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## Liquid Crystals

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# H-shaped dimeric LC compounds: synthesis and thermotropic properties of $\alpha,\omega$ -bis[2,5-bis(4-ethoxyphenoxy)phenoxy]alkanes

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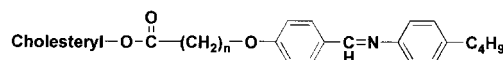
A series of new dimeric liquid crystalline compounds were synthesized and their thermotropic properties studied by differential scanning calorimetry and observation of their melts by polarizing microscopy. These compounds consist of two bis(*p*-ethoxyphenoxy)terephthalate units interconnected through an oxypolymethyleneoxy spacer on the central terephthaloyl units resulting in a structure of 'H-shaped' dimeric twin compounds. The length of spacers was varied from oxytetramethyleneoxy ( $n = 4$ ) to oxyoctamethyleneoxy ( $n = 8$ ). The compound containing the oxydodecamethyleneoxy ( $n = 12$ ) was also included in this study. With the exception only of the dodecamethylene compound, all of the present compounds are monotropically nematic. In contrast, the compound with the oxydodecamethyleneoxy spacer is enantiotropically nematic. It was found that the heats ( $\Delta H_m$ ) of melting of the monotropic compounds are exceptionally high,  $70 \sim 100 \text{ kJ mol}^{-1}$ . The  $\Delta H_m$  value of the compound having the oxydodecamethyleneoxy spacer, however, is much less, about  $17 \text{ kJ mol}^{-1}$ . It is concluded that 'H-shaped' compounds possess less tendency to be thermotropic and also that they tend to vitrify when the spacer length exceeds 6.

## 1. Introduction

A wide variety of liquid crystalline (LC) compounds have been reported especially since the 1960s. In recent years non-conventional LC [1–8] compounds have been attracting a great deal of interest from LC scientists. Among them, dimesogenic compounds [1, 2] (often referred to as Siamese twin mesogens) provide an important new class of LC compounds. Here, two identical mesogenic units are interconnected through a central spacer. Initially these compounds were recognized as excellent model compounds [9, 10] for main chain LC polymers consisting of the same mesogenic units and spacers. Polymethylene [11–16], oligo(oxyethylene) [17–20], and oligosiloxyl groups [21, 22] are representative spacers included in those compounds. Very often the LC behaviour of such compounds is quite

different from that of the corresponding monomesogenic compounds.

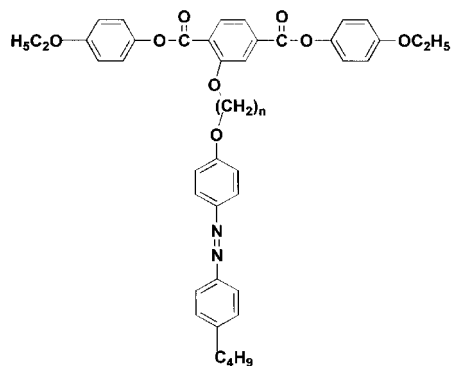
We have recently expanded our research into newer types of dimesogenic compounds in order to establish structure–property relationships for these new types of LC materials [3, 5]. One series of recently reported new dimesogenic compounds [3, 4] consists of two different mesogens interconnected through central spacers:



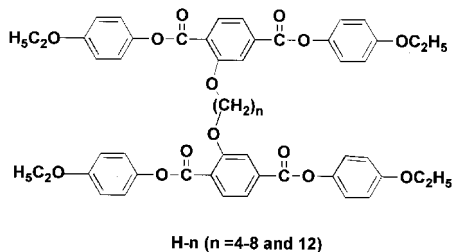
The properties of these compounds reveal a rather complex dependence on the length of spacers. For example, when  $n = 5$ , the compound forms many different phases including incommensurate smectic phases and a twisted grain boundary phase. Another interesting structure is found in 'T-shaped' dimesogenic compounds that can be taken as models [5] for combined-type main

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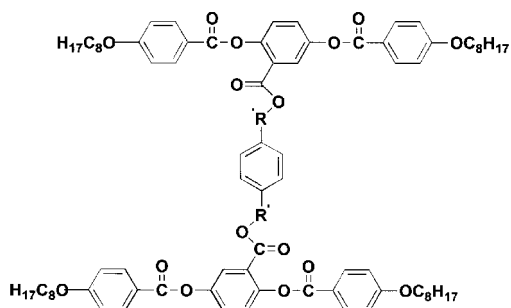
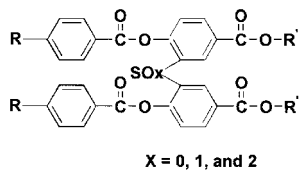
chain/side chain LC polymers:



In this report we describe the synthesis of the following series of 'H-shaped' dimesogenic compounds and discuss their thermotropic properties. The molecules consist of two ester-type mesogenic structures connected through a flexible spacer attached to their central parts:



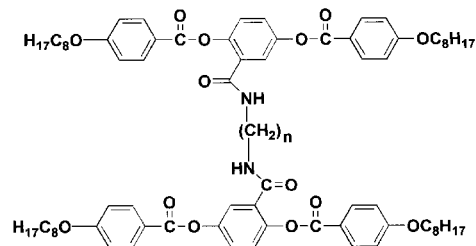
These compounds should be called  $\alpha,\omega$ -bis[2,5-bis-(4-ethoxyphenoxy)carbonyl]phenoxy]alkanes. For the sake of simplicity, they are designated **H-n**, where **H** stands for 'H-shape' and  $n$  for the number of methylene groups in the spacers. These compounds have slightly different structural features from those reported by Demus and co-workers [23, 24].



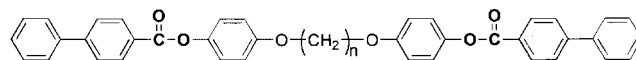
The analogous sulphides, sulphoxide and sulphones have different LC properties. In general sulphones show a greater tendency to form nematic phases enantiotropically,

especially when  $R$  is long, whereas the sulphides are neither LCs nor monotropic. Sulphoxides tend to be monotropic. The twin mesogenic compounds [24] with aromatic bridges form nematic phases enantiotropically. Replacement of the bridge phenylene unit with a 4,4'-biphenylene unit increases the nematic temperature range significantly.

The following compounds [24] have very similar structures to the present series, with the major difference that the bridges are of aliphatic amide rather than ether structure. When  $n$  equals 4 and 5, the compounds form the SmC phase monotropically and nematic phases. The compounds with  $n = 6 \sim 9$  are nematics, whereas those with  $n = 10$  and 12 are monotropically nematic.



The comparison of LC properties of the present series with those of corresponding linearly linked dimesogenic compounds [9, 15, 25–27] and those referred to above is expected to provide more insight on the structure–property relationship of this interesting new class of LC compounds. For example, the following series [9] of linearly linked dimesogenic compounds were found to be enantiotropically nematic and revealed a typical odd–even effect of the central polymethylene spacers on the transition temperatures and also on the thermodynamic parameters for phase transitions.



Such an odd–even effect appears to be general for linearly connected dimesogenic compounds [15, 25–27].

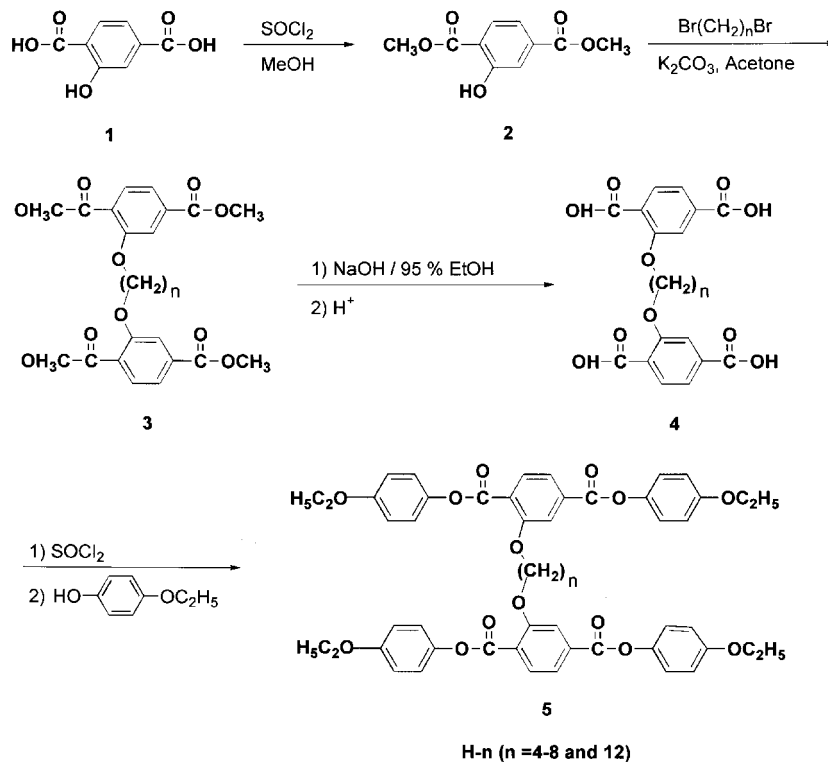
## 2. Experimental

### 2.1. Synthesis

The synthetic route to the new compounds is summarized in the scheme. Experimental details for each step are given below, following the route shown in the scheme. Since the synthetic details are practically the same for each compound, only the procedure for the preparation of **H-4** is described.

#### 2.1.1. Dimethyl 2-hydroxyterephthalate 2

2-Hydroxyterephthalic acid (4.5 g,  $2.5 \times 10^{-2}$  mol) was dissolved in 200 ml of methanol, and 2 ml of purified thionyl chloride was added dropwise. The mixture was stirred for 8 h at room temperature; it was then poured into distilled water and the solution neutralized with



Scheme. Synthetic route to compounds **H-n**.

10%  $\text{NaHCO}_3$ . The precipitate formed was collected on a filter and washed with distilled water. The product yield was 4.9 g (82.6%), m.p. 94–96°C (lit. [28]: 92–93°C).

#### 2.1.2. 1,4-Bis[2,5-di(methoxycarbonyl)phenoxy]butane **3**

Compound **2** (5.3 g,  $2.5 \times 10^{-2}$  mol), 1,4-dibromobutane (1.2 ml,  $1.0 \times 10^{-2}$  mol),  $\text{K}_2\text{CO}_3$  (4.1 g,  $3.0 \times 10^{-2}$  mol) and tetrabutylammonium bromide (0.4 g) were dissolved in 200 ml of acetone. The mixture was heated at reflux for 18 h under a nitrogen atmosphere and cooled to room temperature. The reaction mixture was poured into 0.5M  $\text{K}_2\text{CO}_3$  solution, and the precipitate obtained was thoroughly washed with distilled water. The crude product was recrystallized from a mixture of ethanol and distilled water (1/1, v/v). The product yield was 4.0 g (84.3%), m.p. 105°C. IR (KBr): 2948 (aliphatic C–H stretch), 1727 (C=O stretch), 1290 and 1230  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.85–1.95 (m, 4H,  $\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$ –), 3.88 and 3.92 (s, 12H,  $\text{CH}_3$ ), 4.09–4.15 (t, 4H,  $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$ –), 7.54–7.81 (m, 6H, Ar). Elemental analysis, calc. for  $\text{C}_{24}\text{H}_{26}\text{O}_{10}$  C 60.76, H 5.52; found C 60.85, H 5.60%.

#### 2.1.3. 1,4-Bis[2,5-dicarboxyphenoxy]butane **4**

Compound **3** (4.0 g,  $0.8 \times 10^{-2}$  mol) was dissolved in 50 ml of 95% ethanol, and sodium hydroxide (1.3 g,  $3.3 \times 10^{-2}$  mol) added. The mixture was heated at reflux for 6 h and cooled to room temperature. The

reaction mixture was poured into ice cold water and the solution was acidified with 5M HCl. The precipitate formed was collected on a filter and thoroughly washed with distilled water, then dried. The crude product was recrystallized from a mixture of ethanol and THF (2/1, v/v). The product, yield 2.9 g (82.8%), starts to sublime around 300°C. IR (KBr) 3500–2400 (acid O–H stretch), 1692 (C=O stretch), 1300 and 1243  $\text{cm}^{-1}$  (ether C–O stretch),  $^1\text{H}$  NMR (acetone- $d_6$ ): 1.70–1.90 (m, 4H,  $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$ –), 4.1–4.2 (t, 4H,  $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$ –), 7.55–7.75 (m, 6H, Ar). Elemental analysis, calc. for  $\text{C}_{20}\text{H}_{18}\text{O}_{10}$  C 57.42, H 4.34; found C 57.34, H 4.41%.

#### 2.1.4. 1,4-Bis[2,5-bis(4-ethoxyphenoxy)carbonyl]phenoxy]butane **5 (H-4)**

Compound **4** (0.63 g,  $0.2 \times 10^{-2}$  mol) and 50 ml of purified thionyl chloride were heated under reflux for 4 h. Excess thionyl chloride was then removed by distillation under reduced pressure. The acid chloride formed was dissolved in an ice-chilled mixture of 50 ml of THF and 20 ml of pyridine, to which was added a solution of 4-ethoxyphenol (1.7 g,  $1.2 \times 10^{-2}$  mol) dissolved in 5 ml of dry THF. The mixture was stirred for 20 h at room temperature and for an additional 1 h at 60°C. THF was removed from the mixture using a rotary evaporator. The residue was thoroughly washed with 0.1M HCl, distilled water, 5%  $\text{NaHCO}_3$  solution, and

finally again with distilled water. The crude product, **H-4**, was recrystallized from a mixture of ethanol and acetone (4/1, v/v). The product (**H-4**) yield was 1.0g (76.0%), m.p. 199.5°C. IR (KBr) 3050 and 2927 (aromatic and aliphatic C–H stretch), 1737 (C=O stretch), 1300–1041 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (CF<sub>3</sub>COOD): δ 1.41–1.52 (m, 12H, CH<sub>3</sub>), 2.01–2.21 (m, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>O–), 4.25–4.51 (m, 12H, ArOCH<sub>2</sub>), 7.05–8.30 (m, 22H, Ar). Elemental analysis, calc. for C<sub>52</sub>H<sub>50</sub>O<sub>14</sub> C 69.48, H 5.61; found C 69.18, H 5.69%.

**H-5-8**, and **H-12** were synthesized by the same route, the only difference being that compound **2** was reacted with 1,5-dibromopentane, 1,6-dibromohexane, 1,7-dibromoheptane, 1,8-dibromooctane and 1,12-dibromododecane, respectively, instead of 1,4-dibromobutane in the second step. For that reason only the reaction yields, melting points, spectroscopic data, and the results of elemental analyses of the **H-5** through **H-8** and **H-12** are given below.

#### 2.1.5. 1,5-Bis[2,5-di(methoxycarbonyl)phenoxy]pentane

The product yield was 83.8%, m.p. 63°C. IR (KBr): 2947 (aliphatic C–H stretch), 1726 (C=O stretch), 1297 and 1235 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.56–1.67 (m, 2H, –O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O–), 1.86–1.97 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 3.88 and 3.93 (s, 12H, CH<sub>3</sub>), 4.09–4.16 (t, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>O–), 7.54–7.82 (m, 6H, Ar). Elemental analysis, calc. for C<sub>25</sub>H<sub>28</sub>O<sub>10</sub> C 61.47, H 5.78; found C 61.53, H 5.81%.

#### 2.1.6. 2,5-Bis[2,5-dicarboxyphenoxy]pentane

The product yield was 86.8%, m.p. 290–291°C. IR (KBr): 3400–2400 (acid O–H stretch), 1689 (C=O stretch), 1301 and 1242 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (acetone-d<sub>6</sub>): δ 1.56–1.6 (m, 2H, –O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O–), 1.70–1.92 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 4.1–4.2 (t, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>O–), 7.56–7.73 (m, 6H, Ar). Elemental analysis, calc. for C<sub>21</sub>H<sub>20</sub>O<sub>10</sub> C 58.34, H 4.66; found C 58.55, H 4.81%.

#### 2.1.7. 2,5-Bis[2,5-bis(4-ethoxyphenoxy)carbonyl]phenoxy]pentane **H-5**

The product yield was 77.0%, m.p. 179.0°C. IR (KBr): 3051 and 2925 (aromatic and aliphatic C–H stretch), 1738 (C–O stretch), 1300–1180 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (CF<sub>3</sub>COOD): δ 1.41–1.51 (m, 12H, CH<sub>3</sub>), 1.78–1.90 (m, 2H, –OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 2.01–2.15 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 4.25–4.5 (m, 12H, ArOCH<sub>2</sub>), 7.05–8.31 (m, 22H, Ar). Elemental analysis, calc. for C<sub>53</sub>H<sub>52</sub>O<sub>14</sub> C 69.73, H 5.74; found C 70.19, H 5.79%.

#### 2.1.8. 1,6-Bis[2,5-di(methoxycarbonyl)phenoxy]hexane

The product yield was 82.1%, m.p. 83–84°C. IR (KBr): 2944 (aliphatic C–H stretch), 1715 (C=O stretch), 1300–1500 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.55–1.65 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 1.85–1.95 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 3.88 and 3.90 (s, 12H, CH<sub>3</sub>), 4.09–4.15 (t, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–), 7.54–7.81 (m, 6H, Ar). Elemental analysis, calc. for C<sub>26</sub>H<sub>30</sub>O<sub>10</sub> C 62.15, H 6.01; found C 62.25, H 6.01%.

#### 2.1.9. 1,6-Bis[2,5-dicarboxyphenoxy]hexane

The product yield was 88.8%, m.p. 314–316°C. IR (KBr): 3500–2400 (acid O–H stretch), 1689 (C=O stretch), 1301 and 1242 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (acetone-d<sub>6</sub>): δ 1.55–1.62 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 4.1–4.2 (t, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–), 7.57–7.73 (m, 6H, Ar). Elemental analysis, calc. for C<sub>22</sub>H<sub>22</sub>O<sub>10</sub> C 59.19, H 4.97; found C 58.74, H 5.08%.

#### 2.1.10. 1,6-Bis[2,5-bis(4-ethoxyphenoxy)carbonyl]phenoxy]hexane **H-6**

The product yield was 80%, m.p. 186°C. IR (KBr): 3050 and 2932 (aromatic and aliphatic C–H stretch), 1740 (C=O stretch), 1230–1049 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.35–1.50 (m, 12H, CH<sub>3</sub>), 1.55–1.62 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 1.81–1.95 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>–(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 3.95–4.12 (m, 12H, Ar–CH<sub>2</sub>), 6.85–8.15 (m, 22H, Ar). Elemental analysis, calc. for C<sub>54</sub>H<sub>54</sub>O<sub>14</sub> C 69.96, H 5.87; found C 70.83, H 5.89%.

#### 2.1.11. 1,7-Bis[2,5-di(methoxycarbonyl)phenoxy]heptane

The product yield was 75.1%, m.p. 53°C. IR (KBr): 2945 (aliphatic C–H stretch), 1721 (C=O stretch), 1292 and 1234 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.35–1.45 (m, 2H, –O(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>O–), 1.55–1.65 (m, 4H, –O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>O–), 1.84–1.92 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 3.88 and 3.93 (s, 12H, CH<sub>3</sub>), 4.09–4.14 (t, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>O–), 7.54–7.85 (m, 6H, Ar). Elemental analysis, calc. for C<sub>27</sub>H<sub>32</sub>O<sub>10</sub> C 62.79, H 6.25; found C 63.63, H 6.43%.

#### 2.1.12. 1,7-Bis[2,5-dicarboxyphenoxy]heptane

The product yield was 90%, m.p. 258–259°C. IR (KBr): 3500–2400 (acid O–H stretch), 1693 (C=O stretch), 1299 and 1241 cm<sup>-1</sup> (ether C–O stretch). <sup>1</sup>H NMR (acetone-d<sub>6</sub>): δ 1.35–1.43 (m, 2H, –O(CH<sub>3</sub>)<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>O–), 1.54–1.64 (m, 4H, –O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–(CH<sub>2</sub>)<sub>2</sub>O–), 1.84–1.91 (m, 4H, –OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O–), 4.08–4.13 (t, 4H, –OCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>O–), 7.55–7.88 (m, 6H, Ar). Elemental analysis, calc. for C<sub>23</sub>H<sub>24</sub>O<sub>10</sub> C 59.99, H 5.25; found C 59.82, H 5.12%.

2.1.13. *1,7-Bis[2,5-bis(4-ethoxyphenoxy)carbonyl]-phenoxy]heptane H-7*

The product yield was 87%, m.p. 154.1°C. IR (KBr): 2928 (aliphatic C–H stretch), 1738 (C=O stretch), 1300–1110  $\text{cm}^{-1}$  (ether C–O stretch),  $^1\text{H}$  NMR (tetrachloroethane- $d_2$ ):  $\delta$  1.35–1.45 (m, 14H,  $-\text{O}(\text{CH}_2)_3\text{CH}_2(\text{CH}_2)_3\text{O}-\text{CH}_3$ ), 1.54–1.64 (m, 4H,  $-(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{O}-$ ), 1.84–1.92 (m, 4H,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{O}-$ ), 3.95–4.15 (m, 12H, ArOCH $_2$ -), 6.91–8.09 (m, 22H, Ar). Elemental analysis, calc. for  $\text{C}_{55}\text{H}_{56}\text{O}_{14}$  C 70.19, H 5.99; found C 70.16, H 6.15%.

2.1.14. *1,8-Bis[2,5-di(methoxycarbonyl)phenoxy]octane*

The product yield was 67.3%, m.p. 75–76°C. IR (KBr): 2934 (aliphatic C–H stretch), 1725 (C=O stretch), 1296 and 1234  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.28–1.35 (m, 4H,  $-\text{O}(\text{CH}_2)_3(\text{CH}_2)_2(\text{CH}_2)_3\text{O}-$ ), 1.55–1.66 (m, 4H,  $-\text{O}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{O}-$ ), 1.81–1.91 (m, 4H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_4-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.88 and 3.92 (s, 12H,  $\text{CH}_3$ ), 4.09–4.15 (t, 4H,  $-\text{OCH}_2(\text{CH}_2)_6\text{CH}_2\text{O}-$ ), 7.55–7.86 (m, 6H, Ar). Elemental analysis, calc. for  $\text{C}_{28}\text{H}_{34}\text{O}_{10}$  C 63.39, H 6.46; found C 64.16, H 6.68%.

2.1.15. *1,8-Bis[2,5-dicarboxyphenoxy]octane*

The product yield was 85%, m.p. 272–273°C. IR (KBr): 3500–2400 (acid O–H stretch), 1695 (C=O stretch), 1296 and 1240  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  1.28–1.35 (m, 4H,  $-\text{O}(\text{CH}_2)_3(\text{CH}_2)_2(\text{CH}_2)_3\text{O}-$ ), 1.55–1.65 (m, 4H,  $-\text{O}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2-(\text{CH}_2)_2\text{O}-$ ), 1.82–1.93 (m, 4H,  $-\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{CH}_2\text{O}-$ ), 4.08–4.13 (t, 4H,  $-\text{OCH}_2(\text{CH}_2)_6-\text{CH}_2\text{O}-$ ), 7.54–7.87 (m, 6H, Ar). Elemental analysis, calc. for  $\text{C}_{24}\text{H}_{26}\text{O}_{10}$  C 60.76, H 5.52; found C 60.67, H 5.89%.

2.1.16. *1,8-Bis[2,5-bis(4-ethoxyphenoxy)carbonyl]-phenoxy]octane H-8*

The product yield was 92%, m.p. 146.7°C. IR (KBr): 2930 (aliphatic C–H stretch), 1741 (C=O stretch), 1300–1150  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR (tetrachloroethane- $d_2$ ):  $\delta$  1.28–1.35 (m, 4H,  $-\text{O}(\text{CH}_2)_3-(\text{CH}_2)_2(\text{CH}_2)_3\text{O}-$ ), 1.36–1.50 (m, 16H,  $-(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{O}-$ ,  $\text{CH}_3$ ), 1.81–1.91 (m, 4H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{CH}_2\text{O}-$ ), 3.95–4.16 (m, 12H, Ar–OCH $_2$ -), 6.90–8.05 (m, 22H, Ar). Elemental analysis, calc. for  $\text{C}_{56}\text{H}_{58}\text{O}_{14}$  C 70.47, H 6.12; found C 70.45, H 6.28%.

2.1.17. *1,12-Bis[2,5-di(methoxycarbonyl)phenoxy]-dodecane*

The product yield was 78.5%, m.p. 80°C. IR (KBr): 2917 (aliphatic C–H stretch), 1724 (C=O stretch), 1297 and 1236  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.25–1.55 (m, 16H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{O}-$ ),

3.88 and 3.91 (s, 12H,  $\text{CH}_3$ ), 4.05–4.12 (t, 4H,  $-\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_2\text{O}-$ ), 7.58–7.81 (m, 6H, Ar). Elemental analysis, calc. for  $\text{C}_{32}\text{H}_{42}\text{O}_{10}$  C 65.51, H 7.22; found C 66.19, H 7.50%.

2.1.18. *1,12-Bis[2,5-dicarboxyphenoxy]dodecane*

The product yield was 81%, m.p. 264–266°C. IR (KBr): 3400–2400 (acid O–H stretch), 2925 (aliphatic C–H stretch), 1694 (C=O stretch), 1301 and 1244  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR (DMSO- $d_6$ ): 1.10–1.25 (m, 16H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{O}-$ ), 1.80–1.90 (m, 4H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{O}-$ ), 4.0–4.05 (t,  $-\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_2\text{O}-$ ), 7.50–7.80 (m, 6H, Ar). Elemental analysis, calc. for  $\text{C}_{28}\text{H}_{34}\text{O}_{10}$  C 67.45, H 6.87; found C 67.51, H 7.02%.

2.1.19. *1,12-Bis[2,5-bis(4-ethoxyphenoxy)carbonyl]-phenoxy]dodecane H-12*

The product yield was 72%, m.p. 111.1°C. IR (KBr): 3050 and 2932 (aromatic and aliphatic C–H stretch), 1740 (C=O stretch), 1300–1150  $\text{cm}^{-1}$  (ether C–O stretch).  $^1\text{H}$  NMR (tetrachloroethane- $d_2$ ): 1.10–1.55 (m, 28H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{O}-$  and  $\text{CH}_3$ ), 1.75–1.95 (m, 4H,  $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_8-\text{CH}_2\text{CH}_2\text{O}-$ ), 4.0–4.21 (m, 12H, Ar–CH $_2$ ), 6.89–8.10 (m, 22H, Ar). Elemental analysis, calc. for  $\text{C}_{60}\text{H}_{66}\text{O}_{14}$  C 71.26, H 6.58; found C 71.26, H 6.82%.

## 2.2. Characterization

The infrared and  $^1\text{H}$  NMR spectra were recorded on a Bomen MR-Series FT-IR instrument and an AMS 300 spectrometer, respectively. Elemental analysis was performed by the Korea Basic Science Institute, Seoul, Korea. Thermal properties of the compounds were studied under a nitrogen atmosphere on a differential scanning calorimeter (DSC Perkin-Elmer 7) at the heating and cooling rate of 2°C  $\text{min}^{-1}$ . Thermal transitions and the optical textures of the compounds were also observed through a polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP82HT) controlled automatically by the central unit of a Mettler FP90HT.

## 3. Results and discussion

### 3.1. Synthesis

The present series of compounds (**H-n**) was synthesized following the synthetic route shown in the scheme. 2-Hydroxyterephthalic acid (**1**) was heated under reflux with a mixture of thionyl chloride and methanol to produce the corresponding diester **2**. Compound **2** thus prepared was then refluxed with  $\alpha,\omega$ -dibromoalkanes in acetone in the presence of potassium carbonate to yield the tetraester **3**; this was then hydrolysed to the twin tetracarboxylic acid **4**. Compound **4** was

converted to the corresponding acid chloride before finally being condensed with 4-ethoxyphenol resulting in the formation of the final compound. Pyridine was utilized as an HCl acceptor. The structures of the compounds were confirmed by elemental analysis and IR and  $^1\text{H}$  NMR spectroscopy.

### 3.2. Thermal and liquid crystalline properties

Thermal properties of the present compounds studied by DSC are peculiar. Firstly, all the compounds show broad melting transitions over a range of 5–10°C at a heating rate of  $2^\circ\text{C min}^{-1}$  (see figure 1). Their melting endothermic peaks are highly unsymmetrical; some even appear to consist of overlapping multiple peaks. It is possible that these compounds form more than one crystal structure, i.e. they are polymorphic in the solid state. Secondly, the temperature widths between the peak maximum positions and peak end positions are, however, very narrow, about  $1^\circ\text{C}$ . Thirdly, compounds **H-4** through **H-8** do not exhibit any peaks other than the melting peaks before undergoing thermal decomposition. **H-12**, containing the longest spacers (the dodecamethylene group) is the only compound that shows two endothermic peaks, the larger at a low

temperature and the smaller at a higher temperature. Fourthly, compounds **H-4** through **H-7** reveal multiple exothermic peaks upon cooling the isotropic melts with extremely broad low temperature exotherms covering more than  $20^\circ\text{C}$ , with the only exception of **H-4** that exhibits two rather sharp peaks in the lower temperature region. Fifthly, **H-8** reveals a multiple melting transition on heating, whereas it shows only one broad exothermic transition on cooling the melt. Lastly, **H-12** is unique in that it is the only compound among the present series that exhibits two transitions on heating and one on cooling. This compound tends to solidify into a mesophase glass when the melt is cooled. It shows only one isotropic  $\rightarrow$  nematic transition on cooling the isotropic melt. This behaviour was confirmed also by microscopic observation.

Optical textures and thermal transition behaviour of the compounds were observed in the polarizing microscope. All of the compounds, with the only exception of **H-12**, melted into isotropic melts. However they formed liquid crystalline phases on cooling the isotropic melts. The threaded schlieren textures of the photomicrographs shown in figure 2 indicate that they formed nematic phases, i.e. compounds **H-4** through **H-8** are monotropic nematics. Compound **H-8** was very peculiar in that it formed a nematic phase (figure 3) over only a very narrow range ( $\sim 0.5^\circ\text{C}$ ) of temperature. Moreover, its cooling DSC curve (see figure 1) exhibits a very broad peak covering about  $15^\circ\text{C}$ ; its nematic phase was observed just before solidification.

Among the present series, **H-12** is the only compound that forms a nematic phase reversibly, which is a characteristic of enantiotropic liquid crystalline compounds. The nematic phase formed on cooling the isotropic phase, however, persisted down to room temperature without transition to the crystalline phase. Combining the results of DSC analysis and microscopic observations, we arrive at the conclusion that the small exothermic peaks appearing in the high temperature region in the cooling curves of DSC analysis correspond to the isotropic-to-nematic phase transitions and the large exothermic peaks appearing in the low temperature region to crystallization. As mentioned above, **H-12** fails to crystallize when its nematic melt is cooled to room temperature; it vitrifies into a nematic glassy state.

One question arises as to why only **H-12** is enantiotropic while the rest of these compounds are monotropic. The answer can be found in the table, which compares phase transition temperatures and thermodynamic parameters for transitions. According to the heat of melting data given in the table, the  $\Delta H_m$  value of **H-12** is particularly low when compared with the values for other compounds: its magnitude is only about 20% of the other values. Certainly, the longer spacer is very

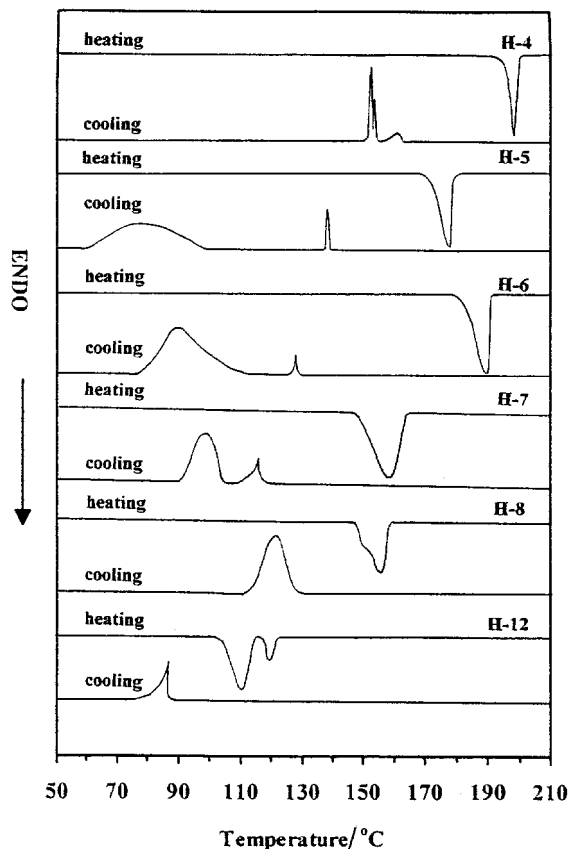
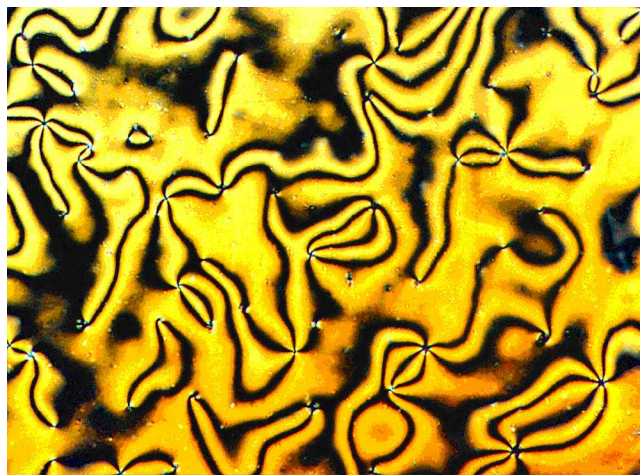
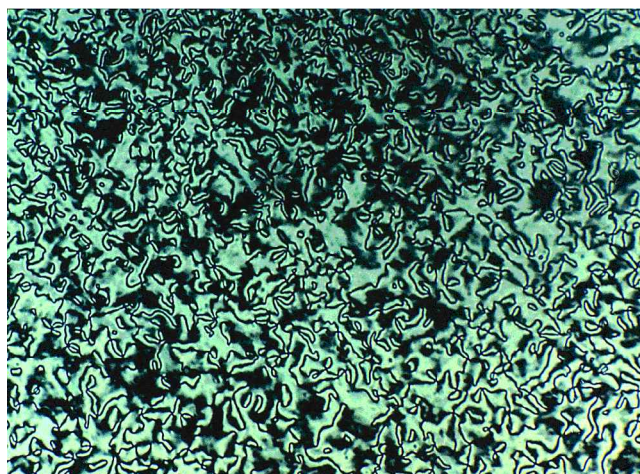


Figure 1. DSC thermograms of compounds **H-n** (heating and cooling rate  $2^\circ\text{C min}^{-1}$ ).





(a)



(b)

Figure 2. Optical photomicrographs of (a) compound **H-5** (129.8°C) and (b) compound **H-6** (104.0°C) (magnification 200×).

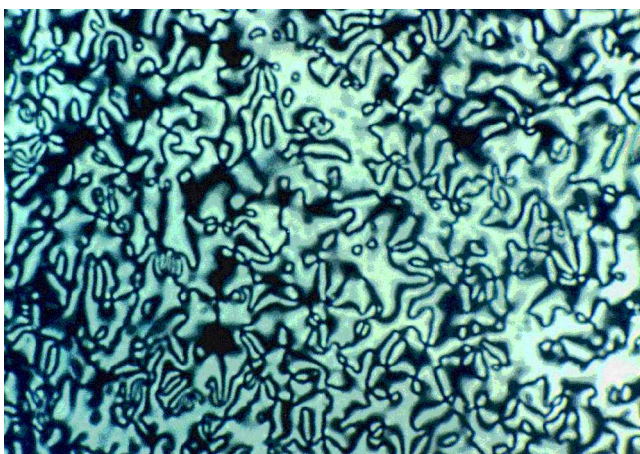


Figure 3. Optical photomicrographs of compound **H-8** (117.8°C) (magnification 200×).

efficient in lowering the  $\Delta H_m$  value, and thus favours the formation of a mesophase upon melting of the crystalline state. It has been observed earlier by us [11–13] that compounds with high  $\Delta H_m$  values tend to be monotropic or non-liquid crystalline. Another point to be noted is that the  $\Delta H_m$  values of **H-4** through **H-8** are much greater than for monomesogenic compounds [29] as well as linearly connected dimesogenic compounds [9, 11, 12, 14]. This is a strong indication that ‘H-shaped’ compounds with shorter lateral spacers form crystals with very strong lattice forces. Relatively large  $\Delta H_m$  values (but smaller than for **H-4** through **H-6**) were reported also by Weissflog *et al.* [24] for similar dimesogenic compounds where the spacers were of aliphatic amide type. Weissflog *et al.* also reported an odd–even dependence of melting and clearing temperatures of their compounds on the length of the spacers. However, we could observe the odd–even effect (figure 4) only for the  $T_m$  values of **H-4** through **H-7**, but not for isotropic–nematic transition temperatures ( $T_{I-N}$ ). The  $T_{I-N}$  value decreases smoothly as the length of the spacers increases. It is not clear why this series and Weissflog’s series reveal such a difference in the dependence of their transition temperatures on the spacers’ length. At the same time, we do not observe any odd–even effect in  $\Delta H_i$ ,  $\Delta S_m$ , and  $\Delta S_i$  values (see the table).

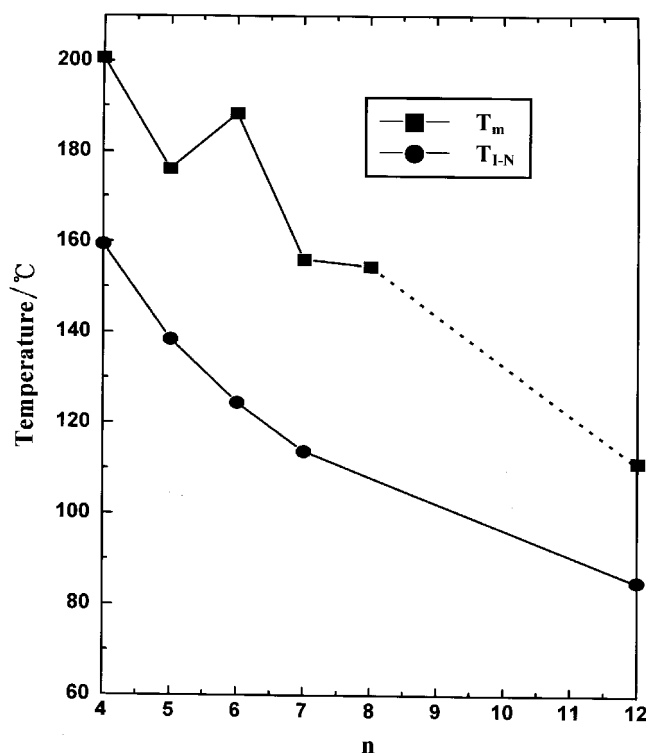


Figure 4. The dependence of transition points  $T_m$  and  $T_{I-N}$  on the length  $n$  of the flexible spacer in the compounds **H-n**.



Table 1. Thermal properties and thermodynamic data for the phase transitions of **H-n** compounds<sup>a</sup>.

<i>n</i>	LC Properties <sup>b</sup>	$T_m/^\circ\text{C}$	$T_i/^\circ\text{C}$	$\Delta H_m/\text{KJ mol}^{-1}$	$\Delta H_i/\text{KJ mol}^{-1}$	$\Delta S_i/\text{J mol}^{-1} \text{K}^{-1}$
4	Mo	200.7	159.5	85.3		
5	Mo	176.2	138.6	85.8	2.74	6.7
6	Mo	188.5	124.6	99.0	2.27	5.7
7	Mo	156.2	113.9	73.0	2.18	5.6
8	Mo	154.7		85.2		
12	En	111.0	(119.7) <sup>c</sup>	17.0	(2.71) <sup>c</sup>	(6.9) <sup>c</sup>
			85		1.17	3.3

<sup>a</sup> Except for the values of  $T_m$  and  $\Delta H_m$ , all the data were obtained from the cooling curves of DSC analysis.  $\Delta H_i$  and  $\Delta S_i$  signify the heat of isotropization and the entropy change for isotropization, respectively.

<sup>b</sup> En and Mo designate enantiotropic and monotropic formation, respectively, of liquid crystal phases.

<sup>c</sup> Values shown in parentheses are those obtained from DSC heating curves.

Since the melting endothermic peaks and the crystallization exothermic peaks of most of the present compounds are so broad, we tried to analyse the structures of their solid states at varying temperatures by X-ray diffraction. The preliminary results obtained, however, are rather complicated and indicate that different phases or crystalline structures coexist. Compounds **H-6** through **H-8** exhibit some possibility of the formation of lamellar or highly ordered LC phases over a very narrow temperature range just before crystallization, but further structural analysis is required before we can draw a final conclusion on this point.

Finally, it is pointed out that LC properties and phase transition behaviour of the linearly linked dimesogenic compounds, as well as of the 'T-shaped' compounds having the same rigid core as in the present series, have not yet been reported. Comparison of the LC properties of those compounds with the present series will provide a clearer picture of the relationship between the structure and properties of the dimesogenic compounds. We are presently undertaking further research in this direction.

#### 4. Conclusion

Although only a limited number of the laterally linked, 'H-shaped', ester-type twin LC compounds have been investigated in this study, their ability to form mesophases appears to be less than for the corresponding linearly joined dimesogenic compounds with the same or similar mesogens. This is ascribed to the unusually high heat of melting of these compounds. All of the compounds reported here form nematic melts either monotropically (**H-4** through **H-8**) or enantiotropically. Although **H-12** is the only enantiotropic LC among the present compounds, it seems safe to say that longer spacers promote the formation of mesophases. All of the present compounds appear to be polymorphic, forming plural crystal morphologies in the solid state.

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