Synthesis and Physical Properties of
Novel Fluorinated Liquid Crystalline Compounds

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Abstract

The synthetic route and physical properties for three-ring derivatives, trans-2,3,2',3'-tetrafluoro-4-alkyl-4'-(4-alkyl-cyclohexyl)-biphenyl and 4-alkyl-cyclohexane carboxylic acid 2,3,2',3',4'-pentafluoro-biphenyl-4-yl ester are presented. They exhibit broad range nematic phases exceeding 30K and low viscosity of nematic liquid crystal mixtures containing these materials. Their viscosity is compared with that of homologues with a lateral isothiocyanate group and show large negative dielectric anisotropies. The threshold voltage V_{th} was low enough to be operated at a driving voltage of 5V. Our novel LC compounds are suitable materials for the improvement of dielectric anisotropy of vertical align liquid crystal displays (VA-LCDs).

1. Introduction

TFT-LCDs are widely utilized information displays, especially in laptop computers, monitors, and TVs due to their excellent resolution quality. However, TFT-LCD has some limitations such as narrow viewing angle and slow response time. Various methods to solve the viewing angle problem such as the addition of birefringence films, the domain divided twisted nematic, the in-plane-switching (IPS) mode, and vertical alignment (VA) mode have been proposed. Among these, newly developed VA-LCD is expected to show improved wide viewing angle and fast response time. [1] These LCDs involve relatively complicated functions, in term of optical anisotropy, elastic constants, dielectric anisotropies, and voltages and cell gap. For example, both dielectric and elastic constants determine the operating voltage, whereas the elastic constant and cell gap determine the switching time. From the viewpoint of molecular structure, the macroscopic properties of phase transition behavior, birefringence, dielectric constant and viscosity are closely interrelated. [2] With the rapid change in the development trend of LCDs the demand for new liquid crystalline materials are increasing. The applied materials use today for these modes are mainly fluorinated liquid crystalline compounds.[3,4] Super fluoro-substituted materials (SFM) are known for their larger dipole moment, high stability, high voltage holding ratio, low threshold voltage and low viscosity.[5] For this reason, many types of SFM were practically used and their properties have been investigated, despite that they have low dielectric and optical anisotropy which are known to deter high speed response. In this work, we report the synthesis of new LC with large negative dielectric anisotropy and the characterization of their physical properties. In addition, we discuss the physical constants of new LC in relation to the calculated molecular parameters.

2. Synthesis

The synthetic procedure that is typically applied in preparing negative dielectric liquid crystalline compound with fluorinate group is depicted in Figure1 and Figure2. All homologues were prepared using the same methods. In Figure 1, the core structure2, the core structure (phenylcyclohexyl group) was introduced by a carbon-carbon coupling reaction from the *trans-*

alkylcylohexanone and organolithium reagent generated from the corresponding halide derivatives, followed by the dehydration, the palladium-catalyzed cross-coupling reaction and reduction reactions. The pure *trans* compounds were obtained in the final stage of the successive recrystallization process(byphenyl group) was successfully introduced by the palladium-catalyzed cross-coupling reaction between boronic acid and aryl bromide [7], followed by deprotection of alcohol and esterification reactions. 2, the core structure (phenylcyclohexyl group) was introduced by a carbon-carbon coupling reaction from the *trans*-alkylcylohexanone and organolithium reagent generated from the corresponding halide derivatives, followed by the dehydration, the palladium-catalyzed cross-coupling reaction and reduction reactions. The pure *trans* compounds were obtained in the final stage of the successive recrystallization process.
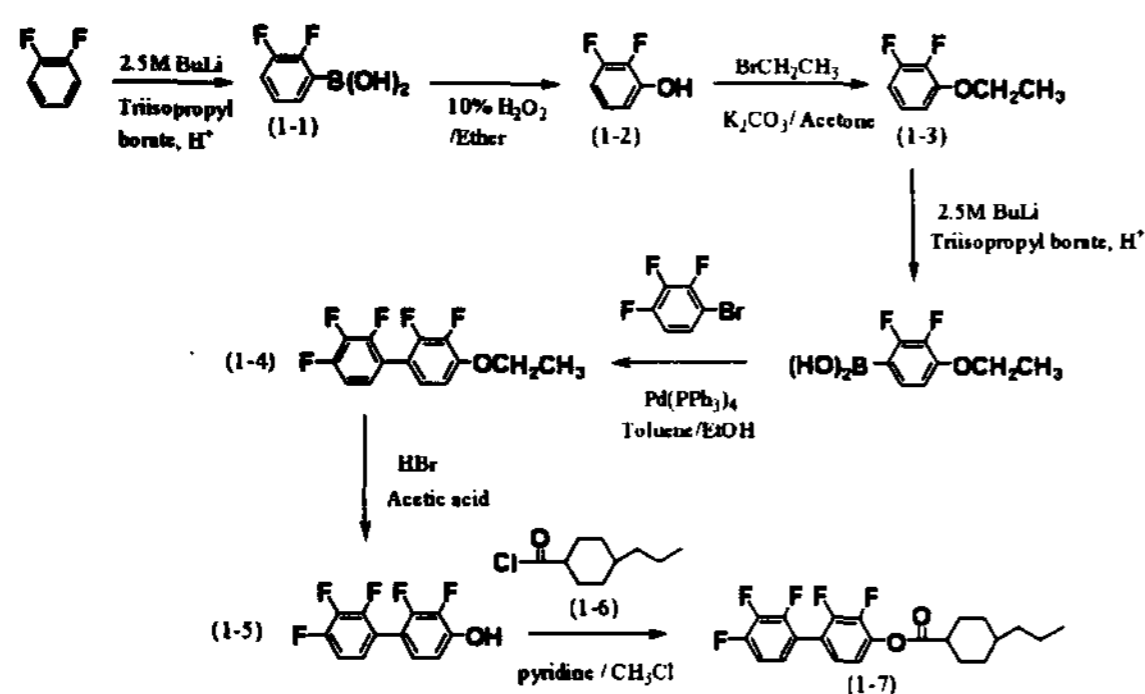

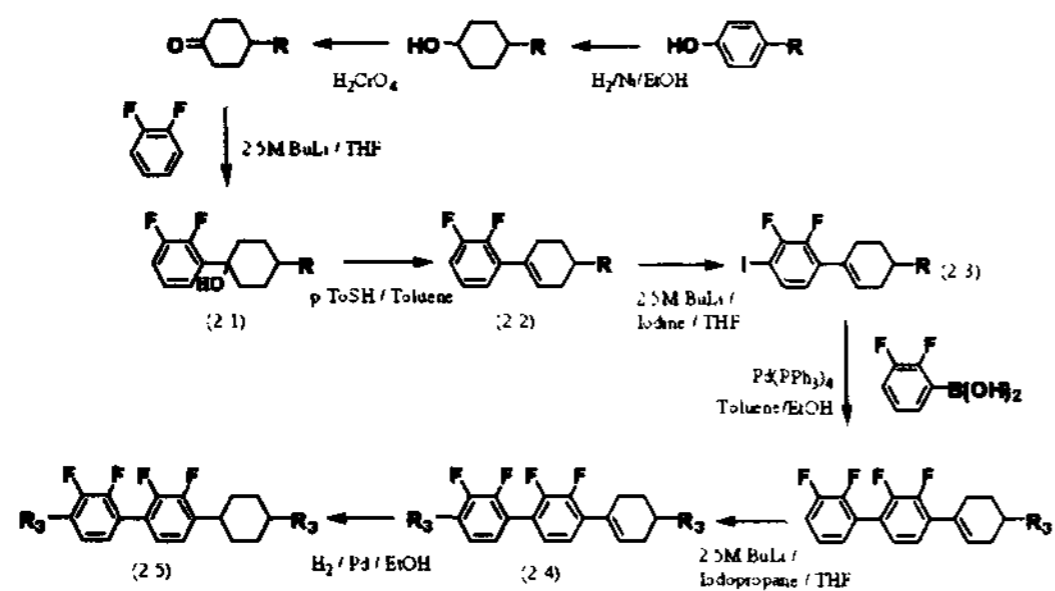**Figure1. Synthetic method of LC compound with Ester group as linking substitute**

Figure2. Synthetic route for alkyl chain as terminal substitute

3. Measurements

The chemical structures of products were confirmed by ^{1}H and ^{13}C NMR spectroscopy (Bruker Avance 400 Spectroscope) 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 DSC-7 / TAC-7). The dielectric anisotropy $\Delta\varepsilon$ was determined by the capacitive method and using impedance analyzer (Hewlett Packard LF impedance analyzer 4172A) at a frequency of 1 kHz. The optical birefringence Δn was measured by using an Abbe's refractometer and the flow viscosity η was obtained by cannon micro viscometer at 20 ℃. All the measurements were carried out at a fixed temperature 20 ℃ on 15wt% solutions of the compound in standard host mixture (MJ 961213) 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 and length-to-breadth ratio data are given, in Table 2 and the calculated molecular parameters such as theμ, $\Delta\alpha$, the angle β between μ and the long molecular axis of the molecule, and measured physical properties are summarized in Table 3.

Table1. Chemical structures and abbreviations for the biphenylcyclohenxane liquid crystal

Abbreviation	Structure
nCcooPFFPFFF	
nCPFFPFFn	

Table2. Phase transition temperatures L/D of biphenylcyclohenxane liquid crystal

Compound	l/d	T_{CN}	T_{NI}
3CcooPFFPFFF	4.1145	67.8	104.48
5CcooPFFPFFF	4.4967	72.7	115.14
3CPFFPFF3	4.3287	-	43.97
5CPFFPFF3	4.7472	43.2	79.41
3CPFFPFF5	4.8929	34.5	59.27
5CPFFPFF5	5.3790	22.5	62.8

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

Compound	$\mu^{1)}$	$\Delta\alpha^{1)}$	$\Delta\alpha/M^{1)}$	$\beta^{1)}$	l/d [1)	$\Delta\varepsilon^{2)}$	$\Delta n^{2)}$	η	Vth
3CcooPFFPFFF	6.11	187.2	0.455	53.09	4.1145	-3.045	0.1098	50.05	2.47
5CcooPFFPFFF	5.27	160.4	0.431	55.46	4.4967	-3.018	0.1062	46.44	2.5
3CPFFPFFF	5.20	150.4	0.408	52.6	3.5560	-2.02	0.0674	20.6	2.6
3CPFFPFF3	4.46	156	0.4	85.8	4.3287	-4.116	0.0918	65.5	2.1
5CPFFPFF3	4.52	162.7	0.387	83.3	4.7472	-4.918	0.1225	53.7	2.08
3CPFFPFF5	5.05	187.9	0.447	88.9	4.8929	-5.550	0.1229	55.90	2.25
5CPFFPFF5	4.42	171.5	0.383	80.9	5.3790	-4.606	0.1197	63.47	2.3

As you can see Table 2, 3CcooPFFPFF, 5CcooPFFPFF, 3CPFFFF5, 5CPFFPFF3, and 5CPFFPFF5 were found to have enantiotropic nematic phases, whereas 3CPFFPFF3 compounds was a non-mesogenic. For the 5CPFFPFF3 compounds, smectic C phase was observed in the heating and cooling processes. It is known that thermal stability is greatly influenced by the molecular parameters such as rigidity, length-to-breadth ratio, packing density, polarizability and enhancement of polarity by conjugation. These factors can explain the effect fluoro substitution on the thermal stability of liquid crystal molecules. As the L/D ratio increases, clearing temperature tend to become high. It is assumed that the larger lateral intermolecular attractive force due to increase of alkyl chain length. The exceptional case of 5CPFFPFF3 that forms a smetic phase is assumed to be the

outcome of the increase of the packing density. We also observed transition temperature of compound with ester group or not. Transition temperature of 3CcooPFFPFFF (104°C) was higher than that of 3CPFFPFFF (94°C). This result is assumed to be the result of the molecular parameters such as l/d and dipole moment and molecular polarizability $\Delta\alpha$ and, viscosity.

As shown in Table 3, the dielectric anisotropy values vary according to core structure, terminal group and alkyl spacer length. This can be explained by the Maier-Meier theory [9] which is based on the Onsager model. The dielectric anisotropy is given by

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_o}\left\{\Delta\alpha + \frac{F\mu^2}{2k_BT}(1-3\cos^2\beta)\right\} \bullet S \quad (1)$$

Here, S is order parameter, N is molecular packing density, h is cavity field factor, F is Onsager reaction field factor, and μ is the

dipole moment forming an angle β with the major inertial axis of the molecule. We observed that nCcooPFFPFFF showed larger negative Δε than those of nCPFFPFFF due to the larger dipole moment μ and anisotropy of molecular polarizability Δα and the angle β. However, nCPFFPFFns showed a larger negative Δε value than those of nCcooPFFPFFF, in spite of smaller dipole moment μ and anisotropy of molecular polarizability Δα. These results imply that dielectric anisotropy was greatly influenced by the angle β of term in equation (1). We also found that negative dielectric anisotropy Δε value is proportional to threshold voltage as shown in Table 3. The threshold voltage is expressed by equation (2) [10, 11], where ε_0 represents the dielectric constant is a vacuum.

$$V_{th} = \pi \left(K \Big/ \varepsilon_0 \Delta\varepsilon \right)^{\frac{1}{2}} \quad (2)$$

The Δn is determined by molecular polarizabilty anisotropy Δα and order parameter S, its density ρ, and n is the average refractive index of the substance, as follows.

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

Asymmetric compounds were seen to have a higher birefringence than those of symmetric as shown Table 3. In terminally alkyl chain compounds, they are classified as either asymmetry or symmetry. This characteristic was also observed in kinematic viscosity in Table 3. Asymmetric compounds (i.e., 3CPFFPFF5, and 5CPFFPFF3) had lower viscosity than that of symmetric compounds (i.e., 3CPFFPFF3, and 5CPFFPFF5).

From Figure 3 below, we can deduce that it is a typical behavior for Δn to increase with the increase of Δε in each group, because of the relationship between two parameters. As shown in equations (1) and (3), dielectric anisotropy Δε and birefringence Δn are in proportion to anisotropy of molecular polarizability Δα and order parameter S. Figure 4 shows the viscosity tendency of LC compounds. By introducing the fluorine group as a lateral substituent in the phenyl ring, the kinematic viscosity is low compared with homologues with the isothiocyanate-substituent. This is explained by the fact that molecular polarizabilty

anisotropy Δα of isothiocyanato group with three non-bonding electron pairs is higher than that of fluorine. This factor enhances the Van der Waal's attraction in molecules.
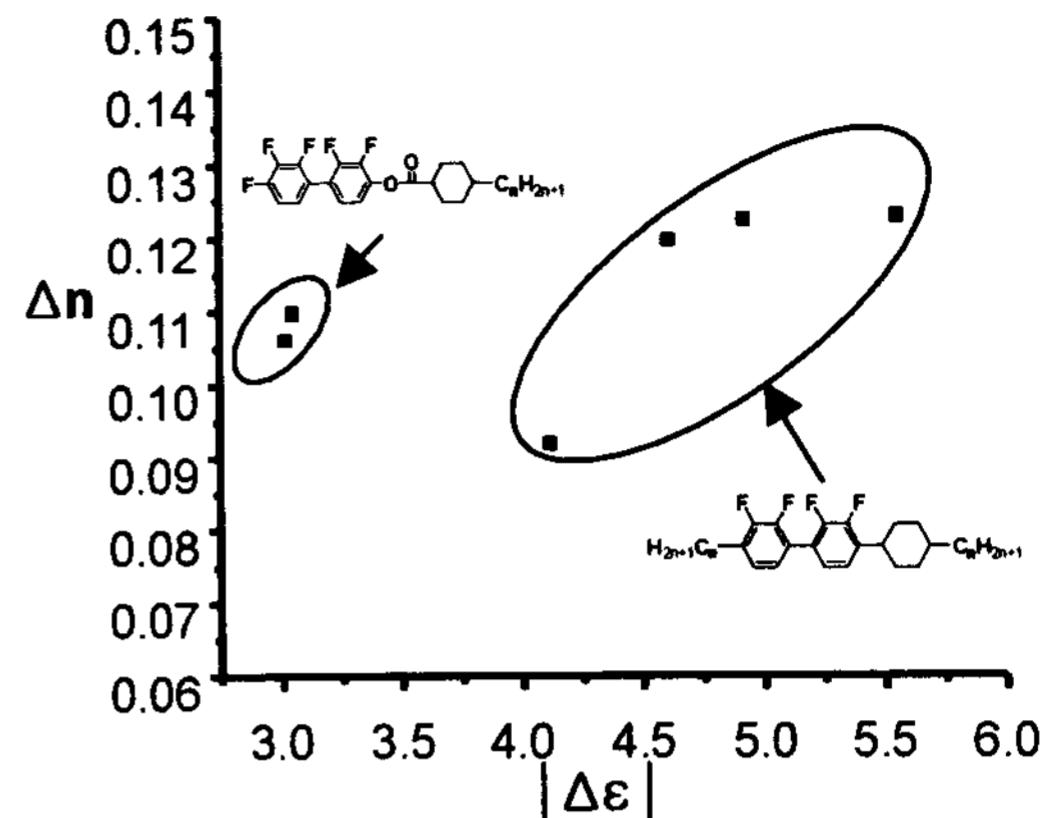

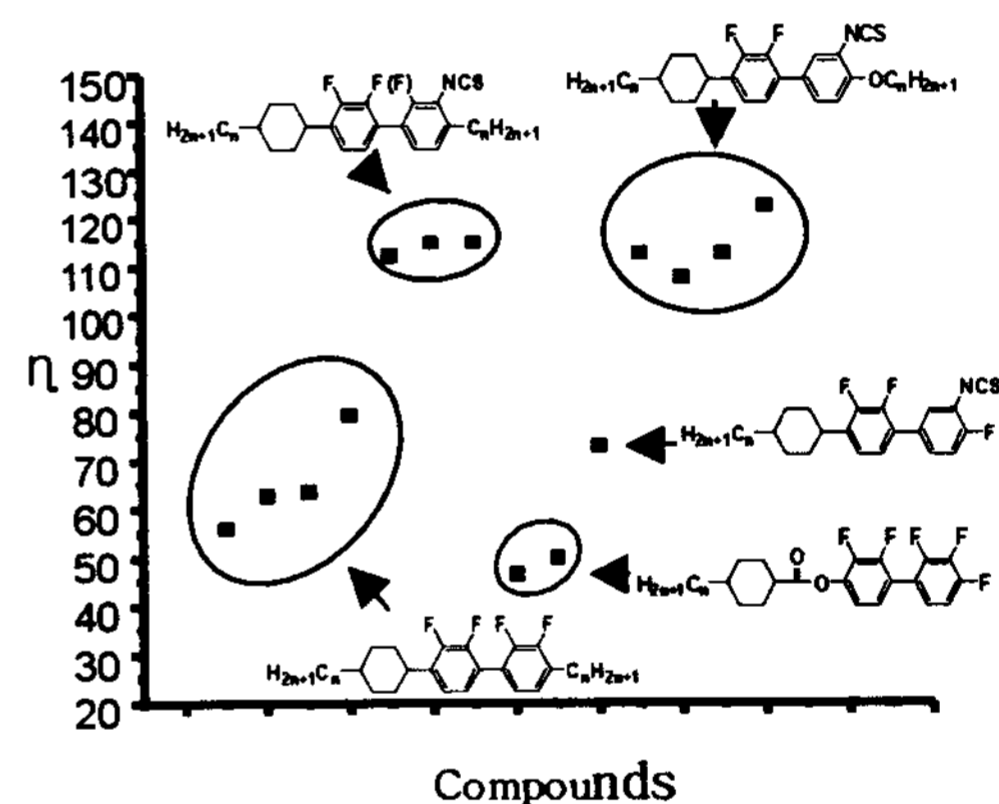**Figure3. Relationship between Δn and Δε for new LC for the experiments**

Figure4. Comparison of the kinematic viscosity between fluorinated LC and isothiocyanate LC

5. Conclusion

The The development of the VA-TFT-LCDs has created a greater demand for the development of new and improved liquid crystalline materials. In this study, we synthesized novel LC compounds, trans-2,3,2',3'-tetrafluoro-4-alkyl-4'-(4-alkyl-cyclohexyl)-biphenyl and 4-alkyl-cyclohexane carboxylic acid 2,3,2',3',4'-pentafluoro-biphenyl-4-yl ester and measured the

physical properties for the purpose of high phase transition We found that the synthesized LC showed low phase transition temperature, relatively low viscosity and large negative dielectric anisotropy And the threshold voltage V_{th} was low enough to operate in TFT-LCD at the driving voltage. The proposed LC compounds are deemed to be suitable materials for the improving dielectric anisotropy of vertical align liquid crystal displays (VA-LCDs).

6. Acknowledgement

7. References

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temperature, large negative dielectric constants, and low viscosity.

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