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Synthesis and Phase Transition Behavior of Novel Liquid Crystal Tetramers

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We synthesized novel liquid crystal tetramers possessing cyanobiphenyl and phenylpyrimidine moieties, and investigated their phase transition behavior. The liquid crystal tetramers exhibited nematic (N) and smectic A (SmA) phases. X-ray diffraction measurements suggest that the SmA phase has an intercalated structure. We discuss the transition behavior of the newly designed tetramers in terms of their molecular shape.

Keywords: liquid crystals; phase transition; tetramers

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 the corresponding low molar mass mesogens [2–5]. For instance, transition properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Furthermore, liquid crystal trimers [6–15] and tetramers [16,17] have been reported. Pronounced odd-even effects have been observed in the transition properties of linear liquid crystal

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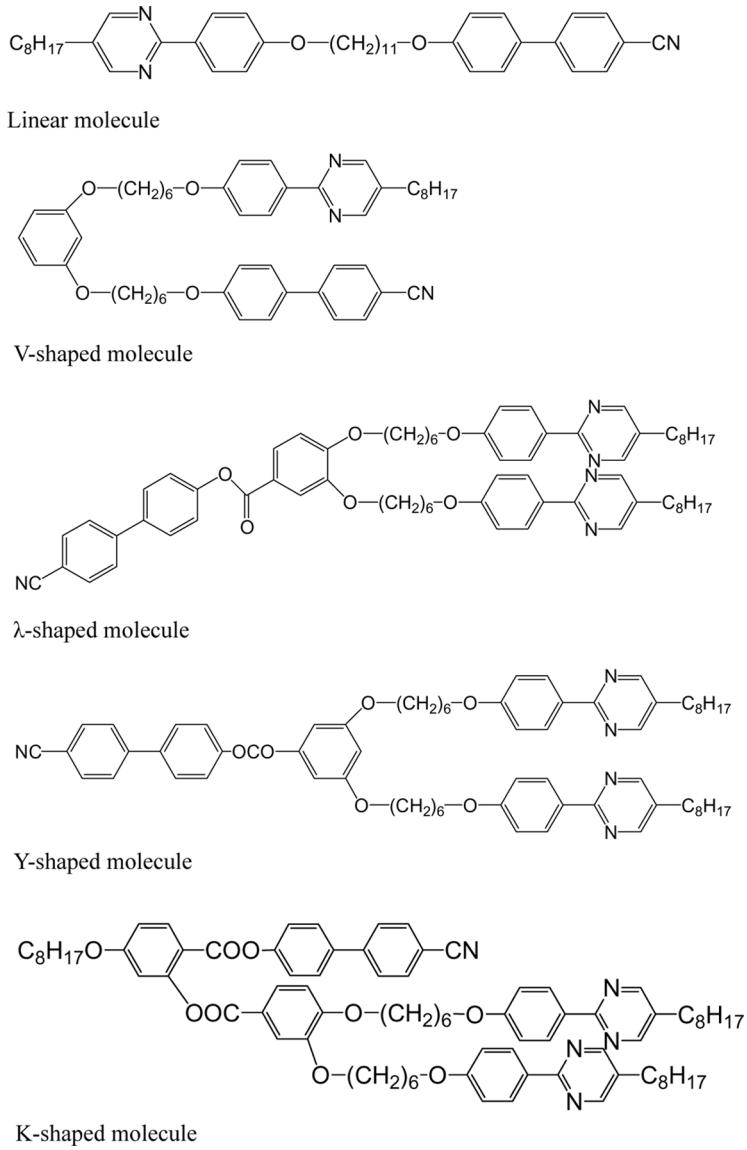


FIGURE 1 Liquid crystal oligomers possessing cyanobiphenyl and phenylpyrimidine units.

oligomers on varying the spacer length. The transition behavior is interpreted in terms of how the spacers control the average molecular shape [12,16].

We have reported liquid crystal oligomers in which cyanobiphenyl and phenylpyrimidine moieties are connected via a flexible spacer [18–20], 1,3-dihydroxybenzene [21], 3,4-dihydroxybenzoic acid [22–24] or 3,5-dihydroxybenzoic acid [25], as shown in Figure 1. Intermolecular interactions between such mesogenic moieties were found to have significant effects on the molecular assemblies in the liquid-crystalline phases: (i) antiparallel interactions between cyanobiphenyl moieties promote the formation of N and SmA phases, (ii) interactions between phenylpyrimidine moieties were found to stabilize smectic phase [26], and (iii) interactions between cyanobiphenyl and phenylpyrimidine moieties are known to induce an SmA phase [27]. Linear compound [18] and the V-shaped compound [21] exhibited a phase sequence of I – N – SmA –SmCanti. The λ-shaped compound [22] was found to show a stable incommensurate SmA phase, however, the Y-shaped compound [25] exhibited a direct transition from isotropic liquid to SmCanti phase. The K-shaped compound [24] showed a monotropic nematic phase.

For the present study, we prepared novel liquid crystal tetramers possessing cyanobiphenyl and phenylpyrimidine moieties, and investigated their phase transition behavior.

2. EXPERIMENTAL

2.1. Spectroscopic Analysis

The structures of the final products were elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-ECA500).

2.2. Preparation of Materials

2.2.1. *1,6-Bis{4-[4-(4-cyanophenyl)phenyloxycarbonyl]-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy} phenyloxy}hexane, I-6*

To a solution of 5-octyl-2-(4-hydoxyphenyl)pyrimidine (2.84 g, 10.0 mmol) and 1,6-dibromohexane (3.42 g, 14.0 mmol) in cyclohexanone (40 ml) was added potassium carbonate (1.38 g, 14.0 mmol). The resulting mixture was stirred at 80°C for 9 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a toluene/ethyl acetate (15/1) mixture as the eluent. Recrystallization from ethanol gave 2-[4-(6-bromohexyloxy)phenyl]-5-octylpyrimidine; yield 2.16 g (4.8 mmol, 48%).

To a solution of 2-[4-(6-bromohexyloxy)phenyl]-5-octylpyrimidine (2.13 g, 4.8 mmol) and ethyl 3,4-dihydroxybenzoate (3.46 g, 19.0 mmol) in cyclohexanone (20 ml) was added potassium carbonate (1.97 g, 14.3 mmol). The resulting mixture was stirred at 70°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 a toluene/ethyl acetate (19/1) mixture as the eluent. Recrystallization from ethanol gave ethyl 4-hydroxy-3-{6-[4-(5-octylpyrimidin-2-yl) phenyloxy]hexyloxy}benzoate; yield 1.15 g (2.1 mmol, 44%).

To a solution of ethyl 4-hydroxy-3-{6-[4-(5-octylpyrimidin-2-yl) phenyloxy]hexyloxy}benzoate (1.10 g, 2.0 mmol) and 1,6-dibromohexane (0.24 g, 1.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (0.28 g, 2.0 mmol). The resulting mixture was stirred at 130°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 a toluene/ethyl acetate (9/1) mixture as the eluent. Recrystallization from ethanol gave 1,6-bis {4-ethyloxycarbonyl-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy} phenyloxy}hexane; yield 1.03 g (0.9 mmol, 88%).

1,6-Bis{4-ethyloxycarbonyl-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy] hexyloxy}phenyloxy}hexane was added to a solution potassium hydroxide (0.90 g, 16 mmol) in ethanol (95%, 20 ml). The resulting mixture was stirred under reflux for 2 h. The solution was acidified with hydrochloric acid. Water (20 ml) was added to the mixture and the aqueous phase was extracted with dichloromethane (3×20 ml). The organic layers were combined, dried over magnesium sulfate, filtered and evaporated. 1,6-Bis{4-carboxy-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy] hexyloxy}phenyloxy}hexane was obtained; yield 0.64 g (0.6 mmol, 71%).

To a solution of 1,6-bis{4-carboxy-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}phenyloxy}hexane (0.56 g, 0.5 mmol) in dichloromethane (30 ml), 4-cyano-4′-hydroxybiphenyl (0.23 g, 1.2 mmol), *N,N′*-dicyclohexylcarbodiimide (0.25 g, 1.2 mmol) and 4-(*N,N*-dimethylamino) pyridine (0.25 g, 1.2 mmol) were added. The resulting solution was stirred at room temperature for 25 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel with a toluene/ethyl acetate (4/1) mixture as the eluent. Recrystallization from ethanol gave the desired product; Yield 84 mg (0.1 mmol, 11%).

δ_H (500 MHz, $CDCl_3$, TMS): 8.55 (s, 4H, Ar-H), 8.33 (d, 4H, Ar-H, $J = 9.1$ Hz), 7.83 (dd, 2H, Ar-H, $J = 8.3$ Hz, 2.0 Hz), 7.72 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.67 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.67 (d, 2H, Ar-H, $J = 2.3$ Hz), 7.62 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.31 (d, 4H, Ar-H, $J = 8.6$ Hz), 6.95 (d, 4H, Ar-H, $J = 9.0$ Hz), 6.93 (d, 2H, Ar-H, $J = 8.2$ Hz), 4.09 (t, 4H, -OCH_2-, $J = 6.6$ Hz),

4.09 (t, 4H, -OCH_2-, $J = 6.6$ Hz), 4.01 (t, 4H, -OCH_2-, $J = 6.3$ Hz), 2.58 (t, 4H, Ar-CH_2-, $J = 7.7$ Hz), 1.90–1.26 (m, 48H, aliphatic-H), 0.87 (t, 6H, -CH_3, $J = 6.9$ Hz). ν/cm^{-1} (KBr): 2927,2855 (C-H), 2225 (C≡N), 1729 (C=O, -COO-), 1606,1584 (C=C).

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. *1,7-Bis{4-[4-(4-cyanophenyl)phenyloxycarbonyl]-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy] hexyloxy}phenyloxy}heptane, I-7*

δ_H (500 MHz, $CDCl_3$, TMS): 8.56 (s, 4H, Ar-H), 8.33 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.83 (dd, 2H, Ar-H, $J = 8.3$ Hz, 2.0 Hz), 7.73 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.67 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.66 (d, 2H, Ar-H, $J = 1.7$ Hz), 7.62 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.31 (d, 4H, Ar-H, $J = 8.6$ Hz), 6.95 (d, 4H, Ar-H, $J = 9.2$ Hz), 6.94 (d, 2H, Ar-H, $J = 9.2$ Hz), 4.10 (t, 4H, -OCH_2-, $J = 6.6$ Hz), 4.07 (t, 4H, -OCH_2-, $J = 6.6$ Hz), 4.02 (t, 4H, -OCH_2-, $J = 6.3$ Hz), 2.58 (t, 4H, Ar-CH_2-, $J = 7.8$ Hz), 1.90–1.26 (m, 50H, aliphatic-H), 0.87 (t, 6H, -CH_3, $J = 6.9$ Hz). ν/cm^{-1} (KBr): 2928,2855 (C-H), 2225 (C≡N), 1728 (C=O, -COO-), 1606,1584 (C=C).

2.2.3. *1,8-Bis{4-[4-(4-cyanophenyl)phenyloxycarbonyl]-2-{6-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}phenyloxy}octane, I-8*

δ_H (500 MHz, $CDCl_3$, TMS): 8.56 (s, 4H, Ar-H), 8.34 (d, 4H, Ar-H, $J = 9.2$ Hz), 7.83 (dd, 2H, Ar-H, $J = 8.3$ Hz, 2.1 Hz), 7.73 (d, 4H, Ar-H, $J = 8.0$ Hz), 7.68 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.67 (d, 2H, Ar-H, $J = 2.3$ Hz), 7.63 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.32 (d, 4H, Ar-H, $J = 8.6$ Hz), 6.96 (d, 4H, Ar-H, $J = 9.2$ Hz), 6.94 (d, 2H, Ar-H, $J = 8.6$ Hz), 4.11 (t, 4H, -OCH_2-, $J = 6.6$ Hz), 4.06 (t, 4H, -OCH_2-, $J = 6.6$ Hz), 4.03 (t, 4H, -OCH_2-, $J = 6.6$ Hz), 2.58 (t, 4H, Ar-CH_2-, $J = 7.5$ Hz), 1.91–1.26 (m, 52H, aliphatic-H), 0.88 (t, 6H, -CH_3, $J = 7.2$ Hz). ν/cm^{-1} (KBr): 2928,2855 (C-H), 2225 (C≡N), 1727 (C=O, -COO-), 1606,1584 (C=C).

2.3. Physical Properties

The initial phase assignments and corresponding transition temperatures for the final 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 $5^{\circ}C\,min^{-1}$ after being encapsulated in aluminum pans. The XRD patterns of the sample on cooling process were obtained using a real-time X-ray diffractometer (D8 Discover; Bruker AXS GmbH) equipped with a hot stage and a temperature-control processor. A sample was put on a convex lens, which was placed in a custom-made temperature stabilized holder (stability within $\pm 0.1^{\circ}C$). The X-ray apparatus was equipped with a cross-coupled Göbel mirror on a platform system with a two-dimensional position-sensitive proportional counter (PSPC) detector (HI-Star; Bruker AXS GmbH). X-rays were generated at 40 kV and 40 mA; a parallel Cu Kα X-ray beam was used to irradiate the sample. Each diffraction pattern was obtained using the PSPC detector at a camera distance of 150 mm for a short counting time of 30 s.

3. RESULTS AND DISCUSSION

3.1. Synthesis

We designed novel liquid crystal tetramers **I-n** (see Fig. 2). Compound **I-6** was prepared by the synthesis outlined in Scheme 1. Purification of the final products was carried out using column chromatography over silica gel with a toluene/ethyl acetate (4/1) mixture as the eluent, followed by the recrystallization from ethanol. The structures were elucidated using IR and ^{1}H NMR measurements.

3.2. Phase Transition Behavior

Transition temperatures and transition enthalpies for compounds **I-n** measured by optical polarized light microscopy and differential scanning calorimetry (DSC) are listed in Table 1. Compound **I-6**

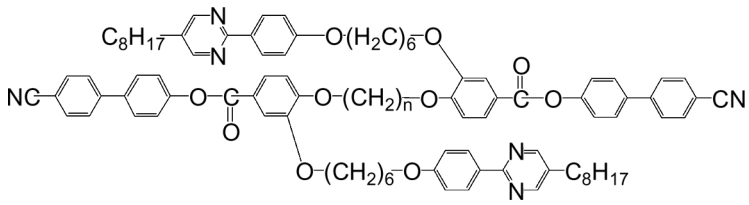
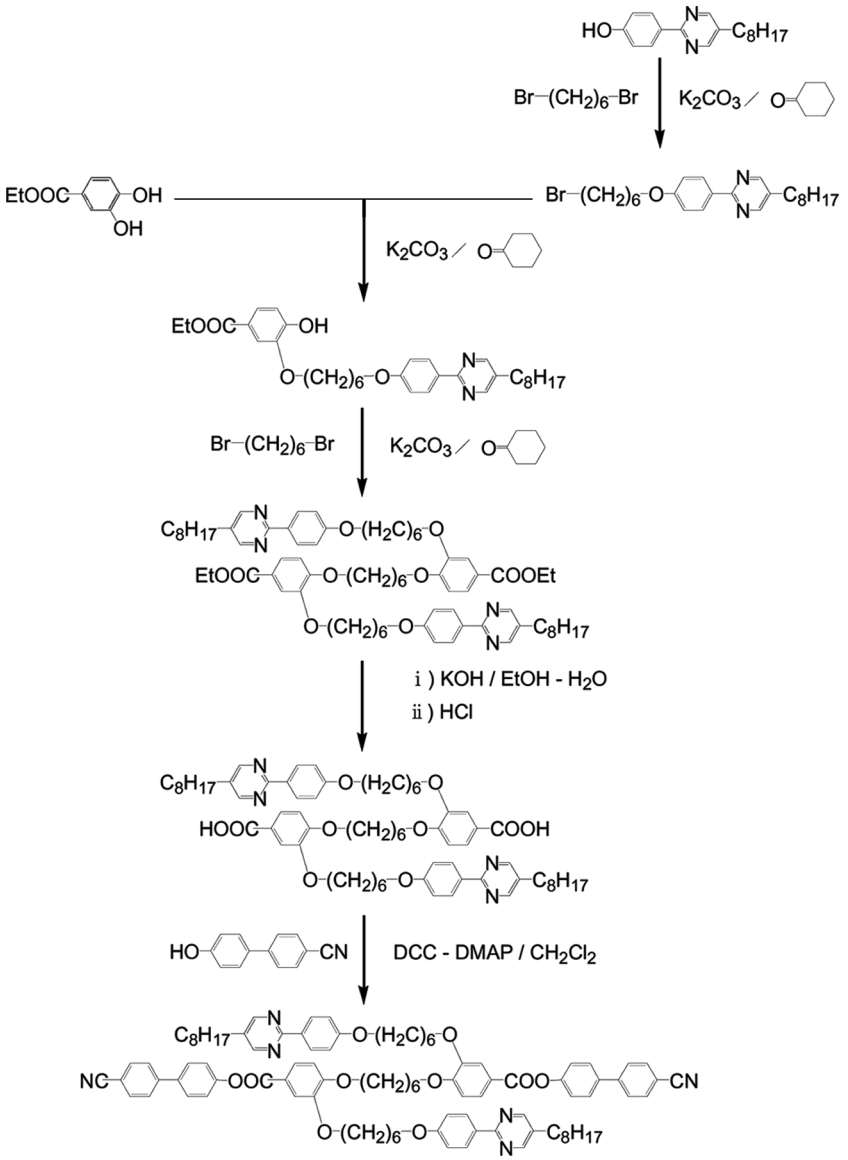


FIGURE 2 Molecular structure of compound **I-n**.



SCHEME 1 The preparative route for the liquid crystal tetramer **I-6**.

exhibited an SmA phase, whereas compounds **I-7** and **I-8** exhibited N and SmA phases. Weissflog *et al*. reported that a dimer possessing two laterally attached substituents exhibits an SmA phase [28]. Imrie and

TABLE 1 Phase Transition Temperatures (°C) and Transition Enthalpies (kJ mol^{-1}) (in Square Brackets) for **I-n**

Compound	Cr	SmA	N	I	mp/°C
I-6	• 172	• 209 [31.2]		•	208
I-7	• 97.8	• 202.6 [a]	• 202.8 [a]	•	191
I-8	• 130	• 191 [14.0]	• 198 [15.8]	•	178

[a] The I-N and N-SmA transitions occurred simultaneously. The total value of both transition enthalpies was 30.4 kJ mol^{-1}.

Henderson discussed that packing constraints depress appearance of an N phase of the dimer [2]. The appearance of the N phase for the compounds **I-7** and **I-8** is thought to be attributed to antiparallel interactions between the neighboring cyanobiphenyl moieties.

3.3. X-Ray Diffraction Studies

In order to understand a structure of the SmA phase, XRD measurements were carried out. Figure 3 shows an X-ray diffraction pattern in the small angle region of compound **I-6** in the SmA phase. A sharp reflection was observed at $2\theta = 3.82°$, corresponding to the spacing of 23.1 Å. Figure 4 shows the expected elongated molecular conformation and length calculated using the MM2 method. Although stability of the configuration from MM2 method is still questionable due to the molecular flexibility, we consider the single configuration to discuss

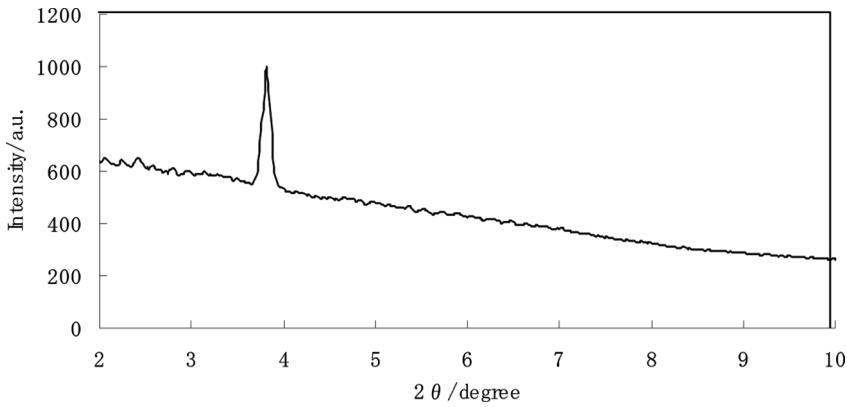


FIGURE 3 X-ray diffraction pattern of compound **I-6** in the SmA phase.

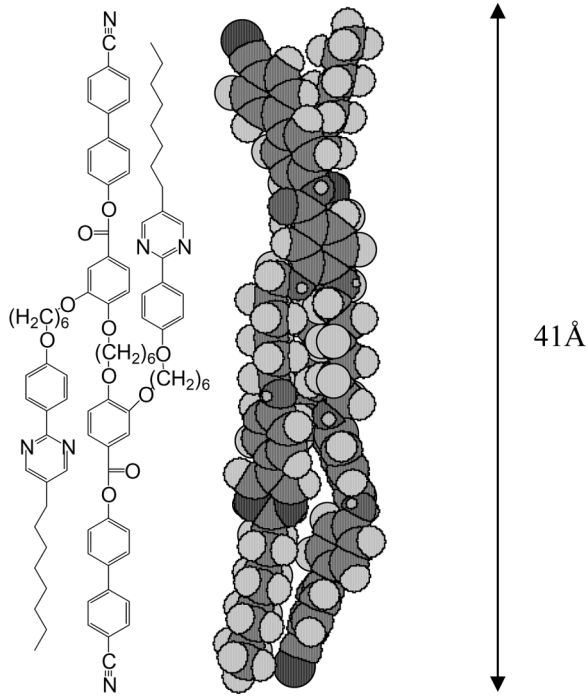


FIGURE 4 Expected molecular configuration and length by the MM2 calculation for compound **I - 6**.

the phase structure at the first approximation. The molecular length was estimated as 41 Å. The obtained layer spacing is shorter than the molecular length. Therefore compound **I - 6** is considered to form an intercalated SmA phase. Figure 5 shows a possible model of molecular organization in the SmA phase. The model suggests that: 1) the close-packed molecular shape produces favorable molecular packing and, 2) intermolecular interactions between cyanobiphenyl and phenylpyrimidine moieties exist in each layer.

4. CONCLUSIONS

We prepared novel liquid crystal tetramers possessing cyanobiphenyl and phenylpyrimidine moieties, and found that they exhibit N and SmA phases. X-ray studies suggest that the SmA phase has an intercalated layer structure composed of the tetramers with a close-packed conformation.

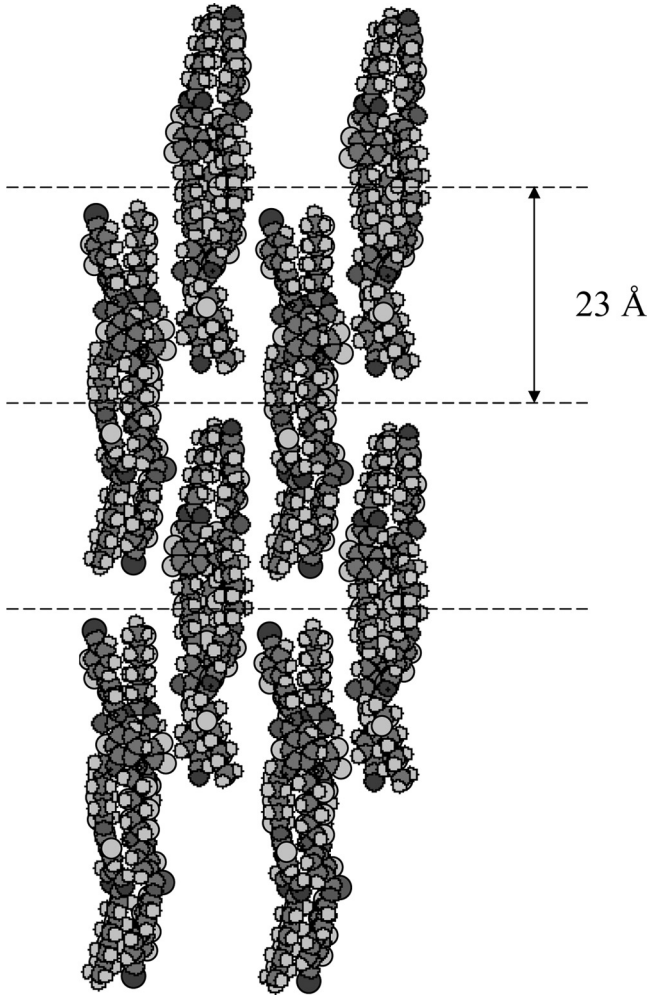


FIGURE 5 Molecular arrangements suggested for compound **I - 6** in the SmA phase.

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