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SYNTHESIS AND THERMAL PROPERTIES OF TWIN DIMERS CONTAINING CYANOSTILBENE GROUPS AS A MESOGENIC GROUP

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Twin dimers (TDs) with a different linking group (ester or ether) between the mesogenic group (cyanostilbene moiety) and the flexible spacer were synthesized to clarify the effect of the linking group on the mesomorphic properties. The sequence of the ester linking group and the position of the cyano group in the mesogenic core made an important contribution to the thermal properties of the twin dimers. A remarkable odd–even effect in the phase transition temperatures and entropy changes from a nematic phase to an isotropic fluid was observed for all the synthesized twin dimers.

Keywords: cyanostilbene; liquid crystal dimer; odd–even effect

INTRODUCTION

Aromatic main chain liquid crystalline polymers (MCLCPs) with wholly aromatic rings or semiflexible moieties have been found primarily as high-performance polymers for molding resins with good mechanical properties. MCLCPs can be classified into three types such as Xyder (Amoco, Augusta), Vectra (Hoechst-Celanese, New Jersey), and X7G (Eastman-Kodak, Tennessee), depending upon their heat distortion temperatures. Especially the chemical constituents of semiflexible MCLCPs like X7G (polyethylene terephthalate modified with rigid p-hydroxybenzoic acid) are the mesogenic rigid core and a flexible spacer. Consequently, semiflexible MCLCPs had lower phase transition temperatures and high solubility. Therefore, semiflexible MCLCPs are suitable candidates for the assessment of reliable correlations between their chemical structural

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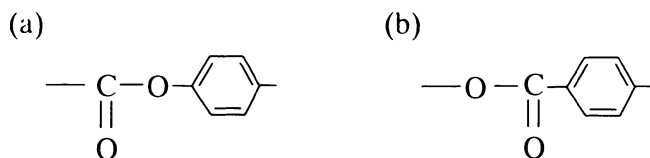


FIGURE 1 Possible chemical structure of ester group linked to phenyl group.

characteristics and physical properties, including thermal properties and formation of mesophases [1].

Thermal properties of semiflexible MCLCPs are dependent upon the chemical structure of rigid core, flexible spacer length, the linking group between the rigid core and a flexible spacer, etc. There are two types of ester linking groups as shown in Figure 1. Asrar et al. reported that the mesomorphic phase structure of the semiflexible MCLCPs is deeply influenced by the sequence of the ester linking bond between the rigid core and the flexible spacer [1]. A nematic phase was exhibited for the semiflexible MCLCPs with the ester linking group, as shown in Figure 1(a), while a smectic phase was displayed for the semiflexible MCLCPs with the ester linking group, as shown in Figure 1(b). Roviello et al. and Blumstein et al. reported that the 4,4'-dihydroxy- α -methylstilbene-aliphatic acid polymers and the 4,4'-dihydroxy-2,2'-dimethylazoxybenzene-alkanedioic acid polymers exhibited a nematic phase [2,3].

We have already reported the synthesis and thermal properties of the 4,4'-dihydroxycyanostilbene-alkanedioic acid polymers shown in Figure 2 [4,5]. These semiflexible MCLCPs exhibited an enantiotropic nematic phase. Thus a nematic phase was easily displayed for the semiflexible MCLCPs with the ester linking group as shown in Figure 1(a). On the other hand, Watanabe et al. reported that a smectic phase was shown for the semiflexible MCLCPs with biphenyl groups as a mesogenic group and the ester linking group as shown in Figure 1(b) [8]; however, the semiflexible MCLCP with the ester linking group as shown in Figure 1(b) is little investigated.

The effect of the flexible polymethylene spacer on the thermal properties of MCLCPs is well assessed in a number of publications. The odd-even effect of melting points (T_m) and clearing points (T_i) is well-known behavior for the MCLCPs with different flexible spacer lengths. Both

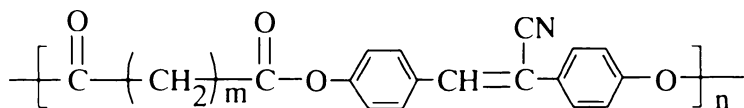


FIGURE 2 Chemical structure of main chain type liquid crystalline polyester containing cyanostilbene moieties.

nematic–isotropic phase transition temperatures and entropy changes from a nematic phase to an isotropic melt decrease with increasing length of the flexible spacer. The odd–even effect would be explained by the different order of the mesogenic groups in the nematic phase, depending upon the number of methylene units with all trans conformation in the flexible spacer. Roviello et al. and Blumstein et al. reported the odd–even effect on the transition temperatures, enthalpy changes, and entropy changes from a nematic phase to an isotropic melt of thermotropic liquid crystalline polyesters [2,3]. The clear odd–even effect on the transition temperatures and entropy changes from a nematic phase to an isotropic melt were also observed for the semiflexible MCLCPs, as shown in Figure 2. Thus the odd–even effect was much like the very familiar thermodynamic properties of the semiflexible MCLCPs. However, it is very difficult to understand the odd–even effect on the transition temperatures and entropy changes from a nematic phase to an isotropic melt, because the semiflexible MCLCPs have structural complexity and a polymeric nature, ie., high molecular weight, molecular weight distribution, etc.

Low molecular weight model compounds having fundamental structural units for the semiflexible MCLCP are used to investigate the odd–even effect on the phase transition temperatures and entropy changes of the semiflexible MCLCPs by experimental and computer-simulation techniques [6,7]. There are two types of model compounds. One is a core model that has a single mesogenic core with two terminal chains. Another is a twin dimeric model (twin dimer) in which two mesogenic cores are linked by a flexible spacer.

Twin dimers are recognized as an exact structural model compound of semiflexible MCLCPs [6]. Abe et al. have found that the different order of the mesogenic group in the nematic phase played an important role in the odd–even effect on the nematic–isotropic phase transition behavior of the twin dimer by the conformation analysis of the spacer [7].

In this report, we synthesized twin dimers having the cyanostilbene moieties as a mesogenic group, as shown in Figure 3, and investigated the thermal properties of the dimers with different linking groups. We also discussed the effect of the position of the cyano group in the mesogen on the thermal properties of the twin dimers.

EXPERIMENTAL

Materials

4-Methoxyphenylacetonitrile was purchased from Midorikagaku Corporation (Tokyo).

Twin dimers (TDs) I–V were prepared according to Schemes 1, 2, and 3. Typical synthetic procedures of the twin dimers were described below.

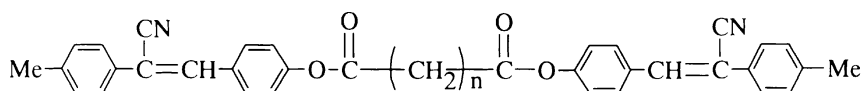
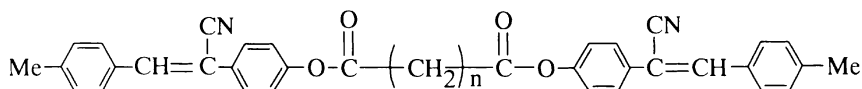
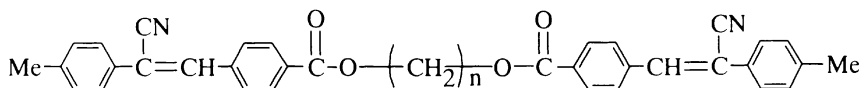
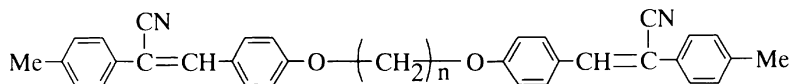
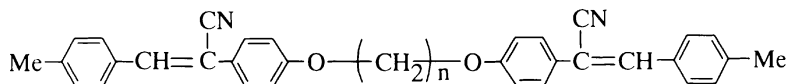
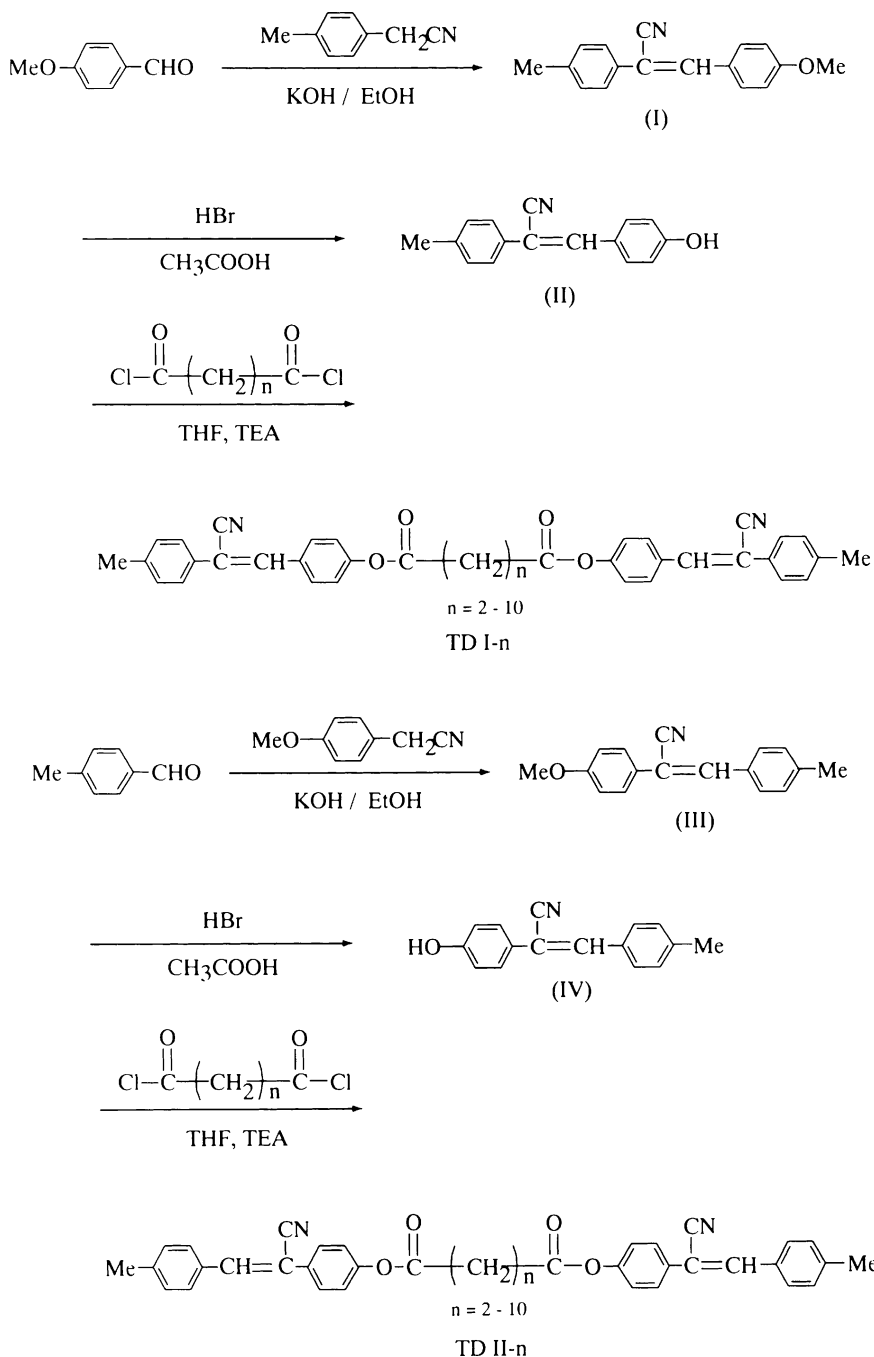
TD I-n, $n = 2 - 10$ TD II-n, $n = 2 - 10$ TD III-n, $n = 2 - 10$ TD IV-n, $n = 2 - 10$ TD V-n, $n = 2 - 10$

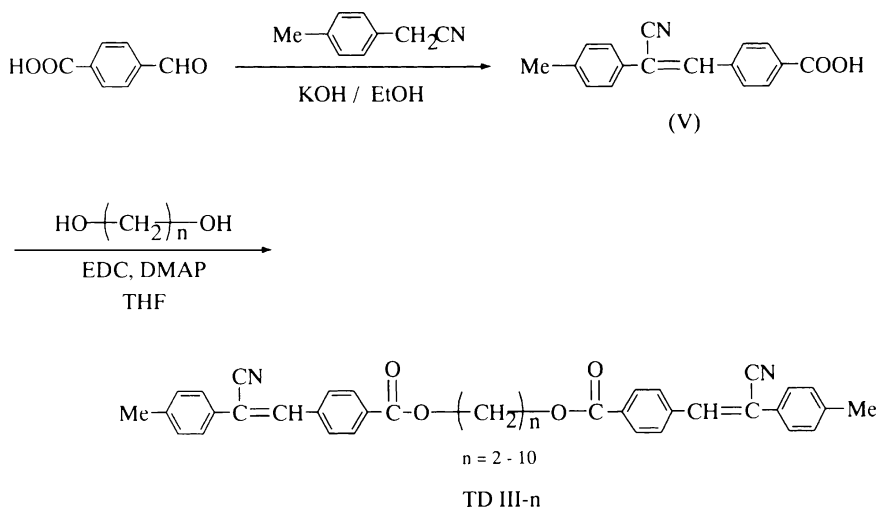
FIGURE 3 Chemical structures of synthesized twin dimers containing cyanostilbene moieties.

4-Methyl-4'-methoxy- α -cyanostilbene (I)

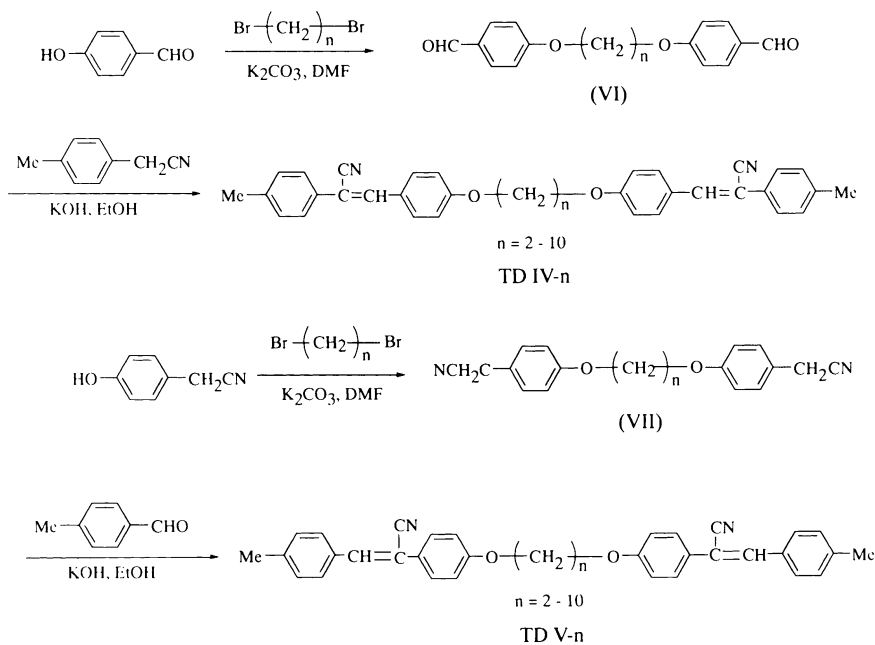
Potassium hydroxide (19.4 g, 0.35 mol) was dissolved in ethanol (450 ml). p-Tolualdehyde (23 ml, 0.19 mol) was dissolved in the ethanol solution. 4-Methoxyphenyl acetonitrile (25 ml, 0.17 mol) was added dropwise to the ethanol solution. After the reaction mixture was stirred for



SCHEME 1 Synthesis of twin dimer I and II series.



SCHEME 2 Synthesis of twin dimer III series.



SCHEME 3 Synthesis of twin dimer IV and V series.

4 at room temperature, the precipitate was washed with aqueous HCl and then with water until a neutral aqueous solution was obtained. The product was purified by recrystallization from a mixed solvent (acetone/methanol = 1/2) and was obtained in a 72.9% yield (39.2 g). $^1\text{H-NMR}$ (CDCl_3) δ ppm: 2.4(s, 3H, CH_3), 3.8(s, 3H, OCH_3), 7.5(s, 1H, $\text{CH}=\text{}$), 7.0–7.9(m, 8H, Ar-H).

4-Hydroxy-4'-methyl-cyanostilbene (II)

The intermediate (I) (20 g, 80.6 mmol) was dissolved in acetic acid (80 ml). A hydrobromic acid aqueous solution (47%, 80 ml) was added to the acetic acid solution. The reaction mixture was heated at 120°C for 12 h and then was poured into water. The precipitate was washed with water until a neutral aqueous solution was obtained. The product was obtained in a 62.1% yield (11.8 g) and was used without further purification. $^1\text{H-NMR}$ (CDCl_3) δ ppm: 2.4(s, 3H, CH_3), 3.9(s, 1H, OH), 7.5(s, 1H, $\text{CH}=\text{}$), 7.0–7.9(m, 8H, Ar-H).

Twin Dimer I ($n = 6$): TD I-6

The intermediate (II) (1.1 g, 4.3 mmol) was dissolved in tetrahydrofuran (THF) (40 ml). Triethylamine (1.8 ml, 12.8 mmol) was added to the THF solution. A THF solution (10 ml) of suberoyl chloride (0.45 ml, 2.1 mmol) was added dropwise to the THF solution. The reaction mixture was stirred at room temperature for 24 h. The precipitate was removed by filtration. THF was evaporated under reduced pressure. The residue was washed with aqueous HCl and with water until a neutral aqueous solution was obtained. After the product was washed with methanol, the product was purified by silica gel column chromatography (eluent chloroform) and was obtained in a 55.5% yield (0.72 g). $^1\text{H-NMR}$ (CDCl_3) δ ppm: 1.3–1.8 (m, 8H, CH_2), 2.4(s, 6H, CH_3), 2.8(t, 4H, OOCCH_2), 7.5(s, 2H, $\text{CH}=\text{}$), 7.1–7.8(m, 16H, Ar-H).

4-Methoxy-4'-methyl- α -cyanostilbene (III)

The intermediate (III) was synthesized from p-anisaldehyde and p-xylylcyanide according to the similar synthetic procedure of the intermediate (I). The product was purified by recrystallization from a mixed solvent (acetone/methanol = 1/2). The product was obtained in a 74.8% yield (40.2 g). $^1\text{H-NMR}$ (CDCl_3) δ ppm: 2.4(s, 3H, CH_3), 3.8(s, 3H, CH_3), 7.3(s, 1H, $\text{CH}=\text{}$), 6.9–7.8(m, 8H, Ar-H).

Intermediate (IV)

The intermediate (IV) was prepared according to the similar synthetic procedure of the intermediate (II). The product was used without further purification. The product was obtained in a 34.8% yield (6.8 g). $^1\text{H-NMR}$

(CDCl₃) δ ppm: 2.4(s, 3H, CH₃), 3.8(s, 1H, OH), 7.5(s, 1H, CH=), 7.0–7.8(m, 8H, Ar-H).

Twin Dimer II (n = 6): TD II-6

The intermediate (IV) (1.1 g, 4.3 mmol) was dissolved in THF (40 ml). Triethylamine (1.8 ml, 12.8 mmol) was added to the THF solution. A THF solution (10 ml) of suberoyl chloride (0.45 ml, 2.1 mmol) was added dropwise to the THF solution. The reaction mixture was stirred at room temperature for 24 h. The precipitate was removed by filtration. THF was evaporated under reduced pressure. The residue was washed with aqueous HCl and with water until a neutral aqueous solution was obtained. After the product was washed with methanol, the product was purified by silica gel column chromatography (eluent chloroform) and was obtained in a 62.5% yield (0.81 g). ¹H-NMR (CDCl₃) δ ppm: 1.5–1.8(m, 8H, CH₂), 2.4(s, 6H, CH₃), 2.6(t, 4H, OOCCH₂), 7.5(s, 2H, CH=), 7.0–7.9(m, 16H, Ar-H).

Intermediate (V)

Potassium hydroxide (19.4 g, 0.35 mol) was dissolved in ethanol (450 ml). p-Terephthalaldehydic acid (25 g, 0.17 mol) was dissolved in the ethanol solution. p-Xylylcyanide (25 ml, 0.19 mol) was added dropwise to the ethanol solution. After the reaction mixture was stirred for 12 h at room temperature, the precipitate was washed with aqueous HCl and then with water until a neutral aqueous solution was obtained. The product was purified by recrystallization from acetone and was obtained in a 76.1% yield (38.2 g). ¹H-NMR (CDCl₃) δ ppm: 2.4(s, 3H, CH₃), 7.2–8.1(m, 9H, Ar-H and =CH), 13.2(s, 1H, COOH).

Twin Dimer III (n = 6): TD III-6

The intermediate (V) (1.4 g, 5.3 mmol), 1,6-hexanediol (0.3 ml, 2.5 mmol) were dissolved in THF (80 ml). 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (2.0 g, 10.4 mmol) and a small amount of 4-dimethylaminopyridine as a catalyst were added to the THF solution. The reaction mixture was stirred at room temperature for 48 h. The precipitate (urea derivative as a by-product) was removed by filtration. THF was evaporated under reduced pressure. The residue was washed with aqueous HCl to remove the remained urea derivative as a by-product of the esterification reaction and with water until a neutral aqueous solution was obtained. After the product was washed with methanol, the product was purified by recrystallization from a mixed solvent (benzene/methanol = 5/1) and was obtained in a 40.7% yield (0.60 g). ¹H-NMR (CDCl₃) δ ppm: 1.6–1.9(m, 8H, CH₂), 2.4(s, 6H, CH₃), 4.4(t, 4H, COOCH₂), 7.5(s, 2H, CH=), 7.2–8.1(m, 16H, Ar-H).

Intermediate (VI)

p-Hydroxybenzaldehyde (2.4 g, 21.2 mmol) and 1,6-dibromohexane (1.5 ml, 10.0 mmol) were dissolved in dimethylformamide (7.5 ml). Potassium carbonate (3.4 g, 25.2 mmol) was added to the solution. After the reaction mixture was heated at 110°C for 4 h, it was poured into water (300 ml). The white precipitate was washed with water and was obtained in a 55.1% yield (1.8 g). The white precipitate was used without further purification. $^1\text{H-NMR}$ (CDCl_3) δ ppm: 1.5–2.0(m, 8H, CH_2), 4.2(t, 4H, OCH_2), 6.0(d, 4H, Ar-H), 7.8(d, 4H, Ar-H), 9.9(s, 2H, CHO).

Twin Dimer IV ($n = 6$): TD IV-6

Potassium hydroxide (8.0 g, 0.12 mol) was dissolved in ethanol (300 ml). p-Xylylcyanide (1.7 ml, 13.3 mmol) and the intermediate (VI) (1.8 g, 5.5 mmol) were added to the ethanol solution. After the reaction mixture was stirred at 60°C for 2 h, the light yellowish precipitate obtained was washed with aqueous HCl and then with water until a neutral aqueous solution was obtained. The product was purified by recrystallization from a mixed solvent (methanol/chloroform = 1/3). The yellow product was obtained in a 72.2% yield (2.2 g). $^1\text{H-NMR}$ (CDCl_3) δ ppm: 1.5–2.0(m, 8H, CH_2), 2.4(s, 6H, CH_3), 4.1(t, 4H, OCH_2), 7.5(s, 2H, $\text{CH}=\text{}$), 6.8–7.8(m, 16H, Ar-H).

Intermediate (VII)

p-Hydroxybenzylcyanide (2.8 g, 21.2 mmol) and 1,6-dibromohexane (1.5 ml) were dissolved in dimethylformamide (5 ml). Potassium carbonate (3.4 g, 25.2 mmol) was added to the mixture solution. The reaction mixture was heated at 110°C for 4 h and then was poured into water (300 ml). The precipitate obtained was washed with water. The white precipitate was purified by silica gel column chromatography (eluent chloroform). The product was obtained in a 34.5% yield (1.2 g). $^1\text{H-NMR}$ (CDCl_3) δ ppm: 1.5–1.7(m, 8H, CH_2), 3.6(s, 4H, CNCH_2), 4.0(t, 4H, OCH_2), 6.8(d, 4H, Ar-H), 7.3(d, 4H, Ar-H).

Twin Dimer V ($n = 6$): TD V-6

Potassium hydroxide (2.0 g, 30.5 mmol) was dissolved in ethanol (150 ml). p-Tolualdehyde (0.4 ml, 3.4 mmol) and the intermediate (VII) (0.51 g, 1.44 mmol) were added to the ethanol solution. After the reaction mixture was stirred at 60°C for 2 h, the light yellowish precipitate obtained was washed with aqueous HCl and then with water until a neutral aqueous solution was obtained. The product was purified by recrystallization from a mixed solvent (methanol/chloroform = 1/3). The yellow product was obtained in a 62.9% yield (0.62 g). $^1\text{H-NMR}$ (CDCl_3) δ ppm: 1.5–2.0(m, 8H, CH_2), 2.4(s, 6H, CH_3), 4.1(t, 4H, OCH_2), 7.5(s, 2H, $\text{CH}=\text{}$), 6.8–7.8(m, 16H, Ar-H).

Characterization

^1H -NMR was carried out with a JEOL JNM-LA 400 spectrometer using CDCl_3 as the solvent. Infrared spectra were recorded on a JEOL JIR 7000 spectrometer. Spectra were collected at 4 cm^{-1} resolution. DSC measurements were conducted with a Mettler DSC821^e. Optical microscopy was performed on a Nikon polarizing optical microscope, OPTIPHOTO-POL, equipped with a Mettler FP80 controller and a FP82 hot stage. Thermal properties of synthesized materials were investigated by optical microscope and DSC measurements. X-ray diffraction patterns were recorded with a RIGAKU RINT2500 series with Ni-filtered $\text{CuK}\alpha$ radiation. The sample in quartz capillary (diameter 1 mm) was held in a temperature-controlled cell (RIGAKU LC high-temperature controller). The mesomorphic structure of twin dimers was investigated by X-ray measurements.

RESULTS AND DISCUSSION

We synthesized twin dimer (TD) series containing cyanostilbene groups. Thermal properties of the TD series were investigated by polarizing optical microscopy and DSC measurements. DSC curves of TD I-5 and I-6 were shown in Figure 4. A peak assigned to the phase transition from the crystal to the isotropic melt was shown on heating run of TD I-5. On the other

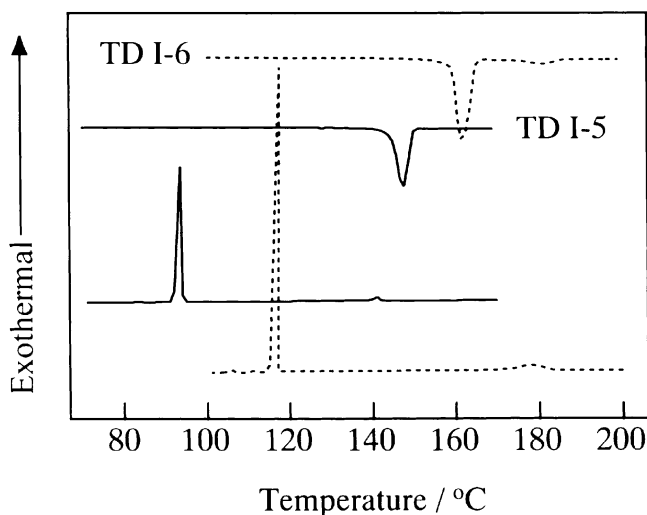


FIGURE 4 DSC curves of twin dimers I (TD I-6, broken line; TD I-5, solid line).

hand, two peaks were detected on the cooling run of TD I-5. A schlieren texture was observed in the temperature range between the two peaks. The two peaks were assigned to the melting and clearing points, respectively. The mesomorphic phase structure of the TD series was examined by X-ray diffraction measurements. TD I-5 displayed a monotropic nematic phase, while TD I-6 exhibited an enantiotropic nematic phase. Phase transition temperatures and entropy changes from a nematic phase to an isotropic melt (ΔS_{NI}) for TD I-*n* are summarized in Table 1. On the heating scan of the TD I series, a nematic phase was exhibited for TD I-(even number) except TD I-2, while TD I-2 and TD I-(odd number) series did not show any mesophases on the heating scan.

Phase transition temperatures and ΔS_{NI} on the cooling scan of the TD I series were summarized in Figures 5(a) and 5(b), respectively. Two peaks were observed in DSC curves on the cooling run of the TD I series except TD I-3, as shown in Figure 5(a). These two peaks were assigned to melting and clearing temperatures, respectively. A schlieren texture was observed in the temperature range between the two peaks detected by DSC measurements of the TD I series. Only a broad peak was observed in the wide-angle region of the X-ray pattern for the TD I series except TD I-3. The reason why TD I-3 did not exhibit any mesophases was not clarified. Clearing points of the TD I series showed a remarkable odd–even effect. The clearing points of the TD I series decreased with increasing flexible spacer length.

The ΔS_{NI} of the TD I series also displayed a remarkable odd–even effect, and the ΔS_{NI} values increased with increasing flexible spacer length. This

TABLE 1 Phase Transition Temperatures and Entropy Changes from a Nematic Phase to an Isotropic Melt of Twin Dimer I Series

<i>n</i>	Heating			Cooling		
	$T_{\text{Cr}}/^{\circ}\text{C}$	$T_{\text{NI}}/^{\circ}\text{C}$	$\Delta S_{\text{NI}}/(\text{Jmol}^{-1}\text{K}^{-1})$	$T_{\text{Cr}}/^{\circ}\text{C}$	$T_{\text{NI}}/^{\circ}\text{C}$	$\Delta S_{\text{NI}}/(\text{Jmol}^{-1}\text{K}^{-1})$
2	212	—	—	193	208	4.9
3	174	—	—	164	—	—
4	191	206	8.0	155	205	6.1
5	147	—	—	94	141	2.6
6	162	182	10.2	120	179	8.4
7	145	—	—	114	135	3.1
8	135	164	12.4	113	163	11.4
9	132	—	—	98	133	4.5
10	127	148	7.7	102	146	10.4

T_{Cr} , melting point; T_{NI} , nematic-isotropic phase transition temperature; ΔS_{NI} , entropy changes based on the phase transition from a nematic phase to an isotropic melt.

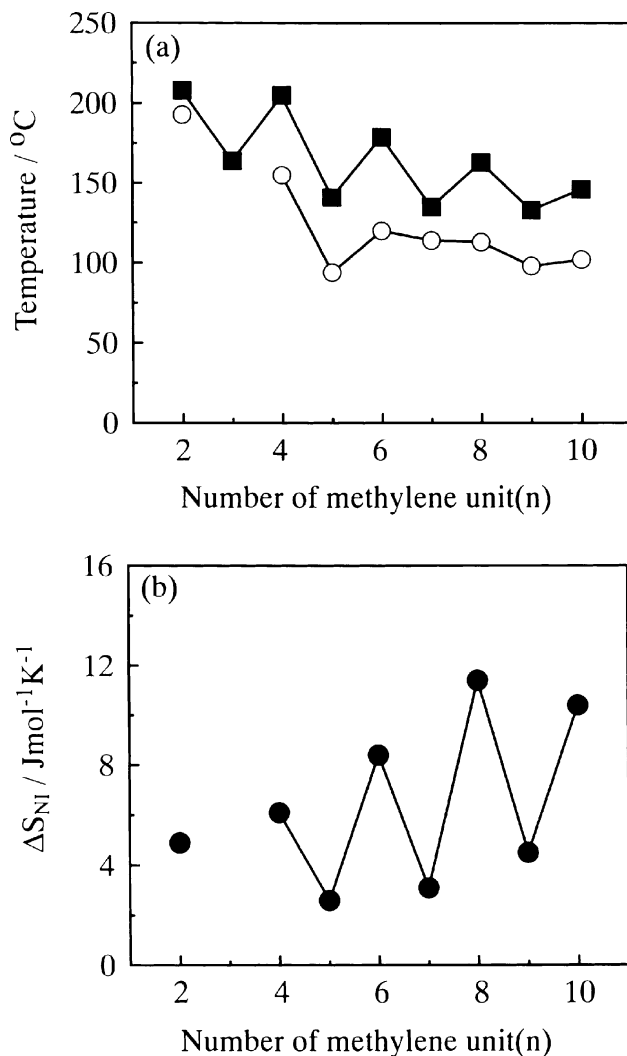


FIGURE 5 (a) Phase transition temperatures and (b) entropy changes of twin dimer I series. Open circles and solid squares represent melting and clearing points, respectively. Closed circles indicate entropy changes based on the phase transition from nematic to isotropic phase.

result indicates that the orientational order of the mesogenic groups in the nematic phase would increase with increasing flexible spacer length.

The difference in the chemical structure between the TD I series and TD II series was the position of the cyano group in the mesogenic core. TD II-4,

TD II-6, and TD II-9 exhibited an enantiotropic nematic phase. On the other hand, the TD II series, with the exception of the above mentioned three TDs, displayed a monotropic nematic phase. Thermal properties of TD II series are summarized in Table 2. Figure 6 shows phase transition temperatures and ΔS_{NI} values of the TD II series on the cooling run. The TD II series have the same linking group between the rigid core and the flexible spacer as the TD I series; however, the position of the cyano group in the mesogenic core of the TD II series was different from that of the TD I series. A schlieren texture was observed for the TD II series. The nematic structure of the TD II series was supported by X-ray measurements. Melting and clearing points for the TD II series displayed a remarkable odd–even effect. The remarkable odd–even effect on melting points was not observed for the TD I series with longer flexible methylene spacer ($n > 6$), as shown in Figure 5(a). However in the case of the TD II series shown in Figure 6(a), the clear odd–even effect on the melting points was displayed. The position of the cyano group in the mesogenic core would play an important role to exhibit the remarkable odd–even effect on the melting point. Both melting and clearing points for the TD II series decreased with increasing flexible spacer length. These clearing points for the TD II series were nearly equal to those of the TD I series, while these melting points of the TD II series were a little higher than those of the TD I series. As a result, the mesomorphic temperature range of the TD I series was wider than that of the TD II series.

The ΔS_{NI} values of the TD II series displayed an odd–even effect, and the ΔS_{NI} values gradually increased with increasing flexible spacer length. Both TD I and TD II series exhibited a nematic phase. However, the ΔS_{NI} values

TABLE 2 Phase Transition Temperatures and Entropy Changes from a Nematic Phase to an Isotropic Melt of Twin Dimer II Series

n	Heating			Cooling		
	$T_{\text{Cr}}/^{\circ}\text{C}$	$T_{\text{NI}}/^{\circ}\text{C}$	$\Delta S_{\text{NI}}/(\text{Jmol}^{-1}\text{K}^{-1})$	$T_{\text{Cr}}/^{\circ}\text{C}$	$T_{\text{NI}}/^{\circ}\text{C}$	$\Delta S_{\text{NI}}/(\text{Jmol}^{-1}\text{K}^{-1})$
2	216	—	—	171	202	4.2
3	171	—	—	156	157	2.1
4	192	202	4.5	182	200	4.9
5	146	—	—	116	135	2.3
6	165	175	5.2	147	170	5.4
7	131	—	—	114	133	2.4
8	156	—	—	142	154	8.0
9	115	148	3.4	95	126	3.7
10	146	—	—	134	146	12.6

T_{Cr} , melting point; T_{NI} , nematic-isotropic phase transition temperature; ΔS_{NI} , entropy changes based on the phase transition from a nematic phase to an isotropic melt.

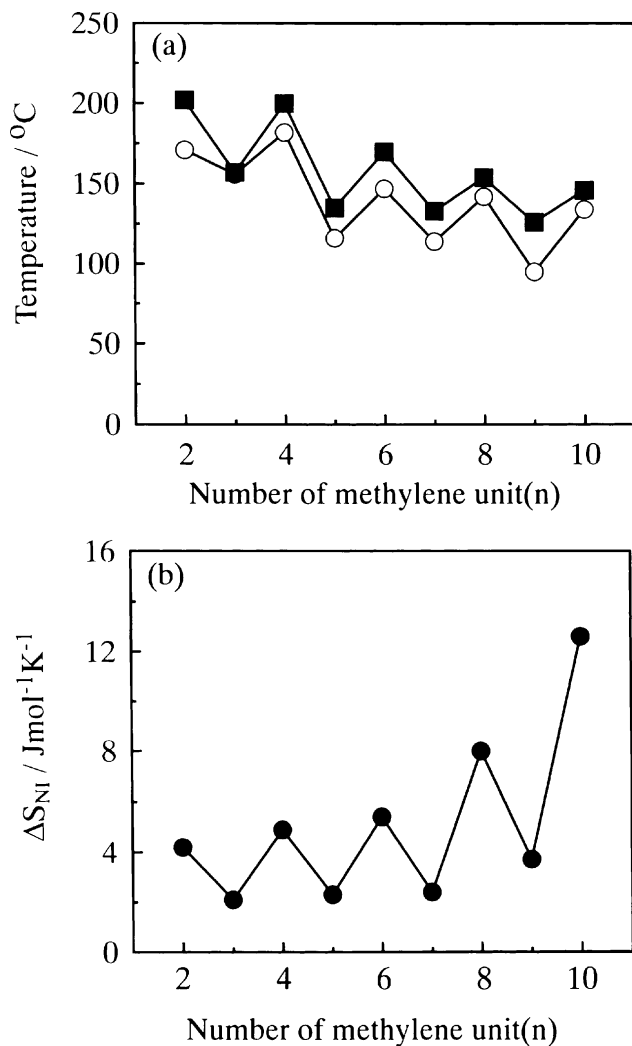


FIGURE 6 (a) Phase transition temperatures and (b) entropy changes of twin dimer II series. Open circles and solid squares represent melting and clearing points, respectively. Closed circles indicate entropy changes based on the phase transition from nematic to isotropic phase.

of the TD I series, except for TD I-10, were larger than those of the TD II series. Furthermore, the magnitude of the odd-even effect for the ΔS_{NI} values of the TD I series was larger than that of the TD II series.

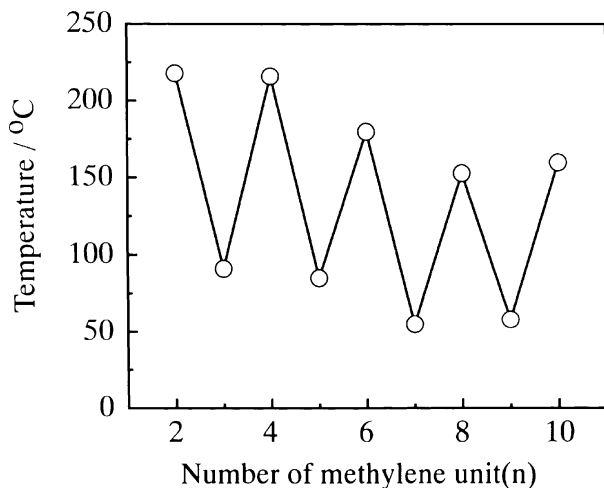


FIGURE 7 Phase transition temperatures of twin dimer III series. Open circles represent melting points.

Figure 7 displayed melting points of the TD III series. The TD III series has same mesogenic core as the TD I series; however, the sequence of the ester linking group of the TD III series is opposite of that of the TD I series. No mesophase was exhibited for the TD III series. A remarkable odd-even effect was shown for the melting points of the TD III series. These results

TABLE 3 Phase Transition Temperatures and Entropy Changes from a Nematic Phase to an Isotropic Melt of Twin Dimer IV Series

n	Heating			Cooling		
	$T_{Cr}/^{\circ}\text{C}$	$T_{NI}/^{\circ}\text{C}$	$\Delta S_{NI}/(\text{Jmol}^{-1}\text{K}^{-1})$	$T_{Cr}/^{\circ}\text{C}$	$T_{NI}/^{\circ}\text{C}$	$\Delta S_{NI}/(\text{Jmol}^{-1}\text{K}^{-1})$
2	190	192	4.0	182	192	5.2
3	156	—	—	141	—	—
4	206	—	—	200	—	—
5	125	—	—	105	109	1.6
6	149	167	11.4	133	167	11.5
7	141	—	—	77	117	3.7
8	155	—	—	109	149	10.8
9	159	—	—	51	120	6.0
10	147	—	—	132	139	9.6

T_{Cr} , melting point; T_{NI} , nematic-isotropic phase transition temperature; ΔS_{NI} , entropy changes based on the phase transition from a nematic phase to an isotropic melt.

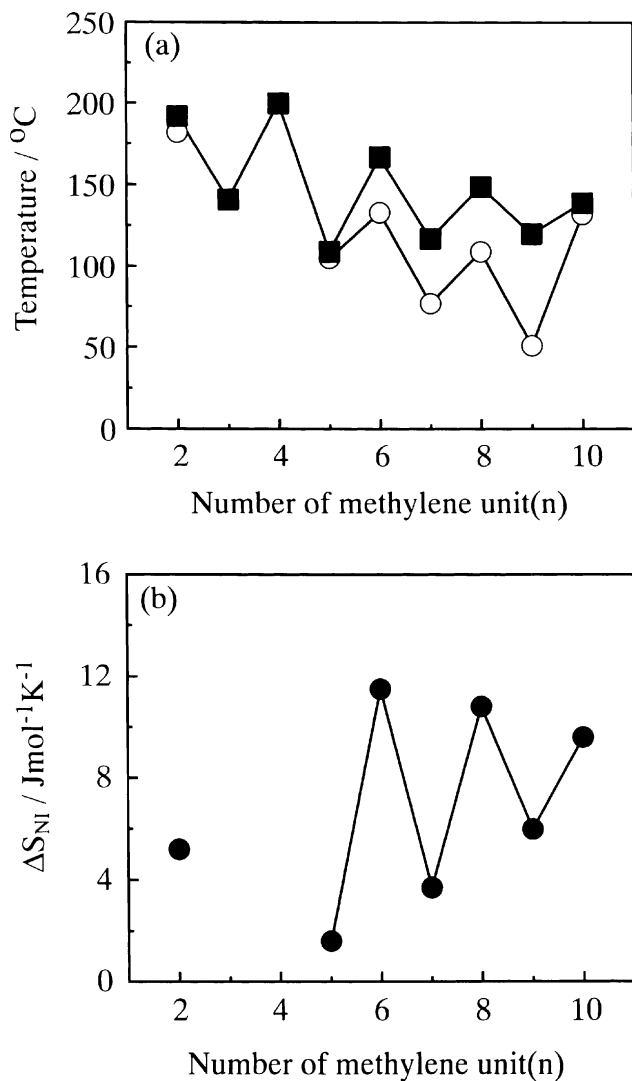


FIGURE 8 (a) Phase transition temperatures and (b) entropy changes of twin dimer IV series. Open circles and solid squares represent melting and clearing points, respectively. Closed circles indicate entropy changes based on the phase transition from nematic to isotropic phase.

suggested that the sequence of the ester linking group for the TD series played an important role to exhibit a mesophase. In the case of the twin dimer series, which has the same sequence of the ester linking group as our

TD III series, the orientation of the mesogenic groups in the smectic phase was controlled by the conformation of the flexible spacer [8]. On the other hand, our TD III series did not display any mesophases.

We prepared the TD IV and TD V series that had the ether linking group between the mesogenic group and the flexible methylene spacer. TD IV-2 and IV-6 exhibited an enantiotropic nematic phase, while a monotropic nematic phase was observed for the TD IV series with a longer methylene spacer ($n > 4$). Thermal properties of TD IV series are summarized in Table 3. Figure 8 displays phase transition temperatures and ΔS_{NI} for the TD IV series on the cooling run. A remarkable odd-even effect was observed for the clearing points, melting points, and ΔS_{NI} values. The TD IV series exhibited a nematic phase, while, as shown in Figure 9, no mesophases were exhibited for the TD V series that had the cyano group at the different position from TD IV series. The π -conjugated system from the oxygen to the cyano group for the TD I and TD IV was longer than that for the TD II and TD V. This result indicated that the position of cyano group in the mesogenic core played an important role in exhibiting a mesophase for the TD series with ether linking group.

With regard to exhibition of the mesophase, the TD I and TD IV series are superior to another TD series. The TD I and TD IV series had the sequence of o-phenyl group as a linking group and the cyano group near the terminal group of the mesogenic core. The π -conjugated length from the oxygen to the cyano group would influence the exhibition of the

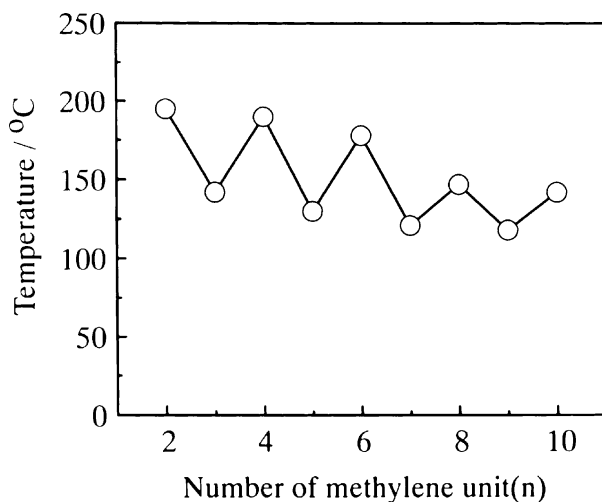


FIGURE 9 Phase transition temperatures of twin dimer V series. Open circles represent melting points.

mesophase for the TD series. In the case of the TD III series, the sequence of the linking group was opposite to that of the TD I series. The donation of the electron from the oxygen atom would not occur in the mesogenic group of the TD III series because the TD III series had the sequence of phenyl-carbonyl, as shown in Figure 1(b). The ΔS_{NI} for TD IV series displayed a remarkable odd-even effect. The ΔS_{NI} values of the TD IV with odd-membered series increased with increasing methylene spacer length, while that of the TD IV with even-membered series decreased with increasing methylene spacer length. As a result, the magnitude of the ΔS_{NI} values for the TD IV series became small. This result indicated that the conformational effect of the flexible spacer on the ΔS_{NI} values decreased with increasing flexible spacer length.

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