Effect of terminal aryl rings of liquid crystal trimers on liquid crystalline properties

Toshio Itahara*

Faculty of Engineering, Kagoshima University, Kagoshima, Japan

(Received 7 January 2014; accepted 23 February 2014)

Liquid crystalline properties of five series of biphenyl derivatives connected with p-nitrophenyl, phenyl, 2-naphthyl, 9-phenanthryl and bromo as the terminal groups via flexible spacers were studied. All the compounds exhibited nematic phase. The nematic–isotropic or isotropic–nematic transition properties resulted in an odd–even effect as the length of the spacers was varied, in which the even members exhibited higher values, for the compounds with p-nitrophenyl, phenyl, 2-naphthyl and 9-phenanthryl groups, while the transitional properties of the compounds substituted with bromo atom as the terminal group instead of the aryl groups did not show such odd–even effect. These results suggest that the aryl rings, such as p-nitrophenyl, phenyl, 2-naphthyl and 9-phenanthryl groups, play a role of mesogen while the terminal bromo atom does not. The effect of the terminal aryl rings on the liquid crystalline properties will be reported.

Keywords: liquid crystal trimer; terminal aryl group; odd–even effect; nematic liquid crystals

1. Introduction

Most of the rod-like liquid crystalline compounds consist of two or more rings, which are bonded directly to one another or connected by linking groups. The rings form the core of the liquid crystalline compounds and the major anisotropy of the compounds, which is necessary for their mesogenisity, results from the core. Therefore, it is important to develop a means to experimentally evaluate the role of the rings as mesogen. In the previous paper, we prepared the nematogens (1) and estimated the role of the p-nitrophenyl group as the mesogen on the basis of odd–even effect of the flexible spacer between the p-nitrophenyl and the biphenyl groups. Similar technique may be applicable to a comparison of the role of terminal rings as mesogen. The outline of the concept is shown in Scheme 1. An odd–even effect of the flexible spacers between the terminal aryl group (X) and the biphenyl group on liquid crystalline properties will be measured, when the terminal ring (X in Scheme 1) plays a role of mesogen. The relationship between the odd–even effect and the structures of the terminal aryl groups was studied.

The remarkable odd–even effect of the flexible spacer between the mesogenic units on liquid crystalline properties is known as the typical behaviour for liquid crystal dimers and trimers, which are the molecules containing two and three mesogenic groups linked flexible spacers, respectively. In the present investigation, four series of compounds (2), (3), (4) and (5) were synthesised (Scheme 2). The transitional properties of series 1, 2, 3 and 4 were studied in order to compare the role of the aryl groups as mesogen, namely 1 (X = p-nitrophenyl), 2 (X = phenyl), 3 (X = 2-naphthyl) and 4 (X = 9-phenanthryl). Various liquid crystal trimers have been prepared since the first report by Imrie and Luckhurst and series 1, 2, 3 and 4 are looked upon as liquid crystal trimers with the terminal aryl groups as the mesogens. Furthermore, the transitional properties of series 5 (X = Br) were compared with those of series 1, 2, 3 and 4. The interesting transitional properties of the nematogens connected with a terminal phenyl group via flexible spacers had been reported by Gray et al., Ennulat et al. and Zannoni et al. Various liquid crystalline molecules containing 2-naphthyl group are also known. However, little attention has been paid to liquid crystalline compounds connected with a terminal 9-phenanthryl group.

2. Experimental details

2.1 Characterisation

Elemental analyses were performed at the Analytical Center of Kyushu University. 1H-NMR spectra (400 MHz) were obtained with a JEOL GSX 400 spectrometer (JEOL Ltd., Tokyo, Japan). The chemical shifts (δ-values) were measured in parts per million (ppm) down-field from tetramethylsilane as an internal reference. Infrared (IR) spectra were recorded with a JASCO FT/IR-420 spectrometer (JASCO Ltd, Tokyo, Japan). Measurements in CDCl3 were made with a 0.1 mm KBr cell. Differential scanning calorimetry (DSC) measurements were carried out with a Shimadzu DSC-60 (Shimadzu Ltd., Kyoto, Japan).

*Email: itahara@be.kagoshima-u.ac.jp

© 2014 Taylor & Francis
Polarising microscopy observations were performed under a Nikon Eclipse E600 POL (Nikon Ltd., Tokyo, Japan) equipped with a hot stage (Linkam LK-600PH; Linkam Scientific Instruments Ltd., Surrey, UK).

2.2 Synthesis

11-(4-cyanobiphenyl-4′-yloxy)undecyl 4′-(ω-bromoalkoxy)-4-biphenylcarboxylate (5)

A mixture of 11-(4-cyanobiphenyl-4′-yloxy)undecyl 4′-hydroxy-4-biphenylcarboxylate [22] (1 mmol) and α,ω-dibromalkane \( (n = 4–12) \) (2 mmol) in \( N,N\)-dimethylformamide (DMF) (50 mL) in the presence of K2CO3 (1 mmol) was stirred at room temperature for 8 h. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of a mixture of chloroform and hexane gave 5a-i in 65–73% yield, although the synthesis of 5h had been already reported.[23]

5a \( (n = 4) \): IR (CDCl3, cm⁻¹) 2931, 2856, 2227 (cyano, CN), 1714 (COO), 1606, 1524, 1495, 1471, 1279, 1248, 1182, 1115. 1H NMR (CDCl3, ppm) \( \delta \) 8.08 (d, 2H, \( J = 8.0 \) Hz), 7.69–7.51 (m, 8H), 7.00–6.97 (m, 6H), 4.33 (t, 2H, \( J = 6.4 \) Hz), 4.05 (t, 2H, \( J = 6.4 \) Hz), 4.00 (t, 2H, \( J = 6.4 \) Hz), 3.51 (t, 2H, \( J = 6.4 \) Hz), 2.15–1.95 (m, 4H), 1.85–1.75 (m, 4H), 1.5–1.3 (m, 14H). Anal. Calcd for C41H46NO4Br: C, 70.68; H, 6.65; N, 2.01%. Found: C, 70.82; H, 6.66; N, 2.01%.

Odd–even effect

| \( X \) | = phenyl, \( p \)-nitrophenyl, 2-naphthyl, 9-phenanthryl |

Scheme 1. The comparison of the role of terminal aryl groups (\( X \)) as mesogen on the basis of odd–even effect.

A mixture of 11-(4-cyanobiphenyl-4′-yloxy)undecyl 4′-hydroxy-4-biphenylcarboxylate [22] (1 mmol) and \( \alpha,\omega \)-dibromalkane \( (n = 4–12) \) (2 mmol) in \( N,N\)-dimethylformamide (DMF) (50 mL) in the presence of K2CO3 (1 mmol) was stirred at room temperature for 8 h. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of a mixture of chloroform and hexane gave 5a-i in 65–73% yield, although the synthesis of 5h had been already reported.[23]

11-(4-cyanobiphenyl-4′-yloxy)undecyl 4′-(ω-bromoalkoxy)-4-biphenylcarboxylate (2)

A mixture of 5a-g (0.5 mmol) and phenol (1 mmol) in DMF (25 mL) in the presence of K2CO3 (0.5 mmol) was stirred at room temperature for 24 h. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of chloroform gave 2a-g in 37–44% yield.

2g \( (n = 10) \): IR (CDCl3, cm⁻¹) 2931, 2856, 2227 (CN), 1709 (ester, OCO), 1604, 1523, 1496, 1471,
1390, 1279, 1182, 1115. $^1$H NMR (CDCl$_3$, ppm) $\delta$ 8.08 (d, 2H, $J$ = 8.0 Hz), 7.70–7.50 (m, 10H), 7.32–7.25 (m, 2H), 7.00–6.88 (m, 7H), 4.33 (t, 2H, $J$ = 6.4 Hz), 4.00 (t, 4H, $J$ = 6.4 Hz), 3.95 (t, 2H, $J$ = 6.4 Hz), 1.90–1.75 (m, 8H), 1.5–1.3 (m, 26H). Anal. Calcd for C$_{53}$H$_{63}$NO$_5$: C, 80.17; H, 8.00; N, 1.76%. Found: C, 80.43; H, 6.98; N, 1.85%.

11-(4-cyanobiphenyl-4'-oxy)undecyl 4'-(o-(naphthyl-2-oxy)alkoxy)-4-biphenylcarboxylate (3)

A mixture of 5a-i (0.5 mmol) and β-naphthol (1 mmol) in DMF (25 mL) in the presence of K$_2$CO$_3$ (0.5 mmol) was stirred at room temperature for 24 h. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of chloroform gave 3a-i in 43–53% yield.

3a ($n$ = 4): IR (CDCl$_3$, cm$^{-1}$) 2931, 2856, 2227 (CN), 1709 (OCO), 1604, 1496, 1468, 1389, 1279, 1248, 1217, 1182, 1119. $^1$H NMR (CDCl$_3$, ppm) $\delta$ 8.08 (d, 2H, $J$ = 8.0 Hz), 7.8–7.5 (m, 13H), 7.43 (t, 1H, $J$ = 8.0 Hz), 7.33 (t, 1H, $J$ = 8 Hz), 7.17–7.12 (m, 2H), 7.02–6.95 (m, 4H), 4.33 (t, 2H, $J$ = 6.4 Hz), 4.18 (t, 2H, $J$ = 6.4 Hz), 4.12 (t, 2H, $J$ = 6.4 Hz), 4.00 (t, 2H, $J$ = 6.4 Hz), 2.10–2.05 (m, 4H), 1.85–1.75 (m, 4H), 1.5–1.3 (m, 14H). Anal. Calcd for C$_{41}$H$_{33}$NO$_5$: C, 80.60; H, 7.03; N 1.84%. Found: C, 80.43; H, 6.98; N, 1.85%.

11-(4-cyanobiphenyl-4'-oxy)undecyl 4'-(o-(phenanthryl-9-oxy)alkoxy)-4-biphenylcarboxylate (4)

A mixture of 5a-g (0.5 mmol) and 9-phenanthrol (1 mmol) in DMF (25 mL) in the presence of K$_2$CO$_3$ (0.5 mmol) was stirred at room temperature for 24 h. The reaction mixture was evaporated to give a residue, which was chromatographed over silica gel. Elution of chloroform gave 4a-g in 28–32% yield.

4g ($n$ = 10): IR (CDCl$_3$, cm$^{-1}$) 2931, 2856, 2227 (CN), 1709 (OCO), 1606, 1525, 1496, 1452, 1281, 1248, 1182, 1119. $^1$H NMR (CDCl$_3$, ppm) $\delta$ 8.65 (d, 1H, $J$ = 8.0 Hz), 8.58 (d, 1H, $J$ = 8.0 Hz), 8.37 (dd, 1H, $H$ = 8.0 Hz, $J$ = 1.5 Hz), 8.08 (d, 2H, $J$ = 8.0 Hz), 7.75–7.45 (m, 15H), 7.05–6.95 (m, 5H), 4.33 (t, 2H, $J$ = 6.4 Hz), 4.24 (t, 2H, $J$ = 6.4 Hz), 4.00 (t, 4H, $J$ = 6.4 Hz), 1.98 (quintet, 2H, $J$ = 6.4 Hz), 1.9–1.3 (m, 32H). Anal. Calcd for C$_{63}$H$_{67}$NO$_5$: C, 81.94; H, 7.55; N 1.57%. Found: C, 81.96; H, 7.52; N, 1.62%. The elemental analyses and spectral data of 2a-f, 3b-i, 4a-f and 5b-g,i are shown as Supplemental data.

3. Results

We previously reported the synthesis of 5h ($n$ = 11).[23] Compounds 5a-g,i ($n$ = 4–10 and 12) were prepared according to a procedure similar to the synthesis of 5h. New series of compounds (2a-g), (3a-i) and (4a-g) were prepared by reactions of series 5 with phenol, β-naphthol and 9-phenanthrol, respectively. The structures of the new compounds were characterised by elemental analyses, $^1$H-NMR and IR spectral data.

The thermal mesomorphic phases of series 2, 3, 4 and 5 were investigated by DSC and polarising microscopy (POM). All the compounds containing series 1[2] exhibited nematic phase, although series 5 showed nematic and S$_A$ phases. The textures of the liquid crystals of 1a, 2a, 3a, 4a and 5a are shown in Figure 1.

The transitional properties of series 5 are summarised in Table 1. The peaks of the S$_A$-nematic transition were very small, but the peaks of nematic–isotropic transition were observed clearly (Figure 2). Previously we reported the odd–even effect of the number ($n$) of carbon atoms in the alkyl chains on the nematic–isotropic transitional properties for series 1.[2] However, the nematic–isotropic transition temperature and the entropy changes associated with the transition depend on the length of the flexible spacer but does not result in such odd–even effect for series 5 (Figure 2 and Table 1). These results indicate that the bromo atom of series 5 does not work as mesogen, although the odd–even effect of the bromine-terminated chains was already reported in relation to that of the methyl-terminated chains.[24] Furthermore, it is interesting to note that their entropy changes of series 5 are characteristic of those seen for dimers.[25]

The compounds (2d), (2e) and (2f) displayed nematic liquid crystal upon both heating and cooling. On the other hand, 2a, 2b, 2c and 2g exhibited nematic phase upon cooling but did not show liquid crystalline properties upon heating. The transitional properties of series 2, 3 and 4 are summarised in Table 2. The isotropic–nematic transition temperature upon cooling is a little lower than the nematic–isotropic transition temperature upon heating, but the associated entropy changes are substantially the same as those of the nematic–isotropic transition for 2d, 2e and 2f. Therefore, we studied the isotropic–nematic transition upon cooling for series 2. Figure 3 shows the DSC thermogram of series 2 upon cooling. The isotropic–nematic transition temperature showed an odd–even effect as the length of the spacers was varied. On the basis of these data, it seems reasonable to assume that the terminal phenyl group of series 2 plays the role of mesogen, although similar odd–even effect of the nematogens connected with the terminal phenyl group are known.[11–14]

The compounds (3a–f), (3h) and (4d–f) displayed nematic liquid crystal upon both heating and cooling. However, 3g, 3i, 4a–c and 4g exhibited nematic phase upon cooling but did not show liquid crystalline properties upon heating. Therefore, the isotropic–nematic transitions were compared for series 3 and 4. Figures 4 and 5 show the DSC thermograms of series
3 and 4 upon cooling, respectively. The isotropic–nematic transition temperature of series 3 and 4 resulted in an odd–even effect as the length of the spacers was varied, in which the even members exhibited higher values. These results suggest that the 2-naphthyl and the 9-phenanthryl groups play a role of mesogen.

The dependence of the transition temperature on the number (n) of carbon atoms in the alkyl chains for series 1, 2, 3 and 4 is illustrated in Figure 6. Although the melting temperature complicate the dependence (Figure 6b), the nematic-isotropic or the isotropic–nematic transition temperature exerts a clear odd–even effect on varying the length and parity of the flexible spacers (Figure 6a). So, we feel a interest in the differences between the odd members and the even members in the nematic–isotropic or the isotropic–nematic transition temperature. However, the differences between the odd members and the even members are attenuated on increasing the number (n) of carbon atoms. Therefore, we estimated the average of the differences between $n = 4$ and $n = 10$. The averages are as follows; ca. 15°C for series 1, ca. 10°C for series 2, ca. 19°C for series 3 and ca. 17.5°C for series 4. However, it can be seen from Figure 6a that the clearing temperatures of series 1, series 3, series 2 and series 4 decrease in that order. It is interesting that series 4 has lower clearing temperatures than series 2.

Table 1. The transitional properties of series 5.

|       | MP/°C | S-N | N-I | ΔSmp/R | ΔSs-n/R | ΔSn-I/R |
|-------|-------|-----|-----|---------|---------|---------|
| S5a   | 128   | 133 | 139 | 14.2    | 0.21    | 1.74    |
| S5b   | 123   | 133 | 136 | 14.8    | 0.29    | 1.77    |
| S5c   | 119   | 130 | 135 | 15.5    | 0.23    | 1.88    |
| S5d   | 109   | 126 | 132 | 15.8    | 0.20    | 1.94    |
| S5e   | 113   | 119 | 129 | 16.0    | 0.09    | 1.98    |
| S5f   | 106   | 112 | 127 | 16.3    | 0.05    | 1.98    |
| S5g   | 115   | –   | 125 | 19.3    | –       | 2.03    |
| S5h   | 106   | –   | 123 | 17.9    | –       | 2.07    |
| S5i   | 117   | –   | 122 | 21.9    | –       | 2.08    |

Note: MP: melting point. S-N: $S_A$-nematic transition. N-I: nematic–isotropic transition.
Table 2. The transitional properties of series 2, 3 and 4.

|   | MP/ºC | N-I | I-N | ΔSmp/R  | ΔS₁-N/R |
|---|-------|-----|-----|---------|---------|
| 2a | 143   | –   | 137 | 20.7    | 2.35    |
| 2b | 125   | –   | 120 | 18.1    | 1.91    |
| 2c | 133   | –   | 130 | 21.6    | 2.42    |
| 2d | 96    | 119 | 117 | 12.8    | 1.94    |
| 2e | 121   | 127 | 125 | 12.9    | 2.40    |
| 2f | 102   | 119 | 116 | 20.0    | 1.98    |
| 2g | 129   | –   | 120 | 26.0    | 2.45    |
| 3a | 151   | 160 | 158 | 16.4    | 2.72    |
| 3b | 112   | 127 | 125 | 16.0    | 1.85    |
| 3c | 130   | 150 | 148 | 12.0    | 2.93    |
| 3d | 100   | 130 | 128 | 12.4    | 1.97    |
| 3e | 128   | 144 | 142 | 23.0    | 3.03    |
| 3f | 97    | 130 | 128 | 15.7    | 2.07    |
| 3g | 138   | –   | 137 | 25.6    | 3.10    |
| 3h | 119   | 129 | 127 | 23.2    | 2.22    |
| 3i | 138   | –   | 133 | 24.4    | 3.08    |
| 4a | 138   | –   | 133 | 13.6    | 1.78    |
| 4b | 152   | –   | 106 | 18.0    | 1.01    |
| 4c | 128   | –   | 127 | 17.8    | 2.03    |
| 4d | 106   | 110 | 108 | 17.8    | 1.12    |
| 4e | 121   | 125 | 123 | 21.6    | 2.13    |
| 4f | 107   | 111 | 109 | 14.2    | 1.17    |
| 4g | 116   | 121 | 119 | 18.3    | 2.11    |

Note: MP: melting point. N-I: nematic-isotropic transition upon heating. I-N: isotropic-nematic transition upon cooling.
Figure 7 shows the dependence of the entropy changes associated with the nematic–isotropic or the isotropic–nematic transitions on the number \(n\) of carbon atoms in the alkyl chains for series 1, 2, 3 and 4. Interestingly, the values of the entropy changes of series 4 are considerably lower than those of series 1 and 2. Averages of the differences between the odd members and the even members in the entropy changes of series 4 are larger than those of series 1 and 2. Averages of the differences between the odd members and the even members in the entropy changes were calculated. In Figure 7, the thick lines show the averages of the differences between \(n = 4\) and \(n = 10\). The averages are as follows: 0.78 for series 1, 0.46 for series 2, 0.99 for series 3 and 0.94 for series 4, although the discussion in terms of the magnitude of the alternation in the entropy changes is essentially analogous to considering scaling the entropy change according to the number of mesogenic units in trimers [6,24] and tetracmers [26,27].

4. Discussion

What is surprising about series 2 is that their alternations are relatively small, compared to those seen by Gray et al. [11,12] and modelled by Zannoni et al. [14]. The entropy changes are typical for even membered dimers but would be considered small for a trimer. Perhaps, this apparently reduced alternation may reflect that in the trimeric-like series 2, the terminal phenyl group is not strongly correlated to the two mesogenic groups by the spacer. This is similar to the observation for trimers [24] and is also the case in tetracmers [28,29].

In series 3 and 4, the alternations in transitional properties are more marked as would be expected for the larger terminal bulky group. It is noteworthy, however, that the entropy values shown by series 3 are larger than those for the corresponding member of 4. This may be attributed to the greater biaxiality of the phenanthryl group. This has been used to account for the similar behaviour of dimers, and trimers.

Figure 5. DSC thermogram of series 4 upon cooling at the rate of 5ºC/min.

Figure 6. The dependence of transition temperature on the number \(n\) of carbon atoms in the alkyl chains for series 1, 2, 3 and 4. *a*: The clearing temperature. *b*: The melting temperature.

Note: ■: series 1. ○: series 2. ▲: series 3. ▼: series 4.
containing more biaxial groups than conventional rod-like units.\[9,25,30–34\]

The present investigation was undertaken to elucidate the relationship between the odd–even effect and the structures of the terminal rings. We were interested in the differences between the odd members and the even members in the clearing temperatures and the associated entropy changes. The differences of series 3 and 4 are larger than those of series 1 and 2, and the differences of series 3 and series 4 are similar to each other. We think that the differences reflect on the size and anisotropy of the terminal aryl groups and the strength of its interactions with the molecular field. However, it can be seen from Figure 6a that the clearing temperatures decrease in the following order; series 1, series 3, series 2 and series 4. Furthermore, the absolute values of the entropies of series 4 are considerably lower than those of series 1, 2 and 3 (Figure 7) because, at least in part, of the greater molecular biaxiality. These results suggest that the role of the naphthyl and the p-nitrophenyl groups as a mesogen is different from that of the phenanthryl group.

5. Conclusion

All the series of 1, 2, 3, 4 and 5 showed nematic phase. The nematic–isotropic or isotropic–nematic transitional properties of series 1, 2, 3 and 4 showed a clear dependence on the length and parity of the flexible spacer. However, the transitional properties of series 5 did not exhibit such odd–even effect. These results suggest that the p-nitrophenyl, phenyl, 2-naphthyl and 9-phenanthryl groups in series 1, 2, 3 and 4 play a role of mesogen but the terminal bromo atom in series 5 does not play a role of mesogen. The differences in the clearing temperatures and the associated entropy changes between the odd members and the even members decrease in the following order: series 3, series 4, series 1, and series 2. However, series 4 has considerably lower clearing temperatures than series 3 and actually lower than series 2. Furthermore, the values of the entropy changes of series 4 are considerably lower than those of series 1, 2 and 3.

Acknowledgements

The author thanks Akihiro Nishino, Shushi Furukawa, Kaoru Kubota, Mayumi Morimoto, Miho Sunose, Jun-ichi Inadome, Hisashi Tamura and Tomohide Uto for the preparation of series 1, 2, 3, 4 and 5.

Supplemental data

Supplemental data (the elemental analyses and spectral data of 2a-f, 3b-i, 4a-f and 5b-g,i) for this article can be accessed http://dx.doi.org/10.1080/02678292.2014.898343

References

[1] Demus D. Chemical structure and mesogenic properties. In: Demus D, Goodby J, Gray GW, Spiess HW, Vill V, editors. Handbook of liquid crystals. 2nd ed. Vol. 1, Chapter VI. Weinheim: Wiley-VCH;1998. p. 133–187.
[2] Itahara T, Nishino A, Furukawa S, Kubota K. Mesogenic behaviour of p-nitrophenyl group linked with biphenyl mesogens via flexible spacers. Liq Cryst. 2013;40:1167–1173. doi:10.1080/02678292.2013.817619
