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Comparison of liquid crystalline properties of dimeric compounds of different skeletal shapes

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Series of dimeric compounds of different skeletal shapes consisting of two triad aromatic ester type mesogenic moieties connected via polymethylene spacers were synthesized and their liquid crystalline properties compared. The two mesogenic units are connected in either H- or T-shape or in linear fashion. In general, it was found that mesophase temperature ranges for the T- and linear-shaped compounds are much wider than for the H-shaped compounds. Moreover, the former are enantiotropic thermotropic materials, whereas the latter tend to be monotropic unless the spacer length is fairly long, i.e. longer than decamethylene. Among the three series, the linearly linked twin compounds had the highest melting and isotropization temperatures. All of the linear and T-shaped dimeric compounds reported in this article form only nematic mesophases.

1. Introduction

Non-conventional liquid crystalline (LC) compounds having either unusual chemical structures or non-linear skeletal structures are attracting a great deal of interest in the liquid crystal community. Non-symmetric dimesogenic compounds [1–16], bent-shaped dimeric mesogens [17–23], laterally branched or T-shaped dimesogens [24–27], compounds consisting of two parallel mesogenic units connected laterally through a spacer or H-shaped dimers [28–35], and LC compounds having multiple tails [36–40] are some examples. Recently, we reported the LC properties of some of H- and T-shaped compounds comprising two mesogenic units connected through a polymethylene spacer [20, 21]. Earlier, the Halle group [25, 26] reported the LC properties of similar H-shaped compounds containing different types of linking spacers between the two mesogenic units. According to the results obtainable from a rather limited number of reports describing the LC properties of this type of compound, the nature and the temperature range of their mesophases appear to depend greatly on the structure and length of the spacers. However, the dependence of their LC properties on the structure of the mesogenic units is not yet clear due to the lack of experimental data available up to the present time.

When the mesogenic units were of the aromatic ester type and the spacers were α, ω-alkylenes as shown below in figure 1, the longer spacers induced the formation of nematic LC phases which were enantiometric, whereas shorter spacers made them monotropic [33, 34]. The shorter spacers, however, favour the formation of smectic LC phases in addition to the nematic phases. Longer tails on the mesogenic units tend to favour the formation of smectic phases and create enantiotropic mesogens.

In this investigation we have prepared the following (figure 2) six dimeric LC compounds and compared their LC properties with those of the corresponding H-shaped counterparts (figure 1) reported earlier by us [33, 34]. The present compounds are either T-shaped or linear (1).

The acronyms shown above and used to describe these series refer to T-shaped or linearly (1) connected dimers having different numbers (4, 8, and 12) of methylene

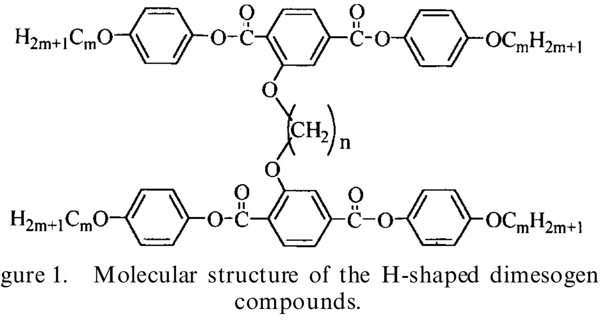

Figure 1. Molecular structure of the H-shaped dimesogenic compounds.

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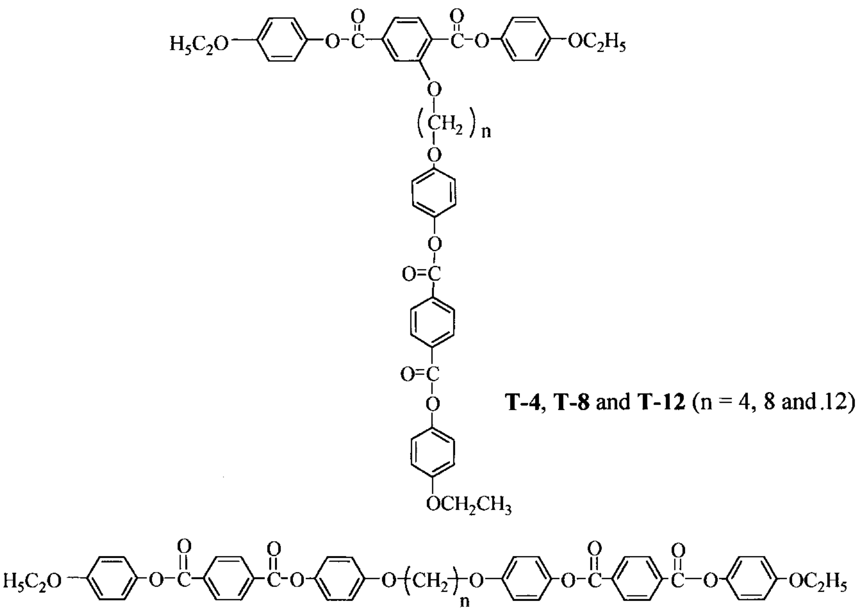


T-4, **T-8** and **T-12** (n = 4, 8 and.12)

l-4, **l-8** and **l-12** (n= 4, 8 and 12)

Figure 2. Molecular structures of the T-shaped and l-shaped dimeric compounds.

groups in the α, ω-alkylene spacers. In this paper, we primarily concentrate upon comparing the mesophase-forming capability, the nature of the mesophase formed, the phase transition temperatures, and the thermodynamic parameters associated with the phase transitions of the three series of dimeric compounds with different skeletal structures.

2. Experimental

2.1. *Synthesis of T-shaped compounds*

The synthetic routes to the compounds are summarized in schemes 1 and 2. Experimental details for each step are given below, following the routes shown in the schemes. Since the synthetic details for members of a specific homologous series are practically the same, only the procedures for the preparation of **T-8** and **l-8** are described.

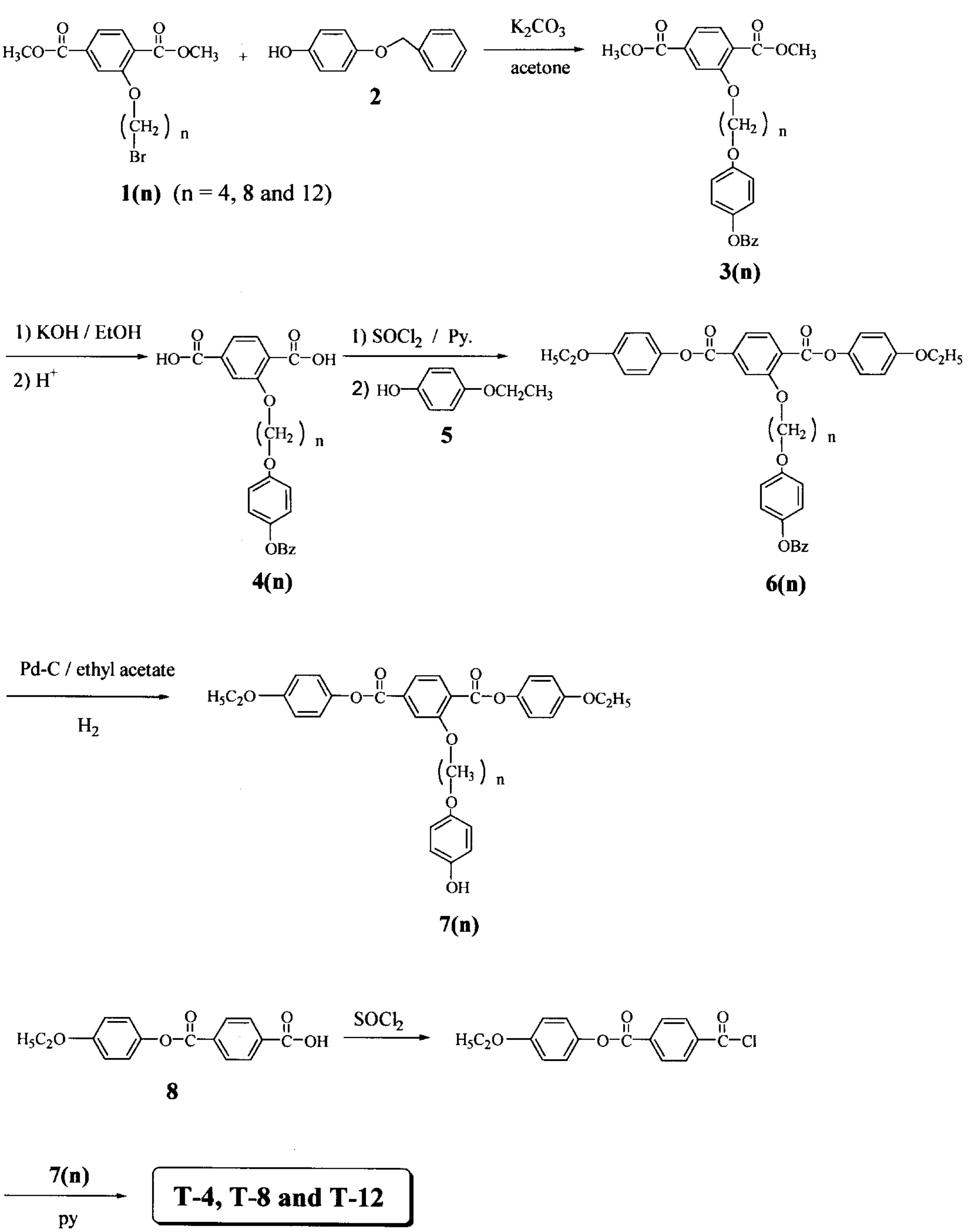
2.1.1. *Dimethyl 2-[8-(4-benzyloxyphenoxy)octyloxy]-terephthalate **3(8)***

Dimethyl 2-(8-bromooctyloxy)terephthalate (**1**, 4.65 g, 1.16×10^{-2} mol) and 4-benzyloxyphenol (**2**, 2.4 g, 1.2×10^{-2} mol) were dissolved in 300 ml of acetone containing 20 g of K_2CO_3 and 0.01 g of tetra-*n*-butylammonium iodide. The mixture was heated at reflux for 36 h. Insoluble precipitates were removed by filtration and acetone was distilled off. The residue was dissolved in methylene chloride and the solution poured into an excess of hexane. The white precipitate formed was collected by filtration and thoroughly washed with hexane before drying at 40°C in a vacuum oven. The compound thus obtained was found to be pure enough by TLC and was used directly in the next step. The yield was 4.95 g (82%), m.p. 74°C. IR (KBr, cm^{-1}): 3046 (aromatic C–H stretch), 2938 (aliphatic C–H stretch), 1725 (C=O stretch), 1513 (aromatic C=C stretch), and 1294, 1250, 1228 (C–O stretch). ^1H NMR ($CDCl_3$, δ ppm): 1.40–1.49 (m, 8H, $-\underline{CH_2}-$), 1.74–1.87 (m, 4H, $Ar-OCH_2\underline{CH_2}-$), 3.90 (s, 3H, $Ar-COO\underline{CH_3}$), 3.94 (s, 3H, $Ar-COO\underline{CH_3}$), 4.09 (t, 2H, $Ar-O\underline{CH_2}-$), 5.01 (s, 2H, $Ar\underline{CH_2}O-$), and 6.81–7.44 (m, 12H, aromatic Hs). Elemental analysis: calc. for $C_{31}H_{36}O_7$ C 71.52, H 6.97; found C 71.57, H 7.01%.

The melting points of the corresponding compounds **3(4)** and **3(12)** containing tetramethylene and dodecamethylene spacers were 56 and 71°C, respectively. Their structures were also confirmed by IR, ^1H NMR spectroscopy and elemental analysis.

2.1.2. *2-[8-(4-Benzyloxyphenoxy)octyloxy]terephthalic acid **4(8)***

Compound **3(8)** (4.48 g, 0.86×10^{-2} mol) was dissolved in 250 ml of 95% ethanol containing 4.8 g of KOH. The mixture was boiled for 5 h. Insoluble material was removed by filtration and the solvent distilled off using a rotary evaporator. The residue was dissolved in distilled water and then the solution was acidified with 1M HCl. The white precipitate formed was filtered off and washed thoroughly with distilled water. The product



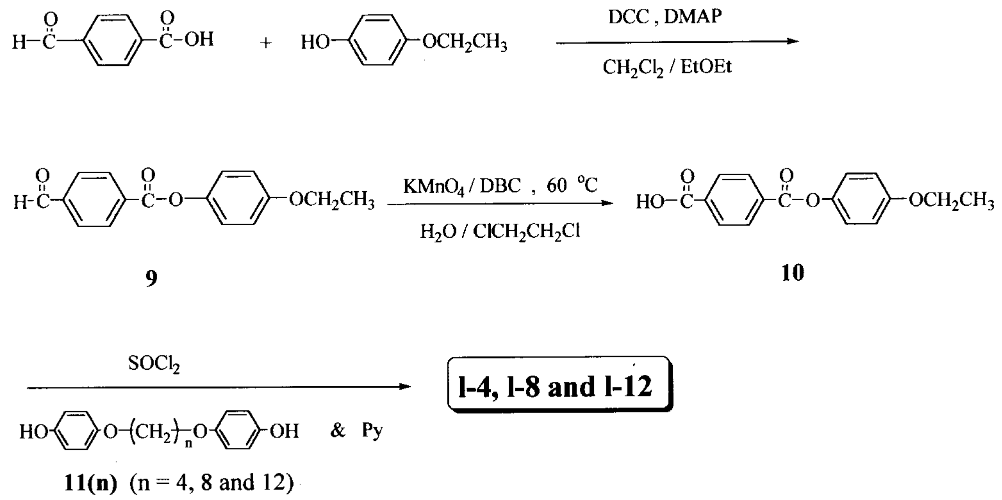
Scheme 1. Synthetic route to T-shaped compounds.

was dried at 60°C in a vacuum oven. The yield was 4.20 g (95%), m.p. 170°C. IR (KBr, cm^{-1}): 2369–3412 (COOH stretch), 2930 (aliphatic C–H stretch), 1739 (C=O stretch), 1513 (aromatic C=C stretch), and 1251, 1223 (C–O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 1.34–1.42 (m, 8H, $-\underline{CH_2}-$), 1.66–1.74 (m, 4H, $Ar-OCH_2\underline{CH_2}-$), 3.87 (t, 2H, $ArO\underline{CH_2}-$), 4.07 (t, 2H, $Ar-O\underline{CH_2}-$), 5.02 (s, 2H, $Ar\underline{CH_2}O-$), and 7.31–7.43 (m, 12H, aromatic Hs). Elemental analysis: calc. for $C_{29}H_{32}O_7$ C 70.71, H 6.55; found C 70.78, H 6.54%.

The melting points of **4(4)** and **4(12)** were 198–199°C and 168–170°C, respectively. Their structures were confirmed spectroscopically and also by elemental analysis.

2.1.3. *Bis(4-ethoxyphenyl) 2-[8-(4-benzyloxyphenoxy)-octyloxy]terephthalate 6(8)*

Compound **4(8)** (3.4 g, 0.69×10^{-2} mol) was dissolved in 21 ml of thionyl chloride and the mixture heated at reflux for 4 h under a dry nitrogen atmosphere. Excess



Scheme 2. Synthetic route to I-shaped compounds.

of thionyl chloride was distilled off under reduced pressure (*c.* 5 torr). To the residue was added 50 ml of dry petroleum ether, and the solvent and any residual thionyl chloride were removed by distillation under reduced pressure. The dicarboxylic acid dichloride was dissolved in 50 ml of dry pyridine and the solution cooled to 0°C. A solution prepared separately by dissolving 2.0 g (1.45×10^{-2} mol) of 4-ethoxyphenol in 100 ml of dry pyridine was added dropwise with vigorous stirring to the acid chloride solution over a period of 1 h. The mixture was slowly warmed to and maintained at 80°C for 24 h. The reaction mixture was poured into an excess of 1M HCl. The precipitate formed was filtered off, followed by thorough washing with distilled water. The crude product was recrystallized from a mixture of ethanol and acetone (1 : 3 by vol.) and then chromatographed on a silica gel column using as eluent a mixture of ethyl acetate and hexane (1 : 2 by vol.). The yield was 3.74 g (70%), m.p. 98°C. IR (KBr, cm^{-1}): 3069 (aromatic C–H stretch), 2930 (aliphatic C–H stretch), 1725 (C=O stretch), 1505 (aromatic C=C stretch), and 1185, 1221, 1287 (C–O stretch). ^1H NMR ($CDCl_3$, δ ppm): 1.36–1.53 (m, 14H, $-ArOCH_2\underline{CH_3}$ and $-\underline{CH_2}-$), 1.70–1.90 (m, 4H, $Ar-OCH_2\underline{CH_2}-$), 3.85–4.19 (m, 8H, $Ar-O\underline{CH_2}-$), 5.01 (s, 2H, $Ar\underline{CH_2}O-$), and 6.80–8.04 (m, 20H, aromatic Hs). Elemental analysis: calc. for $C_{45}H_{48}O_9$ C 73.75, H 6.60; found C 73.73, H 6.64%.

The melting points of **5(4)** and **5(12)** prepared in the same manner were 112 and 99°C, respectively. Their structures were again confirmed by spectroscopy and elemental analysis.

2.1.4. *Bis(4-ethoxyphenyl) 2-[8-(4-hydroxyphenoxy)-octyloxy]terephthalate* ***7(8)***

Compound **5(8)** (3.2 g, 0.44×10^{-2} mol) was dissolved in 200 ml of purified ethyl acetate. Palladium (10 wt %) with activated charcoal (0.1 g) dispersed in 1 ml of dry methylene chloride was mixed with the ethyl acetate solution in a Parr bomb reactor. Hydrogenation was conducted at room temperature for 5 h under a hydrogen pressure of 40 psi (2069 torr). The mixture was filtered through celite. The solvent in the filtrate was removed using a rotary evaporator. The residue was chromatographed through a silica gel column using as eluant a mixture of methylene chloride, ethyl acetate, and hexane (15 : 1 : 7 by vol.). The product was recrystallized from a mixture of methanol and methylene chloride (1 : 3 by vol.). The yield was 2.32 g (82%), m.p. 76°C. IR (KBr, cm^{-1}): 3173–3635 (O–H stretch), 3066 (aromatic C–H stretch), 2931 (aliphatic C–H stretch), 1717 (C=O stretch), 1511 (aromatic C=C stretch), and 1184, 1220, 1291 (C–O stretch). ^1H NMR ($CDCl_3$, δ ppm): 1.25–1.54 (m, 14H, $ArOCH_2\underline{CH_3}$ and $-\underline{CH_2}-$), 1.67–1.89 (m, 4H, $Ar-OCH_2\underline{CH_2}-$), 3.84–4.17 (m, 8H, $Ar-O\underline{CH_2}-$), 4.55 (s, 1H, ArOH), and 6.75–8.04 (m, 15H, aromatic Hs). Elemental analysis: calc. for $C_{38}H_{42}O_9$ C 71.01, H 6.59; found C 71.08, H 6.61%.

Compounds **6(4)** and **6(12)** were prepared similarly. Their melting points were 126 and 103°C, respectively. Their structures were confirmed by spectroscopy and elemental analysis.

2.1.5. *Bis(4-ethoxyphenyl) 2-{8-[4-(4-ethoxyphenoxy-carbonyl)benzoyloxyphenoxy]octyloxy}-terephthalate* ***T-8***

4-(4-Ethoxyphenoxycarbonyl)benzoic acid (**8**, 1.07 g, 0.37×10^{-2} mol) was dissolved in 10 ml of thionyl chloride. The mixture was heated at reflux for 4 h under a nitrogen atmosphere. Excess of thionyl chloride was distilled off under a reduced pressure. Dry petroleum ether (50 ml) was mixed with the residue, and residual thionyl chloride and petroleum ether were removed by distillation under reduced pressure. The acid chloride formed was dissolved in dry pyridine (20 ml). This mixture was cooled down to 0°C. Separately, 2.18 g (0.34×10^{-2} mol) of compound **6(8)** were dissolved in 50 ml of dry pyridine. This solution was added dropwise over a period of 1 h to the acid chloride solution. The mixture was heated with stirring to and maintained at 80°C for 36 h under a nitrogen atmosphere. The reaction mixture was poured into 0.1M HCl with vigorous stirring. The crude product obtained by extraction with methylene chloride followed by evaporation was chromatographed on a silica gel column using as eluent a mixture of methylene chloride, ethyl acetate, and hexane (15 : 1 : 3 by vol.). The product was dissolved in methylene chloride and precipitated into methanol; the precipitate was filtered off, washed thoroughly with methanol, and dried. The yield was 2.75 g (89%), m.p. 147.5°C. IR (KBr, cm^{-1}): 3066 (aromatic C–H stretch), 2934 (aliphatic C–H stretch), 1732 (C=O stretch), 1511 (aromatic C=C stretch), and 1191, 1248, 1292 (C–O stretch). ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.40–1.49 (m, 17H, $\mathrm{ArOCH_2\underline{CH_3}}$ and $-\underline{\mathrm{CH_2}}-$), 1.75–1.92 (m, 4H, $\mathrm{Ar{-}OCH_2\underline{CH_2}}-$), 3.93–4.25 (m, 10H, $\mathrm{Ar{-}O\underline{CH_2}}-$), 6.94–8.05 (m, 19H, aromatic Hs), 8.32 (s, 4H, terephthaloyl aromatic Hs). Elemental analysis: calc. for $\mathrm{C_{54}H_{54}O_{13}}$ C 71.19, H 5.97; found C 71.18, H 5.95%.

The other two T-shaped compounds, **T-4** and **T-12**, were prepared in a similar manner and their structures also were confirmed by spectroscopy and elemental analysis. The melting points of these two compounds were 137.5 and 112°C, respectively.

2.2 *Synthesis of linear twin dimers*

Three linear twin dimers, **l-4**, **l-8**, **l-12**, were prepared by reacting mono-4-ethoxyphenyl terephthalate with α,ω-bis(4-hydroxyphenoxy)alkanes in the presence of a condensing agent. Since the compounds were prepared similarly (scheme 2), only synthetic details for the preparation of **l-8** are given below.

2.2.1. *4-(4-Ethoxyphenoxycarbonyl)benzaldehyde* ***9***

4-Carboxybenzaldehyde (24.0 g, 0.16 mol), 4-ethoxyphenol (22.05 g, 0.159 mol), and 4-*N*,*N*-dimethylaminopyridine (DMAP, 0.21 g) were dissolved in 600 ml of a mixture of methylene chloride and diethyl ether (2 : 1 by vol.) and the solution was cooled to 0°C. Separately, 33.35 g (0.162 mol) of dicyclohexylcarbodiimide (DCC) were dissolved in 150 ml of methylene chloride, and the DCC solution was added dropwise to the solution of the two reactants and DMAP [41]. The whole mixture was stirred at 0°C for 5 h and then at room temperature for 10 h. The insoluble dicyclohexylurea, was removed by filtration. The crude reaction product obtained by distilling off the solvents using a rotary evaporator was purified by chromatography through a silica gel column. A mixture of methylene chloride and hexane (1 : 1 by vol.) was utilized as eluent. The yield was 32.4 g (75%), m.p. 74°C. IR (KBr, cm^{-1}): 2976 (aliphatic C–H stretch), 1748 and 1694 (C=O stretch), 1510 (aromatic C=C stretch), and 1213, 1248, 1277 (C–O stretch). ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.43 (t, 3H, $\mathrm{ArOCH_2\underline{CH_3}}$), 4.05 (q, 2H, $\mathrm{Ar{-}O\underline{CH_2}}-$), 6.93–8.37 (m, 8H, aromatic Hs), 10.15 (s, 1H, $\mathrm{ArCO\underline{H}}$). Elemental analysis: calc. for $\mathrm{C_{16}H_{14}O_4}$ C 71.10, H 5.22; found C 71.08, H 5.24%.

2.2.2. *Mono-4-ethoxyphenyl terephthalate* ***10***

Compound **9** (28.5 g, 9.96×10^{-2} mol) and dibenzo-18-crown-6 were dissolved in 200 ml of 1,2-dichloroethane. Separately, 21.0 g (0.133 mol) of potassium permanganate were dissolved in 100 ml of distilled water [42]. The two solutions were mixed in a 500 ml round bottomed flask and stirred vigorously at 60°C for 4 h. Insoluble matter was removed by filtration. 1,2-Dichloroethane in the filtrate was removed using a rotary evaporator. The remaining aqueous solution was acidified with 1M HCl. The precipitate was filtered off and washed thoroughly with distilled water. Pure product was obtained by recrystallizing the crude product from a mixture of ethyl acetate and hexane (1 : 5 by vol.). The yield was 17.7 g (62%), m.p. 204°C. IR (KBr, cm^{-1}): 2400–3400 (acid–OH stretch), 2977 (aliphatic C–H stretch), 1730 and 1687 (C=O stretch), 1501 (aromatic C=C stretch), and 1191, 1242, 1276 (C–O stretch). ^{1}H NMR (DMSO-$\mathrm{d_6}$, δ ppm): 1.34 (t, 3H, $\mathrm{ArOCH_2\underline{CH_3}}$), 4.03 (q, 2H, $\mathrm{Ar{-}O\underline{CH_2}}-$), 6.98–8.24 (m, 8H, aromatic Hs), 13.48 (s, 1H, $\mathrm{ArCOO\underline{C}}$). Elemental analysis: calc. for $\mathrm{C_{16}H_{14}O_5}$ C 67.13, H 4.93; found C 67.25, H 5.01%.

2.2.3. *1,8-Bis{4-[4-(4-ethoxyphenoxycarbonyl)-benzoyloxy]phenoxy}octane* ***l-8***

Compound **10** (4.0 g, 1.4×10^{-2} mol) was dissolved in 21 ml of thionyl chloride. The solution was heated at reflux for 4 h. Excess of thionyl chloride was removed by distillation under reduced pressure. The acid chloride thus obtained was dissolved in 50 ml of pyridine and the solution cooled to 0°C. To this solution was added dropwise with vigorous stirring a solution of 1,8-bis-(4-hydroxyphenoxy)octane (**11**, 2.14 g, 0.65×10^{-2} mol) dissolved in 100 ml of dry pyridine. The temperature of the solution was raised to and maintained at 80°C overnight. The reaction mixture was poured into 1M HCl. The precipitate was filtered off, washed with distilled water and dried. The crude product thus obtained was dissolved in 100 ml of a mixture of trifluoroacetic acid and chloroform (1 : 1 by vol.), and insoluble matter was removed by filtration. *N*,*N*-Dimethylformamide (DMF) was slowly added to the filtrate with stirring. The precipitate was filtered off and washed with DMF. It was again dissolved in the trifluoroacetic acid/chloroform mixture and reprecipitated by adding DMF. This purification process was repeated once again. Finally, the precipitate was washed thoroughly with hot acetone and dried. The yield was 4.5 g (80%), m.p. 240°C. IR (KBr, cm^{-1}): 3069 (aromatic C–H stretch), 2930 (aliphatic C–H stretch), 1732 (C=O stretch), 1505 (aromatic C=C stretch), 1198 and 1210 (C–O stretch). ^{1}H NMR ($CF_3COOD/CDCl_3$=1/1, δ ppm): 1.50 (m, 14H, $ArOCH_2\underline{CH_3}$ and $-\underline{CH_2}-$), 1.91 (m, 4H, $Ar-OCH_2\underline{CH_2}-$), 4.20–4.31 (m, 8H, $Ar-O\underline{CH_2}-$), 7.12–7.26 (m, 16H, $-CH_2O-\underline{Ar}-OOC-$), 8.43 (s, 8H, terephthaloyl aromatic Hs). Elemental analysis: calc. for $C_{52}H_{50}O_{12}$ C 72.04, H 5.81; found C 72.03, H 5.84%.

The other two linear twin dimers, **l-4** and **l-12**, were prepared similarly; compound **l-12** was purified by recrystallization from DMF. Their structures were confirmed by spectral and elemental analysis. The melting points of these compounds were 282 and 224°C, respectively.

2.3. *Instrumentation*

The IR and ^{1}H NMR spectra of intermediates and final compounds were, respectively, recorded on a Bomm Michelson-series FTIR instrument and a Varian Gemini 300 NMR spectrometer. Differential scanning calorimetric (DSC) thermograms were obtained using a Mettler DSC 821^e using a nitrogen stream. The heating and cooling rate was 5°C min^{-1}. Thermal transitions and optical textures of the compounds were observed by polarizing optical microscopy (Olympus BH-2 equipped with a Mettler FP82HT hot stage controlled automatically by a Mettler FP90HT central unit). Indium was employed as a calibration reference for temperature and enthalpy changes.

3. Results and discussion

3.1. *Liquid crystalline properties of intermediates*

Some of the intermediates synthesized *en route* to the T-shaped compounds were found to be mesomorphic (thermotropic). Among these, all the **6(*n*)** and **7(*n*)** compounds gave monotropic mesophases as shown by their thermal transitions (DSC analysis) and optical textures in melts observed by polarizing microscopy. This is rather surprising, because a large lateral substituent will reduce the axial ratios of the compounds, which is expected to reduce the ability of the compounds to form a mesophase in the melt. Therefore, it is probable that the alkylene spacer groups, due to their high conformational freedom, allow the pendants to orient themselves more or less parallel to the mesogenic aromatic ester core structure. Such a parallel orientation of the lateral substituent will be less detrimental to mesophase formation.

In contrast, the simple compound **8** has much different structural features and exhibits enantiotropic nematic properties. This compound is just an aromatic ester bearing a carboxylic acid group on one end and an ethoxy group on the other. As reported for many aromatic carboxylic acids [43, 44], the compound is expected to exist as a dimer in the melt, which favours formation of a mesophase.

3.2. *Comparison of the LC properties of linearly connected twin compounds with those of the T- and H-shaped compounds*

It should be interesting to compare the LC and thermal properties of dimer compounds of different shapes. As explained in § 1, we reported LC properties for a series of twin compounds which consists of two identical mesogenic units laterally linked to each other through an oxyalkyleneoxy spacer; that is, the H-shaped twins shown in figure 1 [33, 34]. It was observed that, for those compounds, long spacers are needed to obtain enantiotropic LC phases, and when the alkoxy tails are long, the even form smectic phases. Figures 3 and 4 show DSC thermograms for the present T-shaped and linearly linked dimeric compounds. All show two endothermic peaks in the heating cycle: the larger peaks at lower temperatures correspond to melting transitions (T_ms) and the smaller peaks at higher temperatures to mesophase to isotropic phase transitions, i.e. isotropization

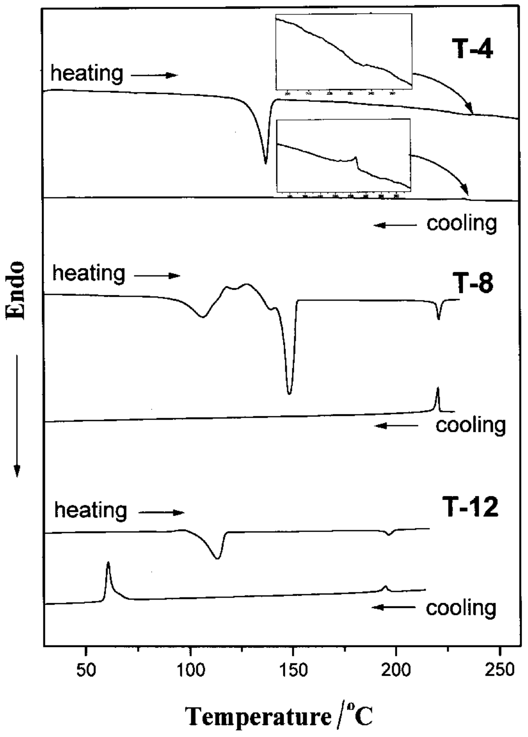


Figure 3. DSC thermograms of the **T-*n*** compounds.

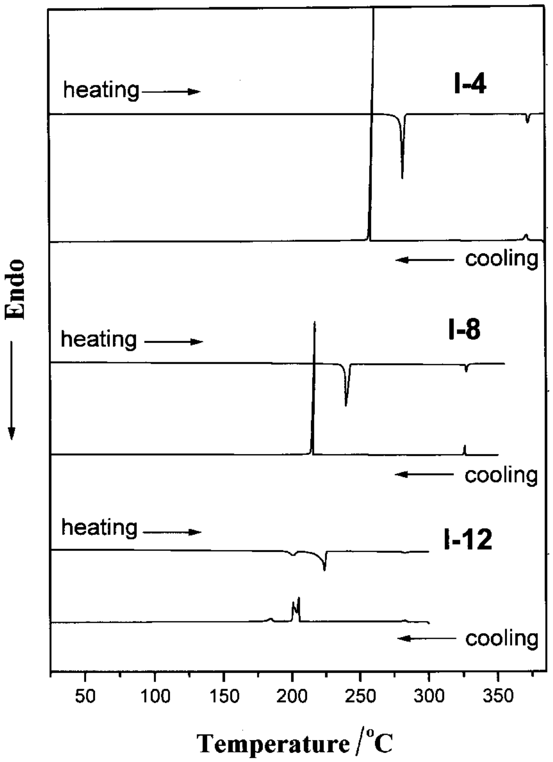


Figure 4. DSC thermograms of the **I-*n*** compounds.

peaks. Among the three T-shaped dimers, only **T-12** undergoes crystallization on cooling the melt, showing a supercooled crystallization exotherm about 50°C lower than the T_m value.

In contrast, the other two T-shaped compounds, **T-4** and **T-8**, solidified from the LC phases only when the melts were cooled to room temperature. The supercooled LC solids, however, underwent further crystallization processes on heating, as reflected by crystallization exotherms appearing on the second heating DSC thermograms. These observations were in agreement with observations by polarizing microscopy. The DSC thermogram obtained in the heating cycle for **T-8** exhibits rather broad and multiple melting endotherms. It is our belief that this compound is polymorphic in the solid state. The compound did not melt until the temperature of the highest of the endothermic peaks. Moreover, heating the supercooled LC states generates multiple exothermic crystallization peaks before reaching the final melting temperature.

The T_m values (see the table) of the T-shaped series demonstrate a rather irregular dependence on the length of the flexible spacer between the two mesogenic units: T_m of **T-4** is 137.5°C, whereas the value for **T-8** is higher, 147.5°C; the T_m value for **T-12** is significantly lower, 112°C. The enthalpy change (ΔH_m) for melting of the compounds, however, decreases steadily with increasing length of the spacer. This implies that a longer spacer may reduce the intermolecular and lattice forces in the solid. A smooth decrease is observed for the isotropization temperatures (T_i): T_i for **T-4** is 232°C and those for **T-8** and **T-12** are 221.5 and 196.5°C, respectively.

The thermodynamic parameters associated with isotropization (ΔH_i and ΔS_i) also show a regular dependence on the length of the spacers. They tend to increase with increasing length of the spacers suggesting that a longer spacer brings about a LC state of higher order. Of course, we need to examine the thermal behaviour of the complete homologous spacer series to discuss any further dependence on spacer length. Recently, we reported [26] the thermal behaviour including the LC properties of two different series of T-shaped compounds and found that these properties depend strongly on the chemical structure of the mesogenic unit and the length of the spacer.

Table 1. LC properties of **H-*n***, **T-*n*** and **I-*n*** dimer LC compounds.

Compounds	$T_m{}^a$/°C	$T_i{}^a$/°C	$\Delta H_m{}^a$/kJ mol^{-1}	$\Delta H_i{}^a$/kJ mol^{-1}	$\Delta S_i{}^a$/J mol^{-1} K^{-1}	LC properties	Optical texture[b]
H-4[c]	199.5	159.5	85.3	—	—	Mo[d]	N Sm
H-8[c]	146.7		85.2	—	—	Mo	N Sm
H-12[c]	110.9	119.6	17.0	2.7	6.9	En[d]	N
T-4	137.4	232.1	55.5	1.1	2.1	En	N
T-8	147.4	221.5	46.4	3.4	6.9	En	N
T-12	112.1	196.4	36.4	4.2	8.9	En	N
I-4	281.8	372.5	105.1	12.6	19.5	En	N
I-8	239.9	327.4	109.3	7.7	12.7	En	N
I-12	223.9	283.1	118.5	5.9	10.7	En	N

[a] DSC thermograms obtained under a nitrogen atmosphere at heating rates of 5°C min^{-1}.

[b] Observed by polarizing microscopy. N and Sm stand for nematic and smectic, respectively.

[c] Quoted from [33].

[d] Monotropic or enantiotropic.

As far as the phase transitions of the linearly linked dimers are concerned, their melting and isotropization temperatures fall with increasing length of the spacers, an effect repeatedly observed earlier [45–49]. The values of the enthalpy changes (ΔH_m) for melting, however, remain almost the same regardless of the spacer length. This is in marked contrast to the H- and T-shaped dimers that show much diminished ΔH_m values for those with longer spacers (see the table). Among the three series, the isotropization temperature (ΔT_i) and the associated enthalpy (ΔH_i) and entropy changes (ΔS_i) are highest for the linear dimers, implying a higher thermal stability of their mesophases. Simply comparing T_i values, the mesophases from the T-shaped compounds appear to have a significantly higher thermal stability than those of the corresponding H-shaped compounds. It is however noted that the ΔS_i values for the linear dimers appear to decrease with spacer length in contrast to those of the T-shaped dimers. Although there are experimental and theoretical reports [50] showing that ΔS_i values increase with spacer length for linear dimers, some of our earlier work and the present results show an irregular [51] or reversed dependence [52] of ΔS_i values on spacer length.

As summarized in the table, all the present compounds form only nematic phases, and a representative optical texture is shown in figure 5. This shows a four- and two-brushed schlieren texture characteristic of the nematic mesophase.

The fact that the T-shaped dimers form nematic phases implies that the two mesogenic units in the molecular are not perpendicular, but in a more or less parallel or inclined geometry in the mesophase. If they were perpendicular to each other, these compounds would tend to form a layered morphology, which is not observed regardless of the length of the spacers linking the two units. Weissflog *et al.* [24, 27] earlier reported the LC properties of some T-shaped dimers, and all of their compounds also formed only nematic phases. Therefore, the terminology, T-shaped dimer, utilized here and in our previous papers is not intended to describe the actual orientation of the two mesogenic units, but to express simply the geometrical shape of the skeletons of their structural formulae. It is however emphasized that some combined-type liquid crystalline polymers consisting of T-shaped repeating units are able to form a layered morphology in the melt, which suggests that their repeating units, corresponding to the present T-shaped dimers, are indeed in the T-shape [53]. Presently, it seems that polymers of T-shaped repeating units have a higher tendency to form a layered structure than low molar mass compounds of T-shape, especially, when the structures of the two mesogenic units are greatly different, for example, in their polarity [54]. This aspect needs to be studied more closely in future work on T-shaped dimesogens. Our previous work [5, 11, 13, 14] clearly demonstrates that dimesogenic compounds consisting of two mesogenic units of vastly different nature can form abundant collection of mesophases, including incommensurate smectic phases and twisted grain boundary phases. Such a wide variety of mesophases do not seem to be induced by T- or H-shaped dimesogenic compounds.

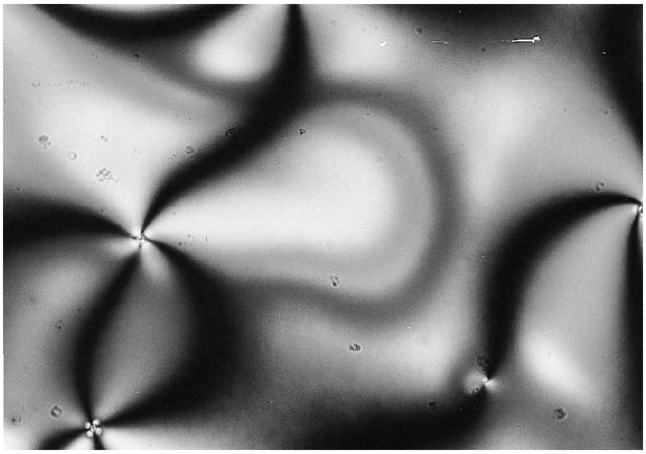


Figure 5. Optical micrograph of **T-12** (194.0°C) (magnification 200×).

4. Conclusion

Among the dimeric LC compounds of three different skeletal shapes studied in this investigation, the linear twin compounds reveal the highest values of T_m and T_i and of other thermodynamic parameters associated with phase transitions. Especially, the higher T_i, ΔH_i, and ΔS_i values of the linearly linked dimers are a strong indication that their nematic mesophases are not only more thermally stable, but also of higher molecular order than those of the H- or T-shaped analogues. Among the three series, the H-shaped compounds have the lowest tendency to be mesomorphic, but they are more prone to form smectic phases.

The T-shaped compounds exhibit a very contrasting dependence of ΔH_i and ΔS_i on spacer length compared with the linear twins. The former values gradually increase in magnitude with increasing spacer length, whereas the opposite occurs for the latter. Although this may seem contradictory if hastily judged, the effects can be ascribed to a common origin, i.e. the higher degree of conformational freedom around C–C single bonds in the spacers of longer length. For T-shaped compounds, a higher degree of conformational freedom will result in a higher possibility that the two mesogenic units in the molecular can orient themselves more or less parallel to one another, so favouring the ordered assembly of mesogens leading to the formation of mesophases. On the contrary, the higher conformational freedom of the spacers in the linearly linked twin dimers will diminish the tendency of the mesogenic units to form ordered domains. Nevertheless, much higher ΔS_i values for the linear dimers may imply the existence of higher order in the mesophase when compared with the T-shaped compounds.

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