**Design and Properties of New Fluorinated Liquid Crystals of Fused Ring Systems for Active Matrix LCD**

TAKATSU Haruyoshi, TAKEHARA Sadao, TAKEUCHI Kiyofumi and IWASHITA Yoshinori

The thermal and physical properties of several new classes of fluorinated liquid crystals of fused ring systems are discussed. The fluorinated phenyldecahydro- naphthalenes have low birefringence and relatively high clearing points. The pentafluorinated tetrahydro- naphthalene has large dielectric anisotropy with relatively low birefringence. The naphthalenes with four fluorine groups, including 1-fluoro-group for the naphthalene ring, have large dielectric anisotropy, large birefringence and low visco-elastic ratio which leads to quick response time in a twisted nematic liquid crystal display (TN-LCD). The introduction of 1-fluoro-group to the naphthalene ring and of 5-fluoro-group to the tetrahydro- naphthalene ring increases the dielectric anisotropy drastically and does not decrease the N-I transition temperature.

1 Introduction

The liquid crystals with a variety of birefringence, a wide temperature range nematic phase, large dielectric anisotropy and low viscosity are required for an active matrix LCD for cellular phones, PDA, note PC or LCD-TV of next generation. We developed and presented new fluorinated liquid crystal materials of fused ring systems. In this paper, the relation of the properties and the chemical structures for the fluorinated decahydro- naphthalenes (1, 2, 3), the tetrahydro- naphthalenes-A (4, 5, 6, 7), the tetrahydro- naphthalenes-B (8, 9), the naphthalenes-A (10, 11, 12, 13) and the naphthalenes-B (14, 15), shown in Fig. 1, are discussed. These LC components have a variety of physical properties and high potentiality to improve the characteristics of liquid crystal mixtures in order to achieve a future highly advanced LCD.

2 Experimental

2.1 Preparation of materials

The decahydro- naphthalenes (1, 2, 3) were prepared from 6-alkyldecahydro- naphthalene-2-on obtained by stereo-selective reduction of 6-propynaphthalene-2-ol and followed by oxidation. The tetrahydro- naphthalenes-A (4, 5, 6, 7) or -B (8, 9) were synthesized by the regio-selective reduction of the corresponding fluoro- naphthalenes. The naphthalenes-A (10, 11, 12, 13) were synthesized by Suzuki-coupling reaction of the corresponding triflate and the phenyl boronic acid. The introduction of a fluoro-group at 1-position of naphthalene ring were achieved by the electrophilic fluorination of the 6-substituted 2-naphthal. The naphthalenes-B (14, 15) with a naphthalene ring at the end of mesogenic moiety were prepared from 4-propylcyclohexanon or 4-propylbicyclohexanon and 1,2-difluoro-6-bromonaphthalene.

2.2 Measurements

Table 1 shows the transition temperatures and the physical properties of the LC components of the fused ring systems. We prepared the liquid crystal mixtures including 20 wt% of each single component in an LC host. The nematic-to-isotropic (N-I) transition temperatures with * marks were determined from the values of the mixtures by extrapolation. The birefringence $\Delta n$ and the dielectric anisotropy $\Delta \epsilon$ were measured at 25°C and the value of each LC component was also determined by extrapolation. The bulk viscosity was measured at 20°C. The visco-elastic ratio $\eta / \eta_a$, which relates to the response time, was determined from the decay response time at 25°C.
3 Results and discussions
3.1 Nematic-to-isotropic (N-I) transition temperatures

For the LC components of Formula I, the thermal stability of nematic phases (N-I transition temperatures) of the fused ring systems are between those of the cyclohexane ring system (-122 °C) and the bicyclohexane ring system (65 °C). The N-I transition temperature (-33 °C) of the decahydronaphthalene 2 is 10 °C and 29 °C higher than those of the naphthalene 10 (-43 °C) and the tetrahydronaphthalene 4 (-62 °C). For the fused ring

<table>
<thead>
<tr>
<th>Table 1 Properties of Liquid Crystal Components of Fused Ring Systems</th>
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<tbody>
<tr>
<td>Transition temp. (°C)</td>
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<tr>
<td></td>
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<tr>
<td>(Decahydronaphthalenes)</td>
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<tr>
<td>1</td>
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<td>2</td>
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<td>3</td>
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<tr>
<td>(Tetrahydronaphthalenes-A)</td>
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<td>4</td>
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<td>6</td>
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<td>7</td>
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<tr>
<td>(Tetrahydronaphthalenes-B)</td>
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<td>9</td>
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<tr>
<td>(Naphthalenes-A)</td>
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<td>10</td>
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<td>11</td>
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<td>12</td>
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<td>13</td>
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<tr>
<td>(Naphthalenes-B)</td>
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<tr>
<td>14</td>
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<tr>
<td>15</td>
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<tr>
<td>(Host LC)</td>
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</tbody>
</table>

Δn*: birefringence at 25 °C obtained by extrapolation
nD*: dielectric anisotropy at 25 °C obtained by extrapolation
□: bulk viscosity at 20 °C (20 wt% in a host LC)
□ / □: visco-elastic ratio at 25 °C (20 wt% in a host LC)
systems of Formula II, the N-I transition temperature (191 °C) of the decahydronaphthalene 3 is also higher than that of the naphthalene 12 (154 °C), and the N-I transition temperature of the fluoronaphthalene 13 (157 °C) is also higher than that of the fluorotetrahydronaphthalene 7 (136 °C). In case of Formula III, having the fused ring at the terminal in an LC core, the N-I transition temperatures of the difluoronaphthalene 14 (23 °C) and the difluoro-tetrahydronaphthalene 8 (20 °C) are similar.

Formula I:

\[
\begin{array}{c}
\text{n-C}_2\text{H}_4 - X - \text{F}
\end{array}
\]

(-122 °C) \quad (-62 °C) \quad (-43 °C) \quad (-33 °C) \quad (63 °C)

Formula II:

\[
\begin{array}{c}
\text{n-C}_2\text{H}_4 - \text{F}
\end{array}
\]

(154 °C) \quad (191 °C) \quad (136 °C) \quad (157 °C)

Formula III:

\[
\begin{array}{c}
\text{n-C}_2\text{H}_4 - X
\end{array}
\]

(20 °C) \quad (23 °C)

Comparing with the component 4 and the component 5 for the tetrahydronaphthalenes of Formula I, the introduction of fluoro-group at 5-position does not decrease the N-I transition temperature. The introduction of fluoro-group at 7-position, however, decreases 27 °C of the N-I transition temperature, comparing the component 5 and the component 6.

The introduction of fluoro-group at 1-position for the naphthalene of Formula I increases the N-I transition temperature from -43 °C of the component 10 to -30 °C of the component 11, while the increase for Formula II compounds are only 3 °C from 154 °C of the component 12 to 157 °C of the component 13.

3.2 Birefringence

The birefringence \( \Delta n \) increases with the increase of \( \pi \)-electron conjugation in an LC molecule. The decahydronaphthalene 2 has 0.051 of the lowest \( \Delta n \) in the fused ring system of Formula I because decahydronaphthalene ring has no \( \pi \)-electron conjugation. The tetrahydronaphthalene 4 has 0.100 of moderate \( \Delta n \) and naphthalene 10 has 0.187 of high \( \Delta n \) due to the \( \pi \)-electron conjugation of the fused ring system. The introduction of fluoro-group to tetrahydronaphthalene ring of Formula I decreases \( \Delta n \) slightly, and the \( \Delta n \) of the difluorotetrahydronaphthalene 6 decreases to 0.084.
3.3 Dielectric anisotropy

The electron attractive group with the dipole moment of the parallel to the molecular axis increases the dielectric anisotropy \( \Delta \varepsilon \) of the LC component. The introduction of 5-fluoro-group to the tetrahydro-naphthalene \( 4 \) in formula I increases the \( \Delta \varepsilon \) from 12.1 to 20.1 of the component \( 5 \), and the introduction of 5,7-difluoro-groups increases to 27.9 of the component \( 6 \). The introduction of 1-fluoro-group to the naphthalene \( 10 \) increases the \( \Delta \varepsilon \) from 10.7 to 23.6 of the component \( 11 \). The increase degree by the introduction of a fluoro-group for the naphthalene ring is larger than that for the tetrahydro-naphthalene ring because of the difference of \( \pi \)-electron conjugation of the fused ring system. The introduction of 1-fluoro-group to the naphthalene \( 12 \) for formula II also increases the \( \Delta \varepsilon \) from 11.4 to 23.0 of the component \( 13 \).

\[
\begin{align*}
\text{Formula I} & : \\
X & < \begin{array}{c}
\text{X} \\
12.1
\end{array} < \begin{array}{c}
\text{X} \\
20.1
\end{array} < \begin{array}{c}
\text{X} \\
27.9
\end{array} \\
\text{Formula II} & : \\
X & < \begin{array}{c}
\text{X} \\
10.7
\end{array} < \begin{array}{c}
\text{X} \\
23.6
\end{array} < \begin{array}{c}
\text{X} \\
11.4
\end{array} < \begin{array}{c}
\text{X} \\
23.0
\end{array} \\
\end{align*}
\]

3.4 Bulk viscosity and visco-elastic ratio

The decahydro-naphthalenes \( 1 \) and \( 2 \) of two ring systems have low bulk viscosity and small values of visco-elastic ratio \( \eta / \eta_s \). The tetrahydro-naphthalene \( 8 \) and the naphthalene \( 14 \) with a fused ring at the end of mesogen moiety have small values of \( \eta / \eta_s \), leading to quick response time of an LCD, in spite of having not so low bulk viscosity. The 1-fluoro-naphthalene \( 11 \) with four fluoro-groups and 23.6 of large \( \Delta \varepsilon \), required for low driving voltage, has a small value of \( \eta / \eta_s \) because of the large elastic constant of splay.

4 Conclusion

The thermal and physical properties of some series of LC components of fused ring systems with a variety of \( \Delta n \) and \( \Delta \varepsilon \) are compared and discussed. The fluorinated phenyl-decahydro-naphthalenes have low birefringence and relatively high clearing points. The pentafluorinated tetrahydro-naphthalene has large dielectric anisotropy with relatively low birefringence. The introduction of 1-fluoro-group to the naphthalene ring and of 5-fluoro-group to the tetrahydro-naphthalene ring increases the dielectric anisotropy drastically.

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References

報文

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