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Liquid Crystals

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Synthesis and physical properties of novel S-shaped liquid crystal oligomers

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We prepared novel S-shaped liquid crystal oligomers, the 4,4′-bis(ω-(2-(ω-(4-(cyanophenyl)-phenyloxy)alkyloxy)phenyloxy)alkyloxybiphenyls (**S-*n***), and investigated their transition behaviour. The oligomer with even-numbered spacers (**S-6**) exhibited a nematic phase, whereas the oligomer with odd-numbered spacers (**S-7**) exhibited nematic and smectic A phases. Transition properties of the S-shaped oligomers are compared with those of the corresponding monomeric and U-shaped dimeric compounds. The entropy changes associated with the I–N transition for the oligomers were found to have small values, similar to that of the monomeric compound. A biaxial smectic phase was induced below the SmA phase in some binary mixtures of **S-6** and a phenylpyrimidine derivative (**8-PYP-6O**). On the other hand, the SmA phase was stabilized in the mixtures of **S-7** and **8-PYP-6O**. We discuss the transition behaivour of the S-shaped oligomers in terms of their molecular shape.

1. Introduction

Supramolecular assemblies composed of oligomeric liquid crystals are current topics in the design of new liquid crystalline materials [1]. Liquid crystal oligomers consist of semi-rigid mesogenic units connected via flexible spacers [2–4]. 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. Furthermore, liquid crystal trimers [5] and tetramers [6] have been reported. Pronounced odd–even effects were observed for the transition properties of linear liquid crystal oligomers on varying the spacer length. The transition behaviour is interpreted in terms of the average molecular shape of those oligomers. U-shaped liquid crystals have been investigated by several research groups [7–10]. Attard and Douglass reported structure–property correlations of the bimesogenic compounds derived from phthalic acid, providing important understanding about the behaviour of U-shaped liquid crystal systems [10]. In 1,3-benzene derivatives first synthesized by Matsunaga *et al.* [11], antiferroelectric and ferroelectric properties have been more recently found in such banana-shaped molecules by Watanabe *et al.* [12, 13]. The banana-shaped system has given new concepts for chirality and phase structures in liquid crystals [14, 15].

We previously designed U-shaped molecules in which two mesogenic moieties are connected via 1, 2-dihydroxybenzene [16]. The pre-organized supermolecule was found to induce smectic-like layer ordering in the nematic phase. Recently we reported pronounced odd–even effects in the transition behaviour of U-shaped systems [17]. We report here the synthesis and transition properties of novel S-shaped molecules in which two U-shaped mesogenic molecules are connected as shown in figure 1. We discuss the effects of the molecular shape on transition behaviour for the novel liquid crystal oligomers.

2. Experimental

2.1. *Preparation of materials*

Purification of the final products was carried out using HPLC (Japan Analytical Industry Co., Ltd., LC9101, JAIGEL-1H column); chloroform was used as eluant. Detection of products was achieved by UV irradiation (λ=254 nm). Recrystallization from ethanol gave the final products; their structures were elucidated using infrared (IR) spectroscopy (FTS-30; Bio-Rad

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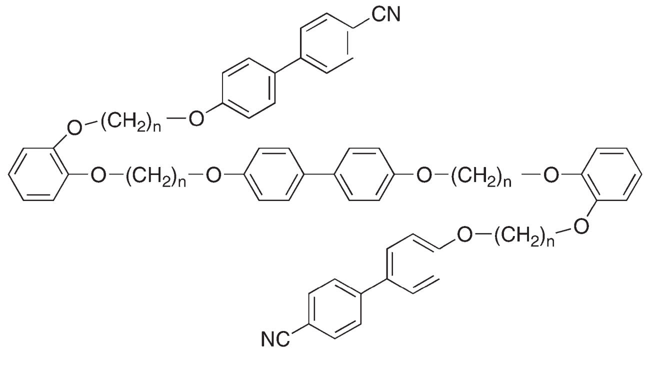


Figure 1. Molecular structure of S-shaped liquid crystal oligomer **S-*n***.

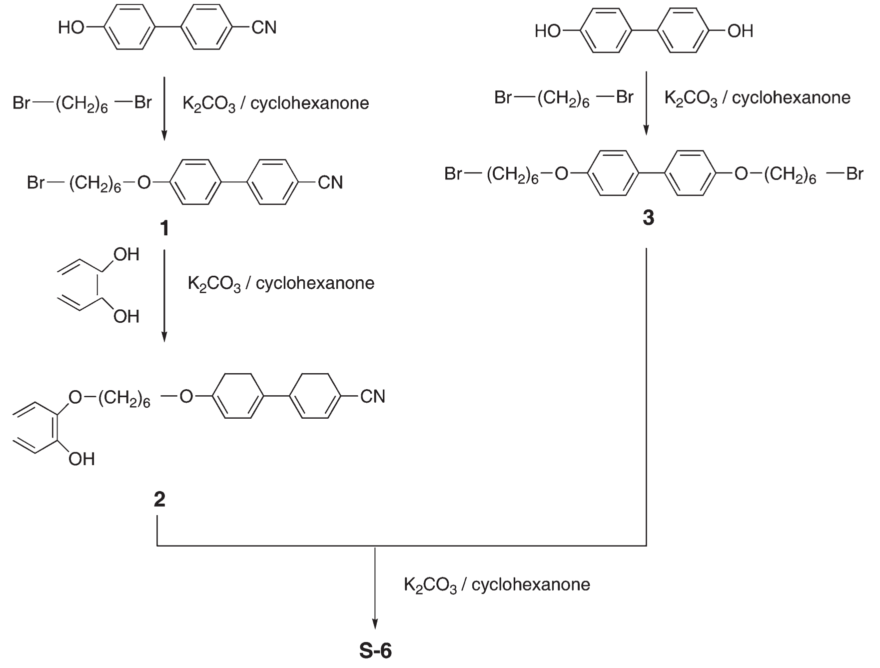
Laboratories, Inc.) and proton nuclear magnetic resonance spectroscopy (JNM-GX270; JEOL or JNM-A-400; JEOL). An outline of the synthesis is given in scheme 1.

2.1.1. 4, 4′-Bis(6-(2-(6-(4-(cyanophenyl)phenyloxy)hexyloxy)phenyloxy)hexyloxybiphenyl (S-6). Potassium carbonate (2.42 g, 17.5 mmol) was added to a solution of 4-cyano-4′-hydroxybiphenyl (2.93 g, 15 mmol) and 1, 6-dibromohexane (4.88 g, 20 mmol) in cyclohexanone (45 ml). The reaction 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 toluene. Recrystallization from ethanol gave 4-cyano-4′-(6-bromohexyloxy)biphenyl (**1**); yield 2.77 g (52%).

Potassium carbonate (1.41 g, 10 mmol) was added to a solution of compound **1** (3.67 g, 10 mmol) and 1,2-dihydroxybenzene (3.38 g, 30 mmol) in cyclohexanone (45 ml). The reaction mixture was stirred at 70°C for 24 h. After filtration of the precipitate, the solvent was removed by evaporation; the residue was purified by column chromatography on silica gel with dichloromethane. 2-(6-(4-(Cyanophenyl)phenyloxy)hexyloxy) phenol (**2**) was obtained; yield 2.19 g (55%).

Potassium carbonate (1.74 g, 12.6 mmol) was added to a solution of 4,4′-dihydroxybiphenyl (1.87 g, 10 mmol) and 1, 6-dibromobenzene (9.76 g, 40 mmol) in acetone (50 ml). The reaction mixture was stirred under reflux for 10 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was reprecipitated with a mixture of chloroform and ethanol to give 4,4′-bis(6-bromohexyloxy)biphenyl (**3**); yield 1.04 g (20 %).

Potassium carbonate (0.28 g, 2.2 mmol) was added to a solution of compound **2** (0.84 g, 2.2 mmol) and compound **3** (0.51 g, 1.0 mmol) in cyclohexanone (40 ml). The reaction mixture was stirred at 120°C for 20 h. After filtration of the precipitate, the solvent was removed by evaporation; the residue was washed with dichloromethane and purified using HPLC with chloroform. Recrystallization from ethanol gave the desired product; yield 0.53 g (47%). ^{1}H NMR (270 MHz,



Scheme 1. Synthesis of **S-6**.

solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.65(d, 4H, Ar–**H**, J=8.6 Hz), 7.59(d, 4H, Ar–**H**, J=8.9 Hz), 7.48(d, 4H, Ar–**H**, J=8.9 Hz), 7.41(d, 4H, Ar–**H**, J=8.4 Hz), 6.97–6.88(m, 16H, Ar–**H**), 4.04–3.94(m, 16H, Ar–OC**H**$_2$–), 1.85–1.52(m, 32H, aliphatic–**H**), IR (KBr) ν_{max}/cm^{-1}: 2940, 2861, 2224, 1601, 1498.

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

2.1.2. 4,4′-Bis(7-(2-(7-(4-(cyanophenyl)phenyloxy)heptyloxy)phenyloxy) heptyloxybiphenyl (S-7).

^{1}H NMR (400 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.66(d, 4H, Ar–**H**, J=8.3 Hz), 7.60(d, 4H, Ar–**H**, J=8.3 Hz), 7.49(d, 4H, Ar–**H**, J=8.3 Hz), 7.42(d, 4H, Ar–**H**, J=8.8 Hz), 6.97–6.89(m, 16H, Ar–**H**), 4.02–3.95(m, 16H, Ar–OC**H**$_2$–), 1.85–1.52(m, 40H, aliphatic–**H**), IR (KBr) ν_{max}/cm^{-1}: 2947, 2856, 2225, 1602, 1499.

2.1.3. 2-(6-(4-(4-Cyanophenyloxy)phenyloxy)hexyloxy)-1-(6-(4-(4-methyloxyphenyloxy)phenyloxy)hexyloxy)benzene (U-I).

^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.68–7.58(m, 4H, Ar–**H**), 7.51–7.40(m, 6H, Ar–**H**), 6.98–6.89(m, 10H, Ar–**H**), 4.04–3.95(m, 8H, Ar–OC**H**$_2$–), 3.83(s, 3H, Ar–OC**H**$_3$), 1.88–1.48(m, 16H, aliphatic–**H**), IR (KBr) ν_{max}/cm^{-1}: 2939, 2859, 2224, 1607, 1500.

2.2. *Physical properties*

The initial phase 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 encapsulating in aluminum pans.

Table 1. Transition temperatures (°C) on cooling and enthalpies (kJ mol^{-1}) of transition in brackets for **S-*n***.

Compound	Transition temperature/°C
S-6	Cr 92(7.5) N 139(0.7) I m.p. 154
S-7[a]	glass 17 Y 77(7.31) X 85(8.83) SmA 100(3.38) N 105 (0.95) I

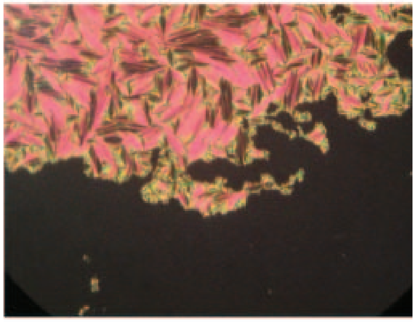
[a]A glass transition was observed at 17°C on heating.

3. Results and discussion

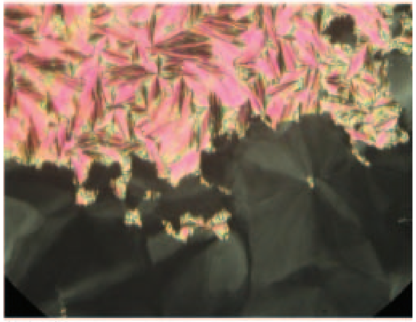
3.1. *Phase transition properties*

Table 1 shows temperatures and enthalpies of transition for the S-shaped compounds determined by optical microscopy and DSC. The oligomer **S-6** with even-numbered spacers exhibited a nematic phase whereas the oligomer **S-7** with odd-numbered spacers exhibited nematic and semctic A phases. On cooling **S-7**, two unidentified phases, X and Y, appeared below the SmA phase. At lower temperatures a glass transition occurred. Figure 2 shows the textures of the SmA, X

(*a*) **SmA (90°C)**



(*b*) **X (80 °C)**



(*c*) **Y (70°C)**

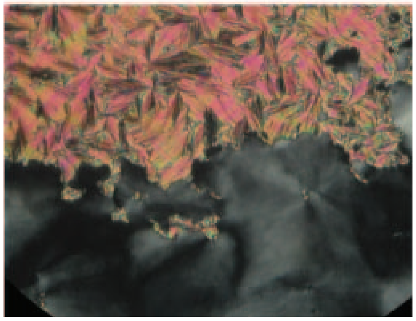
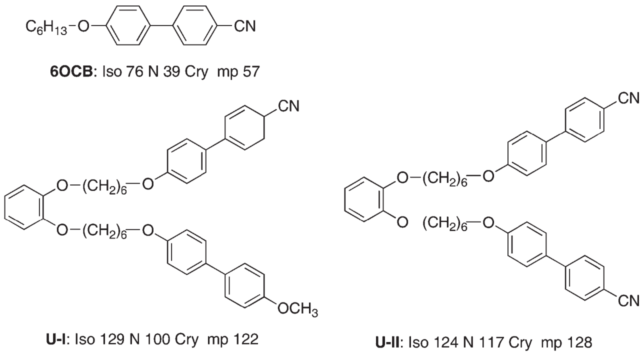


Figure 2. Textures of the SmA, X and Y phases of **S-7**.



6OCB: Iso 76 N 39 Cry mp 57

U-I: Iso 129 N 100 Cry mp 122

U-II: Iso 124 N 117 Cry mp 128

Figure 3. Molecular structures and transition temperatures (°C) on cooling for the corresponding monomeric and dimeric compounds.

and Y phases. The SmA to X transition was accompanied by the increase of birefringence in the homeotropic regions and a large enthalpy change, indicating that the X phase is a biaxial crystalline phase, such as the CrE phase. At present the Y phase has not been identified.

We now compare the transition properties of **S-6** with those of the corresponding monomeric and dimesogenic compounds. The molecular structures are shown in figure 3. All of the corresponding compounds exhibited the phase sequence I–N–Cr. The I–N transition temperatures and the transition entropies ($\Delta S/R$) of the monomeric and oligomeric liquid crystals are listed in table 2. **S-6** shows a higher I–N transition temperature than **6OCB**, non-symmetric dimer **U-I** and symmetric dimer **U-II** [18]. Surprisingly, the transition entropy of **S-6** was found to be of the same magnitude as that of **6OCB**, suggesting that the conformational change of **S-6** at the I–N transition is small.

3.2. *Miscibility studies*

We investigated the transition behaviour of binary mixtures of **6OCB** and **S-*n***. The transition temperatures were determined by optical microscopy. There is no marked difference in the transition behaviour of the binary mixtures of **6OCB** and **S-*n*** between **S-6** and **S-7**.

Table 2. I–N transition temperatures and the transition entropies ($\Delta S/R$) of the monomeric and oligomeric liquid crystals.

Compounds	$T_{\text{I-N}}$/°C	$\Delta S/R$
6OCB	76	0.22
U-I	129	0.41
U-II	124	0.96
S-6	139	0.21

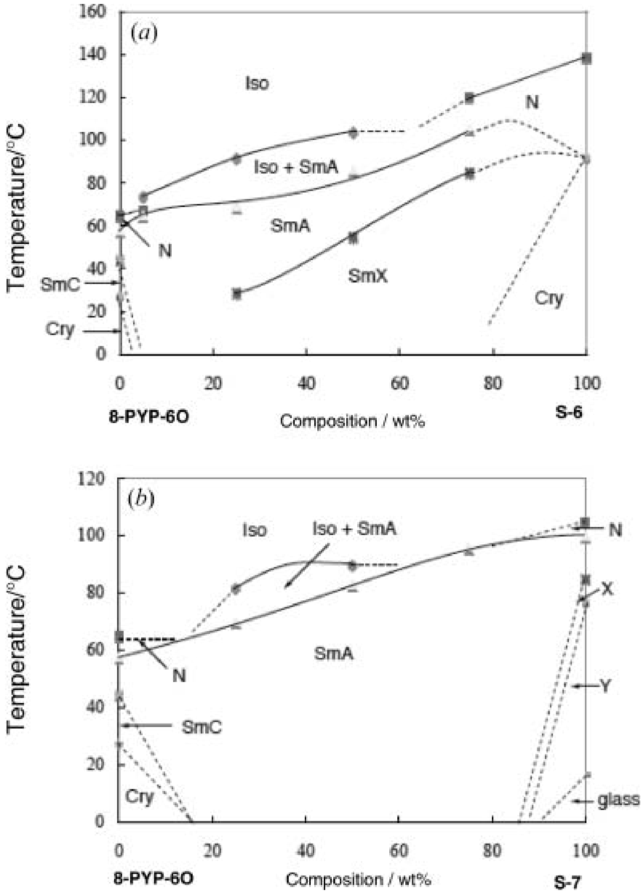
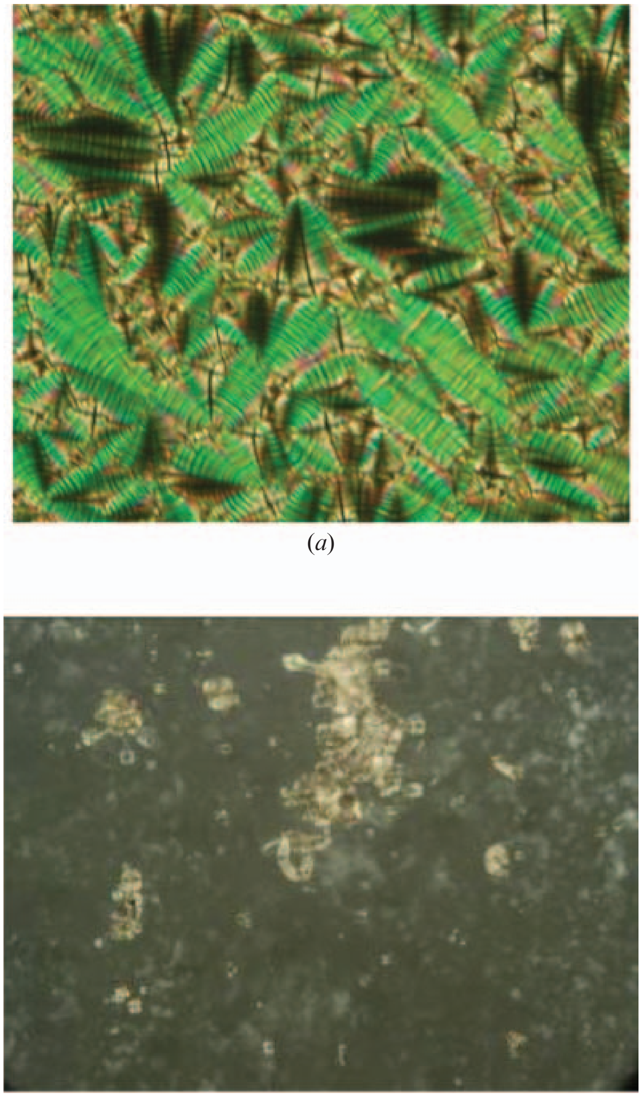


Figure 4. (*a*) Phase diagram between **8-PYP-6O** and **S-6**, and (*b*) phase diagram between **8-PYP-6O** and **S-7**.

The N phases of **6OCB** and **S-*n*** proved to be miscible across the full composition range, suggesting that these N phases may be attributed to inter-molecular antiparallel interactions between cyanobiphenyl moieties. We then investigated the transition behaviour of binary mixtures of 5-octyl-2-(4-hexyloxyphenyl)pyrimidine (**8-PYP-6O**) and **S-*n***. Figure 4 (*a*) shows a phase diagram between **8-PYP-6O** and **S-6**. A SmA phase was induced. Biphasic behaviour with the presence of both an isotropic liquid and the SmA phase is seen for mixtures containing 10–50 wt% of **S-6**. Another smectic phase denoted as SmX was found to be induced below the SmA phase for mixtures containing 25–75 wt% of **S-6**. Figure 4 (*b*) shows a phase diagram between **8-PYP-6O** and **S-7**. The SmA phases for mixtures containing 25–75 wt% of **S-7** did not change to any other phase on cooling and the SmX phase did not appear.

Figure 5 shows (*a*) homogeneously aligned and (*b*) homeotropically aligned textures of the SmX phase. Birefringence in the homeotropic regions increased at the SmA to SmX transition indicating that the SmX



(*a*)

(*b*)

Figure 5. Textures of the SmX phase of the binary mixture of **8-PYP-6O** (50 wt%) and **S-6** (50 wt%) in the (*a*) homogeneously aligned region and (*b*) homeotropically aligned region.

phase is a biaxial phase. Lines appeared in the homogeneous regions. The lines are similar to dichiralization lines that are usually observed in a chiral smectic C (SmC*) phase. The SmA to SmX transition was not accompanied by an enthalpy change, as shown in figure 6. Furthermore, the SmX phase showed fluidity. On the other hand, no ferroelectric switching or spontaneous polarization were detected in the SmX phase under a triangular wave field (80 V peak to peak, 100 Hz, 5 μm). The SmC phase of **8-PYP-6O** is rapidly extinguished upon doping with **S-6**. At present we cannot identify the phase structure.

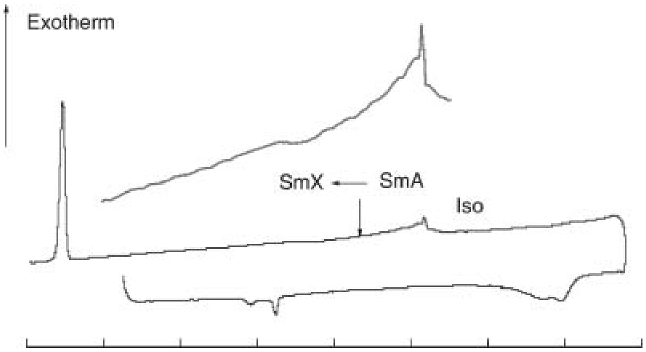


Figure 6. DSC thermogram of the binary mixture of **8-PYP-6O** (25 wt%) and **S-6** (75 wt%); the inset is included for clarity.

3.3. *Possible models for the transition behaviour of S-n*

S-6 with even-numbered spacers exhibited the phase sequence I–N–Cr, whereas **S-7** with odd-numbered spacers showed I–N–SmA–X–Y–glass. T_{IN} of **S-6** is higher than that of **S-7**. Pronounced odd–even effects are seen in the transition behaviour of the S-shaped liquid crystal oligomers.

Tsvetkov *et al.* reported transition properties of a homologous series of linear liquid crystal trimers, 4,4′-bis(ω-4-(4-cyanophenyl)phenyloxy)alkyloxy)biphenyl [19]. All the compounds show phase sequence I–N–Cr, and odd–even effects are seen for the I–N transition temperatures of the trimers on changing the spacer length. The odd–even effects for transition properties of the linear trimers can be interpreted in terms of how the spacers control the average molecular shape [20, 21]. The trimers with odd-membered spacers have a zig-zag shape in which all three mesogenic units are inclined with respect to each other, whereas the trimers with even-membered spacers have a linear shape in which the three mesogenic units are coparallel.

In the case of the present S-shaped oligomers, there is a difference not only in the T_{IN} but also in the phase sequence between **S-6** and **S-7**. Figure 7 shows MM2 models for (*a*) **S-6** and (*b*) **S-7** based on the assumption that intramolecular interactions between the cyanobiphenyl and biphenyl moieties cause the molecules to form a close-packed structure. Although a structure of a mesogenic molecule based on the MM2 calculation does not reflect the real conformation in the liquid crystalline phase, the structure can give some information to discuss the observed structure–property relationships. *L*/*D* ratios for **S-6** and **S-7** are 4.4 and 3.6, respectively. The higher T_{IN} of **S-6** can be interpreted by the larger *L*/*D* ratio. **S-7** is thought to form a broader conformation than **S-6**, which can induce the SmA phase, the biaxial crystalline phase and the glass transition.

Figure 7. MM2 models for (*a*) **S-6** and (*b*) **S-7**, based on the assumption that they exist as their packed structures.

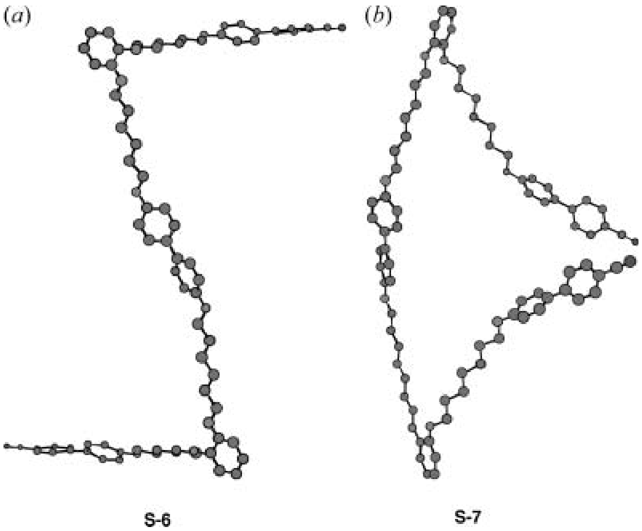


Figure 8. MM2 models for (*a*) **S-6** and (*b*) **S-7** based on the assumption that they exist as their expanded structures.

Now we discuss the transition behaviour of binary mixtures between **8-PYP-6O** and **S-*n***. Induction of the SmA phase observed for both phase diagrams is attributed to intermolecular interactions between phenylpyrimidine and cyanobiphenyl moieties [22]. Figure 8 shows MM2 models for **S-*n*** based on the assumption that the molecules exist in expanded structures. It can be seen from figure 8 that there is an important difference in the conformations between **S-6** and **S-7**; **S-6** can form a twisted structure whereas **S-7** may form a pseudo U-shaped structure. We assume that intermolecular interactions between the cyanobiphenyl moiety of **S-*n*** and the phenylpyrimidine moiety of **8-PYP-6O** cause conformation change of the oligomers from the closer packed structure to the expanded structure. The broader and twisted structure of **S-6** in the mixture with **8-PYP-6O** might induce the biaxial SmX phase, having an unusual phase structure. On the other hand, the pseudo U-shaped structure of **S-7** might prefer a uniaxial SmA phase. This discussion of structure–property relationships in the S-shaped system is consistent with that in our recently reported U-shaped system [17]. We investigated transition properties of the U-shaped dimeric compound, 1,2-bis{ω-[4-(5-alkylpyrimidin-2-yl)phenyloxy]alkyloxy}benzene. The U-shaped compounds with even-numbered spacers, in which the two mesogenic units are estimated to be spread out and coparallel by MM2 calculations, favour a biaxial SmC phase. However, the U-shaped compounds with odd-numbered spacers, in which the two mesogenic units are estimated to form a cross-shape, favour a uniaxial SmA phase. In the case of binary mixtures of **S-*n*** with **6OCB**, there is no marked difference in the transition behaviour between **S-6** and **S-7**; and the N phases of **6OCB** and **S-*n*** are miscible across the full composition range. Therefore, both oligomers may exist as their closer packed structures in the mixtures.

4. Conclusions

We prepared novel S-shaped liquid crystal oligomers. **S-6** with even-numbered spacers exhibited a N phase, while **S-7** with odd-numbered spacers exhibited N and SmA phases with two further unidentified phases. Furthermore, there is an important difference in the phase transition behaviour of the binary mixtures with **8-PYP-6O**, between **S-6** and **S-7**. The unidentified biaxial phase was observed below the SmA phase of some mixtures of **S-6** and **8-PYP-6O**, whereas the SmA phase was stabilized in mixtures of **S-7** and **8-PYP-6O**. The difference in transition behaviour of the binary mixtures of **S-*n*** may be explained in terms of conformation change of **S-*n*** that might be caused by inter-molecular interactions between **S-*n*** and **8-PYP-6O**. Systematic investigations to understand structure–property relationships of a homologous series of the S-shaped oligomers are in progress.

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