

# Synthesis and physical properties of 2-(4-alkylcyclohexylphenyl)-5-alkyl (fluoro)-1,3,2-dioxaborinane derivatives their use in liquid crystals

Jae Ho Lee, Dae Won Park, Jin Ha Kim and Yong Bae Kim

Liquid Crystal Research Center, Department of Chemistry, Division of Natural Sciences,  
KonKuk University 1, Hwayang-dong, Kwangjin-gu, Seoul, 143-701, Korea.

## Abstract

2-[4-(4-alkylcyclohexyl)-phenyl]-5-alkyl-(1,3,2)-dioxaborinane and Fluoro-substituted 1,3,2-dioxaborinane vatives were synthesized and their physical properties were measured. synthesized compound were showed nematic -isotropic transition.

## 1. Introduction

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.<sup>[1]</sup>

Therefore we need the development of various liquid crystalline materials. The major of liquid crystalline molecules consist of carbon, oxygen, nitrogen, and hydrogen atoms. Though a few examples containing heteroatoms are known.<sup>[2]</sup> Liquid crystalline materials containing metal atoms are of special interest since they are expected to have unique properties based on the incorporation of metals having specials electric and magnetic properties.

In this study, we introduced that the synthetic route, the physical and electro-optical properties of the 2-[4-(4-alkylcyclohexyl)-phenyl]-5-alkyl-(1,3,2)-dioxaborinane and fluoro-substituted phenyl 1,3,2-dioxaborinane derivatives and the electro-optic properties of their mixtures.

## 2. Synthesis

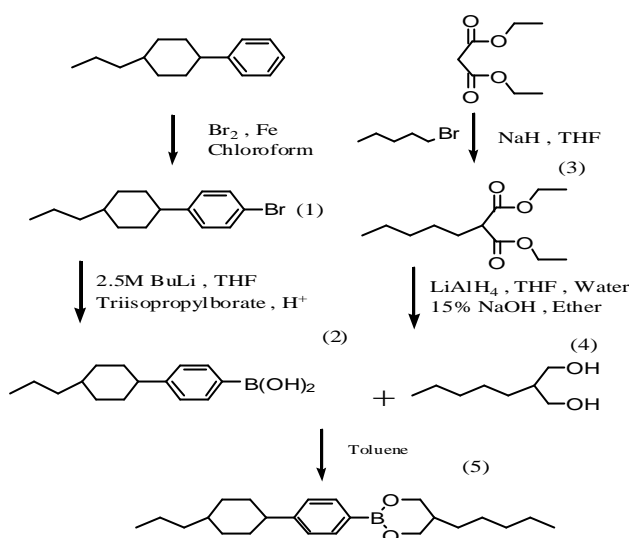
The typical synthetic procedure for the preparation of 2-(4-(4-trans-propyl-cyclohexyl)-phenyl)-5-pentyl-1,3,2-dioxaborinane crystalline compound is depicted in Figure1 and Figure2

### (1) 1-bromo-4-(trans-4-propylcyclohexyl)benzene

1-propyl-4-trans-phenylcyclohexane (16 g, 0.079 mol) and Fe 0.12g in chloroform. While stirring the solution Br<sub>2</sub> 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<sub>4</sub>) and removed in vacuo to give dark brown solid (20 g, yield 93%)

### (2) 4-(trans-4-propyl-cyclohexane)-phenyl boronic acid

The mixture of 1-bromo-4-(trans-4-propyl-cyclohexyl)-benzene (20 g, 0.071 mol) and tetrahydrofuran (250mL) 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 (liquid nitrogen-ethanol bath) and n-butyllithium (30 ml, 0.075 mol, 2.5M solution in hexane) was added rapidly (the rate of addition was adjusted such that the temperature did not momentarily exceed -70). After 0.5 hour, triisopropyl borate (30 ml, 0.13mol) was added the reaction mixture was warmed to room temperature. The mixture was washed with 0.1 N hydrochloric acid and water. The organic layer was dried (anhydrous MgSO<sub>4</sub>) and removed in vacuo to give yellow oil. The product was purified by recrystallised from hexane to give 4-(trans-4-propyl-cyclohexane)-phenylboronic acid (7 g, yield 40%)



**Figure 1. Synthetic method of LC compound 2-(4-(4-trans-propyl-cyclohexyl)-phenyl)-5-pentyl-1,3,2-dioxaborinane**

### (3) Diethyl pentylmalonate

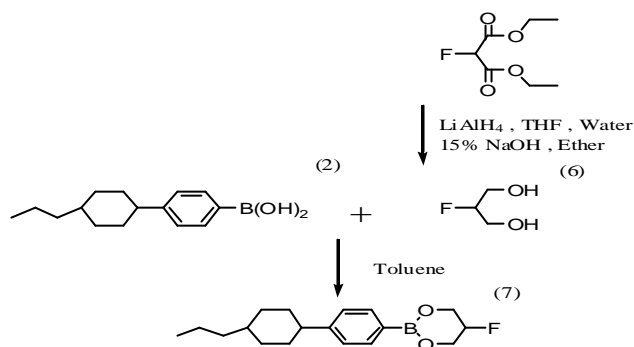
In a dry 500ml round-bottom three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet and reflux condenser attached to a bubble of diethyl malonate (20g 0.125mol) were placed in THF and then of NaH (5g 0.125mol) (60% in mineral oil) was slowly added at ice water. After we confirmed to come out hydrogen from the mixture, 1-Bromo-pentane (18.7g, 0.125mol) was dropped over 15min. Stirring was continued for 4 hours while refluxing at 68°C. The product was isolated by column chromatography (hexane:ether=1:20) (24g, mol, 83%)

### (4) 2-Pentyl-1,3-propane diol

to a suspension of  $\text{LiAlH}_4$  (9.8g, 0.26 mol) in dry THF (250mL), a solution of diethyl pentylmalonate (15g, 0.065 mol) in dry THF was added and the mixture was refluxed (2 H). After cooling, water (9.78 mL), 15% NaOH (9.78 mL), water (29.3 mL) were sequentially added and the suspension filtered onto Celite and washed with ether (200mL). The solvent was dried and evaporated to afford an oil (5g), which was purified by distillation (110 at 0.5mmHg) to give pure 2-Pentyl-1,3-propane diol (4.5 g, yield 47%)<sup>[3]</sup>

### (5) 2-(4-(4-trans-propyl-cyclohexyl)-phenyl)-5-pentyl-1,3,2-dioxaborinane

A mixture of 4-(trans-4-propyl-cyclohexane)-phenyl-boronic acid (2) (5 g, 0.025 mol), 2-Pentyl-1,3-propanediol (4) (3.6 g, 0.025 mol) and toluene (120mL) was stirred under reflux for 2H. During the reaction the water formed removed azeotropically using a Dean-Stark apparatus. When the reaction was completed, toluene was distilled away, and the resultant residue was purified by chromatography on silica gel using ethyl acetate and hexane as an eluant. Recrystallization from hexane gave the corresponding products 2-(4-(4-trans-propyl-cyclohexyl)-phenyl)-5-pentyl-1,3,2-dioxaborinane (5 g, yield 56%)<sup>[4]</sup>



**Figure 2. Synthetic method of LC compound 2-(4-(4-trans-propyl-cyclohexyl)phenyl)-5-fluoro-1,3,2-dioxaborinane**

### (6) 2-Fluoro-1,3-propanediol

The synthesis method is identical with (4) method. It was purified by distillation (80 at 0.5mmHg) to give pure 2-Fluoro-1,3-propanediol (2.8 g, yield 53%)

### (7) 2-(4-(4-trans-propyl-cyclohexyl)phenyl)-5-fluoro-1,3,2-dioxaborinane

The synthesis method is identical with (5) method. It was purified by chromatography on silica gel using ethyl acetate and hexane as an eluant. Recrystallization from ethyl acetate and ethanol gave the corresponding products 2-(4-(4-trans-propyl-cyclohexyl)-phenyl)-5-fluoro-1,3,2-dioxaborinane (3.5 g, yield 52%)

### 3. Measurements

The chemical structures of products were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Bruker Avance 400 Spectroscopy) and GC/Mass spectrometer (Hewlett Packard 6890 series GC system and MSD). The liquid crystalline phase and phase transition temperature were observed through a polarizing microscope (Olympus BX51, BX60), equipped with a heating stage and a controller (Mettler FP90, STC 200D), and Differential Scanning Calorimeter (Perkin-Elmer Diamond DSC / TAC-7). The dielectric anisotropy  $\Delta\epsilon$  was determined by the capacitive method and using impedance analyzer (Hewlett Packard LF impedance analyzer 4172A) at a frequency of 1 kHz using an antiparallel and homeotropic cells with 4 $\mu\text{m}$  thickness. The response times were measured by applying a square-wave AC voltage of 5V at 60 Hz.

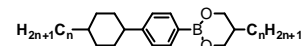
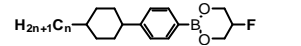
And voltage holding ratio (VHR) were measured using model 6254 Toyo Co. The optical birefringence  $\Delta n$  was measured by using an Abbe's refractometer (at 589nm) and the flow viscosity  $\eta$  was obtained by cannon micro viscometer at 20  $^\circ\text{C}$ . All the measurements were carried out at a fixed temperature 20  $^\circ\text{C}$  on 15wt% solutions of the compound in standard host mixture (ZKC 5081LA) and extrapolated to 100% concentrations, taking into account the variation of the physical parameters of the mixture under investigation. The molecular geometry was calculated using the semi empirical quantum chemical AM1 method (MOPEC 7.0 package).

### 4. Result and discussion

The chemical structures and abbreviations are listed in Table 1. Phase transition temperatures of mesophase of the synthesized compounds shown in Table 2. As you can see Table 2, most of compound were found to have enantiotropic nematic phases, whereas RnCPBF compounds was a non-mesogenic.

All the homologues of RnCPBRn series show high nematic-isotropic transition temperature ( $T_{ni}$ ) points (128.4 ~ 146.1  $^\circ\text{C}$ ) and nematic temperature ranges.

**Table1. Chemical structures and abbreviations for the synthesized liquid crystal compounds**

Abbreviation	Structure
RnCPBRn	
RnCPBF	

**Table2. Phase transition temperatures synthesized liquid crystal compounds**

Abbreviation	Phase Transition Temperature( $^\circ\text{C}$ )			
		C	N	Iso
R3CPBR3	Heat	118.8	146.1	
	Cool	109.7	143.6	
R3CPBR5	Heat	112.6	138.9	
	Cool	105.5	136.9	
R3CPBR7	Heat	108.4	130.2	
	Cool	95.9	128.4	
R3CPBRF	Heat		129.0	
	Cool		106.2	
R5CPBR3	Heat	101.0	142.1	
	Cool	95.9	128.4	
R5CPBR5	Heat	86.3	135.3	
	Cool	71.2	132.8	
R5CPBR7	Heat	93.6	132.3	
	Cool	79.7	131.1	
R5CPBRF	Heat		137.6	
	Cool		114.4	

The calculated molecular parameters such as the  $\mu$ ,  $\Delta a$ , and measured physical properties are summarized in Table 3. [ <sup>1</sup>For the calculations <sup>2</sup>Extrapolated values from 15 wt% host solutions.]

As shown in table 3, transition temperature ( $T_{ni}$ ) of synthesized liquid crystal compound mixtures is (0.2~12.6  $^\circ\text{C}$ ) higher than host mixtures. Dielectric anisotropy ( $\Delta\epsilon$ ) value is similar almost. The dielectric anisotropy values vary according to core structure, terminal group and alkyl spacer length. This can be explained by the Maier-Meier theory [5] which is based on the Onsager model. The dielectric anisotropy is given by

$$\Delta\epsilon = \frac{NFh}{\epsilon_o} \left\{ \Delta a + \frac{Fm^2}{2k_B T} (1 - 3 \cos^2 b) \right\} \cdot S \quad (1)$$

**Table 3. Molecular parameters from molecular modeling calculations, and the measured physical properties of synthesized liquid crystal compounds**

Abbreviation	$Tn^{(2)}$ ( )	$m^{(1)}$ (Debye)	$Da^{(1)}$ (a.u)	$\epsilon^{(2)}$	$n^{(2)}$	$V_{th}^{(2)}$ (V)	$\alpha^{(2)}$ (ms)	$\alpha_{off}^{(2)}$ (ms)	$\alpha_{total}^{(2)}$ (ms)	$\beta^{(2)}$ (mm <sup>2</sup> /s)	VHR <sup>(2)</sup> (%)
HOST	74.6	-	-	+5.21	0.0812	2.2	1.8	12.5	14.3	22.43	99.12
R3CPBR3	81.7	2.07	116.5	+5.08	0.0879	2.3	2.0	12.3	14.3	60.08	98.9
R3CPBR5	84.8	2.11	120.6	+5.09	0.0912	2.3	2.1	11.8	13.9	30.95	98.8
R3CPBR7	85.6	2.12	122.7	+5.12	0.0920	2.4	2.3	12.7	15.0	35.32	99.0
R3CPBF	74.8	0.26	109.5	+5.04	0.0865	2.1	1.8	13.9	15.7	62.06	98.7
R5CPBR3	84.9	2.09	119.8	+5.05	0.0901	2.2	2.2	13.4	15.5	29.45	98.6
R5CPBR5	86.6	2.10	124.3	+5.07	0.0958	2.4	2.5	13.7	16.2	49.14	98.8
R5CPBR7	87.8	2.12	126.1	+5.14	0.0842	2.4	2.4	12.5	14.9	35.34	98.7
R5CPBF	75.6	0.27	112.0	+5.15	0.0812	1.9	1.7	15.4	17.1	63.71	98.4

Here, S is order parameter, N is molecular packing density, h is cavity field factor, F is Onsager reaction field factor, and  $\mu$  is the dipole moment. We observed that RnCPBRn series showed similar  $\Delta\epsilon$ , due to the similar dipole moment  $\mu$  and anisotropy of molecular polarizability  $\Delta\alpha$ . However, RnCPBF series have small dipole moment  $\mu$  and anisotropy of molecular polarizability  $\Delta\alpha$ . In spite of RnCPBF series showed similar  $\Delta\epsilon$ . These results imply that dielectric anisotropy was greatly influenced by the angle  $\beta$  of term in equation (1)

The  $\Delta n$  is determined by molecular polarizability anisotropy  $\Delta\alpha$  and order parameter S, its density  $\rho$ , and n is the average refractive index of the substance, as follows.

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

**Table 4. UV stability test of synthesized liquid crystal compound**

	0	8s	15s	30s	60s	90s
Host	99.12	99.08	99.03	98.91	98.74	98.62
R3CPBR7	99.01	98.98	98.89	98.76	98.60	98.35

We also measured the UV dependence of voltage holding ratio(VHR)of synthesized liquid crystal compound mixture. As listed in Table 4, The VHR values of mixture were stationary.

In this study, we synthesized, trans-2-[4-(4-alkylcyclohexyl)-phenyl]-5-alkyl-(1,3,2)-dioxaborinane and fluoro-substituted phenyl 1,3,2-dioxaborinane derivatives and measured the physical properties for the purpose of high phase transition temperature, high dielectric constants, high stability of UV and low viscosity.

We found that the synthesized LC showed high phase transition temperature and high stability of UV, relatively large viscosity and low dielectric anisotropy.

## 5. Acknowledgement

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## 6. References

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