

Novel Liquid Crystal Compounds and Its Mixtures for VA-TFT-LCD TV Application

Y.B.Kim and S.D.Roh*

Liquid Crystal Research Center, Department of Chemistry, Division of Natural Sciences, Konkuk University 1, Hwayangdong, Kwanjin-ku, Seoul, 143-701, Korea. 82-2-450-3417
rohsudong@kkucc.konkuk.ac.kr

Three-ring types liquid crystalline compounds having fluoro and isothiocyanate substituent were synthesized and their physical and electro-optical properties were measured to evaluate the applications to active matrix VA liquid crystal displays. The tetrakis(triphenylphosphine)palladium(0) catalyzed cross coupling of aryl boronic acids with aryl halides is used to prepare trans-4'-alkoxy-2,3-difluoro-3'-isothiocyanato-4-(4-alkylcyclohexyl)-biphenyl series. The synthesized compounds showed the nematic liquid crystalline phase and the negative dielectric anisotropy. The prepared mixtures showed faster response time and lower threshold voltage than their host mixture.

1. Objectives and Background

The recent concern in the development of liquid crystal display (LCDs) has created strong demand for new liquid crystalline materials with high clearing temperature, high birefringence, high dielectric anisotropy, and low visco elastic ratio.^[1] For active matrix displays, we demand high specific resistance and voltage holding ratio of LC mixtures.^[2] Liquid crystals with fluoro-isothiocyanated phenyl core group meet most of these special features.^[3-4]

Currently, the most TN-TFT-LCD use liquid crystal mixtures with a positive dielectric anisotropy. In contrast, the recently introduced VA-TFT-LCD which offers a superior picture quality with a wide viewing angle ($>160^\circ$), a high contrast, and video-compatible switching times ($<20\text{ms}$) is based on a liquid crystal mixture with negative dielectric anisotropy [5].

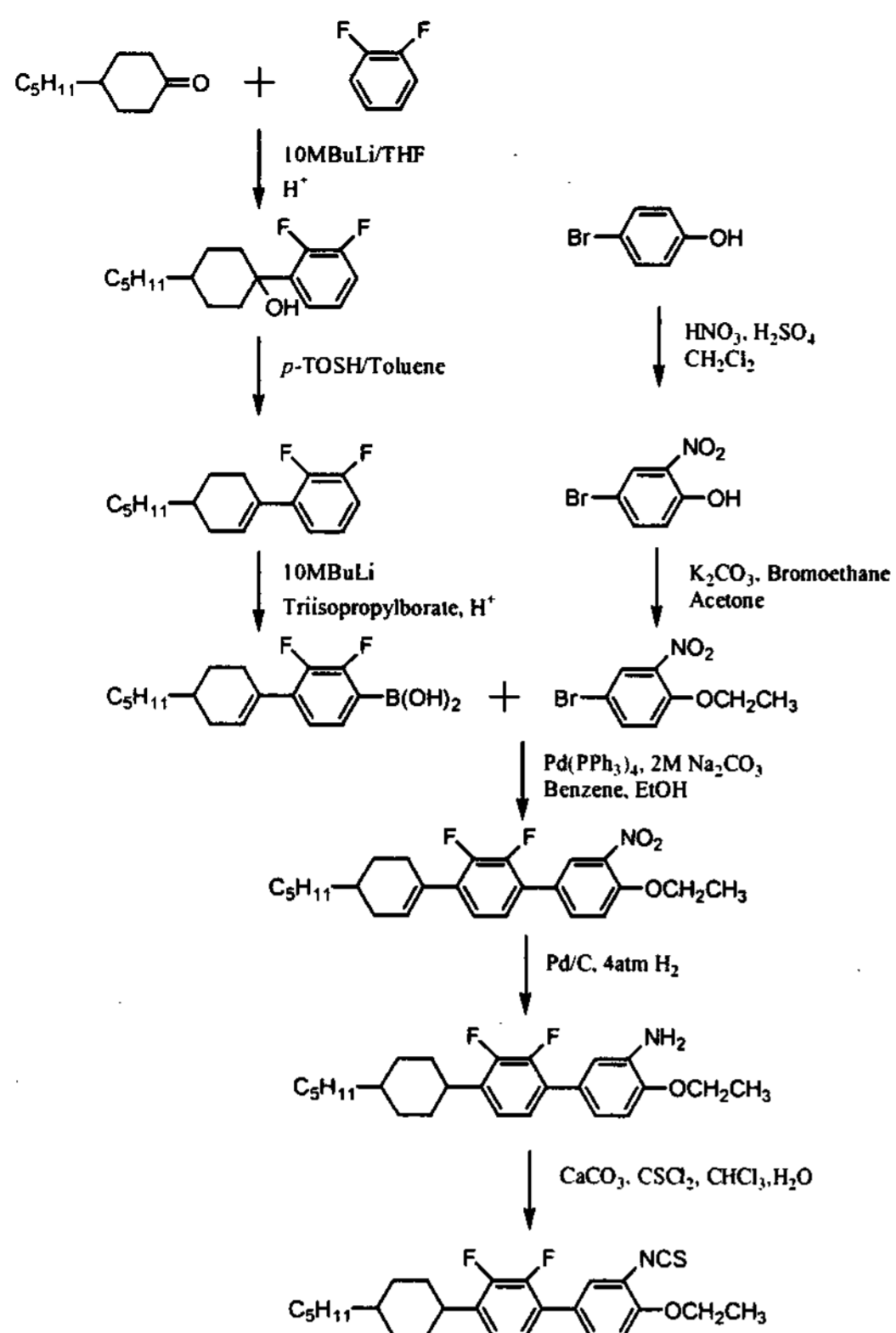
In this work, we introduced that the synthetic route, the physical and electro-optical properties of the new liquid crystalline compounds with the isothiocyanato group in *meta* position of phenyl ring as lateral substituent.

2. Experimental and Measurements

The chemical structures of products were confirmed by ^1H and ^{13}C NMR spectroscopy (Bruker Avance 400 Spectroscope) and EI mass spectrometer (70eV Hewlett Packard 5972 MSD). Their purity were checked by a GLC analysis (Hewlett Packard 6890 series attached to a 30m HP-5MS column) and found to be more than 99.9% pure. The phase transition temperature and liquid crystalline phase were observed with a polarizing microscope (Olympus BH-2) equipped with a heating stage and a controller (Mettler FP82) and Differential Scanning Calorimeter (Perkin-Elmer DSC-7). The dielectric anisotropy $\Delta\epsilon$ is determined by the capacitive method at a frequency of 1 kHz. The optical birefringence Δn is measured using an Abbe refractometer at 20°C . The flow viscosity η is obtained by cannon micro viscometer. The $\Delta\epsilon$, Δn and η of single compounds are extrapolated from 15 wt% solutions in the host mixture. And electro-optic properties (V_{10} , V_{90} , t_{on} , t_{off}) were measured at $4.0\ \mu\text{m}$ VA cell. The measurement has done at 60Hz and 4.5 volt with waveform generator.

3. Synthesis

The typical synthetic procedure of the new liquid crystalline compound with fluoro-isothiocyanate group is depicted in Scheme 1. All homologues were prepared using the same methods, and therefore the general experimental procedures are illustrated using *trans*-4'-ethoxy-2,3-difluoro-3'-isothiocyanato-4-(*trans*-4-pentylcyclohexyl)-biphenyl. They were prepared by a coupling reaction which is the preparation of a boronic acid *via* lithiation *ortho* to a fluorine atom [6,7], and the boronic acid is then coupled with an aryl bromide using tetrakis(triphenylphosphine) palladium(0) as a catalyst [8].



Scheme 1. Synthetic procedure of LC compound with the isothiocyanate group in *meta* position of phenyl ring as lateral substituent.

4. Result and Discussion

The phase transition temperatures of mesophase of the synthesized compounds were listed in Table 1. As can be seen, 5CPFFPSF and 3CPFFPSO1 compounds exhibit monotropic nematic phases. 5CPFFPSO2, 5CPFFPSO1 and 3CPFFPSO2 have enantiotropic nematic phases, whereas 3CPFFPS1, 5CPFFPS1 compounds is a non-mesogenic. For the 5CPFFPSO2, 3CPFFPSO2 compounds, smectic B phase is observed in the cooling process. In the homologous series, the thermal stabilities follows the order the ethoxy > methoxy > fluorine atom > methane substituted in the benzene ring. Their stability is strongly influenced by the molecular parameters such as rigidity, length-to-breadth ratio, packing density, polarizability and enhancement of polarity by conjugation. As the chain length increases, the tendency to form the smectic phase increases. This is due to the larger lateral intermolecular attractive force and the smaller terminal intermolecular cohesions.

Table.1 Phase transition temperature of target compounds.

abbreviation	R ₁		phase transition temperatures (°C)			
	R ₂		Cry	SmB	N	Iso
5CPFFPSF	C ₅ H ₁₁	Heat	•	-	-	52
	F	Cool	•	<-30	-	5.28
5CPFFPSO2	C ₅ H ₁₁	Heat	•	73.4	-	77.9
	OC ₂ H ₅	Cool	•	<-30	63.7	75.8
5CPFFPSO1	C ₅ H ₁₁	Heat	•	62.1	-	86.9
	OCH ₃	Cool	•	<-30	-	85.1
3CPFFPSO2	C ₃ H ₇	Heat	•	-	80.5	92.7
	OC ₂ H ₅	Cool	•	37.6	70.7	91.1
3CPFFPSO1	C ₃ H ₇	Heat	•	-	-	73.9
	OCH ₃	Cool	•	<-30	-	68.4
5CPFFPS1	C ₅ H ₁₁	Heat	•	-	-	34.5
	CH ₃	Cool	•	<-30	-	-
3CPFFPS1	C ₃ H ₇	Heat	•	-	-	72.3
	CH ₃	Cool	•	<-30	-	-

These fluoro-isothiocyanate series exhibit the low clearing temperatures relatively. The low clearing temperature is mainly attributed to the molecular length to breadth ratio.

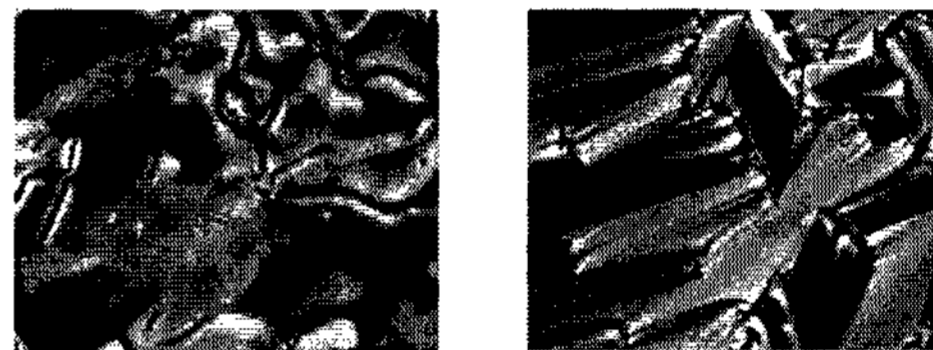


Figure 1. Optical polarizing microscopy texture of *trans*-4'-ethoxy-2,3-difluoro-3'-isothiocyanato-4-(4-pentylcyclohexyl)-biphenyl. (a). nematic phase (75 °C, cooling) (b) smectic B phase (60 °C, cooling).

The physical properties and the molecular parameters of these LC compounds are listed in Table 2. In case of the kind of core group and the length of alkyl spacer in analogue series are same, $\Delta\epsilon$ values of LC compounds shows $-3.1 \sim -5.5$ for the substitution of alkoxy group in terminal position and about zero for alkyl group. On the other hand, 5CPFFPSF has positive $\Delta\epsilon$ of 5.4. This dependency is explained by the Maier-Meier mean field theory^[9] based upon the Onsager model, $\Delta\epsilon$ is given by

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

Here, S is order parameter, N is molecular packing density, h is cavity field factor, and F is Onsager reaction field factor. According to equation (1),

the dielectric anisotropy of a Liquid crystals are mainly determined by the dipole moment μ , its angle β with respect to the principle molecular long axis, if $\beta > 55^\circ$, becomes negative $\Delta\varepsilon$. The reason that 5CPFFPF has positive $\Delta\varepsilon$, even

if it contains 2,3-difluoro moiety, laterally isothiocyanate substituted is present not perpendicularly but parallel to the molecular long axis, in consequence of the result a strong dipole moment generated toward molecular long axis.

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

Abbreviation	$\mu^{1)}$ (Debye)	$\Delta\alpha^{1)}$ (a.u)	$\Delta\alpha/M^{1)}$	$\beta^{1)}$ (Degree)	$l/d^{1)}$ (\square)	ε_{\parallel}	ε_{\perp}	$\Delta\varepsilon^{2)}$	n_e	n_o	$\Delta n^{2)}$	$\eta^{2)}$ (mm^2s^{-1})
5CPFFPSF	4.43	257.2	0.617	54.0	18.64/6.37	12.93	7.53	+5.40	1.6729	1.5394	0.1335	73.0
5CPFFPSO2	5.27	260.5	0.588	84.1	20.76/6.39	5.47	10.97	-5.50	1.6995	1.5301	0.1694	112.8
5CPFFPSO1	5.26	260.0	0.606	78.9	18.65/6.37	7.00	10.10	-3.10	1.6872	1.5387	0.1458	107.7
3CPFFPSO2	5.28	259.8	0.626	80.6	18.48/6.39	5.87	10.97	-5.10	1.6809	1.5348	0.1461	112.8
3CPFFPSO1	5.27	261.1	0.651	77.9	17.03/6.37	6.93	10.63	-3.70	1.7029	1.5448	0.1581	122.4
5CPFFPS1	4.34	251.8	0.609	72.6	18.78/6.43	8.27	7.57	+0.70	1.6669	1.5481	0.1188	115.0
3CPFFPS1	4.35	254.5	0.639	72.4	16.48/6.43	7.67	7.47	+0.20	1.6795	1.5554	0.1241	115.0

μ : dipole moment; $\Delta\alpha$: polarizability anisotropy; β : between dipole moment and molecular long axis; l/d : length to breadth ratio
1): For the calculations, we used semi-empirical quantum method (AM1 Hamiltonian in the MOPAC 5.0)
2): Extrapolated values from 15 wt% host solutions.

The liquid crystal compounds with high Δn value helps to shorten the response time because of the thinner cell gap requirement. The Δn is determined by molecular polarizability anisotropy $\Delta\alpha$ and order parameter S. Accordingly, the Δn value of nematic liquid crystal can be represented in the form of an approximate relationship as following.^[10]

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

Here, M^* is the molecular mass of the nematic liquid crystal compound, ρ is its density, $\Delta\alpha$ is the polarizability anisotropy of the molecule. The optical anisotropy values Δn have 0.1448 ~ 0.1694 for terminally alkoxy LC compounds, the other hand fluoro and alkyl substituted compounds have 0.1188 ~ 0.1335. The Δn values of the alkoxy substituted compounds are higher than the alkyl and fluorine substituted compounds due to the exhibiting high anisotropy of the molecular polarizability as shown Table 2.

We measured the physical and Electro-optic properties of Mixtures with 15wt% fluoro-

isothiocyanated compounds, the results are displayed in table 3.

Table 3. Physical and electro-optic properties of Mixtures with 15wt% fluoro-isothiocyanated compounds.

Mixture	$\Delta\varepsilon$	Δn	η mm^2s^{-1}	V_{10}	V_{90}	τ_{on}	τ_{off}	T_{NI}
				V		ms 60Hz(4.5V)		$^{\circ}C$
Host	-3.39	0.0801	21.36	2.7	5.7	18.6	7.9	74.2
Host+15wt% 5CPFFPSF	-2.07	0.0881	29.11	2.9	5.9	7.2	15.3	61.8
Host+15wt% 5CPFFPSO2	-3.72	0.0934	35.09	2.5	4.9	7.1	15.6	74.9
Host+15wt% 5CPFFPSO1	-3.13	0.0906	34.31	2.5	5.4	6.8	14.1	71.6
Host+15wt% 3CPFFPSO2	-3.69	0.0903	35.09	2.5	4.7	7.0	16.6	76.9
Host+15wt% 3CPFFPSO1	-3.52	0.0918	36.53	2.5	5.8	11.4	13.7	72.6
Host+15wt% 5CPFFPS1	-2.77	0.0859	35.40	2.8	5.9	13.9	13.7	61.0
Host+15wt% 3CPFFPS1	-2.85	0.0867	35.40	2.8	5.9	23.7	11.1	61.4

As can be seen in table 3, V_{10} and V_{90} of mixture of 5CPFFPSO2 series enhanced a little in comparison with host mixtures. And rising time is faster than that of host mixture, but falling time is slower than their host mixture. Because dielectric anisotropy value of the added single compounds in high, threshold voltage is lower and rising time is faster than host mixtures. To optimize switching speed it is important to decrease the viscosity of liquid crystal mixture. As the result of table 3, because of high viscosity, the falling time of Mixtures is slower than host mixture. It is shows that the lower viscosity of this mixture gets falling time to faster. Therefore, when we want to get the faster switching speed, the viscosity yet needs to be improved.

5. Conclusion

The development of the VA-TFT LCDs with its superior picture quality triggered a strong demand for new dielectrically negative liquid crystals. These materials still require optimization with regard to electro-optic, viscoelastic ratio and mesogenic properties. Making use of a combination of molecular modeling and empirical structure-physical property correlations, it is possible to design liquid crystals with negative dielectric anisotropy. The *trans*-4'-alkoxy-2,3-difluoro-3'-isothiocyanato-4-(4-alkylcyclohexyl)-biphenyl series have large negative dielectric anisotropy (-3.1 ~ -5.4) and high birefringence

(0.13~0.17). And their mixtures showed faster response time and lower thresh hold voltage. The series of synthesized compounds can be used for VA-LCDs

6. Acknowledgements

This work was performed Advanced Backbone IT technology development project supported by Ministry of Information & Communication in republic of Korea.

7. Reference

- [1] De Jeu, W. H, 1980, *Physical Properties of Liquid Crystalline Materials* (New York: Gordon & Breach).
- [2] Peer Kirsch, Kazuaki Tarumi. *Angrew. Chem. Int. Ed.* 1998, 37,4
- [3] Y.B.Kim, B.H.Kim. *Society of International Display Digest'00 Digest*, 2000, 12
- [4] Y.B.Kim, I.K.Hur, *Journal of information display.* 2002, 2, 3
- [5] K. Ohmuro, S.Katalka, T.Sasaki, Y.Koike, *SID'97 Digest*, 1997, 845
- [6] B. J. Wakefield, *The Chemistry of Organometallic Compounds*, Pergamon Press, Oxford, 1972, p.39
- [7] G. W Gray, M. Hird, D. Lacey, and K. J. Toyne, *Mol. Cryst. Liq. Crst.*, 1989, 172, 165.
- [8] N. Miqaura, T. Yanagi, and A. Susuki, *Synth. Comm.*, 1981, 3, 1261
- [9] W. Maier, and G. Z. Meier, *Z. Naturforsch Teil A*, 1961, 16, 262.
- [10] M. Klasen, M. Bremer, A. Gotz, A. Manabe, S. Maemura and K. Tarumi, *Jpn. J. Appl. Phys.*, 1998, 37, L945-L948,