the investigation of molecular assembly. Recently molecular topology has attracted much attention as the origin for producing novel self-organizing systems [1]. Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low-molecular mass mesogens [2–4]. On the other hand, we have investigated the microscopic organization of molecules in SmA, SmC^* and SmC^*_A phases by means of C-13 NMR [5–7]. The NMR studies suggest that cooperative motion for the core parts contributes to the orientational order of molecules in each layer. We prepared a U-shaped molecule in which two phenylpyrimidine moieties are connected via catechol (**BOPPHB**).

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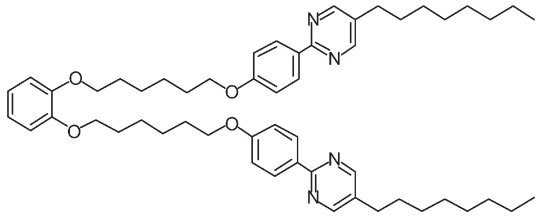
Strong correlation of rotation around the long axis of each mesogenic group is expected. **BOPPHB** was found to have smectic-like layer ordering in the N phase, and unusual enthalpy changes were observed in the N phase on heating from the monotropic SmC phase [8].



BOPPHB

In the present study, we have designed some novel dimeric liquid crystals in which two phenylpyrimidine moieties are connected via (±)-*trans*-1,2-cyclohexanediol or *p*-toluenesulfon amide. Topological effect of the connecting group on phase transition behaviour of the dimeric liquid crystals has been investigated.

2. EXPERIMENTAL

2.1. Materials

(±)-trans-1,2-Bis{6-[4-(5-octylpyrimidin-2-yl)phenoxy]hexyloxy} cyclohexane, 1

To a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (569 mg, 2.0 mmol) and 1,6-dibromohexane (736 mg, 3.0 mmol) in cyclohexanone (10 mL) was added potassium carbonate (280 mg, 2.0 mmol). The reaction mixture was stirred at 70°C for 4 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. 5-Octyl-2-[4-(6-bromohexyl)phenyl]pyrimidine was obtained. Yield: 559 mg (45%).

To a solution of (±)-*trans*-1,2-cyclohexanediol (67 mg, 0.57 mmol) and 5-octyl-2-[4-(6-bromohexyl)phenyl]pyrimidine (1.08 g, 2.4 mmol) in a dimethylsulfoxide–toluene (1:4) mixture (10 mL) was added potassium hydroxide (200 mg, 3.6 mmol). The reaction mixture was stirred at room temperature for 6 hr and then stirred at 60°C for 25 h. After the filtration of participate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a dichloromethane–ethylacetate (14:1) mixture as a eluent. The desired product was obtained. Yield: 41 mg (8%).

^{1}HNMR (270 MHz, solvent $CDCl_3$, standard TMS) $^\delta$H: 8.56 (s, 4H), 8.34 (d, 4H, J = 8.9 Hz), 6.96 (d, 4H, J = 8.9 Hz), 4.01 (t, 4H, J = 6.5 Hz), 3.56 (t, 4H, J = 6.3 Hz), 3.17–3.10 (m, 2H), 2.59 (t, 4H, J = 7.6 Hz), 1.27–1.97 (m, 48H), 0.88 (t, 6H, J = 6.8 Hz); IR (KBr, cm^{-1}) 2928, 2855, 1609, 1585, 797.

N-p-toluensulfonyl-bis{6-[4-(5-octylpyrimidin-2-yl)phenoxy] hexyloxy}amine, 2

To a stirred solution of *p*-toluensulfonamide (77 mg, 0.45 mmol) in *N, N*-dimethyformamide (DMF, 10 mL) was added 60% sodium hydride (52 mg, 1.3 mmol) at 90°C and the reaction mixture was stirred at 90°C for 1 h. Cooling the reaction mixture to room temperature, 5-octyl-2-(4-hydroxyphenyl)pyrimidine (440 mg, 1.0 mmol) was added to the mixture and then the reaction mixture was stirred at room temperature for 5 h. DMF was removed under reduced pressure and solid residue was obtained. Dichloromethane was added to the residue and the suspension was stirred. After the filtration of participate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a dichloromethane-ethylacetate (40:1) mixture as the eluent. Recrystallization from ethanol gave the desired product, yield 265 mg (65%).

^{1}HNMR (270 MHz, solvent $CDCl_3$, standard TMS) $^\delta$H: 8.57 (s, 4H), 8.35 (d, 4H, J = 8.9 Hz), 7.68 (d, 2H, J = 8.4 Hz), 7.27 (d, 2H, J = 8.6 Hz), 6.96 (d, 4H, J = 9.2 Hz), 4.00 (t, 4H, J = 7.7 Hz), 2.59 (t, 4H, J = 6.2 Hz), 2.40(s, 3H), 1.27–1.83 (m, 48H), 0.88 (t, 6H, J = 6.8 Hz); IR (KBr, cm^{-1}) 2928, 2854, 1586, 800.

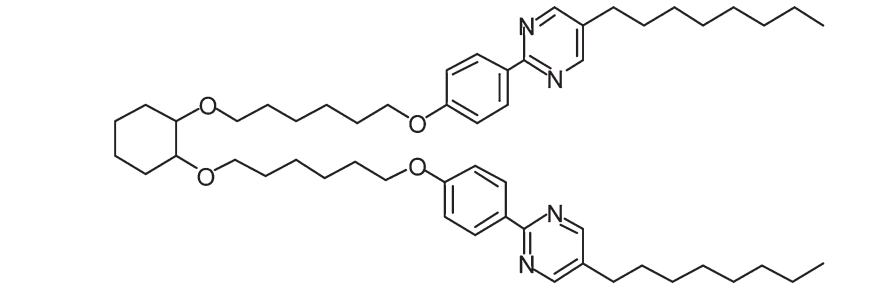
2.2. Liquid-Crystalline Properties

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 5°C min^{-1}. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200.

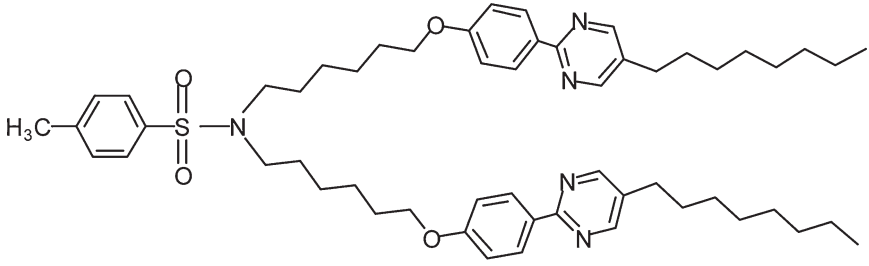
3. RESULTS AND DISCUSSION

3.1. Liquid-Crystalline Properties

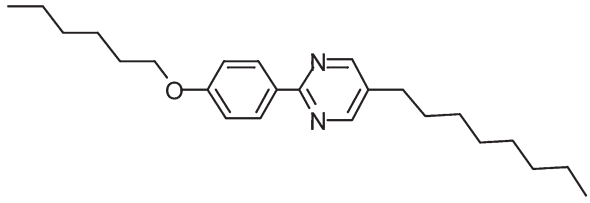
Molecular structures of the novel dimeric materials and the corresponding monomeric compound (**8-PYP-6O**) are shown in Figure 1.



1



2



8-PYP-6O

FIGURE 1 Molecular structures for the novel dimeric liquid crystals and its corresponding monomeric compound.

Temperatures and enthalpies of transition for the compounds and **BOPPHB** determined by optical microscopy and differential scanning microscopy (DSC) are compared in Table 1.

BOPPHB possessing catechol as a connecting group showed N and SmC phases, however, compound **1** was found to show enantiotropic N and SmA phases with markedly low melting temperature. Compound **2** showed only a monotropic SmA phase. Temperature range for the liquid-crystalline phases for compound **1** is similar to that for the monomeric compound, **8-PYP-6O**.

TABLE 1 Transition Temperatures (°C) on Cooling and Enthalpies ($kJmol^{-1}$) of Transition (in brackets) for Compounds under Investigation

Compound	SmC	SmA	N	Iso	mp
1		• 66.3 (1.2)	• 70.9 (3.4)	•	34.5(30.1)
2		• 48.4 (10.6)		•	90.1(60.9)
BOPPHB	• 43.4(0.3)		• 83.3 (3.5)	•	76.0(57.7)
8-PYP-6O	• 44.5	• 57.5(0.4)	• 65.0 (1.7)	•	27.0(27.5)

3.2. Binary Mixture Studies

We investigated the transition behaviour on cooling of binary mixtures between each novel dimeric compound and its corresponding monomeric compound (Fig. 2). There was no biphasic temperature region for the binary mixtures. Figure 2(a) shows a binary phase diagram for mixtures of **8-PYP-6O** and compound **1**. The N and SmA phases of both materials proved to be miscible across the full composition range. Furthermore, the SmC phase was observed even in the mixture containing 7 wt% of compound **1**. The mixtures between **8-PYP-6O** and compound **1** were not crystallized on cooling to –30°C. Figure 2(b) shows a binary phase diagram for mixtures of **8-PYP-6O** and compound **2**. The SmA phase of both materials proved to be miscible, however, the SmC phase disappeared in the mixture containing 25 wt% of compound **2**. Transition temperatures on heating of the mixture containing 25 wt% of compound **2** were Cryst 25°C SmA 47°C N 60°C Iso, however, the mixture containing 75 wt% of compound **2** did not show a liquid-crystalline phase on heating.

Then, we investigated the transition behaviour on cooling of binary mixtures between each dimeric compound and **BOPPHB** (Fig. 3). There was no biphasic temperature region for the binary mixtures. Figure 3(a) shows a binary phase diagram for mixtures of **BOPPHB** and compound **1**. The SmC phase was observed even in the mixture of containing 75 wt% of compound **1**. The SmA and SmC phases observed for the cooling phase diagram did not appear on heating. Transition temperatures on heating of the mixture containing 50 wt% of compound **1** were Cryst 66°C N 79°C Iso. Figure 3(b) shows a binary phase diagram for mixtures of **BOPPHB** and compound **2**. The SmA phase was stable even in the mixture containing 90 wt% of **BOPPHB**, however, the SmC phase of **BOPPHB** was markedly depressed by addition of compound **2**. The SmA and SmC phases did not appear on heating. The mixture containing 25 wt% of compound **2** showed the N phase on heating, however, the mixture containing 50 wt% of compound **2** did not show a liquid-crystalline phase.

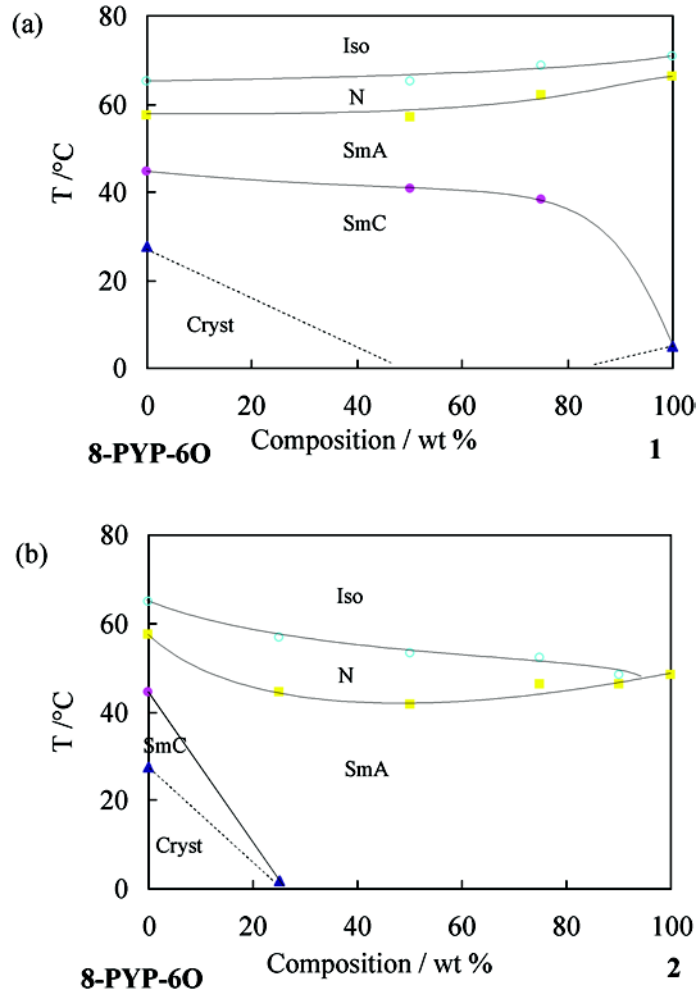


FIGURE 2 (a) Binary phase diagram for mixtures of **8-PYP-6O** and compound **1**. (b) Binary phase diagram for mixtures of **8-PYP-6O** and compound **2**.

Transition behaviour of a 1:1 mixture of compounds **1** and **2** on cooling was Iso 58.3°C N 51.8°C SmA −4.0°C Cryst, indicating that there is no marked difference in microscopic structure of the SmA phase between compounds **1** and **2**. The binary phase diagrams for mixtures between each dimeric compound and **8-PYP-6O** or **BOPPHB** suggest that there is difference in microscopic environment between compounds **1** and **2** in the smectic phases of the binary mixtures.

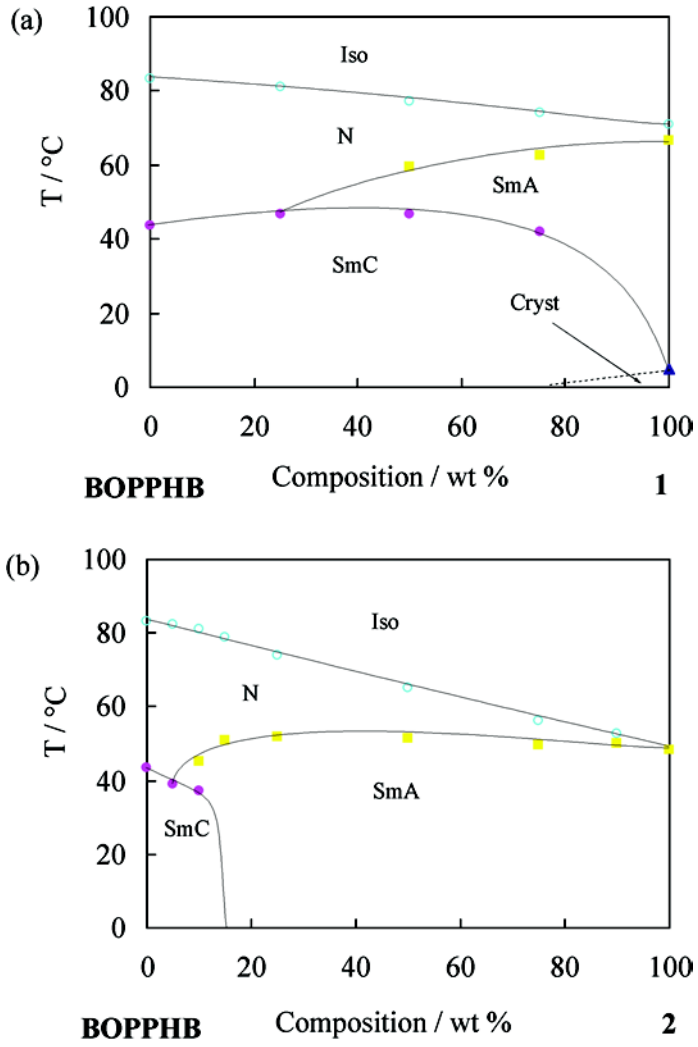


FIGURE 3 (a) Binary phase diagram for mixtures of **BOPPHB** and compound **1**. (b) Binary phase diagram for mixtures of **BOPPHB** and compound **2**.

3.3. Topological Effect

Let us discuss topological effect of the connecting group on transition behaviour for the novel dimeric system. There are two conformers, i.e., diequatrial and diaxial conformers, for *trans*-1,2-disubstituents on chair cyclohexane. MM2 models for the two conformers of compound

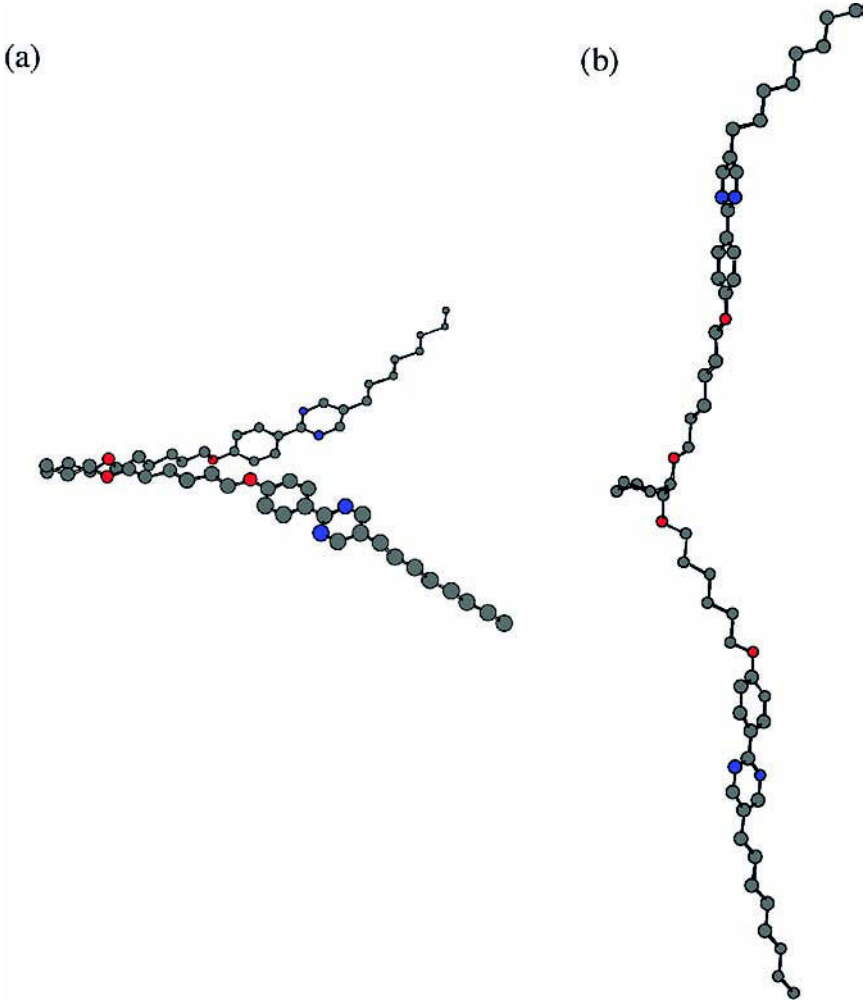


FIGURE 4 A MM2 model for the diequatrial conformation of compound **1** (a) and that for the diaxial conformation of compound **1** (b).

1 are shown in Figure 4. Energy values were estimeted, from the MM2 models, to be about 57 $kJmol^{-1}$ and 58 $kJmol^{-1}$ for the diequatorial conformer (Fig. 4(a)) and the diaxial one (Fig. 4(b)), respectively. The difference in energy values between the two conformers is not so large, thus the conformational change can occur between them in order to stabilize the SmC phase of its binary mixtures with **8-PYP-6O** or **BOPPHB**. On the other hand, the connecting group of compound **2**

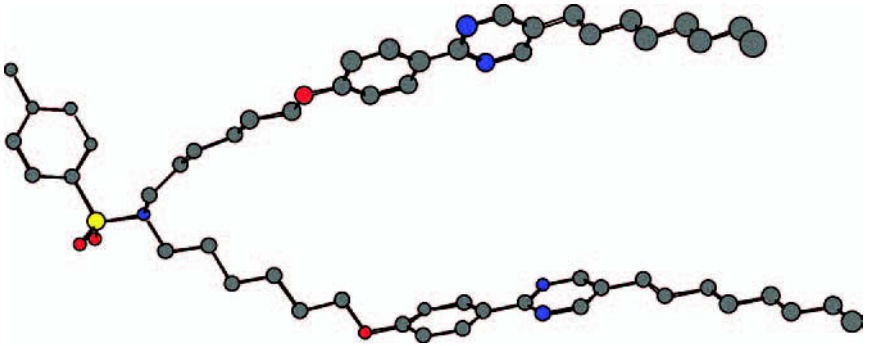


FIGURE 5 A MM2 model for compound **2**.

is thought to be rigid. A MM2 model for compound **2** is shown in Figure 5. The rigid conformation may destabilize the SmC phase of its binary mixtures with **8-PYP-6O** or **BOPPHB**.

4. CONCLUSION

We have prepared novel symmetric dimeric compounds in which two phenylpyrimidine moieties are connected via (±)-*trans*-1,2-cyclohexanediol or *p*-toluenesulfon amide. Compound **1** possessing cyclohexane as the connecting group was found to show enantiotropic N and SmA phases with low melting temperature. The binary mixture studies suggest that compound **1** can stabilize a SmC phase of the mixture. Flexible conformation of compound **1** due to the cyclohexane ring is thought to change its molecular shape in order to stabilize total free energy of the molecular assembly in the system.

REFERENCES

[1] Goodby, J. W., Mehl, G. H., Saez, I. M., Tuffin, R. P., Mackenzie, G., Auzely-Velty, R., Benvegu, T., & Plusquellec, D. (1998). *Chem. Commun*., 2057.
[2] Imrie, C. T. & Luckhurst, G. R. (1998). Liquid crystal dimers and oligomers. In: *Handbook of Liquid Crystals*, Demus, D., Goodby, J. W., Gray, G. W., Spiess, H-.W. & Vill, V. (Eds.), Wiley-VCH: Weinheim, Vol. 2B, p. 801.
[3] Griffin, A. C. & Britt, T. R. (1981). *J. Am. Chem. Soc*., *103* 4957.
[4] Date, R. W., Imrie, C. T., Luckhurst, G. R., & Seddon, J. M. (1992). *Liq. Cryst*., *12*, 203.
[5] Yoshizawa, A., Kikuzaki, H., & Fukumasa, M. (1995). *Liq. Cryst*., *18*, 351.
[6] Yoshizawa, A., Nishiyama, I., Kikuzaki, H., & Ise, N. (1992). *Jpn. J. Appl. Phys*., *31*, L860.
[7] Yoshizawa, A., Yokoyama, A., Kikuzaki, H., & Hirai, T. (1993). *Liq. Cryst*., *14*, 513.
[8] Yoshizawa, A. & Yamaguchi, A. (2002). *Chem. Commun*., 2060.