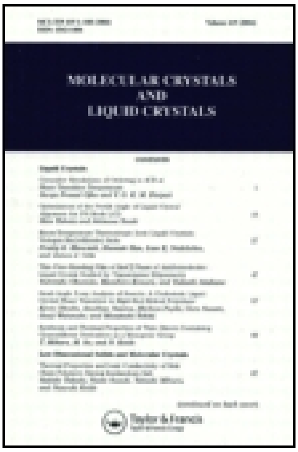

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Synthesis and Properties of Novel Negative Dielectric Liquid Crystal Compounds with a Tetrahydropyran Ring

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Synthesis and Properties of Novel Negative Dielectric Liquid Crystal Compounds with a Tetrahydropyran Ring

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Novel liquid crystal compounds having a tetrahydropyran ring structure have been developed. These compounds show large optical anisotropy, large absolute negative dielectric anisotropy and higher solubility with other LC compounds compared with conventional high birefringent negative dielectric compounds. The two types of tetrahydropyran derivatives have a chair form cyclohexane ring structure with oxygen in different positions, but they show almost the same dielectric value, and their temperature dependence shows almost the same tendency. In order to clarify this the probabilities of the various conformations were determined. Practical mixtures for the VA-LCD application show improved properties suitable for LCD-TV, also three-dimensional.

Keywords Large optical anisotropy; negative dielectric anisotropy; tetrahydropyran derivatives; VA-LCD

1. Introduction

Recent dramatic increase of the applications of negative dielectric nematic liquid crystal mixtures have been derived for LCD-TV purposes due to their superior properties of contrast ratio [1–3]. Moreover, three-dimensional TV, which was launched into the market in 2010 [4,5], has revitalized the market for LCD-TV and made the requirements for the physical properties more stringent, specifically for the properties of viscosity and solubility, which cannot be predicted from chemical structure or quantum chemical calculations.

To satisfy the physical properties of liquid crystal mixtures for VA-LCD to accord with the expansion of the VA-LCD market, we have developed liquid crystal compounds with a tetrahydropyran ring as a key component of the core structure of the rod-like molecules [Mol. Cryst. Liq. Crystal 494, pp. 58–67, 2008]. These compounds are characterized as having large negative dielectric anisotropy ($\Delta\varepsilon$) and superior solubility compared with conventional liquid crystal compounds. However, to meet the requirements of obtaining mixtures that can be used for the application of faster response VA-LCD, compounds with lower viscosity have become important. Using a conventional method to obtain low viscous liquid crystal mixtures,

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the amount of the diluter must be increased. On the other hand, the most effective diluter for liquid crystal mixtures is one that has small optical anisotropy. To obtain high quality images, the values of retardation Δn-d, where Δn is the optical anisotropy and d is the cell gap) must be constant. Therefore, to include the diluter at the maximum percentage, the other components must have a large value of Δn.

Conventional compounds having large Δn include aromatic rings in their structure, but these highly conjugated compounds do not have enough solubility compared to conventional liquid crystal compounds. To overcome these problems, we have developed a novel series of compounds having a tetrahydropyran ring, which can be synthesized by more efficient methods. These compounds show large Δε, large Δn and high solubility all at the same time.

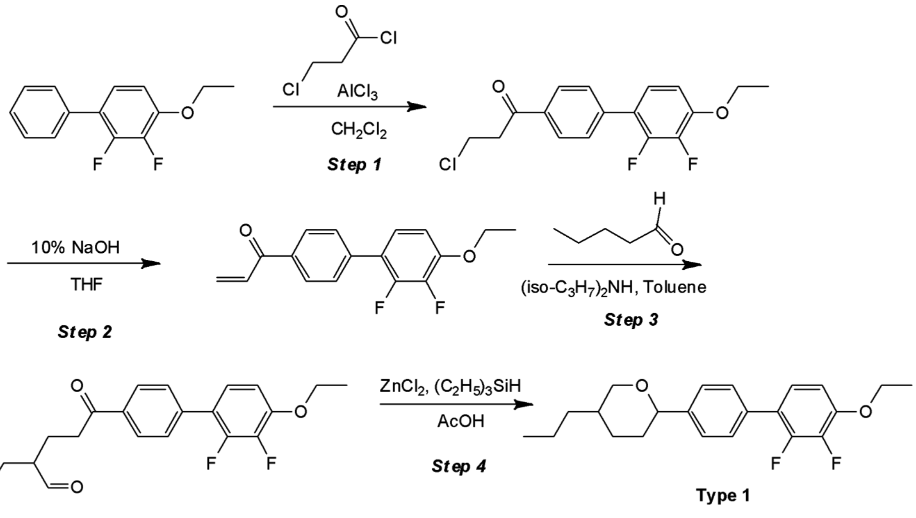
2. Synthesis

The novel liquid crystal compounds were synthesized following the Schemes 1 and 2 below.

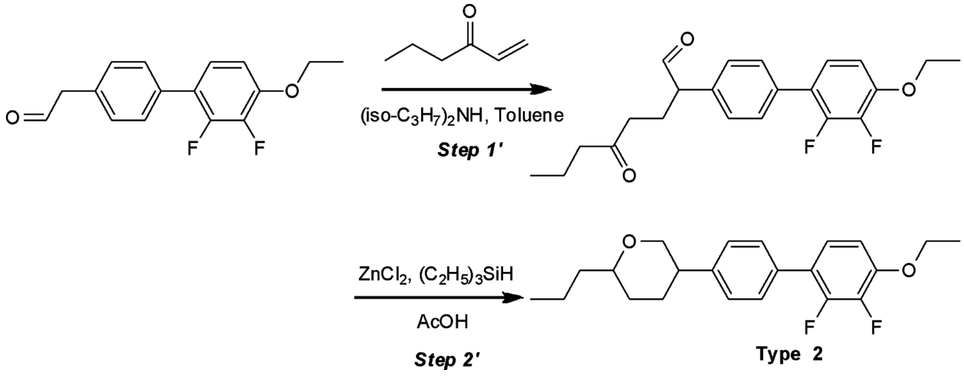
Specifically, oxoaldehyde is obtained by a reaction of enolate anions produced by aldehyde and strong base, together with *α*, *β* unsaturated ketone (Michael addition [6]), after which a cyclization reaction is carried out under acidic conditions to obtain a dihydropyran derivative, and by continuously carrying out reduction, a tetrahydropyran ring can easily be created.

Synthesis of 2-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-propyltetrahydro-*2H*-pyran (type 1, entry 1b in Table 1).

Step 1. 50.0 g of 2,3-Difluoro-4-ethoxybiphenyl (easily prepared from phenylboronic acid and 2, 3-difluoro-4-ethoxybromobenzene) and 31.2 g of anhydrous $AlCl_3$ were dissolved into 200 ml of CH_2Cl_2 at 5°C, into which 32.2 g of 3-chloropropionyl chloride was added while the temperature was maintained. After completion of addition, and after 1 hour of continuous agitation, the reactant was added to 200 ml of 10 wt% hydrochloric acid. After washing the



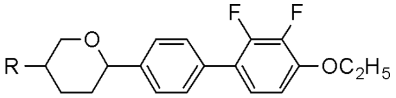
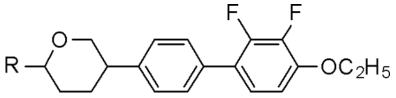
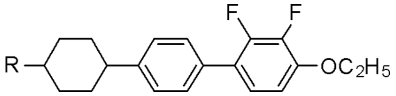
Scheme 1. Synthesis of tetrahydropyran derivatives Type 1.



Scheme 2. Synthesis of tetrahydropyran derivatives Type 2.

organic layer with 100 ml of 10 wt% aqueous sodium hydroxide solution, and then after washing with water until it was neutral, the organic layer was dried over anhydrous $MgSO_4$. Then, after the CH_2Cl_2 was removed in vacuum, the residue was recrystallized from 250 ml of n-hexane to obtain 61.5 g (85%) of 3-chloro-1-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)propan-1-one.

Table 1. Transition temperatures and transition enthalpies of tetrahyrdopyran derivatives types 1, 2 and reference compound 3

Entry	Transition temperatures (°C)	Transition enthalpies (kJ/mol)
	Type 1 	
1a; $R=C_2H_5$	C 92.2 N 133.4 I	C 26.7 N 0.50 I
1b; $R=C_3H_7$	C82.9 N 160.2 I	C 23.0 N 0.66 I
1c; $R=C_4H_9$	C80.4 N 153.9 I	C24.8 N 0.55 I
1d; $R=C_5H_{11}$	C 75.6 (SmB 55.4) N 159.3 I	C25.1 (SmB 2.64) N 0.65 I
	Type 2 	
2a; $R=C_2H_5$	C 68.7 N 109.1 I	C 21.9 N 0.41 I
2b; $R=C_3H_7$	C 72.0 N 137.8 I	C 22.5 N 0.57 I
2c; $R=C_4H_9$	C 65.3 SmA 68.8 N 127.4 I	C 20.8 SmA 0.35 N 0.47 I
2d; $R=C_5H_{11}$	C 66.9 SmA 74.6 N 134.5 I	C 21.6 SmA 0.11 N 0.66 I
	Type 3 	
3a; $R=C_2H_5$	C 77.5 N 142.0 I	C34.2 N 0.61 I
3b; $R=C_3H_7$	C 79.6 N 173.7 I	C 28.4 N 0.71 I
3c; $R=C_4H_9$	C 78.3 SmA 82.9 N 167.5 I	C22.1 SmA 0.78 N 0.64 I
3d; $R=C_5H_{11}$	C73.2 SmA 86.4 N 171.3 I	C 21.4 SmA 0.12 N 0.71 I

^{1}H NMR δ (ppm): 8.02 (dd, $J = 1.7$ Hz, $J = 8.3$ Hz, 2H), 7.63 (dd, $J = 1.3$ Hz, $J = 8.3$ Hz, 2H), 7.13 (ddd, $J = 2.3$ Hz, $J = 7.5$ Hz, $J = 8.4$ Hz, 1H), 6.83 (ddd, $J = 1.8$ Hz, $J = 7.3$ Hz , $J = 8.4$ Hz, 1H), 4.18 (q, $J = 7.0$ Hz, 2H), 3.95 (t, $J = 6.9$ Hz, Hz, 2H), 3.49 (t, $J = 6.9$ Hz, 2H), 1.49 (t, $J = 7.0$ Hz, 3H).

^{19}F NMR δ (ppm): -141.6 (ddd, $J = 1.8$ Hz, $J = 7.3$ Hz, $J = 19.3$ Hz, 1 F), -158.7 (ddd, $J = 2.3$ Hz, $J = 7.5$ Hz, $J = 19.3$ Hz, 1 F).

MS m/z (%) = 324 (M^+, 33.8), 288 (14.1), 261 (100.0), 233 (86.1), 51 (28.9).

Step 2. 50.0 g of 3-Chloro-1-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)propan-1-one was dissolved in 200 ml of THF at room temperature. 100 ml of 10 wt% aqueous sodium hydroxide solution was added to this solution. The temperature of the mixture was raised to 50°C and agitated for 1 hour. 50 ml of toluene was added to the reactant and the product was extracted. After the organic layer was washed with water until it was neutral, it was dried over anhydrous $MgSO_4$. After the toluene and THF was removed in vacuum, the residue was recrystallized from 150 ml of n-hexane to obtain 31.9 g (72%) of 1-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)prop-2-en-1-one.

^{1}H NMR δ (ppm): 8.02 (dd, $J = 1.8$ Hz, $J = 8.3$ Hz, 2H), 7.63 (dd, $J = 1.3$ Hz, $J = 8.3$ Hz, 2H), 7.19 (dd, $J = 10.4$ Hz, $J = 17.1$ Hz, 1H), 7.14 (ddd, $J = 2.4$ Hz, $J = 7.6$ Hz, $J = 8.3$ Hz, 1H), 6.83 (ddd, $J = 1.8$ Hz, $J = 7.3$ Hz, $J = 8.3$ Hz, 1H), 6.49 (dd, $J = 1.7$ Hz, $J = 17.1$ Hz, 1H), 5.95 (dd, $J = 1.7$ Hz, $J = 10.4$ Hz, 1H), 4.18 (q, $J = 7.0$ Hz, 2H), 1.49 (t, $J = 7.0$ Hz, 3H).

^{19}F NMR δ (ppm): -141.7 (ddd, $J = 1.8$ Hz, $J = 7.3$ Hz, $J = 19.3$ Hz, 1 F), -158.8 (ddd, $J = 2.4$ Hz, $J = 7.6$ Hz, $J = 19.3$ Hz, 1 F).

MS m/z (%) = 288 (M^+, 53.2), 260 (19.1), 233 (100.0), 204 (4.8).

Step 3. 20.0 g of 1-(4′-Ethoxy-2′,3′-difluorobiphenyl-4-yl)prop-2-en-1-one and 6.3 g of pentanal were dissolved in 50 ml of toluene. 2.5 g of (iso-$C_3H_7)_2NH$ was added to the solution, which was then agitated at 80°C for 10 hours. Then, after cooling it to room temperature, 200 ml of water was added to the reactant and the organic layer was washed with 100 ml of 10 wt% hydrochloric acid. After washing the organic layer with water until it was neutral, it was dried over anhydrous $MgSO_4$. Then, after the toluene was removed in vacuum, the residue was recrystallized from 150 ml of n-hexane to obtain 20.3 g (78%) of 5-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-oxo-2-propylpentanal.

^{1}H NMR δ (ppm): 9.64 (d, $J = 2.6$ Hz, 1H), 8.01 (dd, $J = 1.6$ Hz, $J = 8.2$ Hz, 2H), 7.61 (dd, $J = 1.3$ Hz, $J = 8.2$ Hz, 2H), 7.13 (ddd, $J = 2.4$ Hz, $J = 7.6$ Hz, $J = 8.3$ Hz, 1H), 6.82 (ddd, $J = 1.7$ Hz, $J = 7.5$ Hz, $J = 8.3$ Hz, 1H), 4.18 (q, $J = 7.0$ Hz, 2H), 3.10–2.95 (m, 2H), 2.44–2.37 (m, 1H), 2.11–2.02 (m, 1H), 2.00–1.92 (m, 1H), 1.76–1.68 (m, 1H), 1.55–1.46 (m, 4H), 1.45–1.36 (m, 2H), 0.95 (t, $J = 7.0$ Hz, 3H).

^{19}F NMR δ (ppm): -141.6 (ddd, $J = 1.7$ Hz, $J = 7.5$ Hz, $J = 19.7$ Hz, 1 F), -158.8 (ddd, $J = 2.4$ Hz, $J = 7.6$ Hz, $J = 19.7$ Hz, 1 F).

MS m/z (%) = 374 (M^+, 2.3), 346 (11.2), 276 (100.0), 261 (35.3), 248 (31.9).

Step 4. 10.0 g of 5-(4′-Ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-oxo-2-propylpentanal was dissolved in 100 ml of acetic acid. 3.6 g of anhydrous $ZnCl_2$ and then 16.9 g of $(C_2H_5)_3SiH$ were added to the solution, which was agitated at 25°C for 10 hours. 200 ml of water was added to the reactant, and the precipitated crystal was extracted with 50 ml of toluene, and the organic layer was washed with 100 ml of 10 wt% hydrochloric acid. After the organic layer was washed with water until it was neutral, it was dried over anhydrous $MgSO_4$. Then after the toluene was removed in vacuum, with n-hexane as element, the residue was purified by column chromatography using silica gel. Then n-hexane was removed in vacuum, and the residue was recrystallized from 20 ml of ethyl acetate to obtain 7.3 g (76%) of 2-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-propyltetrahydro-*2H*-pyran.

^{1}H NMR δ (ppm): 7.47 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.08 (ddd, $J = 2.4$ Hz, $J = 7.6$ Hz, $J = 8.4$ Hz, 1H), 6.78 (ddd, $J = 1.6$ Hz, $J = 7.5$ Hz, $J = 8.4$ Hz, 1H), 4.31 (dd, $J = 1.8$ Hz, $J = 11.5$ Hz, 1H), 4.15 (q, $J = 7.0$ Hz, 2H), 4.10 (ddd, $J = 2.0$ Hz, $J = 4.2$ Hz, $J = 11.2$ Hz, 1H), 3.23 (dd, $J = 11.1$ Hz, $J = 11.2$ Hz, 1H), 2.01–1.96 (m, 1H), 1.93–1.86 (m, 1H), 1.76–1.59 (m, 2H), 1.48 (t, $J = 7.0$ Hz, 3H), 1.43–1.23 (m, 3H), 1.22–1.07 (m, 2H), 0.92 (t, $J = 7.0$ Hz, 3H).

^{19}F NMR δ (ppm): −142.3 (ddd, $J = 1.6$ Hz, $J = 7.5$ Hz, $J = 19.8$ Hz, 1 F), −159.4 (ddd, $J = 2.4$ Hz, $J = 7.6$ Hz, $J = 19.8$ Hz, 1 F).

MS m/z (%) = 360 (M^+, 100), 332 (10.0), 261 (27.5), 247 (22.5), 234 (82.4), 206 (46.1).

Synthesis of 5-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-2-propyltetrahydro-*2H*-pyran (type 2, entry 2b in Table 1)

Step 1′. 10.0 g of (4′-Ethoxy-2′,3′-difluorobiphenyl-4-yl)acetaldehyde (easily prepared from 4-bromophenyacetaldehyde and 2,3-difluoro-4-ethoxyphenylboronic acid) and 4.1 g of hex-1-en-3-one were dissolved in 50 g of toluene. 1.3 g of (iso-$C_3H_7)_2NH$ was added to this solution, which was then agitated for 10 hours at 80°C. Then, after allowing the solution to cool to room temperature, the organic layer was washed with 100 ml of 10 wt% hydrochloric acid. After washing the organic layer with water until it was neutral, it was dried over anhydrous $MgSO_4$. Then, after the toluene was removed in vacuum, the residue was recrystallized from 20 ml of n-hexane to obtain 11.0 g (81%) of 2-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-oxooctanal.

^{1}H NMR δ (ppm): 9.70 (d, $J = 1.3$ Hz, 1H), 7.52 (dd, $J = 1.2$ Hz, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.09 (ddd, $J = 2.4$ Hz, $J = 7.7$ Hz, $J = 8.4$ Hz, 1H), 6.80 (ddd, $J = 1.7$ Hz, $J = 7.6$ Hz, $J = 8.4$ Hz, 1H), 4.17 (q, $J = 7.0$ Hz, 2H), 3.63 (m, 1H), 2.45–2.30 (m, 4H), 2.05–1.97 (m, 1H), 1.62–1.53 (m, 3H), 1.48 (t, $J = 7.0$ Hz, 3H), 0.89 (t, $J = 7.3$ Hz, 3H).

^{19}F NMR δ (ppm): −142.3 (ddd, $J = 1.7$ Hz, $J = 7.6$ Hz, $J = 19.6$ Hz, 1 F), −159.1 (ddd, $J = 2.4$ Hz, $J = 7.7$ Hz, $J = 19.6$ Hz, 1 F).

MS m/z (%) = 374 (M^+, 28.4), 288 (36.1), 260 (100.0), 232(47.2), 219 (8.1).

Step 2′. 10.0 g of 2-(4′-Ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-oxooctanal was dissolved in 100 ml of acetic acid. 3.7 g of anhydrous $ZnCl_2$ and then 17.0 g of $(C_2H_5)_3SiH$ were added to the solution, which was agitated at 25°C for 10 hours. 200 ml of water was added to the reactant mixture, the precipitated crystal was extracted with 50 ml of toluene, and the organic layer was washed with 100 ml of 10 wt% hydrochloric acid. After the organic layer was washed with water until it was neutral, it was dried over anhydrous $MgSO_4$. Then after the toluene was removed in vacuum, with n-hexane as eluent, the residue was purified by column chromatography using silica gel. Then n-hexane was removed in vacuum, and the residue was recrystallized from 20 ml of ethyl acetate to obtain 7.8 g (81%) of 5-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-2-propyltetrahydro-*2H*-pyran.

^{1}H NMR δ (ppm): 7.45 (dd, $J=1.2$ Hz, $J=8.2$ Hz, 2H), 7.27 (d, $J=8.2$ Hz, 2H), 7.08 (ddd, $J=2.2$ Hz, $J=7.6$ Hz, $J=8.4$ Hz, 1H), 6.79 (ddd, $J=1.6$ Hz, $J=7.7$ Hz, $J=8.4$ Hz, 1H), 4.16 (q, $J=7.0$ Hz, 2H), 4.05 (ddd, $J=2.2$ Hz, $J=4.2$ Hz, $J=11.2$ Hz, 1H), 3.44 (dd, $J=11.2$ Hz, $J=11.2$ Hz, 1H), 3.36 (m, 1H), 3.36 (m, 1H), 2.11–2.04 (m, 1H), 1.84–1.74 (m, 2H), 1.61–1.36 (m, 8H), 0.95 (t, $J=7.0$ Hz, 3H).

^{19}F NMR δ (ppm): -142.4 (ddd, $J=1.6$ Hz, $J=7.7$ Hz, $J=19.8$ Hz, 1 F), -159.3 (ddd, $J=2.2$ Hz, $J=7.6$ Hz, $J=19.8$ Hz, 1 F).

MS m/z (%) = 360 (M^+, 79.8), 317 (20.3), 273 (23.1), 260 (58.4), 232 (94.7), 71 (100).

3. Results and Discussion

3.1. *Physical Properties*

Table 1 indicates transition temperatures of the novel series of tetrahydropyran derivatives type 1 and 2 (1a to 1d and 2a to 2d) and conventional negative dielectric compounds type 3 (3a to 3d), with large Δn for comparison. All of the compounds have very similar molecular weight and shapes since there is no significant difference between the ether linkage -O- and the -CH_2- fraction. Contrary to the similar molecular weight and considerable structure of the compounds, type 1 and 2 show a different tendency. Namely, the type 1 series tends to show only a nematic phase and only the case of $R{=}C_5H_{11}$, compound 1d shows a monotropic Sm B phase. On the other hand, type 2 shows a SmA phase where the chain length of R is longer than three. This is a similar tendency to the reference compound type 3. From the comparison of transition temperatures and transition enthalpies, it is obvious that the type 1 series indicates slightly higher melting points, lower nematic to isotropic transition temperatures (TN-Is) and lower transition enthalpies compared with the reference type 3 series. Further, the type 2 series indicates lower melting and TN-Is temperatures when the compounds have a transition sequence of crystal to nematic. From the consideration of the transition temperature, the type 1 series takes a different ordered structure from type 2 and 3 series even though the transition phenomena is similar to type 3 series. The type 2 series forms a lowest ordered smectic phases comparable to type 1 and 3 series.

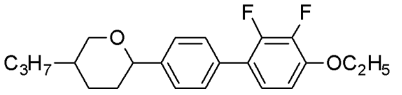
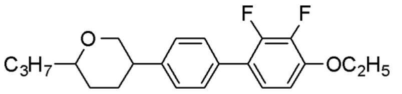
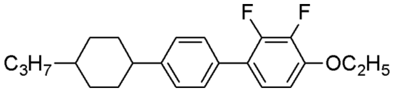
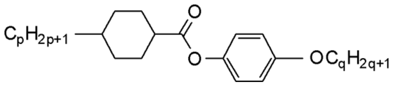
The values for dielectric anisotoropy [7] (Δε) and optical anisotropy [7] (Δn) of synthesized type 1 and type 2 compounds ($R{=}C_3H_7$) are shown with those of the reference compounds in Table 2. These values were obtained by adjusting 85% of a host mixture comprising phenyl cyclohexylcaboxylate and 15% of new liquid crystal compound of types 1, 2 and reference compound, measuring their Δε and Δn, and then directly extrapolating the measurement results [8].

As can be seen clearly from this table, it was determined that type 2 compound shows a very slightly larger Δε than the reference compound, while type 1 compound shows a Δε almost equal to the reference compound. Concerning Δn, it was determined that the 3 types showed almost the same absolute values.

3.2. *Temperature Dependence of the Dielectric Constants $\varepsilon_\perp$ and $\varepsilon_\parallel$*

In order to carry out a detailed investigation into the behavior of types 1 and 2 compounds in a nematic phase, using the host mixture mentioned above a mixture with

Table 2. The extrapolated values for dielectric anisotropy ($\Delta\varepsilon$) and optical anisotopy (Δn) of tetrahyrdopyran derivatives types 1, 2 and reference compound 3

		$\Delta\varepsilon$	Δn
1b		−5.9	0.180
2b		−6.2	0.180
3b		−5.7	0.180
Host mixture		−1.3	0.087
	p = 3, q = 4; 27.6%, p = 4, q = 2; 20.7%, p = 5, c7 = 1; 20.7%, p = 3, qr = 2; 17.2%, p = 5, c7 = 2; 13.8%		

Extrapolated data from mixtures containing synthesized compounds 15% and nematic host mixture 85%.

an even higher concentration (30%) was adjusted and the temperature dependence of the dielectric value was measured. The results of this are shown in Figure 1.

As is clear from these results, it was determined that both liquid crystal mixtures containing types 1 and 2 compounds show almost the same temperature dependence of dielectric value.

3.3. *Results of the Quantum Chemical Calculation of the Tetrahydropyrane Derivatives*

In order to examine the difference between the structures of types 1 and 2 compounds, the potential energy surfaces (30 degree intervals) were obtained along with dihedral angles $\theta 1$ and $\theta 2$ by using density functional theory (DFT) with a B3LYP functional [9] and 6–31G(d) basis sets. All caluculations were carried out using the GAMESS suite of program codes [10].

Boltzmann existence probabilities at 300 K for each conformer was then estimated as shown in Figures 2 and 3. From the results it was determined that for both types 1 and 2 compounds there are 8 stable conformation regions, and that there is no major difference between their existence probabilities. Within these stable regions, it appears that the structures with the most stable conformations for type 1 are when $\theta 1$ is 210 degrees, $\theta 2$ is 30 degrees, and for type 2 are when $\theta 1$ is 0 degrees, $\theta 2$ is 330 degrees. These conformations are shown in Figures 4 and 5.

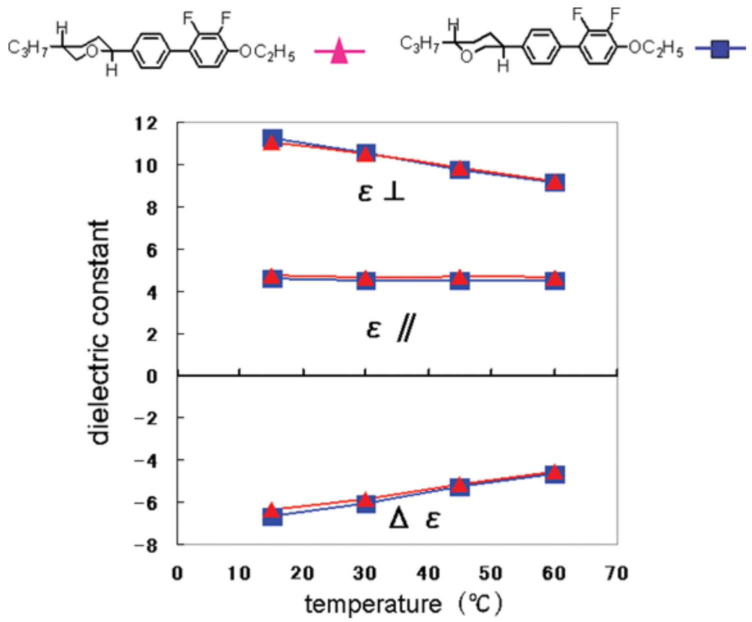


Figure 1. Temperature dependence of the dielectric constants. (Figure appears in color online.)

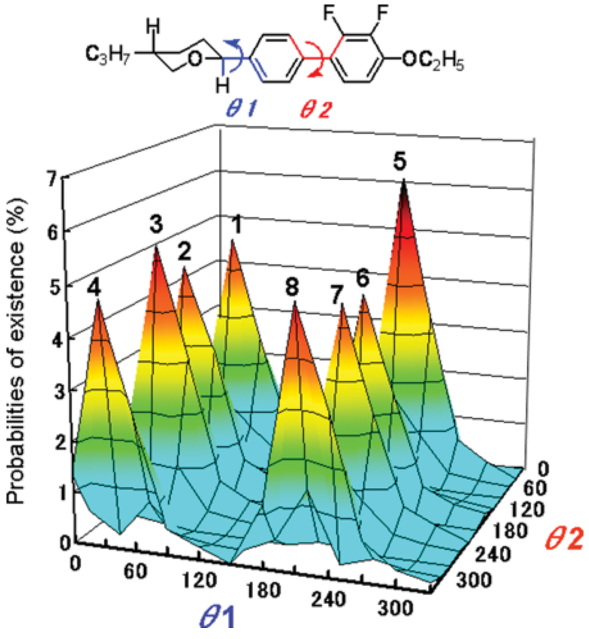


Figure 2. Boltzmann probabilities of existence of type 1 at 300 K. (Figure appears in color online.)

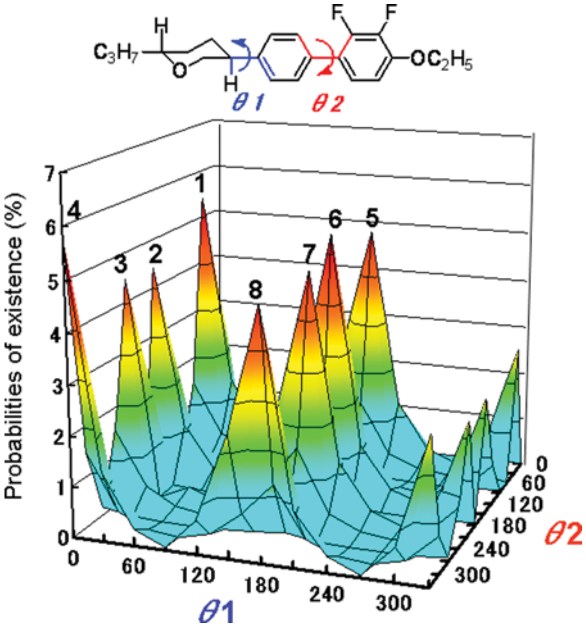


Figure 3. Boltzmann probabilities of existence of type 1 at 300 K. (Figure appears in color online.)

A dipole moment that can be produced by each conformation and an angle β between the long molecular axis and moment of inertia are different for each, and as a result the dielectric value produced by each conformation is different. Tables 3a and 3b show the calculated values for dipole moments and β for each of the eight stable conformations for types 1 and 2, which have high existence probabilities. Also, shown in Tables 3a and 3b is $-\mu^2(1–3\cos^2\beta)$, as the physical quantity proportional to

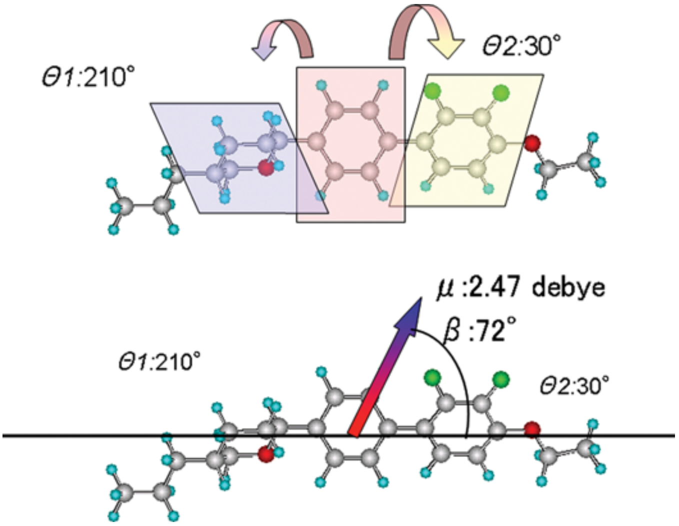


Figure 4. Most stable conformation for type 1. (Figure appears in color online.)

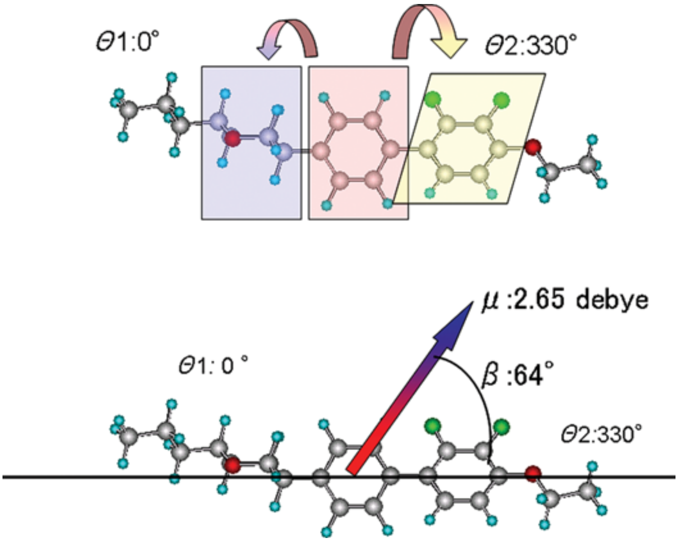


Figure 5. Most stable conformation for type 2. (Figure appears in color online.)

Δε, which can be calculated from the obtained dipole moments and β. However, conformation existence probabilities that can be taken by the two compounds are almost the same, and as a result the average dielectric value of the structure that can be taken can be confirmed. For both compounds this average dielectric value is almost the same. This also supports the measurement result that there is almost no difference between the two compounds for the measured dielectric values (ε⊥ and ε||) mentioned above.

3.4. *Mixtures for the VA-LCD Application*

From the above mentioned results, the novel series of compounds could become components of a practical liquid crystal mixture for VA-LCD application. Model mixtures including types 1 and 2 compounds 16 wt% respectively were prepared

Table 3a. Dihedral angle, dipole moments, (β and $-\mu^2(1–3\cos^2(\beta)$) of 8 stable conformations for type 1

Conformation no.	Dihedral angle $\theta1$ degrees	Dihedral angle $\theta2$ degrees	Dipole moment μ Debye	β degrees	$-\mu^2(1–3\cos^2\beta)$ $\propto \Delta\varepsilon$
1	30	30	4.22	83	−16.93
2	30	150	3.49	73	−8.95
3	30	210	2.48	73	−4.62
4	30	330	3.44	85	−11.55
5	210	30	2.47	72	−4.42
6	210	150	3.49	85	−11.91
7	210	210	4.20	83	−16.77
8	210	330	3.53	72	−8.95

Table 3b. Dihedral angle, dipole moments, β and $-\mu^2$ (1–3cos$^2\beta$) of 8 stable conformations for type 2

Conformation no.	Dihedral angle $\theta 1$ degrees	Dihedral angle $\theta 2$ degrees	Dipole moment μ Debye	β degrees	$-\mu^2(1–3\cos^2\beta) \propto \Delta\varepsilon$
1	0	30	3.82	72	−10.56
2	0	150	4.41	82	−18.36
3	0	210	3.52	80	−11.25
4	0	330	2.65	64	−2.99
5	180	30	3.50	81	−11.27
6	180	150	2.67	64	−2.89
7	180	210	3.76	72	−10.00
8	180	330	4.43	82	−18.56

and their physical properties compared with a conventional liquid crystal mixture including type 3 compound, from the viewpoints of practical application. Their physical properties are shown in Table 4.

As can be seen clearly from this table, it became possible to promote property improvement by using types 1 and 2 compounds as structural components.

Recently, to avoid the problem of image defect at low temperatures, liquid crystal mixtures must have a wide nematic temperature range. Especially at the low temperatures, a liquid crystal mixture must not crystallize and not indicate smectic phase. To confirm the practical applicability of the novel series, low temperature stability (LTS) test for type1 compound was conducted. The LTS test was conducted as follows; 9 mixtures consisting of a base mixture and type 1 compound for testing were prepared according to the ratios shown in Table 5. Nine comparable mixtures consisting of the base mixture and type 3 compound were also prepared for a reference test. The prepared mixtures were stored in glass bottles at −20°C for 30 days. After the preservation period, the conditions of the mixtures were examined with naked eyes. In cases where the mixture remained nematic, it is marked as Ne (Ne), in cases where it had entered smectic phase Sm (Sm), and in case where it had become crystal Cr (Cr). Table 5 shows the results of the low temperature preservation test. It was confirmed that the type 1 novel series has a tendency to prevent the formation of crystal at low temperatures as compared with the reference type 3.

Table 4. Physical properties of model mixtures comprising types 1, 2 and 3

Physical properties	Ref (type 3, 3b)	Mixture A (type 1, 1b)	Mixture B (type 2, 2b)
NI(°C)	80.6	81.4	80.7
$\gamma 1$ (mPa · sec)	60	55	56
Δn	0.103	0.104	0.104
$\Delta\varepsilon$	−2.5	−2.9	−2.9
K_{11}/K_{33}	14.2/13.5	14.2/14.7	13.7/14.1
Vc (V)	2.41	2.4	2.39

Table 5. Results of preservation test at −20°C

Concentration of type 1	1b	1c	1d	Concentration of type 3	3b	3c	3d
10 (wt%)	Ne	Ne	Ne	10 (wt%)	Ne	Ne	Ne
15 (wt%)	Ne	Ne	Ne	15 (wt%)	Cr	Cr	Ne
20 (wt%)	Sm	Ne	Sm	20 (wt%)	Cr	Cr	Cr

4. Conclusions

Novel liquid crystal compounds having a tetrahydropyran ring structure have been developed. These new compounds show large optical anisotropy values arising from the highly conjugated structure of the core part. Further, these derivatives show high absolute negative dielectric anisotropy values and higher solubility with the other liquid crystal compounds compared with conventional high birefringent negative dielectric compounds. The dielectric values of the two novel series indicate almost the same value and same temperature dependency. The two types of tetrahydropyran compounds have a chair form cyclohexane ring structure with oxygen in different positions, but they show almost the same dielectric value, and their temperature dependence shows almost the same tendency.The reason for this being that the existence probabilities of the various conformations that it can take are almost the same, and at the same time that both compounds have almost the same average dielectric values. Practical mixtures for VA-LCD application including novel liquid crystal compounds show improved properties suitable for LCD-TV including three-dimensional displays.

References

[1] Okumura, K., Kataoka, S., Sasaki, T., & Koide, Y. (1997). *SID Symposium Digest Tech Papers*, *28*, 845.

[2] Takeda, A., Kataoka, S., Sasaki, T., Chiba, H., Ohmuro, K., Koide, Y., Sasabayashi, T., & Okamoto, K. (1998). *SID Symposium Digest Tech Papers*, *29*, 1077.

[3] Kim, K. H., Park, S. B., Schim, J. U., & Souk, J. H. (1998). *SID Symposium Digest Tech Papers*, *29*, 1085.

[4] Chen, C.-Y., Chen, Y.-C., Dai, C.-H., Yeh, P.-C., Chiu, C.-H., Su, J.-J., Chen, T.-S., Norio, S., Liau, W.-L., & Lien, A. (2010). *SID Symposium Digest Tech Papers*, 37.1.

[5] Sik-Dae, Park, S.-M., Jung, J.-H., & Hwang, D.-C. (2010). *SID Symposium Digest Tech Papers*, 51.2.

[6] Bergmann, E.D., *et al.* (1959). *Org. React.*, *10*, 179–555.

[7] (a) Okamura, M., & Ichinose, H. (2002). *EKISYO*, *6*, 295; (b) Okamura, M., & Ichinose, H. (2002). *EKISYO*, *6*, 390.

[8] Demus, D., & Inukai, T. (1999). *Liquid Crystal*, *26*, 1257.

[9] Becke, A. D. (1993). *J. Chem. Phys.*, *98*, 5648.

[10] The GAMESS suite of program codes was used. See: Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M., & Montgomery, Jr J. A. (1993). *J. Comp. Chem. 4*, 1347.