

Blending of Novel Liquid Crystal Mixtures for TFT-LCD TV Application

Y. B.KIM and E. J. LIM*

Liquid Crystal Research Center, Department of Chemistry
Division of Natural Sciences, Konkuk University,
1, Hwayangdong, Kwanjin-ku, Seoul, 143-701, Korea.

Abstract

Tree-ring types liquid crystalline compounds having fluoro and isothiocyanate substituent[1] were synthesized and their physical properties were measured to evaluate the applications to TFT-LCD TV.

All synthesized compounds were showed remarkably high T_{ni} point. Birefringence(Δn) and dielectric anisotropy($\Delta\epsilon$) were higher than fluoro analogues and isothiocyanate substituted bicyclohexyl-phenyl compounds.

1. Objectives and Background

A most important parameter for TV application of LCD is a fast switching time for displaying of moving image[2]. Twisted nematic mode is the most matured technology of LCD field. The switching times can be described by the following formula.[3~5]

$$\tau_{on} \propto \left(\frac{d}{\pi}\right)^2 \frac{\gamma_1}{K_{eff}} \left(\frac{1}{(V/V_{th})^2 - 1}\right) \quad (1)$$

$$\tau_{off} \propto \left(\frac{d}{\pi}\right)^2 \frac{\gamma_1}{K_{eff}} \quad (2)$$

$$V_{th} = \pi \sqrt{\frac{(K_{11} + (K_{33} - 2K_{22})/4)}{\epsilon_0 \Delta\epsilon}} = \pi \sqrt{\frac{K_{eff}}{\epsilon_0 \Delta\epsilon}} \quad (3)$$

where τ_{on} , τ_{off} are switching on and off times, V the applied voltage, γ_1 rotational viscosity, d cell gap, $\Delta\epsilon$ the dielectric anisotropy, and K_1, K_2 and K_3 represent V_{th} is the voltage needed of 10% transmittance change from the off voltage state.

The physical properties of nematic liquid crystals for active matrix LCDs application should have wide nematic range, high dielectric

anisotropy, moderate optical anisotropy, low viscosity, high stability, high voltage holding ratio (VHR), and so on. Super fluoro-substituted materials have very high stability, which has a great advantage in the field of AM-LCD applications. However they have low dielectric and birefringence, which limit the development of high-speed response and low power consumption. Recently, it is reported on fluoro - isothiocyanate substituted two ring(cyclohexyl-phenyl) and three ring (bicyclohexyl-phenyl) compounds has high birefringence and dielectric anisotropy.[2]

In this paper we will report the physical properties of fluoro - isothiocyanate substituted cyclohexylbiphenyl liquid crystal compounds and the electro-optic properties of their mixtures

2. Experimental

2-1. Synthesis

The fluoro - isothiocyanate substituted cyclohexylbiphenyl liquid crystal compounds were prepared according to the following scheme depicted in Figure 1.

2-1-1. 4-Bromo-2-fluoro-N,N-dibenzyl aniline

The mixture of 4-bromo-2-fluoroaniline (10.0 g, 0.0526 mol) and benzyl bromide(26.9 g, 0.158 mol) in chloroform (200 mL) was added to a stirred solution of sodium carbonate (21.1 g, 0.211 mol) and *tetra*-butylammonium bromide(0.85 g, 2.63mmol) in water (100 mL). The stirred mixture was heated under reflux for 2 days. The product was washed with water and dried (anhydrous $MgSO_4$). The solvent was removed *in vacuo* to yield a white solid, which was recrystallised from ethanol at room temperature (hexane at $-25^\circ C$ for 4-bromo-2,6-difluoro-N,N-dibenzylaniline) to give colorless crystal (17.1 g, yield 87.9 %). Mass spectrum 369 (M^+), 371 (M^+), 278, 280, 200, 202

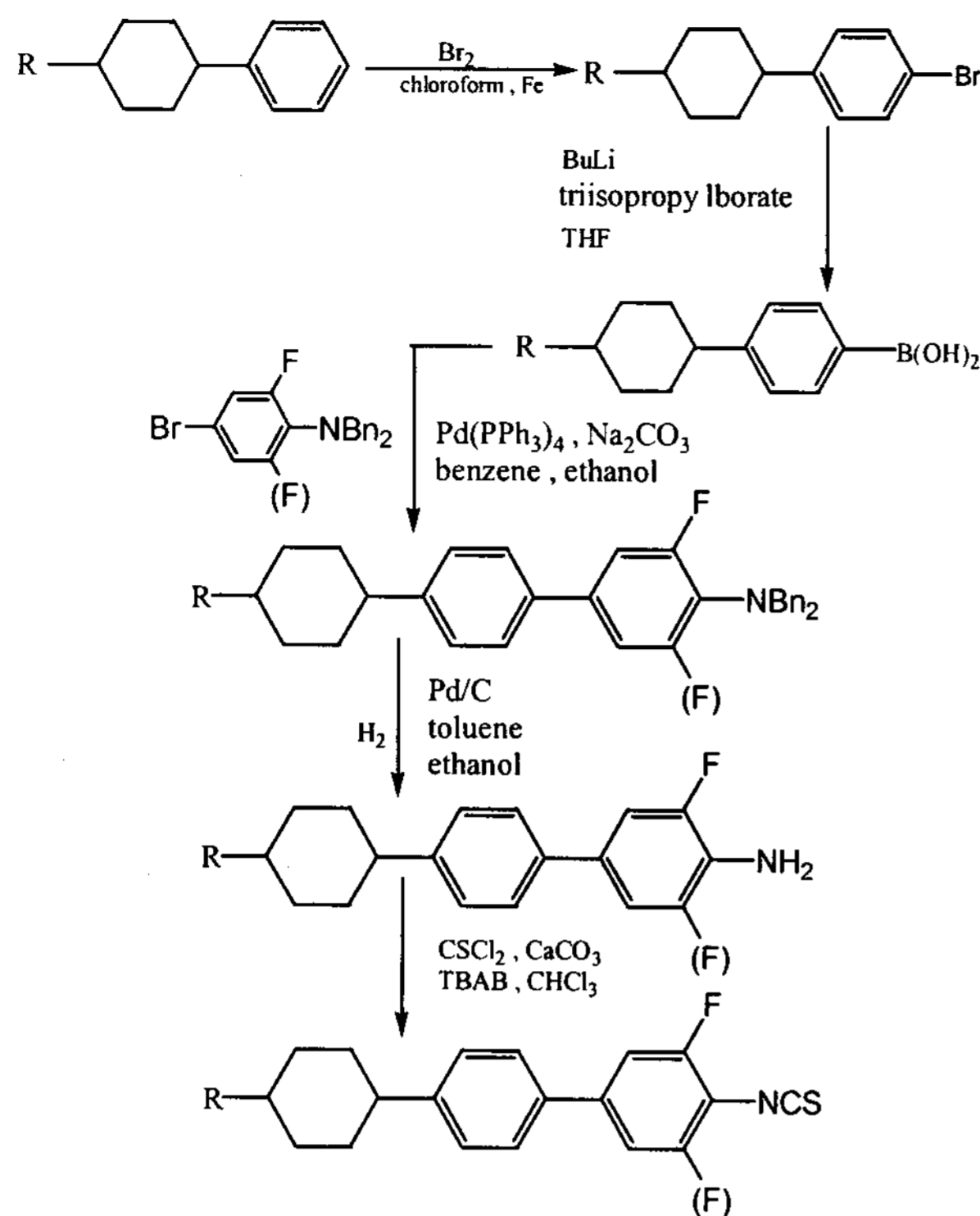


Figure 1. Scheme of trans - 3(5) - (di)fluoro - isothiocyanato-4-(4-n-alkylcyclohexyl) biphenyl.

2-1-2. 1-bromo-4-(trans-4-pentylcyclohexyl) benzene

1-pentyl-4-trans-phenylcyclohexane (16 g, 0.069 mol) and Fe 0.12g in chloroform. While stirring the solution Br_2 was added dropwise. Stirring was then continued for 3 hours at room temperature. The mixture was washed with 1N NaOH and water. The organic layer was dried (anhydrous MgSO_4) and removed *in vacuo* to give dark brown solid (20 g, 0.065 mol)

2-1-3. 4-(trans-4-pentyl-cyclohexane)phenyl boric acid

The mixture of 1-bromo-4-(trans-4-pentyl-cyclohexyl)-benzene (20 g, 0.065 mol) and tetrahydrofuran (150mL, diethyl ether for 4-bromo-2,6-fluoro-N,N-dibenzylaniline because of solubility at low temperature) distilled over lithium aluminum hydride were introduced, under nitrogen, into a three-neck flask equipped with a low-temperature thermometer, addition funnel, magnetic stirrer and nitrogen inlet tube. The reaction mixture was cooled to -78°C

(liquid nitrogen-acetone bath) and n-butyllithium (46.8 ml, 0.075 mol, 1.6M solution in hexane) was added rapidly (the rate of addition was adjusted such that the temperature did not momentarily exceed -70°C). After 1 hour, triisopropyl borate (30 ml, 0.13mol) was added the reaction mixture was warmed to room temperature and poured into ice-cold water (50 mL). The mixture was washed with 0.1 N hydrochloric acid and water. The organic layer was dried (anhydrous MgSO_4) and removed *in vacuo* to give yellow oil. The product was purified by recrystallised from hexane to give 4-(trans-4-pentyl-cyclohexane)-phenylboric acid (7 g, yield 37%)

2-1-4. 4-(trans-4-pentyl-cyclohexyl)-2-fluoro-N,N-dibenzylaniline

The mixture of 4-Bromo-3-fluoro-N,N-dibenzylaniline 10 g and Tetrakis(triphenylphosphine)palladium(0) 0.5 g and benzene 50 ml including 0.5 g 2M sodium carbonate 38 ml. While stirring the solution 4-(trans-4-pentyl-cyclohexane)-phenylboric acid (7 g, 0.025mol) in ethanol 20 ml was added dropwise. Stirring was then continued for 12 hours at 95°C temperature. The mixture was washed with 0.1 N hydrochloric acid and water. The organic layer was dried (anhydrous MgSO_4) and removed *in vacuo* to give dark brown solid. (8.8 g, yield 70%)

2-1-5. 4-(trans-4-pentyl-cyclohexyl)-3-fluoro-4-aminobiphenyl

4-(trans-4-pentyl-cyclohexyl)-2-fluoro-N,N-dibenzylaniline (8.8 g, 0.0175 mol) and Pd/C (0.90g) in toluene (70 mL) and ethanol (70 mL) was stirred for five hours under hydrogen pressure of 4 kg/cm^2 . The Pd/C was filtered off and the filtrate was evaporated *in vacuo* to afford a brown solid. (4.95g, 85%yield). Mass spectrum

2-1-6. 4-(trans-4-pentyl-cyclohexyl)-3-fluoro-4-isothiocyanatobiphenyl

The mixture of water (40 mL) dissolving calcium carbonate (3.2 g, 0.024 mol) and *tetra*-butylammonium bromide (0.1 g, 0.31 mmol) and chloroform (40 mL) including thiophosgene (2.30 g, 0.020 mol) was cooled to 10°C . While stirring the solution of 4-(trans-4-pentyl-cyclohexyl)-3-fluoro-4-aminobiphenyl (4.95 g, 0.015 mol) in chloroform (35 mL) was added

dropwise. Stirring was then continued for 3 hours at room temperature. The reaction mixture was poured into ice-cold water (50 mL). The mixture was washed with 1 % hydrochloric acid and water. The organic layer was dried (anhydrous MgSO₄) and removed *in vacuo* to give dark brown solid. The product was purified by column chromatography (hexane) and recrystallization. (2.5g, 44.6% yield)
 Mass spectrum 381(M⁺),242,255,286
¹H NMR 0.8~2.1(20H, m)2.6(1H, t)
 7.3~7.7(7H, m)

Each product was identified by ¹H NMR spectrometry(Bruker Avance 400) and EI-mass spectrometry(70eV Hewlett Packard 5972 MSD). Differential Scanning Calorimeter(Perkin-Elmer DSC-7) measured the phase transition temperature. Optical anisotropy Δn is measured using an Abbe' refractometer at 589nm. The dielectric anisotropy Δε is measured by the capacitive method with an impedance analyzer(Hewlett-Packard 4192A) using an antiparallel and homeotropic cells with 5um thickness.

The response times were measured by applying a square-wave AC voltage of 5V at 60 Hz. And voltage holding ratio (VHR) were measured using model 6254 Toyo Co.

3. Result & Discussion

The dielectric anisotropy of a liquid crystal are determined by the dipole moment(μ), its angle(β) and order parameter(S), as described by the Maier and Meier theory[6].

$$\Delta\epsilon = \frac{N_A F h}{\epsilon_0} [\Delta\alpha + (\mu^2 / 2kT)(3 \cos^2 \beta - 1)] \cdot S \quad (4)$$

The birefringence is determined by molecular polarizability anisotropy(Δα), order parameter(S), its density(ρ) and n is the average refractive index of the substance, as follows[7]

$$\Delta n = (2\pi / 3n)(n^2 + 2)N_A (\Delta\alpha / M)\rho S \quad (5)$$

Table 1. Molecular parameters of synthesized liquid crystalline compounds

Parameter	Dipole moment (μ ^a)	Angle (β ^a)	Polarizability anisotropy (Δα ^a)	Δα/M ^a
R3CPPFS	3.287	11.4	314.4	0.89
R3CPPFSF	3.879	10.5	303.9	0.82
R5CPPFS	3.295	13.4	315.7	0.83
R5CPPFSF	3.889	7.6	313.1	0.78

a: for the calculations, we decided to use semi-empirical quantum chemical methods (AMI Hamiltonian in the MOPAC 5.0 package)

We expected that these compounds have high Δn and Δε than isothiocyanate substituted bicyclohexyl-phenyl compounds, because they have more higher polarizability anisotropy(Δα) and Δα/M as shown Table 1. In the case of isothiocyanate substituted bicyclohexyl-phenyl compounds, polarizability anisotropy(Δα) is about 185~201, and Δα/M is about 0.48~0.53.[8]

T_{ni}, birefringence(Δn) and dielectric anisotropy(Δε) of synthesized compounds were listed in Table 3. Birefringence(Δn) and dielectric anisotropy(Δε) values of the synthesized compounds are higher than corresponding the fluoro-isothiocyanate bicyclohexylphenyl LC compounds.[8]

Table 2. Physical properties of synthesized compounds at 20 °C

Spec	Phase transition temperatures [°C]			Δn ^a [589nm]	Δε ^a [1kHz]
	Cry	N	Iso		
R3CPPFS	103.8	-	220.96	0.29	12.6
R3CPPFSF	56.22	-	200.16	0.27	15.9
R5CPPFS	88.89	-	215.45	0.27	14.1
R5CPPFSF	50.61	-	195.12	0.26	15.2

a : extrapolated values from 15% solution in host mixture

Table 3 shows the physical and electro-optical properties of novel LC mixture (host mixture LC1 + synthesized liquid crystalline compounds). ML series were designed to have the Δn value of between 0.12 and 0.13.

Table 3. physic and electro optical properties of practical LC mixtures

	LC-1	ML-1	ML-2	ML-3	ML-4
T _{ni}	76.2	94.19	93.5	92.3	90.4
Δn	0.096	0.125	0.123	0.122	0.12
Δε	4	6.09	5.29	5.32	5.7
K _{eff}	4.3	7.8	5.7	5.8	5.1
Cell gap	3.2	3.2	3.8	3.2	3.3
V _{th}	1.1	1.2	1.1	1.1	1.0
V ₁₀	1.6	1.7	1.6	1.6	1.5
V ₉₀	2.8	2.8	2.6	2.8	2.6
τ _{on}	2.1	1.5	1.13	1.3	1.2
τ _{off}	11.5	8.4	7.6	7.5	7.8
τ _{all}	13.6	9.9	8.73	8.8	9.0
VHR	99	98	98	97	95

*measurement temp=25°C,

* τ (apply voltage: 0~5, τ_{on}=10%~90%, τ_{off}=90%~10%, τ_{all}=τ_{on}+τ_{off})

*K_{eff} values got from solved an equation(3)

As shown in Table 3, our novel NLC mixtures have significantly higher clearing point (T_{ni}), dielectric anisotropies (Δε) values compared with host mixture. Especially, clearing point of them are 14~18°C higher and dielectric anisotropies are about 30~50% higher than host mixture.

The total switching times were improved from 27% to 36% in comparison to the host mixture LC 1. Their total switching times were less than 10ms, enough to be addressed in 16.7ms frame time.

The improvement of switching time is due to small viscoelastic ratio. The viscoelastic ratio γ_1/K_{eff} is directly proportional to switching time in the LC panel as described by equation (1) and (2). We calculated K_{eff}, by solved an equation (3), describe to the threshold voltage (V_{th}) depends on dielectric anisotropies(Δε) and a set of elastic constants.

As shown in Table 3, the threshold voltage of LC mixtures similar, this result showed that K_{eff} was increased, an extent increase dielectric anisotropies(Δε).

Comparing the K_{eff} of LC-1 with ML-1,2,3,4 shows that the blending of fluoro-isothiocyanated LC compounds lead to increase of K_{eff} of ML-1,2,3,4 mixture. Therefore, because large K_{eff} value lead to low γ_1/K_{eff} and quick switching time τ_{off}.

By using the newly fluoro-isothiocyanated LC compound having high potentiality to improve characteristics for a switching speed, high T_{ni} point of TFT-LCD TV.

4. Conclusion

To achieve the requirement of faster switching times, the novel LC single materials with large birefringence(0.26~0.29), high clearing temperatures(195~220°C), broad nematic range and dielectric anisotropies(12~15) were synthesized.

Blending of fluoro-isothiocyanated LC compounds have a good properties for a fast switching speed of active matrix transmissive TN-LCD TV.

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6. References

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