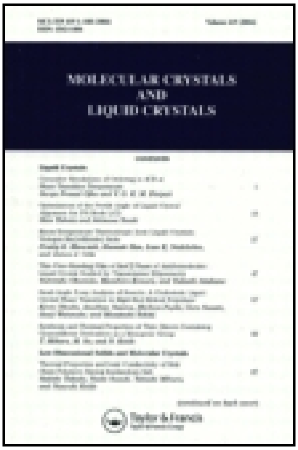

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Comparison of Liquid-Crystalline Properties of Symmetric and Nonsymmetric Liquid Crystal Trimers

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Comparison of Liquid-Crystalline Properties of Symmetric and Nonsymmetric Liquid Crystal Trimers

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A series of nonsymmetric liquid crystal trimers, ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-co-(4-cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylates, were prepared. The compounds exhibited enantiotropic nematic behavior. The melting points, the nematic–isotropic transition temperatures, and the entropy changes associated with the nematic–isotropic transition showed remarkable odd–even effects as the length of the spacers was varied, in which the even members exhibited higher values. The liquid-crystalline properties were compared with those of analogous symmetric trimers. The nematic–isotropic transition temperatures and the associated entropy changes of the nonsymmetric trimers exhibited lower values in comparison with those of the symmetric trimers.

Keywords: liquid crystals; melting point; nematic–isotropic transition; nonsymmetric trimers; odd–even effects

INTRODUCTION

Liquid crystal trimers are defined as molecules containing three mesogenic units joined by two flexible spacers [1] and have been extensively studied as model compounds for liquid-crystalline polymers [1–20]. A comparison of the liquid-crystalline properties of nonsymmetric and symmetric liquid crystal oligomers [4] containing trimers is of interest in connection with the effect of the symmetry of the molecules on the molecular aggregation and liquid-crystalline behavior. However, the investigations have dealt almost exclusively with nonsymmetric and symmetric liquid crystal dimers [4,13,17]. In the present article, data is presented that compare the liquid-crystalline

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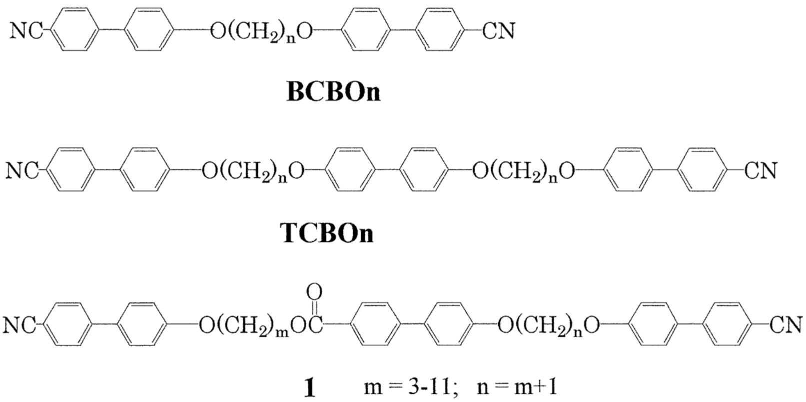


SCHEME 1 Structures of BCBOn, TCBOn, and compounds (**1**).

properties of nonsymmetric liquid crystal trimers with those of symmetric liquid crystal trimers.

4-Cyano-4′-alkoxybiphenyl derivatives are typical liquid-crystalline molecules. Furthermore, it is known that liquid crystal dimers containing two 4-cyanobiphenyl groups, such as BCBOn, exhibit unusual transition behavior [21,22]. In this connection, symmetric liquid crystal trimers such as TCBOn, which are derivatives of BCBOn and contain three biphenyl groups as the mesogenic units, have been prepared [1–3,6,14]. We report the synthesis and characterization of new nonsymmetric liquid crystal trimers (**1**) ($n = m + 1$, $m = 3$–11) containing three biphenyl groups as the mesogenic units (Scheme 1). The nonsymmetry of **1** was achieved by the introduction of one ester group into TCBOn. The thermodynamic data of **1** were compared with those of TCBOn, for which data are available [1].

EXPERIMENTAL

Elemental analyses were performed in the Analytical Center of Kyoto University. The ^{1}H NMR spectra (400 MHz) were obtained with a Jeol GSX 400 spectrometer. The chemical shifts (δ values) were measured in parts per million (ppm) downfield from tetramethylsilane as internal reference. The IR spectra were recorded with a Jasco FT / IR-420 spectrometer. The measurements in $CDCI_3$ were made at room temperature with a 0.1-mm KBr cell. Differential scanning calorimetry (DSC) measurements were carried out with a Shimadzu DSC-60. Microscopy observations were performed under a Nikon Eclipse E600 POL equipped with a hot stage (Linkam LK-600PH).

TABLE 1 Yields and IR Spectral Data of ω-(4-Cyanobiphenyl-4′-yloxy)alkyl 4′-Hydroxy-4-biophenylcarboxylate (**3**)

n	Yield (%)	cm^{-1} ($CDCl_3$)
3	53	3610, 2933, 2858, 2227, 1714, 1606, 1495, 1279, 1180
4	55	3602, 2935, 2856, 2227, 1712, 1605, 1495, 1279, 1180
5	57	3604, 2929, 2856, 2227, 1713, 1605, 1495, 1281, 1180
6	55	3604, 2936, 2860, 2227, 1713, 1605, 1495, 1279, 1180
7	50	3591, 2935, 2858, 2227, 1714, 1606, 1497, 1279, 1180
8	55	3593, 2933, 2858, 2227, 1714, 1606, 1497, 1280, 1180
9	52	3593, 2933, 2858, 2227, 1713, 1606, 1497, 1281, 1180
10	50	3596, 2931, 2856, 2227, 1711, 1606, 1495, 1281, 1180
11	48	3593, 2931, 2856, 2227, 1711, 1606, 1497, 1281, 1180

ω-(4-Cyanobiphenyl-4′-yloxy)alkyl 4′-Hydroxy-4-biophenylcarboxylate (3)

A mixture of α-bromo-ω-(4-cyanobiphenyl-4′yloxy)alkane (**2**) [23,24] (5.0 mmol) and 4′-hydroxy-4-biphenylcarboxylic acid (6.0 mmol) in N,N-dimethylformamide (200 ml) in the presence of K_2CO_3 (5.0 mmol) was stirred for 24 h at room temperature. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of chloroform resulted in the recovery of **2**. Further elution of a mixture of chloroform and methanol (9:1) gave **3**. The yields of **3** (n = 3–12) are shown in Table 1.

ω-(4-Cyanobiphenyl-4′-yloxy)alkyl 4′-[ω-(4-Cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylate (1)

A mixture of **2** (1.0 mmol) and **3** (1.0 mmol) in N,N-dimethylformamide (40 ml) in the presence of K_2CO_3 (1.0 mmol) was stirred for 24 h at room temperature. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of chloroform gave the liquid crystal trimers (**1**), and small amounts of **2** and **3** were also recovered. The yields of **1** ($n = m + 1$, $m = 3–11$) are shown in Table 2.

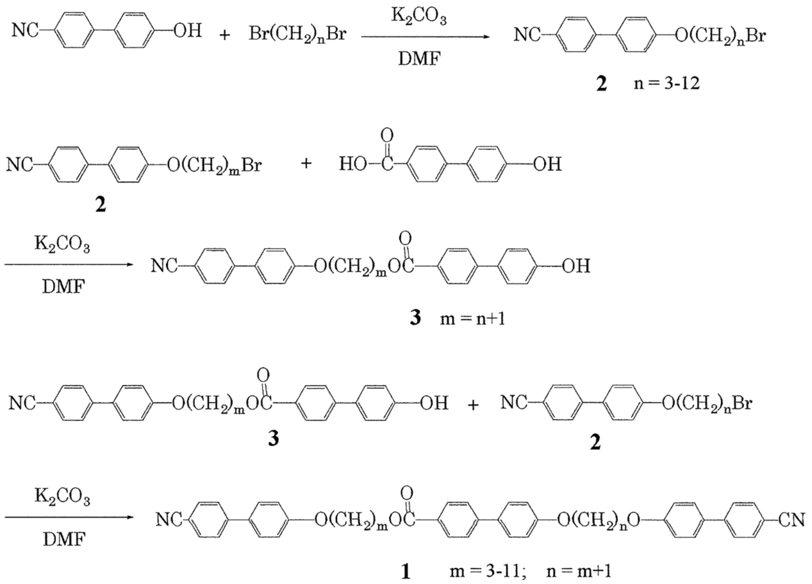
RESULTS AND DISCUSSION

Liquid crystal trimers contain two flexible spacers. To study the dependence of the flexible spacers of liquid crystal trimers on liquid-crystalline properties, a series of compounds (**1**) ($n = m + 1$) in which the number of atoms of the two flexible spacers is equal was prepared.

TABLE 2 Elemental Analyses and Yields of ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-[ω-(4-Cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylate **(1)**

m	n	Yield (%)	Calcd.	Found
3	4	64	$C_{46}H_{38}N_2O_5$: C, 79.06; H, 5.48; N, 4.01%	C, 78.83; H, 5.33; N, 3.39%
4	5	62	$C_{48}H_{42}N_2O_5$: C, 79.32; H, 5.82; N, 3.85%	C, 79.07; H, 5.83; N, 3.85%
5	6	63	$C_{50}H_{46}N_2O_5$: C, 79.55; H, 6.14; N, 3.71%	C, 79.39; H, 6.08; N, 3.65%
6	7	57	$C_{52}H_{50}N_2O_5$: C, 79.77; H, 6.44; N, 3.58%	C, 80.02; H, 6.44; N, 3.58%
7	8	60	$C_{54}H_{54}N_2O_5$: C, 79.77; H, 6.71; N, 3.45%	C, 79.99; H, 6.67; N, 3.48%
8	9	59	$C_{56}H_{58}N_2O_5$ 1/2 H_2O: C, 79.31; H, 7.01; N, 3.30%	C, 79.44; H, 6.91; N, 3.31%
9	10	59	$C_{58}H_{62}N_2O_5$: C, 80.34; H, 7.21; N, 3.23%	C, 80.44; H, 7.20; N, 3.19%
10	11	56	$C_{60}H_{66}N_2O_5 \cdot 1/2H_2O$: C, 79.70; H, 7.47; N, 3.10%	C, 79.65; H, 7.44; N, 3.07%
11	12	57	$C_{62}H_{70}N_2O_5 \cdot 1/2H_2O$: C, 79.88; H, 7.68; N, 3.00%	C, 79.98; H, 7.66; N, 3.03%

The new liquid crystal trimers were synthesized according to the procedure shown in Scheme 2. The reaction of 4-cyano-4′-hydroxybiphenyl with α,ω-dibromoalkanes gave α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkanes (**2**) [23,24]. The treatment of **2** with 4′-hydroxy-4-biphenylcarboxylic acid in N,N-dimethylformamide in the presence of



SCHEME 2 Synthesis of nonsymmetric liquid crystal trimers (**1**).

TABLE 3 ^{1}H NMR Spectral Data of ω-(4-Cyanobiphenyl-4′-yloxy)alkyl-4′-Hydroxy-4-biophenylcarboxylate (**3**)

n	δ (CDCl$_3$)
3	8.07 (d, 2H, $J = 8$ Hz), 7.69 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.53 (d, 2H, $J = 8$ Hz), 7.51 (d, 2H, $J = 8$ Hz), 7.00 (d, 2H, $J = 8$ Hz), 6.93 (d, 2H, $J = 8$ Hz), 4.98 (s, 1H, OH), 4.57 (t, 2H, $J = 6$ Hz), 4.21 (t, 2H, $J = 6$ Hz), 2.32 (quintet, 2H, $J = 6$ Hz).
4	8.06 (d, 2H, $J = 8$ Hz), 7.69 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.53 (d, 2H, $J = 8$ Hz), 7.51 (d, 2H, $J = 8$ Hz), 7.00 (d, 2H, $J = 8$ Hz), 6.93 (d, 2H, $J = 8$ Hz), 5.01 (s, 1H, OH), 4.44 (broad, 2H), 4.11 (broad, 2H), 2.01 (broad, 4H).
5	8.07 (d, 2H, $J = 8$ Hz), 7.69 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.52 (d, 2H, $J = 8$ Hz), 7.51 (d, 2H, $J = 8$ Hz), 6.99 (d, 2H, $J = 8$ Hz), 6.93 (d, 2H, $J = 8$ Hz), 4.96 (s, 1H, OH), 4.39 (t, 2H, $J = 6$ Hz), 4.06 (t, 2H, $J = 6$ Hz), 1.91 (quintet, 4H, $J = 6$ Hz), 1.68 (quintet, 2H, $J = 6$ Hz).
6	8.07 (d, 2H, $J = 8$ Hz), 7.68 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.51 (d, 4H, $J = 8$ Hz), 6.98 (d, 2H, $J = 8$ Hz), 6.92 (d, 2H, $J = 8$ Hz), 4.92 (s, 1H, OH), 4.36 (t, 2H, $J = 6$ Hz), 4.03 (t, 2H, $J = 6$ Hz), 1.84 (quintet, 4H, $J = 6$ Hz), 1.5–1.4 (m, 4H).
7	8.07 (d, 2H, $J = 8$ Hz), 7.68 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.52 (d, 4H, $J = 8$ Hz), 6.99 (d, 2H, $J = 8$ Hz), 6.92 (d, 2H, $J = 8$ Hz), 4.89 (s, 1H, OH), 4.35 (t, 2H, $J = 6$ Hz), 4.02 (t, 2H, $J = 6$ Hz), 1.82 (quintet, 4H, $J = 6$ Hz), 1.5–1.4 (m, 6H).
8	8.07 (d, 2H, $J = 8$ Hz), 7.68 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.51 (d, 4H, $J = 8$ Hz), 6.99 (d, 2H, $J = 8$ Hz), 6.92 (d, 2H, $J = 8$ Hz), 4.90 (s, 1H, OH), 4.34 (t, 2H, $J = 6$ Hz), 4.01 (t, 2H, $J = 6$ Hz), 1.82 (quintet, 4H, $J = 6$ Hz), 1.5–1.4 (m, 8H).
9	8.07 (d, 2H, $J = 8$ Hz), 7.68 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.52 (d, 4H, $J = 8$ Hz), 6.99 (d, 2H, $J = 8$ Hz), 6.92 (d, 2H, $J = 8$ Hz), 4.92 (s, 1H, OH), 4.33 (t, 2H, $J = 6$ Hz), 4.01 (t, 2H, $J = 6$ Hz), 1.80 (quintet, 4H, $J = 6$ Hz), 1.6–1.4 (m, 10H).
10	8.07 (d, 2H, $J = 8$ Hz), 7.68 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.52 (d, 4H, $J = 8$ Hz), 6.99 (d, 2H, $J = 8$ Hz), 6.92 (d, 2H, $J = 8$ Hz), 4.86 (s, 1H, OH), 4.33 (t, 2H, $J = 6$ Hz), 4.00 (t, 2H, $J = 6$ Hz), 1.79 (quintet, 4H, $J = 6$ Hz), 1.6–1.4 (m, 12H).
11	8.07 (d, 2H, $J = 8$ Hz), 7.69 (d, 2H, $J = 8$ Hz), 7.63 (d, 2H, $J = 8$ Hz), 7.60 (d, 2H, $J = 8$ Hz), 7.52 (d, 4H, $J = 8$ Hz), 6.99 (d, 2H, $J = 8$ Hz), 6.92 (d, 2H, $J = 8$ Hz), 4.84 (s, 1H, OH), 4.33 (t, 2H, $J = 6$ Hz), 4.00 (t, 2H, $J = 6$ Hz), 1.79 (quintet, 4H, $J = 6$ Hz), 1.6–1.4 (m, 14H).

K_2CO_3 gave compounds **3**. The IR spectral data of **3** showed the presence of a phenolic OH group at ca. $3600\,cm^{-1}$ and an ester group at $1711–1715\,cm^{-1}$ (Table 1). The ^{1}H NMR spectral data of **3** are summarized in Table 3. The absorptions of **3** at δ 4.84–5.03 (s, 1H, D_2O exchangeable) were assigned to the phenolic OH. These IR and ^{1}H NMR spectral data suggest that the structures of **3** were ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-hydroxy-4-biophenylcarboxylates, not 4′-[ω-(4-cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylic acids. The reaction of **3** with **2** in N,N-dimethylformamide in the presence of K_2CO_3 gave a new liquid crystal, trimer (**1**). The yields and the elemental analyses of **1** ($n = m + 1$, $m = 3–11$) are shown in Table 2. The structures of **1** were further confirmed on the basis of IR spectral data (Table 4) and ^{1}H NMR spectral data (Table 5).

The thermal mesomorphic phases of **1** ($n = m + 1$, $n = 3–11$) were analyzed by means of differential scanning calorimetry (DSC) and polarizing microscopy. All the compounds exhibited enantiotropic nematic behaviors. The nematic phases had a Schlieren optical texture. The transition properties of **1** are listed in Table 6. The thermodynamic data of **1** were compared with those of TCBOn [1]. Figure 1 shows the dependence of the transition temperatures on the number (k) of atoms of the flexible spacers for **1** and TCBOn. In Table 1, k is $n + 2$ and $m + 3$ for **1** and k is $n + 2$ for TCBOn. The melting points and nematic–isotropic transition temperatures of both **1** and TCBOn exhibited an odd–even effect as the number (k) of atoms of the flexible spacers was varied, in which the even numbers exhibited higher values. The odd–even effects of TCBOn are explained on the basis of the all-*trans* conformation [1]. The odd–even effects of **1** and TCBOn were similar to each other, but the nematic–isotropic

TABLE 4 IR Spectral Data of ω-(4-cyanobiphenyl-4′-yloxy)alkyl 4′-[ω-(4-Cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylate **(1)**

m	n	cm^{-1} ($CDCl_3$)
3	4	2940, 2875, 2228, 1714, 1605, 1495, 1396, 1279, 1248, 1180, 1115
4	5	2940, 2873, 2227, 1714, 1606, 1495, 1396, 1277, 1248, 1180, 1115
5	6	2941, 2875, 2227, 1714, 1605, 1495, 1396, 1279, 1248, 1180, 1115
6	7	2941, 2862, 2227, 1711, 1606, 1495, 1396, 1279, 1248, 1180, 1115
7	8	2937, 2860, 2227, 1713, 1606, 1495, 1394, 1279, 1248, 1180, 1115
8	9	2935, 2858, 2227, 1714, 1606, 1495, 1394, 1280, 1248, 1180, 1115
9	10	2933, 2858, 2227, 1711, 1605, 1495, 1394, 1279, 1248, 1180, 1115
10	11	2931, 2856, 2227, 1711, 1606, 1495, 1392, 1281, 1250, 1180, 1115
11	12	2929, 2856, 2227, 1712, 1606, 1495, 1396, 1281, 1250, 1180, 1115

TABLE 5 ^{1}H NMR Spectral Data of ω-(4-Cyanobiphenyl-4′-yloxy)alkyl 4′-[ω-(4-Cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylate (**1**)

m	n	δ ($CDCl_3$)
3	4	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.04–6.98 (m, 6H), 4.56 (t, 2H, $J = 6$ Hz), 4.3–4.1 (m, 6H), 2.32 (quintet, 2H, $J = 6$ Hz), 2.04 (broad 4H).
4	5	8.06 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.03–6.96 (m, 6H), 4.44 (t, 2H, $J = 6$ Hz), 4.11 (t, 2H, $J = 6$ Hz), 4.06 (t, 4H, $J = 6$ Hz), 2.01 (broad 4H), 1.92 (quintet, 4H, $J = 6.0$ HZ), 1.71 (quintet, 2H, $J = 6$ Hz).
5	6	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.05–6.95 (m, 6H), 4.39 (t, 2H, $J = 6$ Hz), 4.06 (t, 2H, $J = 6$ Hz), 4.04 (t, 4H, $J = 6$ Hz), 1.87 (m, 4H), 1.6–1.5 (m, 12H).
6	7	8.06 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.00–6.95 (m, 6H), 4.36 (t, 2H, $J = 6$ Hz), 4.03 (t, 2H, $J = 6$ Hz), 4.02 (t, 2H, $J = 6$ Hz), 4.01 (t, 2H, $J = 6$ Hz), 1.84 (m, 4H), 1.6–1.4 (m, 16H).
7	8	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.00–6.96 (m, 6H), 4.35 (t, 2H, $J = 6$ Hz), 4.02 (t, 6H, $J = 6$ Hz), 1.83 (m, 4H), 1.6–1.3 (m, 18H).
8	9	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.00–6.96 (m, 6H), 4.34 (t, 2H, $J = 6$ Hz), 4.01 (t, 2H, $J = 6$ Hz), 4.00 (t, 4H, $J = 6$ Hz), 1.81 (m, 4H), 1.6–1.3 (m, 22H).
9	10	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.00–6.96 (m, 6H), 4.33 (t, 2H, $J = 6$ Hz), 4.00 (t, 6H, $J = 6$ Hz), 1.81 (m, 4H), 1.6–1.3 (m, 26H).
10	11	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.00–6.96 (m, 6H), 4.33 (t, 2H, $J = 6.5$ Hz), 4.00 (t, 6H, $J = 6.5$ Hz), 1.81 (m, 4H), 1.6–1.3 (m, 30H).
11	12	8.07 (d, 2H, $J = 8$ Hz), 7.7–7.5 (m, 16H), 7.00–6.96 (m, 6H), 4.33 (t, 2H, $J = 6.5$ Hz), 4.00 (t, 6H, $J = 6.5$ Hz), 1.81 (m, 4H), 1.6–1.3 (m, 34H).

TABLE 6 Transition Properties of ω-(4-Cyanobiplienyl-4′-yloxy)alkyl-4′-[ω-(4-Cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylate (**1**)

m	n	T_{CN} (°C)	T_{NI} (°C)	$\Delta S_{CN}/R$	$\Delta S_{NI}/R$
3	4	210	279	13.6	2.48
4	5	168	178	14.5	0.35
5	6	211	248	14.0	2.79
6	7	163	177	16.0	0.43
7	8	202	214	12.5	2.84
8	9	149	171	16.8	0.81
9	10	179	195	17.5	2.85
10	11	144	164	19.0	1.07
11	12	160	176	19.2	3.32

CN: melting point; NI: nematic–isotropic transition.

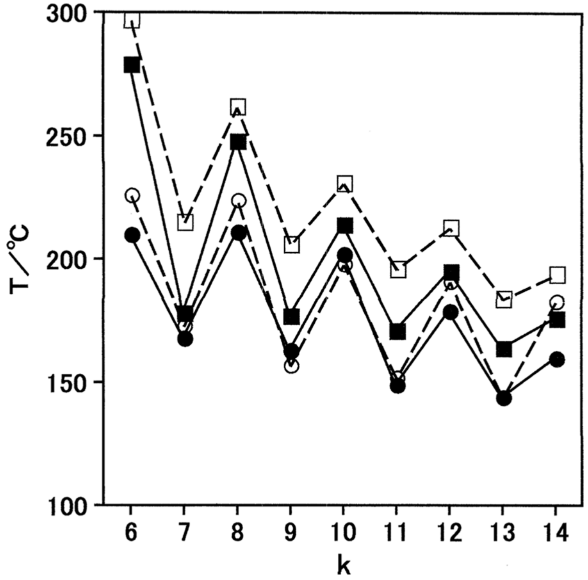


FIGURE 1 Dependence of the transition temperatures on number (k) of atoms of flexible spacers for compounds **(1)** and TCBOn. k = m + 3 = n + 2 for compounds **(1)** and k = n + 2 for TCBOn [1]. ●: melting points of TCBOn. ■: nematic–isotropic/transition temperatures of compounds **(1)**. □: nematic–isotropic transition temperatures of TCBOn.

transition temperatures of **1** clearly exhibited lower values in comparison with those of TCBOn.

Figure 2 shows the dependence of the entropy change ($\Delta S_{CN}/R$) associated with the melting transition on the number (k) of atoms of the flexible spacers for **1** and TCBOn. In spite of the observation of the odd–even effects of the melting points (Fig. 1), Fig. 2 did not show similar odd–even effects. However, $\Delta S_{CN}/R$ of **1** roughly exhibited lower values in comparison with those of TCBOn. Figure 3 shows the dependence of the entropy change ($\Delta S_{NI}/R$) associated with the nematic–isotropic transition on the number (k) of atoms of the flexible spacers for **1** and TCBOn. Figure 3 unquestionably shows the odd–even effects of $\Delta S_{NI}/R$ for **1** and TCBOn. The odd–even effects of **1** closely resembled those of TCBOn. On the other hand, it can be seen from Figs. 1 and 3 that the nematic–isotropic transition temperatures and the values of $\Delta S_{NI}/R$ of **1** were clearly lower than those of TCBOn. It is thought that the differences between **1** and TCBOn result from polarizability and shape of the liquid-crystalline molecules.

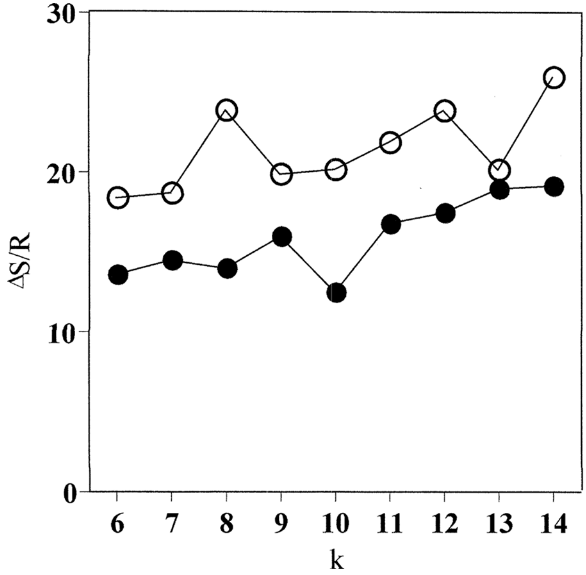


FIGURE 2 Dependence of entropy change associated with melting point on number (k) of atoms of flexible spacers for compounds **(1)** and TCBOn. $k = m + 3 = n + 2$ for compounds **(1)** and $k = n + 2$ for TCBOn [1]. ●: Compounds (**1**). ○: TCBOn.

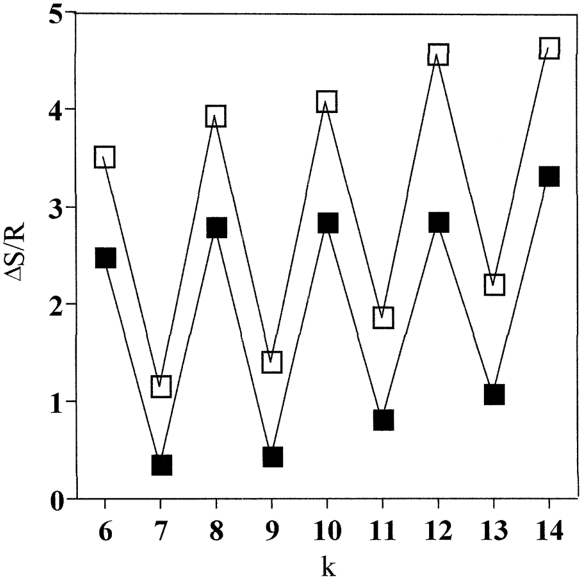


FIGURE 3 Dependence of entropy change associated with nematic–isotropic transition on number (k) of atoms of flexible spacers for compounds **(1)** and TCBOn. k = m + 3 = n + 2 for compounds **(1)** and k = n + 2 for TCBOn [1]. ■: compounds (**1**). □: TCBOn.

CONCLUSION

A series of nonsymmetric liquid crystal trimers, ω-(4-cyanobiphenyl-4′ yloxy)alkyl 4′-[ω-(4-cyanobiphenyl-4′-yloxy)alkoxy]-4-biphenylcarboxylates, were prepared from 4-cyano-4′-hydroxybiphenyl, 4′-hydroxy-4-biphenylcarboxylic acid, and α,ω-dibromoalkanes. Compounds (**1**) (n = m + 1) exhibited enantiotropic nematic behavior. The transition properties of **1** were compared with those of symmetric liquid crystal trimers, such as TCBOn. The melting points, the nematic–isotropic transition temperatures, and the entropy change associated with the nematic–isotropic transition (ΔS_{NI} / R) of both **1** and TCBOn exhibited an odd–even effect as the number (k) of atoms of the flexible spacers was varied, in which the even numbers exhibited higher values, although the entropy change associated with the melting transition (ΔS_{CN} / R) did not exhibit an odd–even effect. The odd–even effects of **1** and TCBOn were similar to each other, but the nematic–isotropic transition temperatures and ΔS_{NI}/R of **1** clearly exhibited lower values in comparison with those of TCBOn. Therefore, it may be concluded from the results of this investigation that the introduction of nonsymmetry into the symmetric liquid crystal trimer will result in a lowering of the nematic–isotropic transition temperatures and the associated entropy changes.

REFERENCES

[1] Imrie, C. T. & Luckhurst, G. R. (1998). *J. Mater. Chem.*, *8*, 1339.
[2] Furuya, H., Asahi, K., & Abe, A. (l986). *Poly. J.*, *18*, 779.
[3] Tsvetkov, N. V., Zuev, V. V., & Tsvetkov, V. N. (1997). *Liq. Cryst.*, *22*, 245.
[4] Imrie, C. T. & Luckhurst, G. R. (1998). In: *Handbook of Liquid Crystals*, Demus, D., Goodby, J., Gray, W. G., Spiess, H. W., & Vill, V. (Eds.), Vol. 2B, Chapter X, Wiley-VCH: Weinheim and references therein, 801.
[5] Liu, P., He, C, Booth, C. J., & Griffin, A. C. (1999). *Mol. Cryst. Liq. Cryst.*, *332*, 243.
[6] Abe, A., Takeda, T., Hiejima, T., & Furuya, H. (l999). *Poly. J.*, *31*, 728.
[7] Kumar, S. & Manickam, M. (1999). *Liq. Cryst.*, *26*, 939.
[8] Kang, D. S., Mahajan, M. P., Zhang, S. Y., Petschek, R. G., Rosenblatt, C., He, C. B., Liu, P. W., & Griffin, A. C. (1999). *Phys. Rev. E*, *60*, 4980.
[9] Yelamaggad, C. V., Hiremath, U. S., & Prasad, S. K. (2000). *Chem. Commun.*, 57.
[10] Sentman, A. C. & Gin, D. L. (200l). *Adv. Mater.*, *13*, 1398.
[11] Yelamaggad, C. V., Nagamani, S. A., Rao, D. S. S., & Prasad, S. K. (2001). *J. Chem. Res.*, 493.
[12] Yelamaggad, C. V., Nagamani, S. A., Hiremath, U. S., Rao, D. S. S., & Prasad, S. K. (2001). *Liq. Cryst.*, *28*, 1581.
[13] Imrie, C. T. & Henderson, P. A. (2002). *Curr. Opin. Colloid Interface Sci.*, *7*, 298.
[14] Abe, A., Hiejima, T., Takeda, T., & Nakafuji, C. (2003). *Polymer*, *44*, 3117.
[15] Henderson, P. A., Cook, A. G., & Imrie, C. T. (2004). *Liq. Cryst.*, *31*, 1427.
[16] Imrie, C. T., Henderson, P. A., & Seddon, J. M. (2004). *J. Mat. Chem.*, *14*, 2486.
[17] Abe, A., Furuya, H., Zhou, Z. P., Hiejima, T., & Kobayashi, Y. (2005). *Adv. Polym. Sci.*, *181*, 121.
[18] Imrie, C. T. & Henderson, P. A. (2005). *Liq. Cryst.*, *32*, 673.
[19] Yoshizawa, A., Kinbara, H., Narumi, T., Yamaguchi, A., & Dewa, H. (2005). *Liq. Cryst.*, *32*, 1175.
[20] Yoshizawa, A., Nakata, M., & Yamaguchi, A. (2006). *Liq. Cryst.*, *33*, 605.
[21] Emsley, J. E., Luckhurst, G. R., Shilstone, G. N., & Sage, I. (1984). *Mol. Cryst. Liq. Cryst. Lett.*, *102*, 223.
[22] Ferrarini, A., Luckhurst, G. R., Nordio, P. L., & Roskilly, S. J. (1993). *Chem. Phys. Lett.*, *214*, 409.
[23] Attard, G. S., Imrie, C. T., & Karasz, F. E. (1992). *Chem. Mater.*, *4*, 1246.
[24] Itahara, T. (2005). *Liq. Cryst.*, *32*, 115.