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Yoshinori Iwashita ^a , Yasuo Umezu ^a , Shotaro

Kawakami ^a , Kiyofumi Takeuchi ^a , Tetsuo Kusumoto ^a , Sadao Takehara ^a & Haruyoshi Takatsu ^a ^a Liquid Crystal Materials Division, Dainippon Ink &

^a Liquid Crystal Materials Division, Dainippon Ink & Chemicals Inc., Kitaadachi-Gun, Saitama, Japan

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LIQUID CRYSTAL MIXTURES WITH LOW BIREFRINGENCE FOR ACTIVE-MATRIX LCD

Yoshinori Iwashita, Yasuo Umezu, Shotaro Kawakami, Kiyofumi Takeuchi, Tetsuo Kusumoto, Sadao Takehara, and Haruyoshi Takatsu Liquid Crystal Materials Division, Dainippon Ink & Chemicals Inc., 4472-1 Komuro, Ina-Machi, Kitaadachi-Gun, Saitama 362-8577, Japan

The liquid crystal (LC) mixtures with fused ring systems such as Decahydronaphthalenes and Tetrahydronaphthalenes for reflective or transflective active-matrix liquid crystal display (AM-LCD) have higher durability than LC mixtures with ester-components. These LC mixtures also have some problems such as low nematic-isotropic transition temperature T_{NI} and high driving voltage. The improvement for driving voltage was carried out by using Tetrahydronaphthalene-component with moderate birefringence Δn and large dielectric anisotropy $\Delta \epsilon$. However, It was difficult to obtain LC mixtures with sufficiently low driving voltage, because of low T_{NI} and the comparatively high Δn of tetrahydronaphthalene.

We have improved these problems by introducing some newly developed LC components and optimization. We obtained the LC mixtures with low Δn and low driving voltage; less than 0.075 of Δn and about 4 V or less of driving voltage. These LC mixtures have high durability with stable nematic phase at low temperature.

Keywords: decahydronaphthalenes; fused ring; reflective LCD; tetrahydronaphthalenes; transflective LCD

INTRODUCTION

Recently, reflective or transflective active matrix liquid crystal display (AM-LCD) for mobile instruments such as PDA or cellular phones, demands high characteristics such as quick response and very Δn with low driving voltage.

Address correspondence to Tetsuo Kusumoto, Liquid Crystal Materials Division, Dainippon Ink & Chemicals Inc., 4472-1 Komuro, Ina-Machi, Kitaadachi-Gun, Saitama 362-8577, Japan.

We are interested in the liquid crystals of fused-ring systems [1–3] with some positions which can be substituted by the fluoro groups. We developed some kind of fused ring components and evaluated the properties of these LC components and LC mixtures with fused ring components [4–7]. In this paper, we have developed new series of LC components such as tetrahydronaphthalenes of fused ring systems which are quite new especially as LC components for AM-LCD. The physical and electro-optical properties of these components were evaluated. The physical and electro-optical properties of the LC mixtures with Decahydronaphthalenes and Tetrahydronaphthalenes for reflective or transflective AM-LCD were also evaluated.

EXPERIMENTAL, RESULTS AND DISCUSSION

Fused Ring Components

We have developed liquid crystal components with fused ring structure as a mesogen moiety shown in Figure 1.

Decahydronaphthalenes have low Δn and small $\Delta \varepsilon$. Tetrahydronaphthalenes and Naphthalenes with some fluoro-substituents to increase the dipole moment of the parallel to the molecular axis have large $\Delta \varepsilon$. Tetrahydronaphthalenes have moderate Δn and Naphthalenes have high Δn due to the π -electron conjugation. Therefore, decahydronaphthalenes and Tetrahydronaphthalenes are suitable to improve the electro-optical properties of reflective or transflective LCD.

Table 1 shows properties of some fluorinated LC components of fused ring systems. We have newly developed a liquid crystalline tetrahydronaphthalene, T3. The LC mixtures including 20 wt% of each single component into host LC mixture were prepared. We carried out the following measurements by using the LC mixtures;

The Nematic-isotropic phase transition temperature, $T_{\rm NI}$, the crystal-, the birefringence Δn and the dielectric anisotropy $\Delta \varepsilon$ were measured. The measurements of Δn and $\Delta \varepsilon$ were carried out at 25 °C. The values of Δn and $\Delta \varepsilon$ are obtained by extrapolation.

$$- \underbrace{\hspace{1cm} \stackrel{F}{\longleftarrow} \hspace{1cm} \stackrel{F}{\longleftarrow}$$

Decahydronaphthalenes Tetrahydronaphthalenes Naphthalenes

FIGURE 1 Mesogenic core structure of fused ring components.

	•	•	Ü	
Component	Structure	$T_{ m NI}[^{\circ}{ m C}]$	Δn	Δε
D1	n-C ₃ H ₇ F	-8	0.059	5.4
D2	n-C ₃ H ₇ -	190	0.091	5.7
T1	n-C ₃ H ₇	-90	0.076	27.9
T2	n-C ₃ H ₇	21	0.067	7.4
Т3	n-C ₃ H ₇ -	157	0.072	9.7

TABLE 1 Properties of Some Fluorinated LC Components of Fused Ring Systems

Decahydronaphthalene D1 has low Δn and D2 has high $T_{\rm NI}$. Tetrahydronaphthalene T1 has very large $\Delta \varepsilon$ and T3 has high $T_{\rm NI}$. Therefore, the LC mixtures with large $\Delta \varepsilon$ *i.e.* low driving voltage and low Δn should be obtained by using these Decahydronaphthalenes and Tetrahydronaphthalenes.

Figure 2 shows the relationship between $\Delta \varepsilon$ and Δn for fused ring components and non-polar components of low viscosity. Decahydronaphthalenes

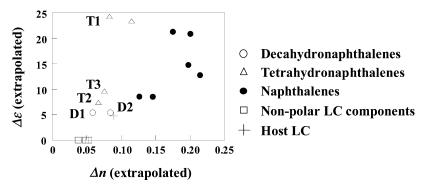


FIGURE 2 Relationship between dielectric anisotropy and birefringence for fused ring LC components.

have small $\Delta \varepsilon$ and low Δn . Naphthalenes have large $\Delta \varepsilon$ and high Δn . It is general behavior that Δn increases with the increase of $\Delta \varepsilon$ because of the relationship of two parameters. Some of tetrahydronaphthalenes, however, indicate an unique relationship between $\Delta \varepsilon$ and Δn , *i.e.*, these components have large $\Delta \varepsilon$ with relatively low Δn . We have already developed the non-polar Bicyclohexanes having low Δn . Consequently, a range of large $\Delta \varepsilon$ and low Δn which is required for reflective LCD materials, can be covered by the LC mixtures including these LC components.

Table 2 shows the transition temperatures of a mixture consisting of non-polar LC components MN1, a LC mixture containing fused ring components, MF1 and a LC mixture containing conventional fluorinated components for an active matrix LCD, MC1. MF1 containing fused ring components has a wide nematic temperature range showing a nematic phase at -10 °C. On the other hand, the conventional MC1 does not show a nematic phase even at room temperature. The difference of stability of a nematic phase may come from the deviation of the rotating axis of a fused ring component from the combination position of each mesogenic unit.

TABLE 2 Comparison of the Nematic Temperature Ranges

Components	MN1	MC1	MF1
C_2H_5 F	-	-	25%
<i>n</i> -C ₃ H ₇ -⟨\F	-	-	25%
C_2H_5 \leftarrow \rightarrow \leftarrow \rightarrow	-	25%	-
<i>n</i> -C ₄ H ₉ −	-	25%	_
n-C ₅ H ₁₁	50%	25%	25%
	50%	25%	25%
$T_{ m NI}$ [°C]	103	106	137
$T_{ ightarrow N}$ [°C]	58	30	-10
Phase at R.T.	Smectic	Smectic	Nematic

Figure 3 shows a schematic representation of the aggregation structure of the LC mixtures MN1, MC1 and MF1. When the conventional LC components are added to non-polar LC mixtures, the conventional LC components hardly break the smectic-order of the LC mixture MN1. Therefore, the LC phase of MC1 is still smectic. On the other hand, in the case of adding fused ring LC components into MN1, because the fused ring components have large exclusive volume to break smectic-order of MN1, the LC mixture MF1 indicates nematic phase at lower temperature than MC1.

Because of the good stability of a nematic phase at low temperature for a mixture of the fused ring components and non-polar components with low viscosity, the mixture of the fused ring components with high concentration of non-polar Bicyclohexanes with low viscosity can be obtained. Therefore, the LC mixtures for reflective TFT-LCD with low Δn and sufficiently low viscosity can be achieved.

Liquid Crystal Mixtures for Reflective LCD

The LC component with large $\Delta \varepsilon$ and low Δn is required for reflective LCD. The most LC components with large $\Delta \varepsilon$ have tendency to reduce the voltage holding ratio (VHR) and to increase in ion density (ID) of LC mixtures. Using ester components is a conventional method to improve the stability of a nematic phase at low temperature and to reduce Δn for LC mixtures. However, the ester components also reduce the VHR and increase in ID.

Table 3 shows the VHR of T1, a conventional TFT-LC component C1 and a fluorinated ester E1. T1 with five fluoro-substituents and large dielectric anisotropy has almost same high VHR as C1 with two fluoro-substituents. The VHR of T1 is much higher than that of a conventional fluorinated LC

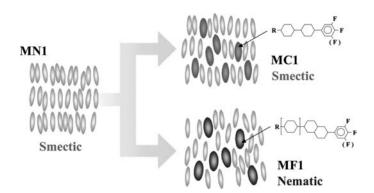


FIGURE 3 Schematic representation of the aggregation structure of the LC mixtures MN1, MC1 and MF1.

Component		$\Delta arepsilon^*$	Voltage holding ratio [%]		
	Structure		Initial	Heat	UV
T1	n-C ₃ H ₇ F F F	24.3	92.7	93.2	92.8
C2	F n-C ₃ H ₇ -⟨\rightarrow\righta	5.2	92.5	93.1	92.3
E1	n -C ₅ H ₁₁ \longrightarrow O F O \frown F	5.1	90.9	90.5	90.7
Host		3.7	92.5	92.2	91.7

TABLE 3 Comparison of the Voltage Holding Ratios

ester of low Δn E1. T1 with relatively low Δn and large dielectric anisotropy shows good solubility, therefore, T1 is useful to reduce the driving voltage of LC mixtures for a reflective LCD.

Figure 4 show the heating time dependence of ID of T1 and a conventional LC component C2. The ID of C2 increased extremely as heating time passed. On the other hand, the ID of T1 also increased. But the increasing ratio was smaller than the one of C2.

Consequently, the LC mixtures with low Δn , large $\Delta \varepsilon$, stable nematic phase at low temperature and sufficient durability for high temperature should be obtained by using the fused ring components such as Decahydronaphthalenes and Tetrahydronaphthalenes instead of using conventional LC components.

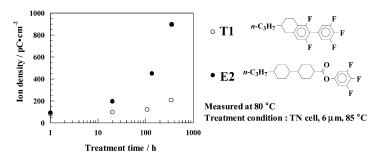


FIGURE 4 Heating time dependence of ion density for LC mixtures containing LC components T1 and E2.

	M1	M2	М3	M4	M5
$T_{\rm NI}/^{\circ}{\rm C}$	86.3	88.3	86.9	89.4	84.4
$T_{\rightarrow N}/^{\circ}C$	-31	-39	-47	-48	-28
Δn	0.075	0.071	0.067	0.064	0.062
$\Delta \varepsilon$	7.8	4.8	5.1	3.8	3.0
η/mPa⋅s	44	35	42	26	22
γ₁/mPa·s	192	139	173	113	84
$V_{\rm th}/{ m V}$	1.34	1.58	1.54	1.81	2.00

TABLE 4 Properties of LC Mixtures with Low Birefringence

 $d=6\,\mathrm{\mu m}$

Table 4 shows the properties of LC mixtures with low Δn . $T_{\rm N}$ is the transition temperature to the nematic phase. η is the flow viscosity γ_1 is the rotational viscosity. Vth is the threshold voltage at the condition of 6 μ m of TN cell. Each mixture has a sufficient temperature range of nematic phase and low Δn for the applications of a reflective LCD without any Esters. M1, M2 and M3 can be driven by 4 V or less. M4 and M5 have very low Δn and small γ_1 .

Figure 5(a), (b) shows the wavelength dependence of Δn and the normalized retardation of LC mixture M1 and M5, respectively. The retardations were normalized by 589.3 nm. M5 has with low Δn has small wavelength dependence of Δn . Therefore, the LC mixture M4 and M5 may improve color-reproductivity and response time for reflective LCD.

CONCLUSION

We have prepared a new series of liquid crystalline tetrahydronaphthalene derivative of low birefringence with positive dielectric anisotropy.

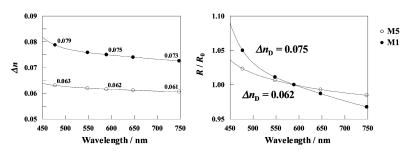


FIGURE 5 Wavelength dependence of (a) birefringence and (b) normalized retardation of LC mixture M1 and M5, where retardations were normalized by 589.3 nm.

High voltage holding ratio and low ion density of Tetrahydronaphthalene with large dielectric anisotropy were confirmed.

We discussed about good solubility of fused ring components at low temperature and concluded that large exclusive volume of fused ring components may occurs good solubility to other kind of components.

We have achieved LC mixtures with low birefringence, low driving voltage and wide operating temperature range. These LC mixtures including no ester as a component improve the reliability of a reflective LCD for cellular phones or PDA which are used under severe conditions and demanded low consumption of electricity. We found that the LC mixtures with very low Dn have small wavelength dependence of Δn which improve the colour-reproductivity for reflective LCD.

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