

## Bent-shaped Liquid Crystal Dimers: Effect of Molecular Shapes on Mesomorphic Properties

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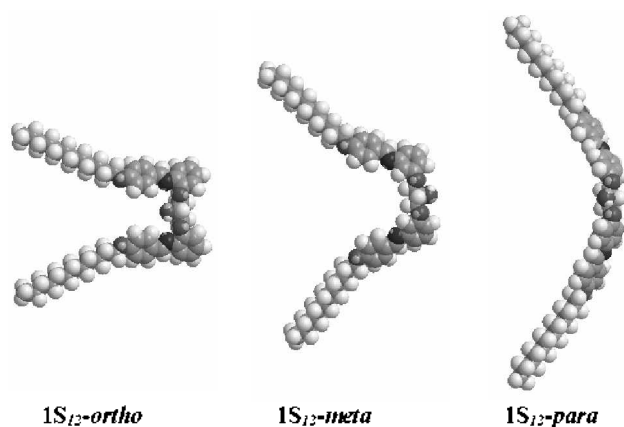
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For the past two decades, the liquid crystal compounds having obtuse and acute angled configurations have been attracting attention.<sup>1,2</sup> Through the sterically induced packing of the bent molecules new smectic modifications can occur, which have no counterpart in the field of calamitic liquid crystals. Especially, the recent discovery of banana-shaped liquid crystal materials *i.e.*, mesogenic compounds bent symmetrically along the middle of the molecules<sup>3,4</sup> have boosted up the studies in this field. Niori *et al.*<sup>5</sup> reported a liquid crystallinity for the compounds having linear, bent, and U-shaped hydrogen bonded mesogenic cores.

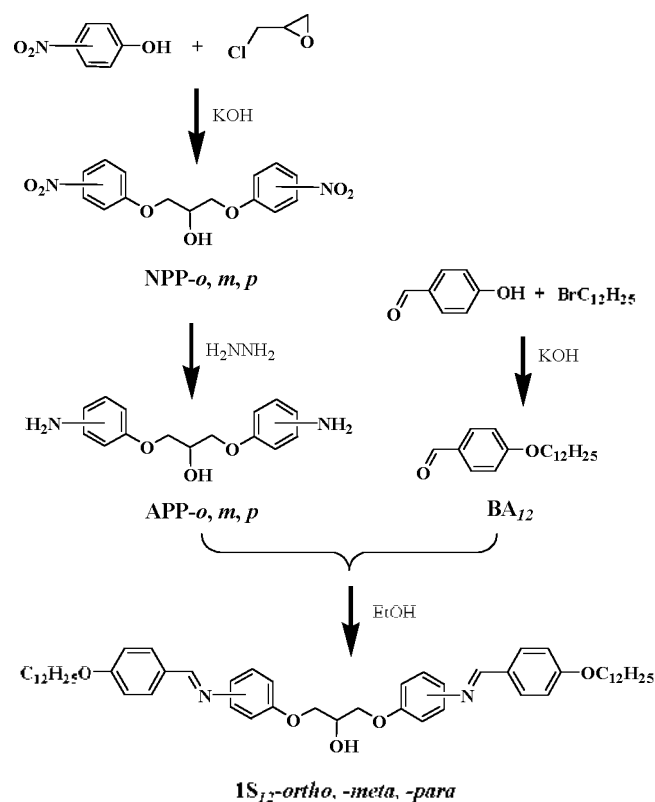
Generally dimers with an even-numbered spacer exhibit SmA phases and/or nematic phases while homologous compounds with odd-numbered spacer exhibit SmC phases.<sup>8</sup> Contrarily to this a mesomorphism in the bent-shaped symmetric dimers with odd-numbered flexible spacer has been reported recently.<sup>6-8</sup> Therefore, we have designed and synthesized three bent-shaped liquid crystal dimers. All of these molecules have two Schiff base mesogenic units with dodecyloxy terminal chain (-OC<sub>12</sub>H<sub>25</sub>) symmetrically linked via 2-hydroxypropylene short spacer. The three compounds differ only in the patterns to join the spacer and mesogenic units. In these compounds the central spacer is attached on the 4-, 3-, and 2-position of two mesogenic units and they are represented as the 1S<sub>12</sub>-*para*, 1S<sub>12</sub>-*meta* and 1S<sub>12</sub>-*ortho*, respectively. Figure 1 shows the most probable atomic configurations of the compounds.



**Figure 1.** Molecular configurations for 1S<sub>12</sub>-*ortho*, 1S<sub>12</sub>-*meta* and 1S<sub>12</sub>-*para* compounds.

### Experiment Section

The synthesis process for the designed molecules is outlined in the Scheme 1. The dinitro compounds (NPP-*o*-, *m*-, *p*-) were firstly synthesized by reacting epichlorohydrin with *o*-, *m*-, *p*-nitrophenols, respectively, according to the similar method described in the literature.<sup>8</sup> The dinitro compounds thus obtained were then converted to the corresponding diamines (APP-*o*-, *m*-, *p*-) by the reduction reaction with hydrazine monohydrate in the presence of palladium on active carbon. In the meanwhile the aldehyde BA<sub>12</sub> was obtained from the conventional etherification of 4-hydroxybenzaldehyde with a dodecyl bromide. Finally, the diamines APP-*o*-, APP-*m*- and APP-*p*- were reacted with the aldehyde BA<sub>12</sub> using PTSA



**Scheme 1.** Synthesis procedure for 1S<sub>12</sub>-*para*, 1S<sub>12</sub>-*meta* and 1S<sub>12</sub>-*ortho* compounds.

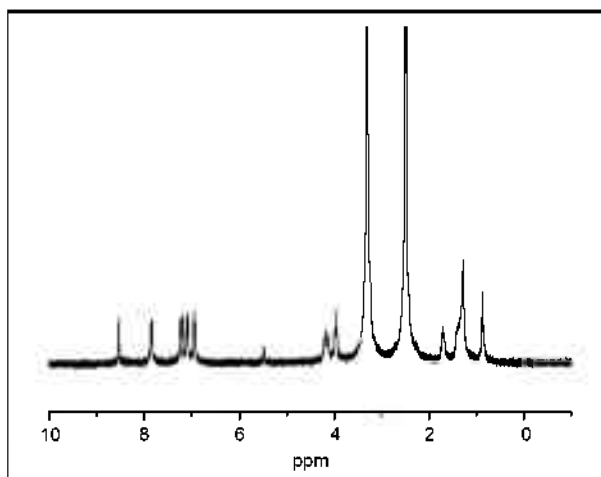


Figure 2.  $^1\text{H}$  NMR spectrum of  $1\text{S}_{12}\text{-para}$  ( $\text{DMSO-}d_6$ ).

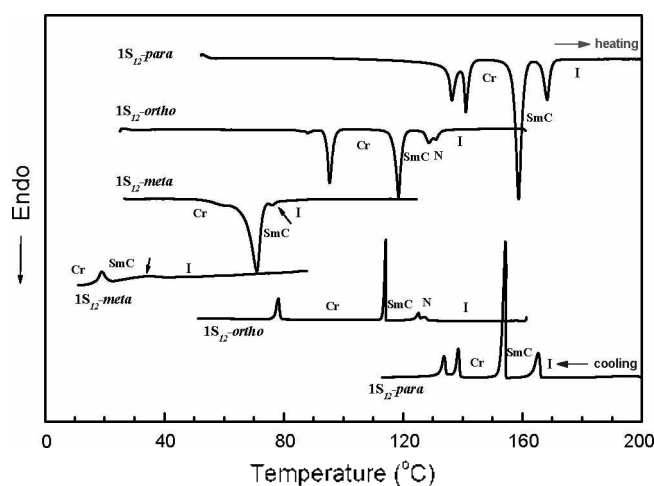
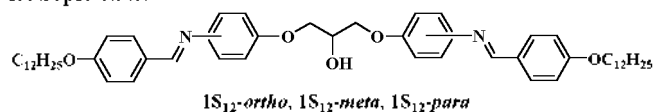


Figure 3. DSC thermograms of  $1\text{S}_{12}\text{-ortho}$ ,  $-meta$  and  $-para$  compounds.

catalyst in anhydrous EtOH, to yield the target compounds  $1\text{S}_{12}\text{-ortho}$ ,  $1\text{S}_{12}\text{-meta}$  and  $1\text{S}_{12}\text{-para}$ , respectively. All the intermediates and the final products were confirmed by elemental analysis, FT-IR, and  $^1\text{H}$  NMR spectroscopy (See Figure 2). IR spectra were recorded with a Perkin-Elmer 1000 FT-IR spectrophotometer on KBr pellets.  $^1\text{H}$ -NMR spectra were recorded by using a Varian Mercury 300 (300 MHz) NMR spectrometer. Differential scanning calorimetric measurements were performed using a TA instruments 910S DSC apparatus under dry nitrogen flow at the scanning rates of  $10\text{ }^\circ\text{C}/\text{min}$ . The transition temperatures were taken at the maximum point of the peaks for each sample. The transition enthalpies were evaluated from the integrated area of the endothermic peaks using a reference indium sample as the standard. Optical microscopy observation was carried out using a Nikon Labophot-2 polarizing microscope fitted with a RTC-1 temperature controller (Instec Inc., Broomfield, Co.) and a Mettler FP-82HT hot stage.

Figure 3 represents the DSC thermodiagrams obtained for both the heating and cooling traces. In Table 1 are summarized the phase transitions and associated enthalpy changes of

Table 1. Phases transition temperatures of the synthesized compounds: Cr = crystalline state, Sm C = smectic C, N = nematic, I = isotropic state.



	Phase and transition temperatures / $^\circ\text{C}$	
	( $\Delta H$ , kJ/mol)	Heating / Cooling
$1\text{S}_{12}\text{-para}$	Cr 158.7 (27.5) SmC 168.3 (14.4) I I 165.2 (15.1) SmC 154.3 (59.1) Cr	
$1\text{S}_{12}\text{-ortho}$	Cr 118.5 (49.5) SmC 128.7 (15.5) N 130.9 (7.1) I I 127.0 (6.5) N 125.1 (14.4) SmC 114.2 (49.3) Cr	
$1\text{S}_{12}\text{-meta}$	Cr 71.0 (83.5) SmC 76.1 (1.0) I I 34.1 (7.8) SmC 19.1 (21.2) Recr	

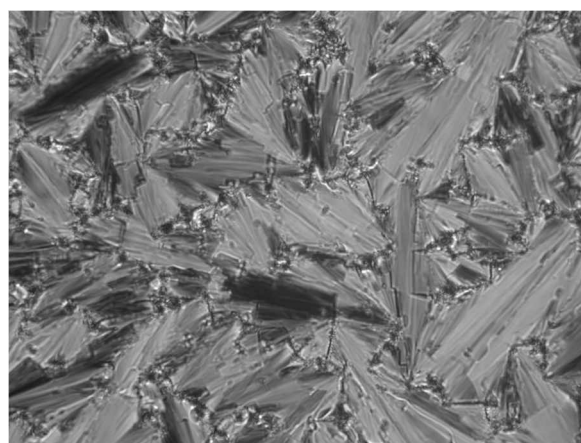
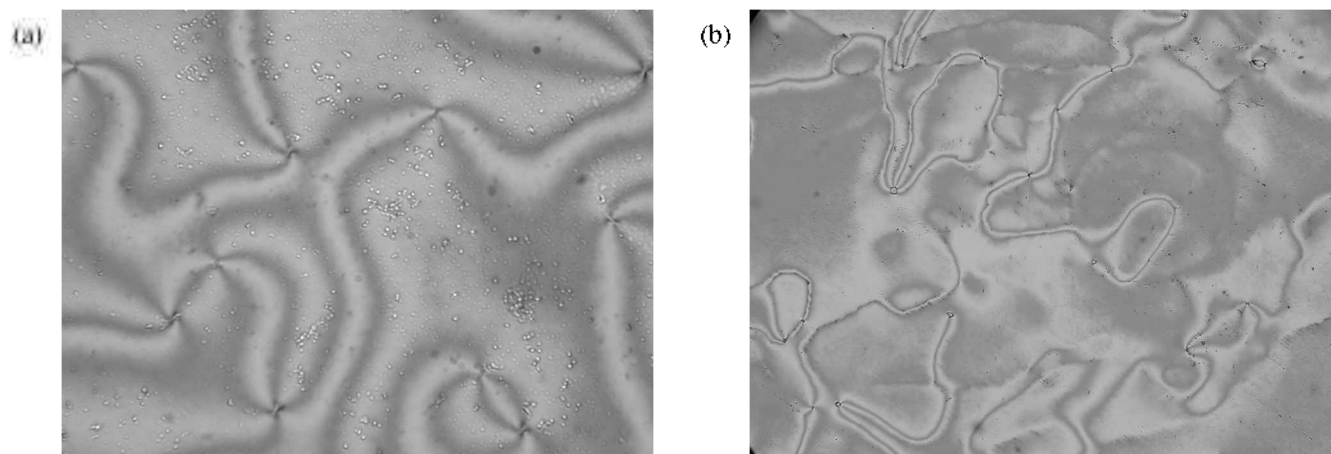


Figure 4. Polarizing optical micrographs of  $1\text{S}_{12}\text{-para}$  ( $165.3\text{ }^\circ\text{C}$ ) ( $\times 100$ ).

dimesogens through the crystalline, smectic and nematic transitions. The compound  $1\text{S}_{12}\text{-para}$  shows an enantiotropic SmC phase (Fig. 4), broken fan-shaped texture) similarly to the results in the  $2\text{S}_n$  series.<sup>8</sup>

When compared to the  $1\text{S}_{12}\text{-para}$  compound the clearing and melting points of the  $1\text{S}_{12}\text{-meta}$  decrease by about  $92\text{ }^\circ\text{C}$  and  $88\text{ }^\circ\text{C}$  respectively. The changes in the phase transition temperatures can be ascribed to the modification of the atomic configurations: The linking position between mesogens and spacer changes from the *meta* in the  $1\text{S}_{12}\text{-meta}$  to the *para* in the  $1\text{S}_{12}\text{-para}$ . Due to this molecular configuration characteristic, the compound  $1\text{S}_{12}\text{-meta}$  shows only enantiotropic SmC phase (schlieren texture) of short range order at low temperature. On the while in the  $1\text{S}_{12}\text{-ortho}$  having the *ortho*-linking, the clearing and melting points decrease by about  $37\text{ }^\circ\text{C}$  and  $45\text{ }^\circ\text{C}$ , respectively. And this compound shows the enantiotropic SmC (Fig. 5(a), schlieren texture) as well as N (Fig. 5(b), schlieren texture) phases.

The observation of liquid crystallinity in the U- or V-shaped molecular shape with polymethylene spacer in mesogenic moiety as in  $1\text{S}_{12}\text{-ortho}$  and  $1\text{S}_{12}\text{-meta}$  are firstly reported in



**Figure 5.** Polarizing optical micrographs of (a) SmC (124.5 °C) and (b) N (129.6 °C) of 1S<sub>12</sub>-ortho (× 100).

this study. Texture analysis using X-ray diffraction will be carried out to understand the characteristic features of dimers in more detail.

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#### References

1. Imrie, C. T. *Structure and Bonding* **1999**, *95*, 149.
2. Date, R. W.; Imrie, C. T.; Luckhurst, G. R.; Seddon, J. M. *Liq. Cryst.* **1992**, *12*, 203.
3. Attard, G. S.; Date, R. W.; Imrie, C. T.; Luckhurst, G. R.; Roskilly, S. J.; Seddon, J. M.; Taylor, L. *Liq. Cryst.* **1994**, *16*, 529.
4. Watanabe, J.; Komura, H.; Niori, T. *Liq. Cryst.* **1993**, *13*, 455.
5. Niori, T.; Adachi, S.; Watanabe, J. *Liq. Cryst.* **1995**, *19*, 139.
6. (a) So, B.-K.; Jang, M.-C.; Park, J.-H.; Lee, K.-S.; Song, H. H.; Lee, S.-M. *Opt. Mater.* **2003**, *21*, 685. (b) Kim, W.-J.; So, B.-K.; Lee, S.-M. *92nd National Meeting of the Korean Chem. Soc.* **2002**, *92*, 100.
7. So, B.-K.; Kim, Y.-S.; Choi, M.-M.; Lee, S.-M.; Kim, J.-E.; Song, H. H.; Park, J.-H. *Liq. Cryst.* **2004**, *31*, 169.
8. So, B.-K.; Kim, W.-J.; Lee, S.-M.; Jang, M.-C.; Song, H.-H.; Park, J.-H. *Dyes and Pigment* **2007**, *75*, 619.