

Dimesogenic Compounds with Chiral Tails: Synthesis and Liquid Crystalline Properties of a Homologous Series of α,ω -Bis[4-(4'-(S)-(-)-2-methylbutoxycarbonyl)biphenyl-4-oxycarbonyl]phenoxy]alkanes

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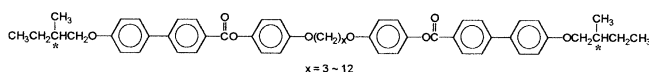
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A series of new liquid crystalline dimesogenic compounds with chiral tails was synthesized, and their thermal and liquid crystalline properties were studied. The chain length of the central polymethylene spacers (x) was varied from dimethylene (2) to decamethylene (12). These compounds were characterized by elemental analysis, IR and NMR spectroscopy, differential scanning calorimetry (DSC), and cross-polarizing microscopy. All compounds were found to be enantiotropically liquid crystalline, and the values of melting (T_m) and isotropization temperature (T_i) as well as enthalpy change (ΔH_i) and entropy change for isotropization (ΔS_i) decreased in a zig-zag fashion revealing the so-called odd-even effect as x increases. Their mesomorphic properties fall into three categories depending upon x ; (a) compounds with $x=2$ and 4 formed two different mesophases, smectic and cholesteric phases in that order on heating, and vice versa on cooling, (b) compounds with $x=3, 7, 8, 10$ and 11 reversibly formed only the cholesteric phase, and (c) compounds with $x=5, 6, 9$ and 12 exhibited only a cholesteric phase on heating, whereas on cooling they formed two different mesophases, cholesteric and smectic phases, sequentially.

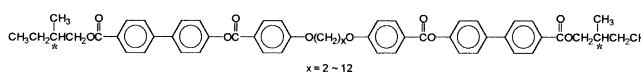
Introduction

Since Meyer¹ proposed that chiral smectic C (Sm^*C) phase could show ferroelectric property, much attention has been paid to structural design of chiral compounds capable of forming smectic phase with the view of potential application for electro-optical devices.²⁻⁵ Over the past few years, a large number of studies have been made to establish the structure-property relationship of monomesogenic compounds which have a mesogenic core, a flexible spacer and a chiral tail.⁶⁻⁸ On the other hand, only a few attempts have so far been made at chiral dimesogenic compounds consisting of two mesogenic units linked through a central spacer.^{9,10} Recently, we¹¹ have synthesized homologous chiral twin compounds varying the chain length of the central spacer (x) and their mesomorphic properties were evaluated: their smectic liquid crystallinities were sensitive to x , revealing a clear odd-even effect in melting (T_m) and isotropization temperatures (T_i) as well as in ΔH_i and ΔS_i values.



In this study, a new series of dimesogenic compounds containing two identical mesogenic units with chiral tails, linked through a central polymethylene spacer, was synthesized. These compounds contain the ester groups whose ester linkages are reversed as compared with the above compounds, *i.e.*, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ vs. $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$. As a part of our continuing

efforts to delineate structure-property relationship of chiral dimesogenic compounds, the effect of the chain length of the central polymethylene spacers (x) of the compounds on their thermal and liquid crystalline properties were investigated.



Experimental Section

Synthesis. The synthetic route to the present compounds is shown in Scheme 1. Because the syntheses of ethyl 4'-hydroxybiphenyl-4-carboxylate¹⁰ (compound **1**) and 4,4'-disubstituted- α,ω -diphenoxyalkanes¹² (compounds **7-9**) have been reported previously, only the synthetic procedures used for remaining synthetic steps are described in the following sections.

Ethyl 4'-benzyloxy-4-biphenylcarboxylate (2). Ethyl 4'-hydroxy-4-biphenylcarboxylate (5.00 g; 20.7 mmole) was dissolved in 100 mL of acetone. To this solution were added K_2CO_3 (4.15 g; 30.0 mmole) and benzyl bromide (3.54 g; 20.7 mmol) at room temperature. The mixture was stirred at 80 °C for 24 hours. After the reaction mixture was cooled to room temperature, the KBr-precipitate formed was filtered off, and then the filtrate was concentrated using a rotatory evaporator. The crude product of solid residue was recrystallized from ethanol. Yield was 6.60 g (96.0%); m.p., 140 °C.

IR (KBr): 3050, 2980, 2850 (C-H), 1603, 1587 (C=C), 1602, 1715 (C=O), 1439 (CH_2), 1251, 1190, 1160, 1070, 1025 cm^{-1} (C-O).

^1H NMR (200 MHz, CDCl_3 , δ): 8.11-8.15 (2H, d, Ar-H), 7.59-7.68 (4H, q, Ar-H), 7.41-7.49 (5H, m, Ar-H), 7.09-7.13 (2H, d, Ar-H), 5.19 (2H, s, OCH_2), 4.39-4.50 (2H, q, CO_2CH_2), 1.42-1.49 (3H, t, CH_3).

4'-Benzyloxy-4-biphenylcarboxylic acid (3). Compound **2** (4.00 g; 12.0 mmole) was added to 225 mL of a 10% (w/v) solution of KOH in 95% ethanol. The mixture was refluxed for 4 hours. It was then diluted with a 1 : 1 (v/v) mixture of ethanol and water, and warmed to 60 °C to dissolve potassium salt of the product. This warm solution was acidified with concentrated HCl. After it was kept at room temperature overnight, the precipitate was collected as white solid by filtration. The collected solid was washed with water thoroughly. The crude product was recrystallized from glacial acetic acid. Yield was 3.33 g (91.0%); m.p., 271 °C. Upon the DSC measurement the compound **3** showed an isotropization endotherm at 292 °C as well as the melting endotherm at 271 °C.

IR (KBr): 3400-2400 (O-H), 3033, 2930, 2850 (C-H), 1685 (C=O), 1604, 1528 (C=C), 1433 (CH_2), 1252, 1200 cm^{-1} (C-O).

^1H NMR (200 MHz, $\text{CDCl}_3/\text{CF}_3\text{COOD}=1 : 1$ v/v, δ): 12.93 (1H, s, CO_2H), 7.73-8.01 (4H, q, Ar-H), 7.41-7.77 (5H, m, Ar-H), 7.11-7.38 (4H, q, Ar-H), 5.18 (2H, s, OCH_2).

(S)-(-)-2-Methylbutyl 4'-benzyloxy-4-biphenylcarboxylate (5). The compound **3** (20.1 mmole) was dissolved in 10 mL of SOCl_2 and the solution was refluxed for 4 hours. The excess SOCl_2 was removed by distillation under a reduced pressure. Compound **4** prepared in this way was dissolved into a mixture (70 mL) of dichloromethane and pyridine (25 : 45 v/v). To this solution was added dropwise a solution of (S)-(-)-2-methyl-1-butanol (2.12 g; 24.1 mmole) in 5 mL of dichloromethane, and then the mixture was stirred vigorously at ambient temperature for 4 hours. The reaction mixture was then poured into a large excess of 0.1 M HCl. The precipitate formed was washed thoroughly with water. The crude product was recrystallized from 95% ethanol. Yield was 5.55 g (91.0%); m.p., 100 °C.

IR (KBr): 3040, 2968, 2850 (C-H), 1708 (C=O), 1604, 1510 (C=C), 1420 (CH_2), 1255, 1193 cm^{-1} (C-O).

^1H NMR (200 MHz, CDCl_3 , δ): 8.00-8.04 (2H, d, Ar-H), 7.49-7.57 (4H, t, Ar-H), 7.38-7.29 (5H, m, Ar-H), 6.98-7.03 (2H, d, Ar-H), 5.06 (2H, s, OCH_2), 4.03-4.21 (2H, m, CO_2CH_2), 1.77-1.87 (1H, m, CH), 1.16-1.50 (2H, m, CH_2), 0.87-0.98 (6H, m, CH_3).

(S)-(-)-2-Methylbutyl 4'-hydroxy-4-biphenylcarboxylate (6). Compound **5** (6.50 g; 14.7 mmol), 0.60 g of 10% palladium on carbon, and a mixture (650 mL) of ethanol and ethyl acetate (42 : 23 v/v) were placed in a 1 L pressurized reaction vessel at 25 °C. Under 100 psi of hydrogen pressure, the mixture was stirred vigorously at 25 °C for 20 hours. After the reaction vessel was relieved from the hydrogen pressure, the catalyst was filtered off. And then the filtrate was concentrated using a rotatory evaporator. The crude product of solid residue was recrystallized from a 1 : 1 (v/v) mixture of ethanol and water. Yield was 4.01 g (96.0%); m.p., 120 °C.

IR (KBr): 3400 (O-H), 3025, 2965, 2845 (C-H), 1681 (C=O), 1603, 1514 (C=C), 1420 (CH_2), 1268, 1191 cm^{-1} (C-O).

^1H NMR (200 MHz, Acetone- d_6 , δ): 8.66 (1H, s, OH), 7.91-7.97 (2H, d, Ar-H), 7.59-7.65 (2H, d, Ar-H), 7.46-7.51 (2H, d, Ar-H), 6.82-6.86 (2H, d, Ar-H), 3.95-4.10 (2H, m, CO_2CH_2), 1.73 (1H, m, CH), 1.14-1.44 (2H, m, CH_2), 0.80-0.92 (6H, m, CH_3).

α,ω -Bis[4-(4'-(S)-(-)-2-methylbutoxycarbonylbiphenyl-4-oxycarbonyl)phenoxy]alkanes (10). Since the synthetic methods used in the preparation of compounds **10** were essentially the same, only a representative example is given here. 4,4'-Dichloroformyl- α,ω -diphenoxypentane (**9**; 0.5 mmole) prepared from compound **8** with SOCl_2 was dissolved in 5 mL of dichloromethane. To this solution was added slowly with vigorously stirring a solution of compound **6** (0.34 g; 1.20 mmole) dissolved in a mixture (10 mL) of pyridine and dichloromethane (1 : 80 v/v) at room temperature. And then the mixture was refluxed for 4 hours. After the mixture was cooled to room temperature and washed with 0.1 M HCl and distilled water in turn, only the dichloromethane soluble fraction was collected and dried over anhydrous MgSO_4 . After dichloromethane was removed by evaporation using a rotatory evaporator, the crude product of solid residue was further purified by means of column chromatography using silica gel as the stationary phase and a mixture of chloroform and ethyl acetate (99 : 1 v/v) as an eluent.

$x = 2$. Yield 62%; m.p. 187 °C. Anal. Calcd. for $\text{C}_{52}\text{H}_{50}\text{O}_{10}$: C, 74.80; H, 6.04; O, 19.19%. Found: C, 72.79; H, 6.45; O, 20.79%. ^1H NMR (200 MHz, CDCl_3 , δ): 8.03-8.16 (8H, q, Ph- CO_2), 7.58-7.71 (8H, q, Ph-Ph), 7.23-7.27 (4H, d, CO_2 -Ph), 6.97-7.03 (4H, d, O-Ph), 4.41 (2H, s, OCH_2O), 4.04-4.22 (4H, m, CO_2CH_2), 1.77-1.84 (2H, m, CH), 1.20-1.49 (4H, m, CH_2), 0.87-0.99 (12H, m, CH_3).

$x = 3$. Yield 64%; m.p. 169 °C. Anal. Calcd. for $\text{C}_{53}\text{H}_{52}\text{O}_{10}$: C, 74.89; H, 6.17; O, 18.85%. Found: C, 73.42; H, 6.04; O, 20.54%. ^1H NMR (200 MHz, CDCl_3 , δ): 8.02-8.13 (8H, q, Ph- CO_2), 7.57-7.61 (8H, q, Ph-Ph), 7.22-7.26 (4H, d, CO_2 -Ph), 6.93-6.98 (4H, d, O-Ph), 4.26-4.04 (8H, m, OCH_2 , CO_2CH_2), 2.28-2.34 (2H, m, OCH_2CH_2), 1.80-1.84 (2H, m, CH), 1.23-1.48 (4H, m, CH_2), 0.87-0.98 (12H, m, CH_3).

$x = 4$. Yield 76%; m.p. 196 °C. Anal. Calcd. for $\text{C}_{54}\text{H}_{54}\text{O}_{10}$: C, 75.15; H, 6.31; O, 18.54%. Found: C, 75.83; H, 6.17; O, 18.00%. ^1H NMR (200 MHz, CDCl_3 , δ): 8.03-8.13 (8H, q, Ph- CO_2), 7.57-7.62 (8H, q, Ph-Ph), 7.25-7.27 (4H, d, CO_2 -Ph), 6.91-6.96 (4H, d, O-Ph), 4.04-4.22 (8H, m, OCH_2 , CO_2CH_2), 2.01 (4H, m, OCH_2CH_2), 1.80-1.84 (2H, m, CH), 1.20-1.53 (4H, m, CH_2), 0.87-0.99 (12H, m, CH_3).

$x = 5$. Yield 87%; m.p. 143 °C. Anal. Calcd. for $\text{C}_{55}\text{H}_{56}\text{O}_{10}$: C, 75.32; H, 6.44; O, 18.24%. Found: C, 76.03; H, 6.14; O, 17.83%. ^1H NMR (200 MHz, CDCl_3 , δ): 8.00-8.12 (8H, q, Ph- CO_2), 7.56-7.77 (8H, q, Ph-Ph), 7.21-7.26 (4H, d, CO_2 -Ph), 6.88-6.94 (4H, d, O-Ph), 4.01-4.21 (8H, m, OCH_2 , CO_2CH_2), 1.80-1.90 (6H, m, OCH_2CH_2 , CH), 1.20-1.65 (6H, m, CH_2), 0.86-0.98 (12H, m, CH_3).

$x = 6$. Yield 74%; m.p. 154 °C. Anal. Calcd. for $\text{C}_{56}\text{H}_{58}\text{O}_{10}$:

C, 75.48; H, 6.56; O, 17.96%. Found: C, 75.35; H, 6.59; O, 18.06%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.12 (8H, q, Ph-CO₂), 7.57-7.71 (8H, q, Ph-Ph), 7.22-7.29 (4H, d, CO₂-Ph), 6.90-6.94 (4H, d, O-Ph), 3.99-4.22 (8H, m, OCH₂, CO₂CH₂), 1.74-1.83 (6H, m, OCH₂CH₂, CH), 1.18-1.53 (8H, m, CH₂), 0.87-0.98 (12H, m, CH₃).

$x = 7$. Yield 79%; m.p. 136 °C. Anal. Calcd. for $\text{C}_{57}\text{H}_{60}\text{O}_{10}$: C, 75.64; H, 6.68; O, 17.68%. Found: C, 75.26; H, 6.79; O, 17.95%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.12 (8H, q, Ph-CO₂), 7.57-7.62 (8H, q, Ph-Ph), 7.22-7.29 (4H, d, CO₂-Ph), 6.90-6.94 (4H, d, O-Ph), 3.97-4.22 (8H, m, OCH₂, CO₂CH₂), 1.74-1.87 (6H, m, OCH₂CH₂, CH), 1.14-1.56 (10H, m, CH₂), 0.87-0.98 (12H, m, CH₃).

$x = 8$. Yield 80%; m.p. 173 °C. Anal. Calcd. for $\text{C}_{58}\text{H}_{62}\text{O}_{10}$: C, 75.79; H, 6.80; O, 17.41%. Found: C, 74.72; H, 6.78; O, 18.50%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.12 (8H, q, Ph-CO₂), 7.57-7.61 (8H, q, Ph-Ph), 7.22-7.29 (4H, d, CO₂-Ph), 6.90-6.94 (4H, d, O-Ph), 3.97-4.22 (8H, m, OCH₂, CO₂CH₂), 1.72-1.84 (6H, m, OCH₂CH₂, CH), 1.19-1.39 (12H, m, CH₂), 0.81-0.95 (12H, m, CH₃).

$x = 9$. Yield 77%; m.p. 140 °C. Anal. Calcd. for $\text{C}_{59}\text{H}_{64}\text{O}_{10}$: C, 75.94; H, 6.91; O, 17.15%. Found: C, 73.79; H, 6.73; O, 19.48%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.12 (8H, q, Ph-CO₂), 7.57-7.62 (8H, q, Ph-Ph), 7.21-7.26 (4H, d, CO₂-Ph), 6.90-6.94 (4H, d, O-Ph), 3.96-4.22 (8H, m, OCH₂, CO₂CH₂), 1.74-1.80 (6H, m, OCH₂CH₂, CH), 1.20-1.39 (14H, m, CH₂), 0.87-0.98 (12H, m, CH₃).

$x = 10$. Yield 88%; m.p. 156 °C. Anal. Calcd. for $\text{C}_{60}\text{H}_{66}\text{O}_{10}$: C, 75.08; H, 7.02; O, 16.89%. Found: C, 75.72; H, 7.07; O, 17.21%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.11 (8H, q, Ph-CO₂), 7.57-7.61 (8H, q, Ph-Ph), 7.19-7.26 (4H, d, CO₂-Ph), 6.89-6.94 (4H, d, O-Ph), 3.96-4.28 (8H, m, OCH₂, CO₂CH₂), 1.70-1.87 (6H, m, OCH₂CH₂, CH), 1.20-1.39 (16H, m, CH₂), 0.87-0.98 (12H, m, CH₃).

$x = 11$. Yield 72%; m.p. 137 °C. Anal. Calcd. for $\text{C}_{61}\text{H}_{68}\text{O}_{10}$: C, 76.22; H, 7.13; O, 16.65%. Found: C, 75.70; H, 6.92; O, 17.38%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.11 (8H, q, Ph-CO₂), 7.57-7.62 (8H, q, Ph-Ph), 7.21-7.26 (4H, d, CO₂-Ph), 6.89-6.94 (4H, d, O-Ph), 3.96-4.16 (8H, m, OCH₂, CO₂CH₂), 1.73-1.84 (6H, m, OCH₂CH₂, CH₂), 1.20-1.39 (18H, m, CH₂), 0.87-0.98 (12H, m, CH₃).

$x = 12$. Yield 84%; m.p. 163 °C. Anal. Calcd. for $\text{C}_{62}\text{H}_{70}\text{O}_{10}$: C, 76.36; H, 7.23; O, 16.41%. Found: C, 75.32; H, 7.08; O, 17.60%. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 8.03-8.11 (8H, q, Ph-CO₂), 7.57-7.61 (8H, q, Ph-Ph), 7.21-7.26 (4H, d, CO₂-Ph), 6.89-6.93 (4H, d, O-Ph), 3.96-4.18 (8H, m, OCH₂, CO₂CH₂), 1.73-1.83 (6H, m, OCH₂CH₂, CH), 1.18-1.50 (20H, m, CH₂), 0.86-0.95 (12H, m, CH₃).

Analysis and Measurements. Structures of the intermediates and the final compounds were confirmed by IR (Jasco, FT-IR-300E) and NMR (Bruker, AMX 200 MHz) spectroscopy, and by elemental analysis (Leco CHNS-932). The NMR spectra were recorded at 25 °C in CDCl_3 with TMS as an internal standard.

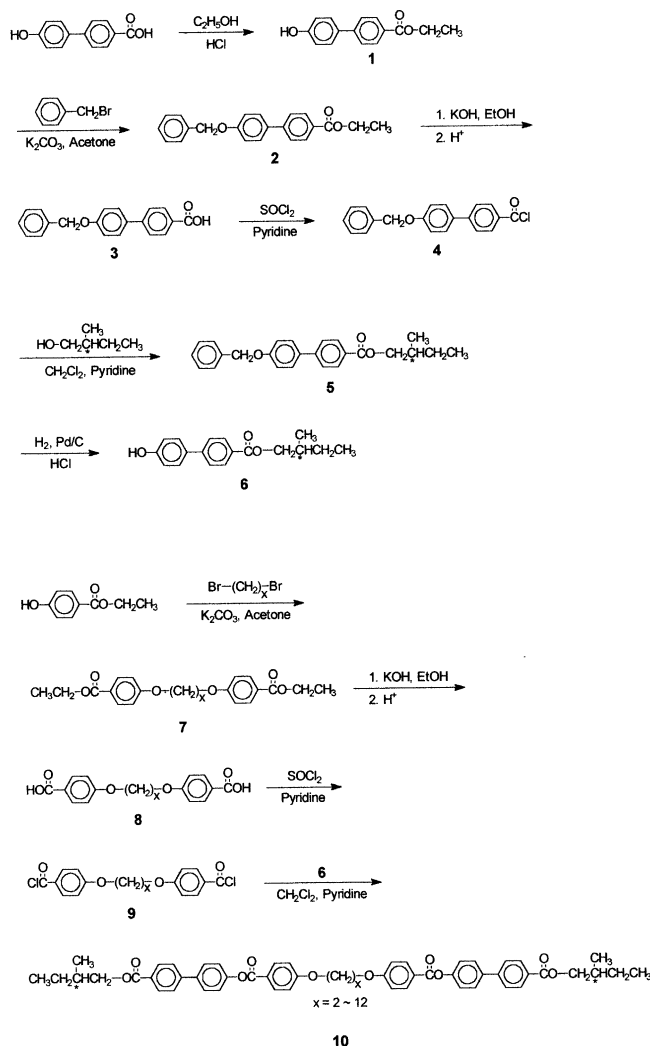
Thermal transition behavior of the compounds was studied under a N_2 atmosphere on a du Pont's differential scanning calorimeter (DSC model 910) with a heating and cooling

rate of 2 °C/min. The optical textures of the melts were examined on a cross-polarizing microscope (Zeiss, Jenapol) equipped with a Mettler hot stage FP-82H. Magnification was 250 \times . Indium was employed as a reference for temperature calibration and estimation of thermodynamic parameters for the phase transitions.

Results and Discussion

Synthesis and thermal behavior of chiral dimesogenic compounds. The synthetic route to the chiral dimesogenic compounds **10** is presented in Scheme 1. All reaction steps were monitored by TLC method carried out on silica gel plates using a UV lamp. Each reaction product was purified either by recrystallization or chromatography followed by recrystallization. All of the IR and NMR spectra of the compounds were consistent with those of expected structures for all the compounds.

The thermal properties of the compounds were studied by DSC. The DSC thermograms of the compounds are shown in Figures 1 and 2. The transition temperatures obtained



Scheme 1. Synthetic Route to Liquid Crystalline Compounds **10**.

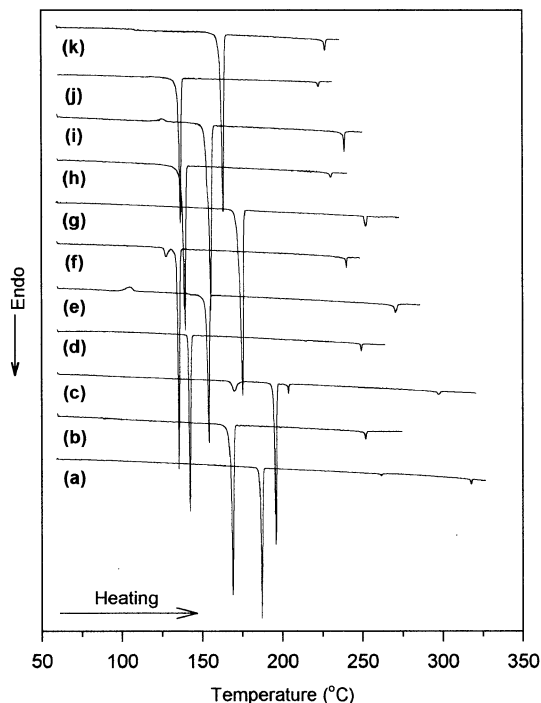


Figure 1. DSC thermograms of compounds **10** at the heating rates of 2 °C/min: (a) $x = 2$; (b) $x = 3$; (c) $x = 4$; (d) $x = 5$; (e) $x = 6$; (f) $x = 7$; (g) $x = 8$; (h) $x = 9$; (i) $x = 10$; (j) $x = 11$; (k) $x = 12$.

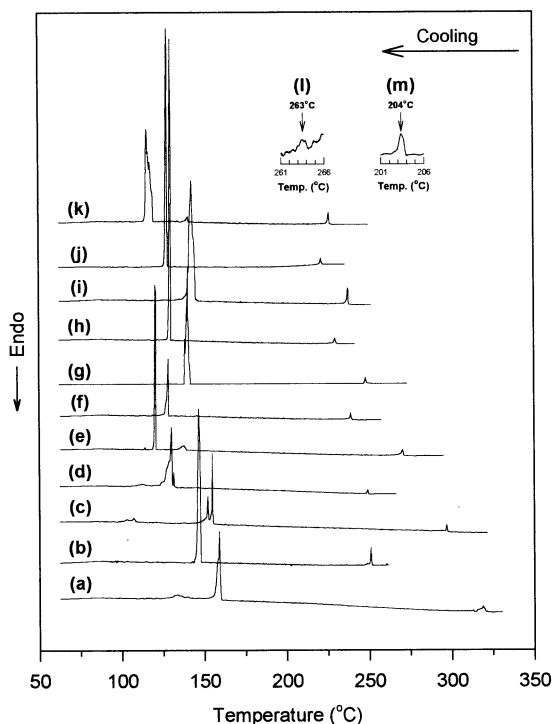


Figure 2. DSC thermograms of compounds **10** at the cooling rates of 2 °C/min: (a) $x = 2$; (b) $x = 3$; (c) $x = 4$; (d) $x = 5$; (e) $x = 6$; (f) $x = 7$; (g) $x = 8$; (h) $x = 9$; (i) $x = 10$; (j) $x = 11$; (k) $x = 12$. Reexamined DSC thermograms with a high sensitivity (cooling rate, 2 °C/min): (l) $x = 2$; (m) $x = 4$.

from these thermograms are schematized in Table 1 to show phase transition sequences. Exceptionally, for the compound

Table 1. The Phase Sequences and the Transition Temperatures for Compounds **10**

x	phase sequence and transition temperature (°C) ^a
2	Cryst $\xrightleftharpoons[159]{187}$ SmX $\xrightleftharpoons[263]{262}$ Ch $\xrightleftharpoons[319]{319}$ Iso
3	Cryst $\xrightleftharpoons[146]{169}$ Ch $\xrightleftharpoons[251]{251}$ Iso
4	Cryst $\xrightleftharpoons[155]{196}$ SmX $\xrightleftharpoons[204]{204}$ Ch $\xrightleftharpoons[297]{298}$ Iso
5	Cryst $\xrightleftharpoons[130]{143}$ Ch $\xrightleftharpoons[249]{249}$ Iso Cryst $\xrightleftharpoons[134]{130}$ SmX $\xrightleftharpoons[134]{134}$ Ch
6	Cryst $\xrightleftharpoons[121]{154}$ Ch $\xrightleftharpoons[270]{271}$ Iso Cryst $\xrightleftharpoons[138]{121}$ SmX $\xrightleftharpoons[138]{138}$ Ch
7	Cryst $\xrightleftharpoons[128]{136}$ Ch $\xrightleftharpoons[239]{240}$ Iso
8	Cryst $\xrightleftharpoons[140]{173}$ Ch $\xrightleftharpoons[250]{252}$ Iso
9	Cryst $\xrightleftharpoons[130]{140}$ Ch $\xrightleftharpoons[230]{231}$ Iso Cryst $\xrightleftharpoons[136^b]{130}$ SmX $\xrightleftharpoons[136^b]{136^b}$ Ch
10	Cryst $\xrightleftharpoons[143]{156}$ Ch $\xrightleftharpoons[237]{239}$ Iso
11	Cryst $\xrightleftharpoons[128]{137}$ Ch $\xrightleftharpoons[221]{223}$ Iso
12	Cryst $\xrightleftharpoons[116]{163}$ Ch $\xrightleftharpoons[226]{227}$ Iso Cryst $\xrightleftharpoons[140]{116}$ SmX $\xrightleftharpoons[140]{140}$ Ch

^aSmX stands for the unidentified smectic phase. ^bThe value in the parentheses was obtained from observation by cross-polarized microscopy attached with a hot-stage.

with $x = 9$, a cholesteric-to-smectic phase (Ch-Sm) transition was observed on a polarizing microscopy, which could not be determined by DSC analysis because of its very low peak intensity. In general, the thermal transition behavior is very sensitive to the length of spacer (x) showing three features. First, on the heating DSC cycle, the two compounds with $x = 2$ and 4 exhibited three endothermic peaks (see Figure 1) and on cooling they again showed the corresponding three exothermic peaks (see Figure 2). It should be noted that, in spite of high temperature values of their isotropization temperatures (T_i s), the Ch-Sm transition peaks for the compounds with $x = 2$ and 4 could be defined by cooling cholesteric melt before thermal degradation. Instead, the Ch-Sm transition temperatures of the other compounds were obtained by cooling the isotropic melts. On heating the strong endotherms appeared at low temperature for melting (Cryst-Sm) transition, the weak peaks at medium temperatures for the Sm-Ch transitions and the final peaks at higher temperatures for isotropization (Ch-Iso) transitions. Corresponding peaks existed also on cooling. Secondly, the compounds with $x = 3, 7, 8, 10$ and 11 revealed two different endothermic peaks,

corresponding to melting and isotropization transitions on heating, and on cooling two the exothermic peaks for reverse transitions. Thirdly, on heating, the compounds with $x = 5, 6, 9$ and 12 showed only a cholesteric phase before the isotro-

pization, whereas, when their isotropic melt was cooled, the compounds exhibited three transitions in the order of Iso-Ch, Ch-Sm and solidification (Sm-Cryst). Namely, they formed the smectic phases monotropically. Moreover, multiple crys-

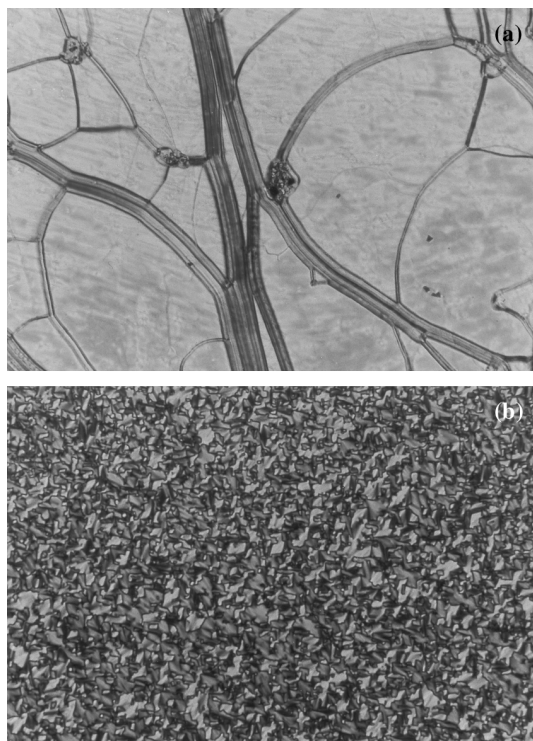


Figure 3. Photomicrographs of compounds **10** on heating (magnification of $\times 250$): (a) $213\text{ }^\circ\text{C}$ with $x=3$; (b) $260\text{ }^\circ\text{C}$ with $x = 6$.

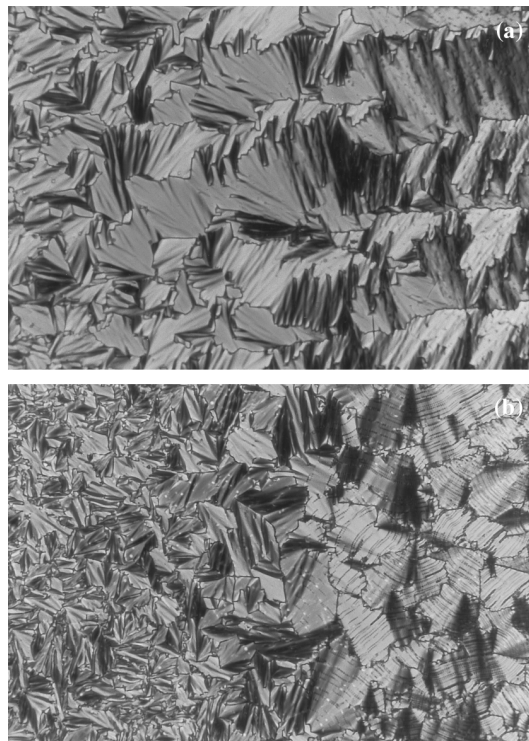


Figure 5. Photomicrographs of compound **10** with $x = 4$ on cooling (magnification of $\times 250$): (a) $256\text{ }^\circ\text{C}$; (b) $156\text{ }^\circ\text{C}$.

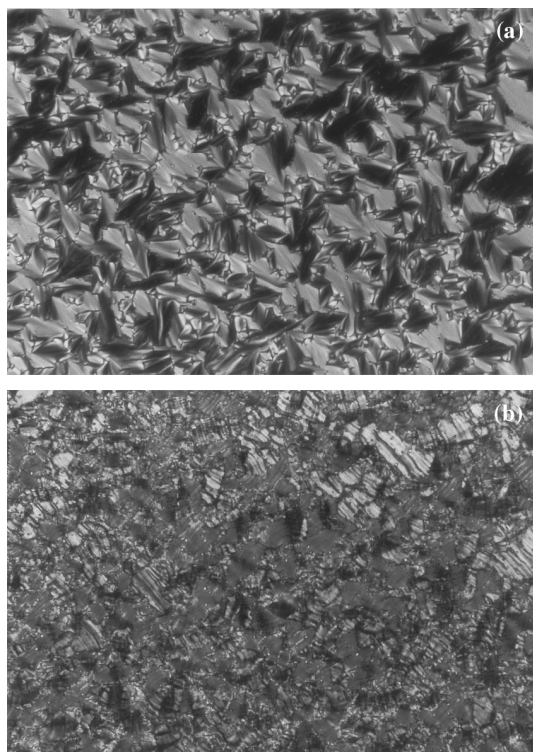


Figure 4. Photomicrographs of compound **10** with $x = 2$ on cooling (magnification of $\times 250$): (a) $300\text{ }^\circ\text{C}$; (b) $219\text{ }^\circ\text{C}$.

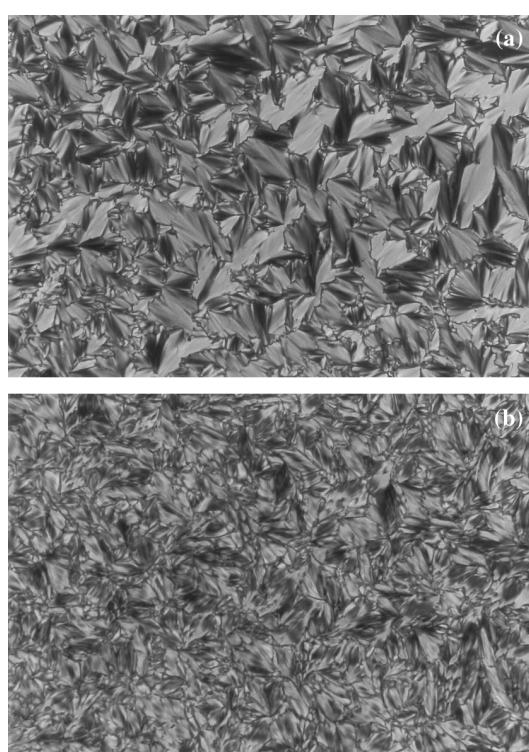


Figure 6. Photomicrographs of compound **10** with $x = 5$ on cooling (magnification of $\times 250$): (a) $226\text{ }^\circ\text{C}$; (b) $131\text{ }^\circ\text{C}$.

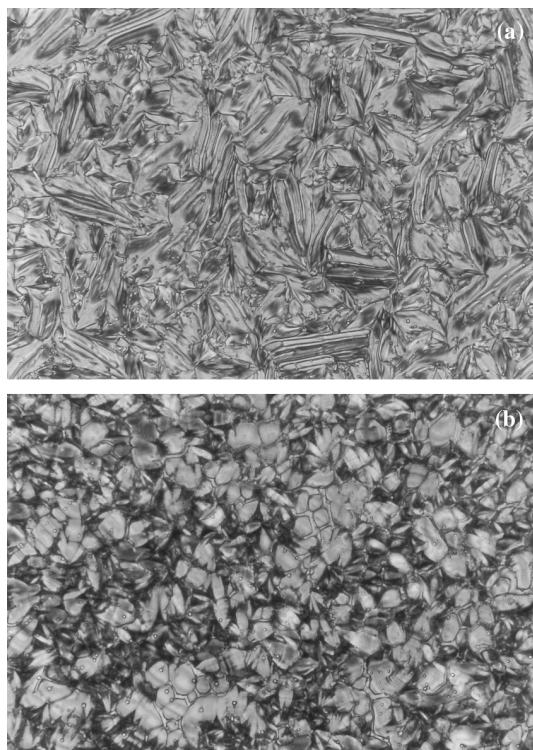


Figure 7. Photomicrographs of compound **10** with $x = 6$ on cooling (magnification of $\times 250$): (a) 158 °C; (b) 126 °C.

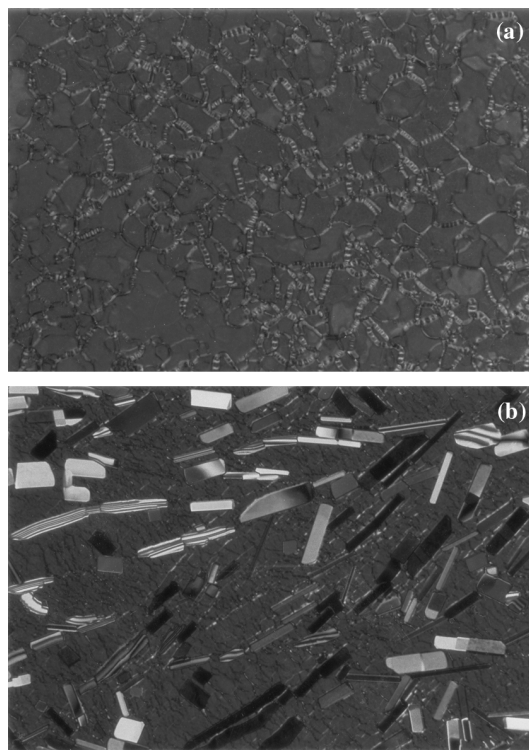


Figure 9. Photomicrographs of compound **10** with $x = 9$ on cooling (magnification of $\times 250$): (a) 137 °C; (c) 135 °C.

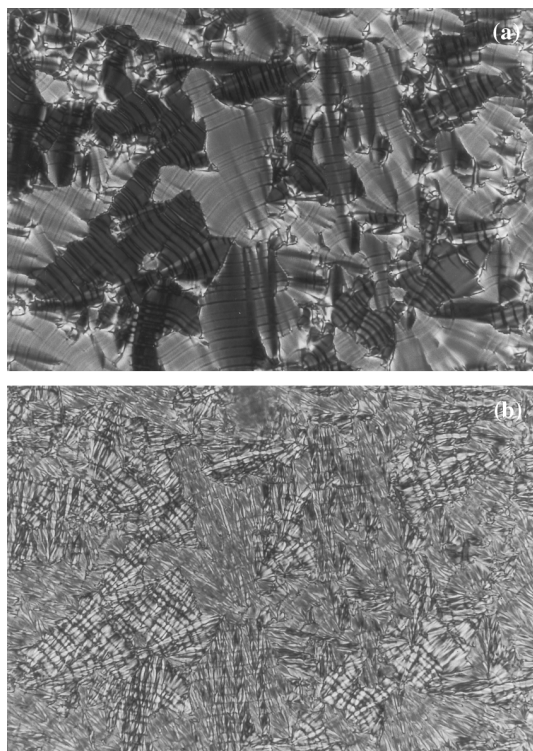


Figure 8. Photomicrographs of compound **10** with $x = 8$ on cooling (magnification of $\times 250$): (a) 235 °C; (b) 177 °C.

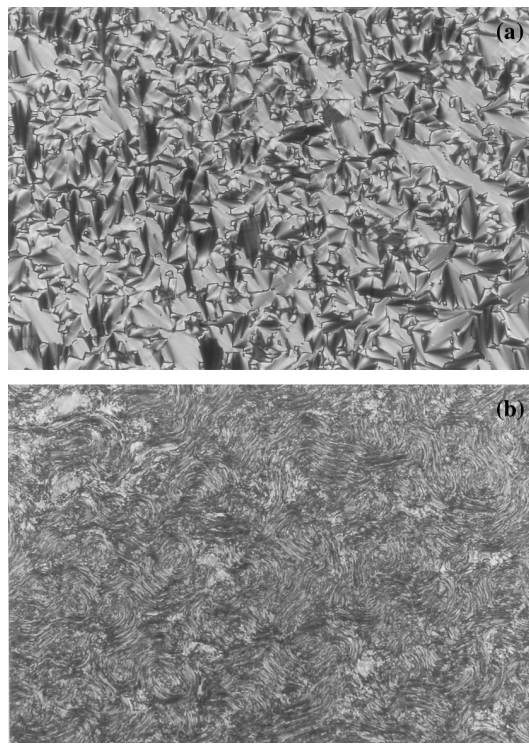


Figure 10. Photomicrographs of compound **10** with $x = 12$ on cooling (magnification of $\times 250$): (a) 223 °C; (b) 133 °C.

tallization peaks appearing on the cooling DSC thermograms are ascribed to occurrence of a slight thermal degradation during thermal analysis.

Nature of mesophases. The thermal transitions observed by DSC analysis were further examined using a polarizing microscope equipped with a hot-stage. The DSC results

could be reconfirmed through the microscopic observation. All of the thermal transitions and transition temperatures coincided very well with microscopic observations except for $x = 9$ as described above. The nature of mesophases formed by each compound was judged by their optical textures in the melts. According to their optical textures, all of the compounds displayed either an oily-streak or a fan-shaped texture in their cholesteric melts as shown in Figure 3. The two compounds with $x = 2$ and 4, on heating, showed a homeotropic nature in their smectic regions. And on cooling they could also form a smectic phase with the banded fan-shaped texture judged to be either chiral smectic A or C (Sm^*A or C) phase (see Figures 4 and 5). Particularly, the compounds with $x = 6$ and 9 displayed mosaic textures corresponding to smectic G and smectic B phases, respectively (see Figures 7 and 9). The compound with $x = 5$ could form the smectic phase over the narrowest temperature range of 4 °C among all of the compounds (see Figure 6). The compound of $x = 12$ revealed the polygonal texture with the appearance of a solid texture (see Figure 10). The possibility that the compound was solidified at 140 °C could be excluded by DSC characterization. Actually, on its cooling DSC thermogram, the weak exothermic peak at 140 °C corresponds to the Ch-Sm transition. Interestingly enough, the compound of $x = 8$, upon cooling its cholesteric melt, underwent change of color at 209 °C from blue to green with the same persisting optical texture, as shown in Figure 8.

Thermodynamics of phase transitions. The dependence of transition temperature on the length of the central spacer is illustrated in Figures 11 and 12. These figures illustrate that, on heating, only two compounds, i.e., those with $x = 2$ and 4, show the mesophase-1-to-mesophase-2 transition, while, on cooling, six compounds among eleven exhibit this transition. It is interesting to compare the mesomorphic transition behavior of the compounds **10** in this study with that of the dimesogenic compounds with chiral tails previ-

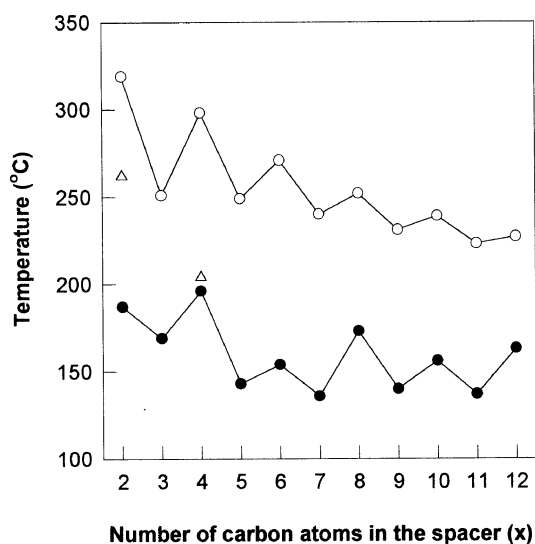


Figure 11. The dependence of transition temperatures of the series on the length of the central polymethylene spacer (x) on heating scan: ● = T_m ; △ = $T_{SmX \rightarrow ch}$; ○ = T_i .

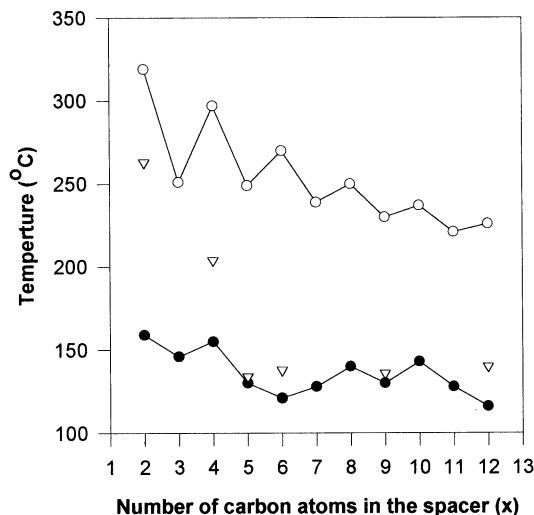
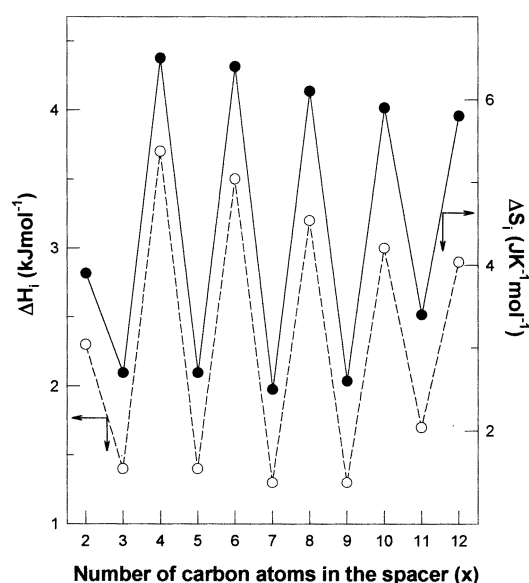


Figure 12. The dependence of transition temperatures of the series on the length of the central polymethylene spacer (x) on cooling scan: ○ = T_i ; ▽ = $T_{Ch \rightarrow SmX}$; ● = T_c (crystallization temperature).

ously reported by us.¹¹ The only difference of structures between two the compounds is the linking order of ester group, as already described. Upon heating, the latter compounds with long spacer ($x = 6-12$) showed smectic phase, whereas the former compounds with short spacer ($x = 2$ and 4) are apt to form smectic phase. Upon cooling, eight-tenth the latter compounds showed Ch-Sm transition, whereas six-eleventh the former compounds display this transition. In general, on cooling, compounds could form more diverse liquid crystalline phases than on heating. In other words, they have a tendency to form monotropic LC phases. Supercooled stabilization of new LC phases could account for this polymorphic nature of the liquid crystalline compounds on cooling. The figures show that the transition temperatures, T_m and T_i , of the compounds decreased in a zig-zag fashion, revealing the so-called odd-even effect,¹³⁻¹⁵ as x increased. On heating, these temperatures were consistently higher for the compounds with even numbers of methylene units in the spacer than those of odd numbers. On cooling, the compounds with $x = 6$ and 12 formed a smectic phase monotropically and, thus, their crystallization temperatures did not fall on the zig-zag line. The compounds with $x = 2$ and 4 enantiotropically formed a smectic phase in a wide temperature range, while the compounds with $x = 5$ and 9 monotropically formed a smectic phase over a very narrow temperature range. In Table 2, the values of enthalpy (ΔH) and entropy changes (ΔS) for phase transitions are summarized. Figure 13 shows how the values of the thermodynamic parameters for isotropization, ΔH_i and ΔS_i , of the compounds change with x . The figure reveals a definite odd-even effect in ΔH_i as well as in ΔS_i for the compounds. Considering the unique conformation of the spacers examined previously by others,^{16,17} the higher values of ΔH_i and ΔS_i for even members than for those of odd ones can be associated with a stronger intermolecular interaction and a higher degree of order in their mesophase, respectively. The com-

Table 2. Thermodynamic Data of Compounds **10**

x	ΔH_m (kJ/mol)	ΔH_i (kJ/mol)	ΔS_m (J/mol · K)	ΔS_i (J/mol · K)
2	48.6	2.3	106	3.9
3	38.9	1.4	88	2.7
4	53.8	3.7	115	6.5
5	44.2	1.4	106	2.7
6	54.4	3.5	127	6.4
7	52.5	1.3	128	2.5
8	60.3	3.2	135	6.1
9	62.8	1.3	152	2.6
10	71.3	3.0	166	5.9
11	70.3	1.7	171	3.4
12	77.4	2.9	178	5.8

**Figure 13.** The dependence of the values of ΔH_i (○···○) and ΔS_i (●—●) of the series on the length of the central polymethylene spacer (x) on heating scan.

compound with $x = 8$ was an exception. Against our expectation, the values of ΔH_m and ΔS_m for the compound of $x = 8$ are smaller than ones for the compound of $x = 9$. At the present moment it is not easy to explain this discrepancy without further study, for example, its crystal structure. It, however, should be noted that the values are significantly higher than those of the preceding compound with $x = 7$. Although we can not draw out a univocal relationship between the mesomorphic property and the structure of the compounds or the length of the spacers, we could realize that the mesomorphic property and transition behavior of these compounds greatly depend on the length of the spacer.

Conclusion

The following conclusions can be drawn from the present

work:

1. All the chiral dimesogenic compounds were liquid crystalline, and showed an odd-even dependence of T_m and T_i as well as ΔH_i and ΔS_i on the number of carbon atoms in the spacer (x).

2. On heating, all of the compounds except the compounds with $x = 2$ and 4 formed only a cholesteric phase. The compounds with $x = 2$ and 4, upon heating, showed smectic and cholesteric phases sequentially before their isotropization.

3. On cooling, the compounds with $x = 2, 4, 5, 6, 9$ and 12 underwent two different transitions of isotropic-to-cholesteric and cholesteric-to-smectic phases sequentially before they crystallized, whereas the compounds with $x = 3, 7, 8, 10$ and 11 formed only a cholesteric phase before crystallization.

4. A smectic phase could be monotropically formed on cooling the compounds with $x = 5, 6, 9$ and 12, while the phase transitions for the remaining compounds were reversible.

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