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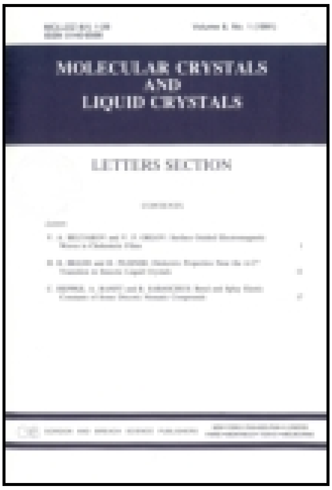

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Synthesis and Physicochemical Properties of Novel Liquid Crystal Compounds with Negative Dielectric Anisotropy with a Tetrahydropyran Ring: Part 2

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Synthesis and Physicochemical Properties of Novel Liquid Crystal Compounds with Negative Dielectric Anisotropy with a Tetrahydropyran Ring: Part 2

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With the aim of improving the properties of liquid crystal (LC) mixtures for VA-LCD and PSA-LCD, JNC has newly synthesized 2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-5-alkenyltetrahydro-2H-pyran derivatives with alkenyl substituents as side chains, and then measured various physicochemical properties to compare their properties to LC compounds with alkyl substituents as side chains. We have shown that several LC compounds with side-chain alkenyl substituents lead to the development of a larger negative dielectric anisotropy ($\Delta\varepsilon$) than for side-chain alkyl substituents. We considered the reason for this using a quantum chemical calculation. As a result, it was found that, compared to alkylated compounds, there exist several LC compounds with side-chain alkenyl substituents, which have a higher existence probability of conformers with a β angle, making expression of a larger $|\Delta\varepsilon|$ possible in an effective manner. It was understood from this study that the physicochemical properties of LC mixtures for VA-LCD and PSA-LCD, which consist of LC compounds as a structural component, newly developed by JNC, show useful properties.

Keywords Alkenyl substituent; negative dielectric anisotropy; PSA-LCD; quantum chemical calculation; tetrahydropyrane derivatives; VA-LCD

Introduction

Generally, LCD-TVs apply the vertical alignment (VA) mode and polymer sustained vertical alignment (PSA) mode in an active matrix type driving system, with the feature that LC mixtures having negative dielectric anisotropy ($\Delta\varepsilon$) are driven. Further, with the aim of improving transmittance, the use of LC mixtures having negative $\Delta\varepsilon$ for smart phones and tablet PCs has recently expanded. It is well known, that to increase response speed in VA-LCD and PSA-LCD, it is essential to develop novel LC mixtures having three properties: large $|\Delta\varepsilon|$, high optical anisotropy (Δn), and low viscosity.

JNC reported that that 2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-5-alkyltetrahydro-*2H*-pyran derivatives with a tetrahydropyran ring exhibit a large $|\Delta\varepsilon|$ as well as favorable solubility in other kinds of LC compounds, showing their usefulness as structural components of VA-LCD LC mixtures [1]. Conventionally, it has been reported that applicability of the Maier-Meier Theory was limited to LC compounds with positive $\Delta\varepsilon$ [2–5]. In the case of LC compounds with negative $\Delta\varepsilon$, there exist a number of structural parts which

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express dipoles; and changes in conformers largely effect dipole variation. Therefore, use of the Maier-Meier Theory for calculation of dielectric anisotropy $\Delta\varepsilon$ using a parameter from a single-conformer molecular calculation is impossible.

We previously reported, that amongst conformers developed by rotating bond axes containing dipole expression structural parts under specified conditions, eight conformers with high existence probabilities were identified, in order to calculate each $\Delta\varepsilon$ under the Maier-Meier Theory. The results show a relatively favorable correlation between calculated $\Delta\varepsilon$ values of 8 conformers in average and measured $\Delta\varepsilon$ values [1].

For the purpose of improving properties of LC mixtures, JNC has newly synthesized 2-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-alkenyltetrahydro-2H-pyran derivatives with various alkenyl substituents as side chains, and then measured various physicochemical properties to compare their properties to LC compounds with alkyl substituents as side chains. Of these derivatives, several compounds with side-chain alkenyl substituents lead to the development of a larger negative $\Delta\varepsilon$ than for compounds with side-chain alkylated substituents. We considered the reason for this using a quantum chemical calculation.

To enhance the precision of the calculated values of $\Delta\varepsilon$ using this quantum chemical calculation, the $\Delta\varepsilon$ for each of 144 conformers, which were developed by rotating bond axes containing dipole expression structural parts under specified conditions, were calculated under the Maier-Meier Theory. The existence probability for each of the 144 conformers was calculated based on the relative energy of each conformer, using the Boltzmann distribution, to achieve the weighted average efficiency of $\Delta\varepsilon$ for each LC compound. As a result, the value of $\Delta\varepsilon$ for each LC compound for which its conformer existence probability was incorporated into the calculation, showed a favorable correlation with each $\Delta\varepsilon$ measured.

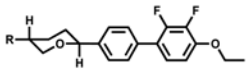
As a result of analysis, we found that amongst LC compounds with side-chain alkenyl substituents, there exist certain LC compounds which have a high existence probability of conformers with both a dipole and β angle (angle of molecule dipole moment with the long molecular axis), making the effective development of a larger $|\Delta\varepsilon|$ more easily possible, than for side-chain alkylated compounds. That is, the research shows that the calculation of $\Delta\varepsilon$ using the Maier-Meier Theory is applicable not only to LC compounds with positive $\Delta\varepsilon$, but also to those with negative $\Delta\varepsilon$ by incorporating each conformer existence probability into such calculation. The LC mixtures containing newly-developed LC compounds showed favorable material properties suitable for VA-LCD and PSA-LCD.

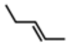
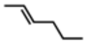
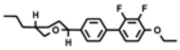
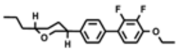
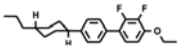
Experimental

Instrumentation

All reagents used for synthesis were bought from either SIGMA-ALDRICH G.K. or Tokyo Chemical Industry Co., Ltd. All reactions were executed in a stream of gaseous nitrogen; and reaction temperature was directly measured. Mass spectra was measured at 200°C using a Shimadzu gas chromatography/mass spectrometer (GC/MS) QP2010 ultra, using both the Electron Impact (EI) Method and Chemical Ionization (CI) Method. Also, ^{1}NMR, ^{19}FNMR and ^{13}CNMR were measured using a Bruker DRX-500 spectrometer, using the internal standard method with the aid of tetramethylsilane. Reactive intermediate and final product was purified using spherical silica gels (40 $\mu\sim 64$ μm), which used solvent mixture *n*-heptane/ethyl acetate as a developing solvent. Melting point and transition temperature were individually measured using a Mettler FP82HT Hot-stage (with FP90 central processor) on which a Nikon ECLIPSE LV100 POL polarization microscope was mounted. The values $\Delta\varepsilon$ [6] and Δn [7] of the newly synthesized LC compounds were extrapolated from measured

Table 1. Transition temperatures and transition enthalpies of 2-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-alkenyltetrahydro-2*H*-pyran



Entry	$R =$	Transition temperatures (°C)	Transition enthalpies (kJ/mol)
A		C 78.2 N 148.4 I	C 23.71 N 0.67 I
B		C 111.3 N 199.2 I	C 25.21 N 0.97 I
C		C 73.7 N 152.4 I	C 25.01 N 0.83 I
D		C (83.9 N) 86.1 I	C 36.56 (N 0.25) I
E		C 94.6 N 182.3 I	C 27.10 N 0.68 I
F		C 86.1 N 169.6 I	C 25.85 N 1.37 I
Ref. 1		C 82.9 N 160.2 I	C 23.00 N 0.66 I
Ref. 2		C 72.0 N 137.8 I	C 22.50 N 0.57 I
Ref. 3		C 79.6 N 173.7 I	C 28.40 N 0.71 I

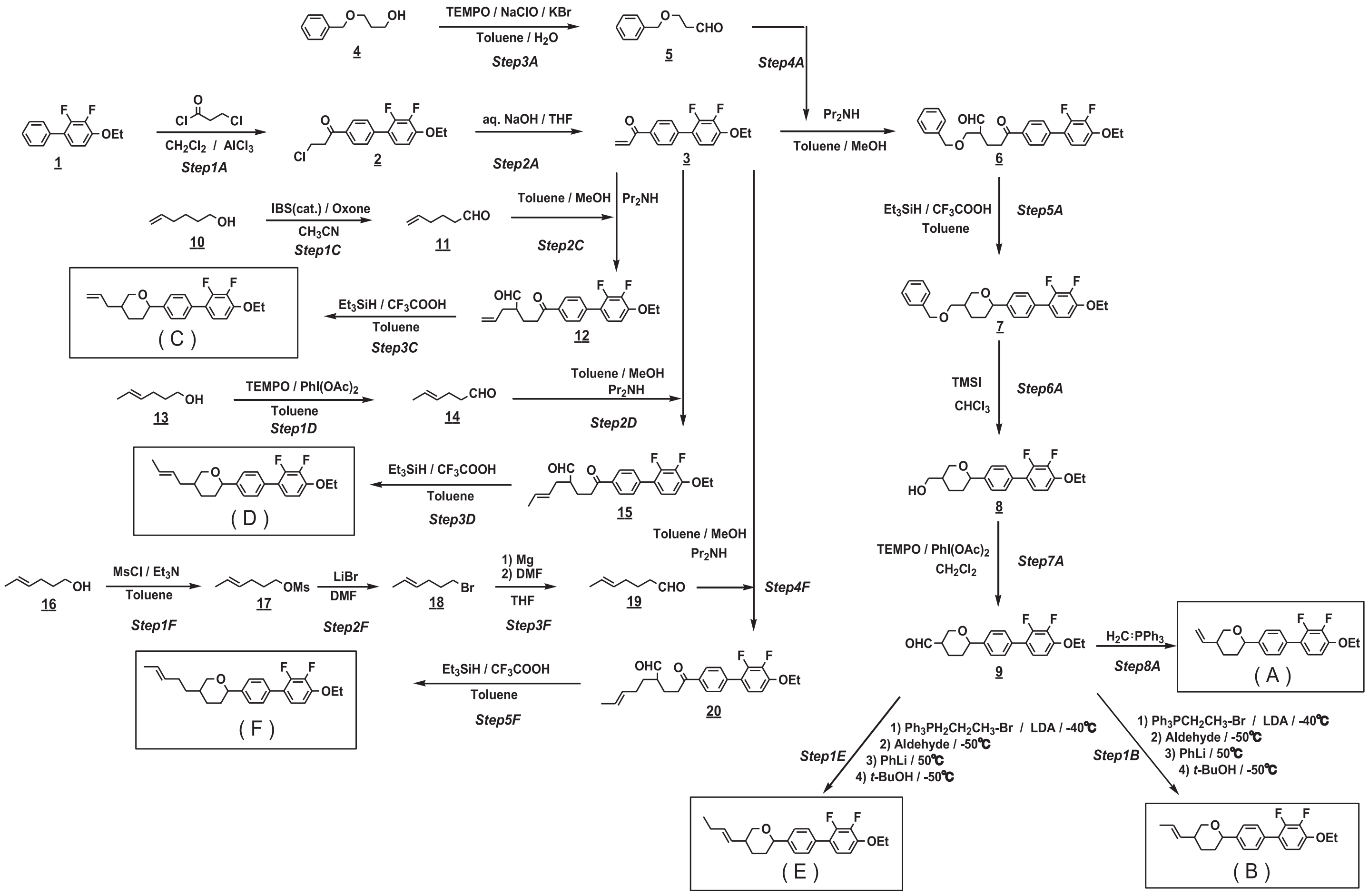
values of the LC mixtures, which were created by adding the concerned LC compounds to phenyl cyclohexyl carboxylate-based nematic LC mixtures. Elastic constants [8] and rotational viscosity were also measured through methods described in previous reports [9].

Synthesis

The LC compounds (A) to (F) newly developed by JNC, as shown in Table 1, were synthesized in conformity with Scheme 1. A key reaction in synthesizing all the LC compounds concerned was developed under a crucial process to synthesize oxoaldehyde through the Michael reaction [10] with the α, β unsaturated ketones and the enolate anions generated by reaction with aldehyde and strong base. A cyclization reaction under an acidic condition was executed to obtain a dihydropyran derivative. Subsequently, a reduction reaction was executed. As a result, tetrahydropyran derivatives were obtained.

Synthesis of 5-ethenyl-2-(4’-ethoxy-2’,3’-difluorobiphenyl-4-yl)tetrahydro-2*H*-pyran (compound A in Table 1)

Step 1A. 4-ethoxy-2,3-difluorobiphenyl (234.14 g, 1.0 mol), was dissolved in CH_2Cl_2 (500 mL), and then $AlCl_3$ (147 g, 1.1 mol) was added at one time while cooling at 5°C or less. Next, a solution created by dissolving 3-Chloropropionylchloride (152 g, 1.2 mol) in CH_2Cl_2 (80 mL), was slowly dropped into this, so that the reaction temperature did not exceed 10°C. After dropping had been completed, this was then agitated for 30 min at 10°C or less, and then for 2 hr at 15∼20°C. Afterward, 10 wt% hydrochloric acid 1.5 L and iced water 800 mL was poured into the resultant mixture. Then, the organic layer was separated from it. The organic layer was washed in the following order: using water 300 mlL, 10 wt% $NaHCO_3$ solution 300 mL, and water 300 mL. After drying using $MgSO_4$, the CH_2Cl_2



Scheme 1. Synthesis of alkenyltetrahydropyrane derivatives.

was concentrated. The concentrate was recrystallized from a solvent mixed with toluene 350 mL and *n*-heptane 700 mL. As a result, 3-chloro-1-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)propan-1-one (**2**, 258.4 g, 0.8 mol, yield: 80%) was obtained.

Step 2A. The ketone derivative (**2**, 258.4 g, 0.8 mol) obtained through Step 1A was dissolved in THF 500 mL. 10 wt% NaOH solution 300 mL was slowly dropped into the resultant mixture, so that the reaction temperature did not exceed 30°C. After agitation for 4 hr at ambient temperature, 10 wt% hydrochloric acid 180 mL was added into the resultant mixture. Then, the solid material precipitated was extracted using ethyl acetate 600 mL. The organic layer was washed twice using 5 wt% $NaHCO_3$ solution 100 mL and brine 200 mL. After drying using $MgSO_4$, the ethyl acetate was concentrated. The concentrated residue was recrystallized by a solvent mixed with ethyl acetate 500 mL and *n*-heptane 600 mL, to obtain 1-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)prop-2-en-1-one (**3**, 197.9 g, 0.69 mol, yield: 86%).

Step 3A. 3-(benzyloxy)propan-1-ol (**4**, 55.4 g, 0.33 mol) was added to a mixed solution containing toluene 340 mL and water 100 mL. Subsequently, TEMPO (522 mg, 3.3 mmol) and KBr (4.0 g, 34 mmol) were added, and then the resultant mixture was cooled at 10°C or less. While, the mixture was being vigorously agitated, a mixture containing 15 wt% NaOCl solution (300 g, 0.6 mol), $NaHCO_3$ (14.2 g, 0.17 mol), and water 100 mL was dropped into it, so that the reaction temperature did not exceed 10°C. After the dropping was completed, the agitation was continued for a further 10 min. The organic layer was washed twice using water 200 mL, once using 10 wt% hydrochloric acid 180 mL, twice using saturated $Na_2S_2O_3$ aqueous solution 100 mL, and finally twice using brine 100 mL. After drying using $MgSO_4$, the toluene was concentrated. As a result crude 3-(benzyloxy)propanal (**5**, 47.9 g, 0.29 mol, yield: 88%) was obtained.

Step 4A. The aldehyde derivative (**5**, 47.9 g, 0.29 mol) obtained in Step 3A, and the keto-vinyl derivative (**3**,57.01 g, 0.198 mol) obtained in Step 2A were dissolved in toluene 200 mL. $(n\text{-}C_3H_7)_2NH$ (2.0 g, 19.8 mmol), methanol 31 mL was added to the solution, and this was heated to 40°C while being agitated, for 12 hr. After cooling, and adding water 100 mL and ethyl acetate 300 mL, the organic layer was extracted. The organic layer was washed twice using brine 100 mL. After drying using $MgSO_4$, the toluene was concentrated. As a result, crude 2-[(benzyloxy)methyl]-5-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-5-oxopentanal (**6**, 72.5 g, 0.16 mol, yield: 81%) was obtained.

Step 5A. The aldehyde derivative (**6**, 72.5 g, 0.16 mol) obtained in Step 4A was dissolved in toluene 300 mL. The mixture obtained after adding Et_3SiH (69.8 g, 0.6 mol) was cooled to 0°C or less. Into this mixture, CF_3COOH (96.1 g, 1.0 mol) was slowly dropped. After dropping was completed, the temperature was allowed to rise slowly to ambient temperature, and the resultant mixture was agitated for 7 hr. After adding acetone 30 mL to the reactant, the resultant mixture was poured into 20 wt% $NaHCO_3$ solution 500 mL. Toluene 200 mL was used to extract an oily substance, which was then washed twice with water 200 mL. After drying using $MgSO_4$, the toluene was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 20:1 as a developing solvent.

As a result, crude 5-[(benzyloxy)methyl]-2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)tetrahydro-2*H*-pyran (**7**, 74.4g, GC-purity: 67%, *cis*-isomer/*trans*-isomer ratio = 12:88) was obtained.

Step 6A. The benzylether derivative (**7**, 74.4 g, 0.117 mol) obtained in Step 5A was dissolved into $CHCl_3$ 250 mL and the solution was cooled with ice. $(CH_3)_3SiI$ (34.1 g, 0.17 mol) was dropped into this solution, so that the reaction temperature did not exceed 10°C. After agitating the resultant mixture at 10°C or less for 5 hr, the resultant mixture was poured into 5 wt% $NaHCO_3$ solution 500 mL. The organic layer was washed twice using water 100 mL. After drying using $MgSO_4$, the $CHCl_3$ was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 2:1 as a developing solvent.

As a result, crude [6-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)tetrahydro-2*H*-pyran-3-yl]methanol (**8**, 15.9 g, 0.046 mol, yield: 39%) was obtained.

Step 7A. The methanol derivative (**8**, 14.5 g, 0.042 mol) obtained in Step 6A was dissolved in CH_2Cl_2 140 mL, to which was added $PhI(OAc)_2$ (26.04 g, 0.05 mol) and TEMPO (0.65 g, 4.15 mmol). The resultant mixture was agitated for 3 hr at ambient temperature. This resultant mixture was then poured into 10 wt% $NaHCO_3$ solution 500 mL, and the reactant extracted using ethyl acetate 300 mL. The precipitated undissolved substance was filtered out, and the organic layer was washed twice using brine 100 mL. After drying with $MgSO_4$, the ethyl acetate was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 4:1 as a developing solvent.

As a result, crude 6-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)tetrahydro-2*H*-pyran-3-carbaldehyde (**9**, 8.7 g, 0.025 mol, yield: 60%, *cis*-isomer/*trans*-isomer ratio = 12:88) was obtained.

Step 8A. To THF 100 mL was added *t*-BuOK (3.4 g, 0.31 mol), and this was cooled in an ice bath. After confirming that the temperature of the liquid had cooled to 0°C or less, Ph_3PCH_2Br (14.2 g, 0.403 mol) was added. After agitating this for 1 hr at 0°C or less, it was dropped into a solution of the aldehyde derivative (**9**, 8.7 g, 0.025 mol) obtained in Step 7A dissolved in THF 50 mL, at a speed such that the reaction temperature did not exceed 5°C. After 30 min, methyl isobutyl ketone 5 g was added, and to this resultant mixture water 100 mL was also added. Using toluene 100 mL, the reactant was extracted. The precipitated undissolved substance was filtered out, and the organic layer was washed twice using brine 100 mL. After drying with $MgSO_4$, the ethyl acetate was concentrated. The concentrated residue was purified using silica gel column chromatography, which used n-heptane as a developing solvent. The solution distillate was concentrated and the resultant residue recrystallized twice from ethanol 20 mL.

As a result, the target compound (A) (3.93 g, 0.012 mol, yield: 54%) was obtained.

^{1}HNMR ($CDCl_3$) σ 7.48 (d, $J = 7.5$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 2H), 7.08 (ddd, $J =$ 8.5, 7.6, 2.3 Hz, 1H), 6.78 (ddd, $J = 8.5$, 7.7, 1.8 Hz, 1H), 5.69 (ddd, $J = 17.0$, 9.3, 6.9 Hz, 1H), 5.12 (ddd, $J = 17.0$, 1.3, 1.1 Hz, 1H), 5.06 (dd, $J = 9.3$, 1.3 Hz, 1H), 4.33 (dd, $J =$ 11.2, 1.7 Hz, 1H), 4.15 (q, $J = 7.0$ Hz, 2H), 4.10 (ddd, $J = 11.2$, 4.4, 2.0 Hz, 1H), 3.39 (dd, $J = 11.2$, 11.2 Hz, 1H), 2.46-2.38 (m, 1H), 2.05-2.01 (m, 1H), 1.97-1.93 (m, 1H), 1.69 (dddd, $J = 13.1$, 12.9, 11.4, 3.7 Hz, 1H), 1.56 (dddd, $J = 13.3$, 13.1, 11.2, 3.4 Hz, 1H), 1.48 (t, $J = 7.0$ Hz, 3H).

^{19}FNMR ($CDCl_3$) σ -142.30 (dd, $J = 19.9$, 7.6 Hz, 1F), -159.39 (dd, $J = 19.9$, 7.7 Hz, 1F).

^{13}CNMR ($CDCl_3$) σ 150.31, 148.34, 148.02, 142.75, 139.15, 134.39, 129.12, 129.10, 126.48 × 2, 124.04, 123.35, 115.65, 109.88, 79.83, 73.23, 65.80, 40.51, 33.79, 30.38, and 15.19.

MS (EI^+) Calcd for $C_{21}H_{22}F_2O_2$ $[M]^+$:*m/z* 344.16. Found: *m/z* 343.95

MS (CI^+) Calcd for $C_{21}H_{22}F_2O_2$ $[M]^+$:*m/z* 344.16. Found: *m/z* 344.15

Synthesis of 2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-5-[(1E)-prop-1-en-1-yl]tetra hydro-2*H*-pyran (compound B in Table 1)

Step 1B. $Ph_3PC_2H_5Br$ (14.1 g, 0.038 mol) was added to THF 50 mL. This was cooled to −40°C using an acetone dry ice bath, and LDA (2M/THF solution 18 mL, 0.036 mol) was dropped into it. After dropping, the temperature of the resultant mixture was maintained at −40°C and agitated for 30 min, and then agitated for 1 hr at 0°C. This was then cooled to −50°C, and a solution of the previously mentioned aldehyde derivative (9, 8.7 g, 0.025 mol) dissolved into THF 50 mL, was dropped into it. After agitating for 30 min, PhLi (1.6M/Bu_2O solution 22.5 mL, 0.036 mol) was dropped into this. And then, after a further 30 min of agitation, *t*-BuOH 5 g and THF 10 mL were dropped into this. After allowing the temperature to rise gradually, at a temperature of 0°C water 100 mL and brine 100 mL were added. The precipitated crude crystal was extracted using toluene 200 mL. The organic layer was washed twice with 10 wt% hydrochloric acid 50 mL, brine 100 mL, 5 wt% $NaHCO_3$ solution 100 mL, and finally brine 100 mL. After drying with $MgSO_4$, the toluene was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 10:1 as a developing solvent. The solution distillate was concentrated, and the resultant residue recrystallized twice from ethanol 20 mL, and the target compound (B) (4.71 g, 0.013 mol, yield: 53%) was obtained.

^{1}HNMR ($CDCl_3$) σ 7.47 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.08 (ddd, $J = 8.5, 7.7, 2.2$ Hz, 1H), 6.78 (ddd, $J = 8.5, 7.6, 2.4$ Hz, 1H), 5.55 (ddt, $J = 15.3, 6.0, 1.0$ Hz, 1H), 5.27 (ddd, $J = 15.3, 7.1, 1.4$ Hz, 1H), 4.31 (dd, $J = 11.3, 2.0$ Hz, 1H),4.15 (q, $J = 7.0$ Hz, 2H), 4.05 (ddd, $J = 11.3, 4.4, 2.0$ Hz, 1H), 3.32 (dd, $J = 11.3, 11.2$ Hz, 1H), 2.38-2.32 (m, 1H), 2.01-1.96 (m, 1H), 1.95-1.90 (m, 1H), 1.68 (d, $J = 6.0$ Hz, 3H), 1.67 (dddd, $J = 13.0, 12.4, 11.5, 3.7$ Hz, 1H), 1.51 (dddd, $J = 13.3, 12.4, 11.3, 3.6$ Hz, 1H), 1.45 (t, $J = 7.0$ Hz, 3H).

^{19}FNMR ($CDCl_3$) σ -142.30 (dd, $J = 19.8, 7.7$Hz, 1F), -159.41 (ddd, $J = 19.8, 7.6, 2.4$ Hz, 1F).

^{13}CNMR ($CDCl_3$) σ 147.98, 147.93, 143.12, 142.88, 134.33, 131.85, 129.10, 129.08, 126.48, 126.36, 124.03, 124.00, 123.37, 109.89, 79.79, 73.72, 65.80, 39.63, 33.94, 31.00, 18.59, and 15.19.

MS (EI^+) Calcd for $C_{22}H_{24}F_2O_2$ $[M]^+$:*m/z*. 358.17. Found: *m/z* 357.95.

MS (CI^+) Calcd for $C_{22}H_{24}F_2O_2$ $[M]^+$:*m/z*. 358.17. Found: *m/z* 358.25.

Synthesis of 5-but-3-en-1-yl-2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)tetrahydro-2*H*-pyran (compound C in Table 1)

Step 1C. Na_2SO_4 (150 g, 1.06 mol) was well dried by decompression in advance. To this was added OXONE® (110.7 g, 0.36 mol), potassium 2-iodo-5-methylbenzenesulfonate (1.66 g, 5 mmol), and CH_3CN 800 mL. And to this was added 5-hexene-1-ol (**10**, 30 g, 0.3 mol). This was then gently heated to reflux for 12 hr. This was then cooled, and after adding water 800 mL, the precipitated oily substance was extracted using Et_2O 100 mL. The organic layer was washed with 5 wt% $NaHCO_3$ solution 100 mL and water 100 mL. After drying with $MgSO_4$, the Et_2O was concentrated. Distilling the concentrated residue by decompression, 5-hexenal (**11**, 7.99 g, 0.075 mol, yield: 27%, bp.: 83∼84.5°C/210hpa) was obtained.

Step 2C. To the 5-hexenal (**11**, 7.99 g, 0.075 mol) obtained in Step 1C was added toluene 150 mL, keto-vinyl derivative (**3**, 22.2 g, 0.068 mol), $(n\text{-}C_3H_7)_2NH$ (8.5 g, 0.084 mol) and methanol 10 mL, which was then agitated at ambient temperature for 12 hr. To this was then added 10 wt% hydrochloric acid 50 mL, which was then agitated. The organic layer was washed using brine 30 mL, 5 wt% $NaHCO_3$ solution 30 mL, and water 100 mL. After drying with $MgSO_4$, the toluene was concentrated. As a result crude (4E)-2-[3-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-3-oxopropyl]hex-4-enal (**12**, 28.9 g, 0.078 mol, yield: 100%) was obtained.

Step 3C. The aldehyde derivative (**12**, 34.3 g, 0.078 mol) obtained in Step 2C was dissolved in toluene 120 mL and after adding Et_3SiH (29.1 g, 0.25 mol), the resulting mixture was cooled to 0°C or less. CF_3COOH (46.1 g, 0.4 mol) was then slowly dropped into this mixture. After dropping, the temperature was then allowed to increase slowly to ambient temperature and the mixture agitated for 7 hr. After adding acetone 10 mL to the reactant, the resultant mixture was poured into 5 wt% $NaHCO_3$ solution 100 mL and water 500 mL. The precipitated crystal was extracted using toluene 200 mL, and washed twice using water 200 mL. After drying with $MgSO_4$, the toluene was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 20:1 as a developing solvent. The solution distillate was concentrated and the resultant residue recrystallized twice from ethanol 20 mL. As a result, the target compound (C) (14.9 g, 0.04 mol, yield: 51%) was obtained.

^{1}HNMR ($CDCl_3$) σ 7.47 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.08 (ddd, $J = 8.6, 8.6, 2.4$ Hz, 1H), 6.78 (ddd, $J = 8.6, 7.7, 2.3$ Hz, 1H), 5.82 (ddt, $J = 17.1, 10.7, 6.8$ Hz, 1H), 5.04 (dd, $J = 17.1, 1.8$ Hz, 1H), 4.98 (dd, $J = 10.7, 1.8$ Hz, 1H), 4.31 (dd, $J = 11.3, 2.0$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.12 (ddd, $J = 11.4, 4.3, 2.0$ Hz, 1H), 3.24 (dd, $J = 11.4, 11.1$ Hz, 1H), 2.17-2.01 (m, 3H), 1.94-1.89 (m, 1H), 1.75-1.67 (m. 1H), 1.65 (dddd, $J = 13.3, 13.0, 11.3, 3.9$ Hz, 1H), 1.48 (t, $J = 7.1$ Hz, 3H), 1.35-1.27 (m. 3H).

^{19}FNMR ($CDCl_3$) σ -142.30 (dd, $J = 19.9, 8.6$ Hz, 1F), -159.42 (ddd, $J = 19.9, 7.7, 2.3$ Hz, 1F).

^{13}CNMR ($CDCl_3$) σ 148.34, 147.99, 143.24, 141.15, 139.02, 134.31, 129.09, 126.48×2, 124.63, 123.97, 123.39, 115.06, 109.90, 80.22, 74.36, 65.81, 35.51, 34.29, 32.07, 31.25, 31.17, and 15.19.

MS (EI$^+$) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 372.19. Found: *m/z* 371.90.

MS (CI$^+$) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 372.19. Found: *m/z* 372.15.

Synthesis of 5-[(2E)-but-2-en-1-yl]-2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)tetrahydro-2*H*-pyran (compound D in Table 1)

Step 1D. trans-4-hexene-1-ol (**13**, 50.0 g, 0.5 mol) and TEMPO (7.9 g, 0.05 mol) were dissolved in toluene 250 mL. This was cooled with ice, and $PhI(OAc)_2$ (176.9 g, 0.55 mol) was added, keeping the reaction temperature at 20°C or less. After agitating for 1 hr, this was washed three times using brine 500 mL, twice using 5 wt% $NaHCO_3$ solution 500 mL and water 500 mL, before drying with $MgSO_4$. As a product, a toluene solution containing *trans*-4-hexenal (**14**) was used in that state in the following step.

Step 2D. The keto-vinyl derivative (**3**, 45.1 g, 0.14 mol) referred to above was dissolved in the toluene solution obtained in Step 1D. This was cooled with ice, and $(n\text{-}C_3H_7)_2NH$ (15.4 g, 0.15 mol) was added. To this was then added methanol 85 mL, and then the resultant mixture was agitated for 10 hr at ambient temperature. To this resultant mixture 10 wt% hydrochloric acid 150 mL was added, and the resultant mixture agitated for 10 min. The organic layer was washed three times using brine 300 mL, before drying with $MgSO_4$. The (5E)-2-[3-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-3-oxopropyl]hept-5-enal (**15**) in a toluene solution obtained was used in the following step.

Step 3D. The toluene solution obtained in Step 2D was cooled with ice. To this was added Et_3SiH (48.4 g, 0.42 mol), and the mixture was cooled to 0°C or less. CF_3COOH (79.2 g, 0.69 mol) was slowly dropped into this mixture. After dropping was completed, the temperature was allowed to rise gradually to ambient temperature. Then after agitating for 10 hr, this resultant mixture was poured into 20 wt% $NaHCO_3$ solution 500 mL. The organic layer was washed three times using brine 300 mL. After drying using $MgSO_4$, the toluene was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 20:1 as a developing solvent. The solution distillate was concentrated and the resultant residue recrystallized three times from ethanol 30 mL. As a result, the target compound (D) (19.5 g, 0.05 mol, yield: 37%) was obtained.

^{1}HNMR ($CDCl_3$) σ 7.47 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.07 (ddd, $J = 8.5, 7.4, 2.2$ Hz, 1H), 6.78 (ddd, J = 8.5, 7.5, 2.4 Hz, 1H), 5.49-5.38 (m, 2H), 4.30 (dd, $J = 11.4, 2.0$ Hz, 1H), 4.15 (q, $J = 7.0$ Hz, 2H), 4.10 (ddd, J = 11.4, 4.3, 2.1 Hz, 1H), 3.23 (dd, $J = 11.4, 11.1$ Hz, 1H), 2.01-1.97 (m, 1H), 1.93-1.82 (m, 3H), 1.76-1.69 (m, 1H), 1.67 (d, $J = 5.5$ Hz, 3H), 1.63 (dddd, $J = 13.0, 11.5, 11.5, 3.8$ Hz, 1H), 1.47 (t, $J = 7.0$ Hz, 3H), 1.30 (dddd, $J = 12.9, 11.5, 11.4, 3.8$ Hz, 1H).

^{19}FNMR ($CDCl_3$) σ -142.30 (dd, $J = 19.8, 7.4$ Hz, 1F), -159.42 (ddd, $J = 19.8, 7.5, 2.4$ Hz, 1F).

^{13}CNMR ($CDCl_3$) σ 142.98, 134.27, 129.08, 129.06, 128.84, 127.05 × 2, 126.47 × 2, 124.03, 124.00, 123.40, 123.31, 109.90, 80.15, 74.26, 65.80, 36.36, 36.12, 34.42, 31.02, 18.33, and 15.19.

MS (EI$^+$) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 372.19. Found: *m/z* 371.95.

MS (CI$^+$) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 372.19. Found: *m/z* 372.20.

Synthesis of 5-[(1E)-but-1-en-1-yl]-2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)tetra hydro-2*H*-pyran (compound E in Table 1)

Step 1E. $Ph_3PC_2H_5Br$ was replaced with $Ph_3PC_3H_7Br$ (14.45 g, 0.038 mol), and following a method similar to that for compound B, synthesis was carried out. The resultant residue was recrystallized three times from ethanol 20 mL. As a result, target compound (E) (3.25 g, 8.4 mmol, yield: 33.5%) was obtained.

^{1}HNMR ($CDCl_3$) σ 7.47 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.08 (ddd, $J = 8.3, 7.7, 2.3$ Hz, 1H), 6.78 (ddd, $J = 8.3, 7.5, 2.3$ Hz, 1H), 5.57 (dt, $J = 15.5, 6.3$ Hz, 1H), 5.24 (dd, $J = 15.5, 7.2$ Hz, 1H), 4.31 (dd, $J = 11.3, 2.0$ Hz, 1H), 4.15 (q, $J = 7.0$ Hz, 2H), 4.05 (ddd, $J = 11.3, 4.5, 2.1$ Hz, 1H), 3.32 (dd, $J = 11.3, 11.3$ Hz, 1H), 2.36-2.31 (m, 1H), 2.02 (dq, $J = 7.4, 6.3$ Hz, 2H), 2.01-1.97 (m, 1H), 1.95-1.90 (m, 1H), 1.67 (dddd, $J = 13.2, 11.3, 11.3, 3.5$ Hz, 1H), 1.52 (dddd, $J = 13.3, 13.2, 11.3, 3.7$ Hz, 1H), 1.47 (t, $J = 7.0$ Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H).

^{19}FNMR ($CDCl_3$) σ -142.30 (dd, $J = 19.6, 7.7$ Hz, 1F), −159.42 (ddd, $J = 19.6, 7.5, 2.3$ Hz, 1F).

^{13}CNMR ($CDCl_3$) σ 148.36, 148.00, 143.11, 141.27, 134.33, 133.51, 129.53, 129.10, 129.08, 126.49 × 2, 124.04, 123.97, 109.88, 79.80, 79.79, 65.80, 39.54, 33.96, 31.06, 26.17, 15.19, and 14.20.

MS (EI$^+$) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 372.19. Found: *m/z* 371.95.

MS (CI$^+$) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 372.19. Found: *m/z* 372.20

Synthesis of 2-(4’-ethoxy-2’,3’-difluorobiphenyl-4-yl)-5-[(3E)-pent-3-en-1-yl]tetra hydro-*2H*-pyran (compound F in Table 1)

Step 1F. *trans*-4-hexene-1-ol (**16**, 40.0 g, 0.4 mol) and Et_3N (48.5 g, 0.48 mol) were dissolved in toluene 400 mL. MsCl (50.3 g, 0.44 mol) was then dropped into this solution, which was cooled with ice, keeping the reaction temperature at 25°C or less. After agitating for 1 hr, brine 200 mL was added. The organic layer was washed twice using 5 wt% $NaHCO_3$ solution 500 mL and water 500 mL. After drying with $MgSO_4$, the toluene was concentrated. As a result, 4-hexene-1-mesylate (**17**, 69.5 g, 0.39 mol, yield: 97.5%) was obtained as a colorless, oily substance.

Step 2F. LiBr (41.6 g, 0.48 mol) was added to DMF 150 mL and agitated at 50°C for 1 hr. After cooling to ambient temperature, the mesylate (**17**, 69.5 g, 0.39 mol) obtained in Step 1F was added, the temperature raised to 70°C, and the resultant mixture agitated for 1 hr. Then after cooling to ambient temperature, water 100 mL was added. A liberated oily substance was extracted using Et_2O 100 mL. The organic layer was washed twice using 10 wt% hydrochloric acid, 5 wt% $NaHCO_3$ solution 200 mL, and water 200 mL. After drying with $MgSO_4$, the Et_2O was concentrated. As a result, 1-bromo-hexene (**18**, 61 g, 0.38 mol, yield: 96.4%) was obtained as a colorless, oily substance.

Step 3F. The solution formed by dissolving 1-bromo-hexene (**18**, 61 g, 0.38 mol) obtained in Step 2F in THF 120 mL was dropped into Mg (7.7 g, 0.32 mol) combined with THF 75 mL, so the reaction temperature did not exceed 30°C. After dropping was completed, the resultant mixture was agitated for 1 hr, and Grignard reagent was prepared. After cooling with ice, DMF (25.7 g, 0.35 mol) was dropped into the resultant mixture, at 20°C or less. 10 wt% hydrochloric acid 200 mL was slowly added, and then the precipitated oily substance was extracted using toluene 100 mL. The organic layer was washed twice using 5 wt% $NaHCO_3$ solution 500 mL and water 500 mL, and then dried using $MgSO_4$. The 5-heptenal (**19**) toluene solution obtained was used in this state in the following step.

Step 4F. The keto-vinyl derivative (**3**, 45.0 g, 0.14 mol) previously referred to was dissolved in the 5-heptenal (**19**) toluene solution obtained in Step 3F, then cooled with ice before adding $(n\text{-}C_3H_7)_2NH$ (15.4 g, 0.15 mol). To this was added methanol 80 mL, and the resultant mixture was agitated for 24 hr at ambient temperature. 10 wt% hydrochloric acid 150 mL was added to this resultant mixture, and agitated for 10 min. The precipitated oily substance was extracted using toluene 300 mL. The organic layer was washed twice using 5 wt% $NaHCO_3$ solution 200 mL and water 200 mL, before drying using $MgSO_4$. Toluene solution obtained of (5E)-2-[3-(4’-ethoxy-2’,3’-difluorobiphenyl-4-yl)-3-oxopropyl]hept-5-enal (**20**) was used in this state in the following step.

Step 5F. The aldehyde derivative (**20**) toluene solution obtained in Step 4F was cooled with ice. Et_3SiH (48.4 g, 0.42 mol) was added to this and the mixture cooled to 0°C or less. CF_3COOH (79.2 g, 0.69 mol) was slowly dropped into this mixture. After dropping was completed, the temperature was allowed to rise gradually to ambient temperature. Then after 10 hr of agitation, the resultant mixture was poured into 20 wt% $NaHCO_3$ solution 500 mL. The organic layer was washed three times with brine 300 mL. After drying with $MgSO_4$, the toluene was concentrated. The concentrated residue was purified using silica gel column chromatography, which used solvent mixture *n*-heptane/ethyl acetate 20:1 as a developing solvent. The solution distillate was concentrated and the resultant residue recrystallized three times from ethanol 30 mL. As a result, the target compound (F) (23.6 g, 0.062 mol, yield: 44%) was obtained.

^{1}HNMR ($CDCl_3$) σ 7.47 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.07 (ddd, J = 8.7, 8.1, 2.4 Hz, 1H), 6.78 (ddd, J = 8.7, 7.5, 2.3 Hz, 1H), 5.49-5.39 (m, 2H), 4.30 (dd, J = 11.4, 2.1 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.11 (ddd, J = 11.3, 4.3, 2.0 Hz, 1H), 3.23 (dd, J = 11.3, 11.1 Hz, 1H), 2.07-1.97 (m, 3H), 1.93-1.88 (m, 1H), 1.73-1.60 (m, 2H), 1.66 (d, J = 4.8 Hz, 3H), 1.47 (t, J = 7.1 Hz, 3H), 1.33-1.16 (m, 3H).

^{19}FNMR ($CDCl_3$) σ -142.31 (dd, J = 19.0, 8.1 Hz, 1F), -159.42 (ddd, J = 19.0, 7.5, 2.3 Hz, 1F).

^{13}CNMR ($CDCl_3$) σ 148.33, 147.99, 143.23, 142.98, 134.29, 131.47, 129.09, 129.07, 126.49 × 2, 125.55, 124.00, 123.38, 109.87, 80.22, 74.42, 65.79, 35.46, 34.32, 32.76, 31.20, 30.04, 18.37, and 15.19.

MS (EI^+) Calcd for $C_{24}H_{28}F_2O_2$ $[M]^+$:*m/z* 386.21. Found: *m/z* 385.95.

MS (CI^+) Calcd for $C_{23}H_{26}F_2O_2$ $[M]^+$:*m/z* 386.21. Found: *m/z* 386.15

Results and Discussion

Physicochemical Properties

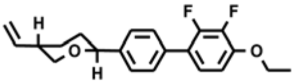
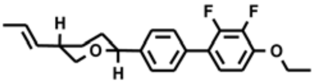
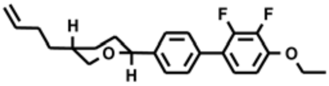
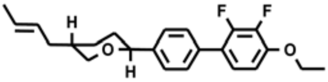
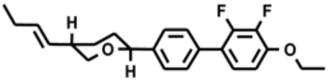
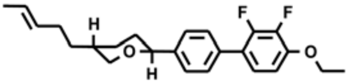
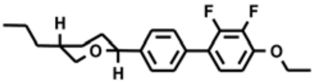
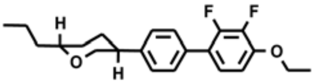
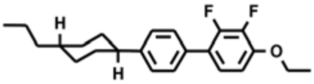
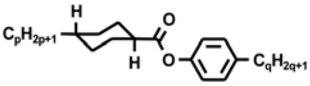
Table 1 shows transition temperatures and transition enthalpies of newly-synthesized 2-(4'-ethoxy-2',3'-difluorobiphenyl-4-yl)-5-alkenyltetrahydro-2*H*-pyran. Amongst such synthesized compounds, only compound D shows a monotropic nematic phase, while others except for compound D fully show enantiotropic nematic phases. The rise in the CN point (transition temperature of crystal-nematic phase) or melting point is considered to be due to the stability of crystal structure of LC molecules being increased by the introduction of double bonds, so that the phase transition may be shifted to the higher temperature side, as compared to alkylated compounds with the same carbon number [1]. Further, a wider temperature range for the nematic phase, as compared to alkylated compounds with the same carbon number, is evident. In particular, compound A with side-chain vinyl substituents exhibits a nematic phase temperature range that is about 30° larger than compounds with side-chain ethyl substituents. This is because double bonds at the ends of molecules significantly affect the stability of crystal structure of LC molecules. It is found that the CN point and NI point vary significantly according to the position of double bonds, even with the same carbon number. Amongst compounds C, D, and E, compound E shows the highest NI point (transition temperature of nematic-isotropic). Similarly, as mentioned earlier, it can be assumed that double bonds located nearer to the molecular skeleton lead to greater enhancement in the stability of crystal structure of LC molecules.

Table 2 shows $\Delta\varepsilon$ and Δn values for each LC compound, which were extrapolated from the measured values of LC mixtures obtained by dissolving tetrahydropyrane derivatives in a nematic LC mixture consisting of several kinds of phenyl cyclohexyl carboxylate. Compounds B, C, D, E, and F show a positive correlation between the height of NI point and magnitude of $\Delta\varepsilon$, giving results that accord with the Maier-Meier Theory discussed below. Amongst these compounds obtained, compound A showed the largest $|\Delta\varepsilon|$. We tried to clarify the reason for this using the quantum chemical calculation given in Section 3.

Results of Quantum Chemical Calculations for Tetrahydropyran Derivatives

For each of the 144 conformers obtained by rotating dihedral angles θ_1 and θ_2 of Tetrahydropyrane derivatives 360° at intervals of 30°, individual partial structures optimized

Table 2. Extrapolated values of $\Delta\varepsilon$ of 2-(4′-ethoxy-2′,3′-difluorobiphenyl-4-yl)-5-alkenyltetrahydro-2*H*-pyran

		$\Delta\varepsilon$	Δn
A		−6.25	0.194
B		−6.18	0.212
C		−5.78	0.186
D		−5.11	0.154
E		−5.60	0.194
F		−5.40	0.196
Ref. 1		−5.90	0.180
Ref. 2		−6.20	0.180
Ref. 3		−5.70	0.180
Host mixture		−1.30	0.087
	$p = 3, q = 4$; 27.6%, $p = 4, q = 2$; 20.7%, $p = 5, q = 1$; 20.7%, $p = 3, q = 2$; 17.2%, $p = 5, q = 2$; 13.8%		

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

through the calculation at the level of B3LYP/6-31G(d) [11] were sought. Subsequently, quantum chemical calculations for total energies, molecular polarizability and dipole, and β angle were also obtained at the level of B3LYP/6-31G(d). All the calculations were executed using the GAMESS suite of program codes [12].

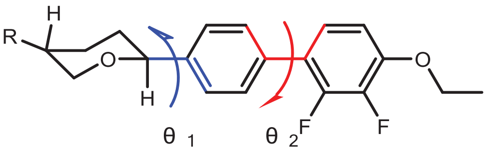


Table 3. Parameters from molecular modeling calculations and calculated values of $\Delta\ \varepsilon$

Entry	α_{av} (Å^3)	$\Delta\alpha$ (Å^3)	μ (DEBYE)	β (deg.)	$-\mu^2(1-\cos^2\beta)$	P_2	$\Delta\varepsilon_{(c.)}$
A	36.08	23.63	3.2995	84.5	−11.01	0.697	−4.19
B	38.15	25.25	3.3518	77.2	−9.83	0.706	−3.50
C	39.41	24.84	3.3048	82.9	−10.81	0.700	−3.65
D	39.61	22.58	3.3518	77.3	−9.69	0.683	−3.20
E	39.95	25.85	3.3506	76.8	−9.66	0.704	−3.23
F	41.41	26.18	3.3465	76.8	−9.57	0.702	−2.99
Ref. 1	37.76	22.67	3.3542	77.7	−10.06	0.694	−3.47
Ref. 2	37.88	23.52	3.5443	74.4	−10.57	0.692	−3.75
Ref. 3	37.86	23.45	3.2964	86.2	−10.69	0.692	−3.61

Then, the $\Delta\varepsilon$ ($= \varepsilon_{//} - \varepsilon_{\perp}$) of each of the 144 conformers was calculated using the Maier-Meier Theory as follows:

$$\varepsilon_{//} = 1 + (\mathrm{NhF}/\varepsilon_0)[\alpha_{av} + 2/3\Delta\alpha \mathrm{P}_2 + \mathrm{F}(\mu^2/3k_B\mathrm{T})(1 - \{1 - 3\cos^2\beta\}\mathrm{P}_2)] \quad (1) \quad [13]$$

$$\varepsilon_{\perp} = 1 + (\mathrm{NhF}/\varepsilon_0)[\boldsymbol{\alpha}_{av} - 1/3\boldsymbol{\Delta\alpha}\mathrm{P}_2 + \mathrm{F}(\boldsymbol{\mu}^2/3k_B\mathrm{T})(1 + 1/2\{1 - 3\cos^2\boldsymbol{\beta}\}\mathrm{P}_2)] \quad (2) \quad [13]$$

$$\mathrm{P}_2 = 0.363\ \log\ \mathrm{T}_{\mathrm{NI}} : \text{using the } \mathrm{T}_{\mathrm{NI}} \text{of the mixtures} \quad (3) \quad [14]$$

Subsequently, the existence probability of each of the 144 conformers at 300 K was obtained using the Boltzman distribution, based on the relative energy of each conformer, which was calculated by use of the DFT method. The $\Delta\varepsilon$ value for each of the 144 conformers in which existence probabilities were incorporated was calculated. By totalizing each value, we achieved the weighted average efficiency of $\Delta\varepsilon$ of each of the compounds. Table 3 shows individual parameters and their results.

Figure 1 shows the correlation between measured and calculated values of $\Delta\varepsilon$ for each of the compounds, showing a relatively favorable correlation between the measured and calculated values. As a result of regression analysis, correlation coefficient R was found to be 0.785. By comprehensively evaluating the results obtained, it was shown that calculation of dielectric anisotropy $\Delta\varepsilon$ using the Maier-Meier Theory was applicable to LC compounds having negative $\Delta\varepsilon$ by incorporating each conformer existence probability using the Boltzmann distribution. This finding has reversed the conventional idea that calculation of $\Delta\varepsilon$ using the parameters derived from single-conformer molecules, by applying the Maier-Meier Theory as it was, was impossible. As previously reported, this was on the grounds that there are multiple structural parts which express each dipole, and that changes in conformers significantly affect dipoles.

Tetrahydropyran derivatives A to F which have the newly developed alkenyl substituents as side chains, as well as Ref.1, 2 and 3 compounds, as shown in Table 3, have very similar molecular skeletons which express $\Delta\varepsilon$. And each compound also shows a dipole within the same level. Specifically, however, certain compounds show large $|\Delta\varepsilon|$. The chain length dependency of $-\mu^2(1-3\cos^2\beta)$, equivalent to $\Delta\varepsilon$, is plotted as shown in Fig. 2. It can be implied from the side-chain length that $-\mu^2(1-3\cos^2\beta)$ has a large variation. In other words, this suggests that that the side-chain significantly impacts changes in the β angle.

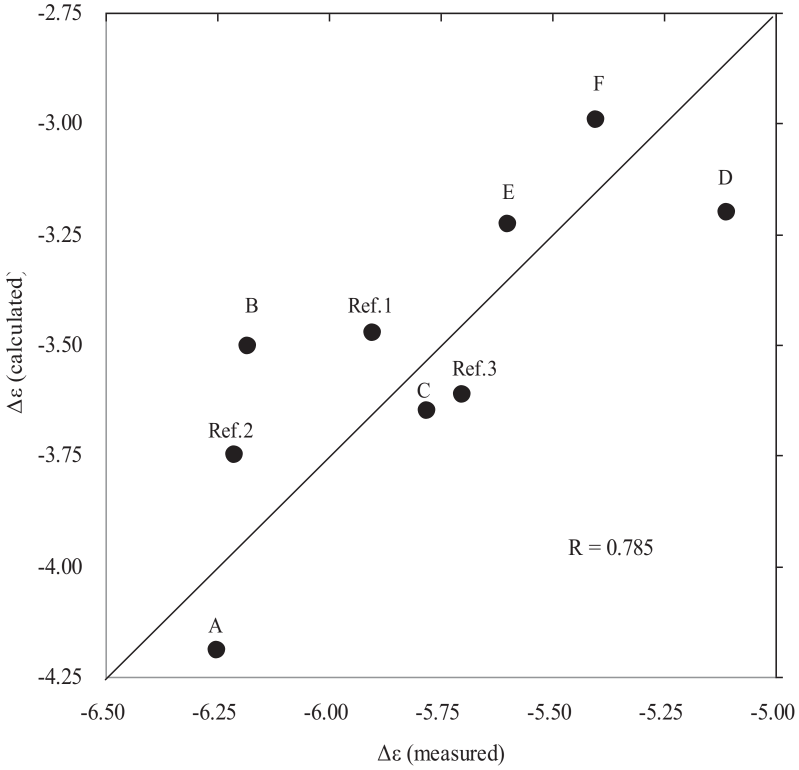


Figure 1. Calculated Δ ε vs. measured values.

Concerning tetrahydropyrane derivatives A and D which have the newly-developed alkenyl substituents as side chains, as well as compound Ref.1, Fig. 3 shows distributions of estimated values of $\Delta\varepsilon$ for the 144 conformers, which were obtained by rotating dihedral angles θ_1 and θ_2 of tetrahydropyrane compounds 360° at intervals of 30°, as well as Boltzmann-based existence probabilities, and β angles.

For the concerned derivatives and compound indicated in Fig. 3, while there is no specific difference in each conformer existence probably using the Boltzmann distribution, which was denoted in the middle region, each conformer β angle showed a large variation, which was denoted in the lower region. The β angle of compound A showed a distribution of nearly 90° in all regions, while the β angle for each of compounds D and Ref 1 showed a small value in the regions with a relatively high existence probability of each conformer. This gap in the β angle is a major reason for the gap in $\Delta\varepsilon$. That is, compound A showed a variation of nearly 90° in the β angle, which is formed by long axis of molecule and inertia moment of molecule, leading to the expression of a large $|\Delta\varepsilon|$.

Mixtures for VA-LCD and PSA-LCD Application

Based on a comprehensive evaluation of the research presented here, it is considered that the novel LC compounds newly synthesized by JNC, show useful properties as structural components of LC mixtures for VA-LCD and PSA-LCD. To ascertain their usefulness, we prepared a model mixture containing 15 wt% compound A having a nearly 90° β angle, as

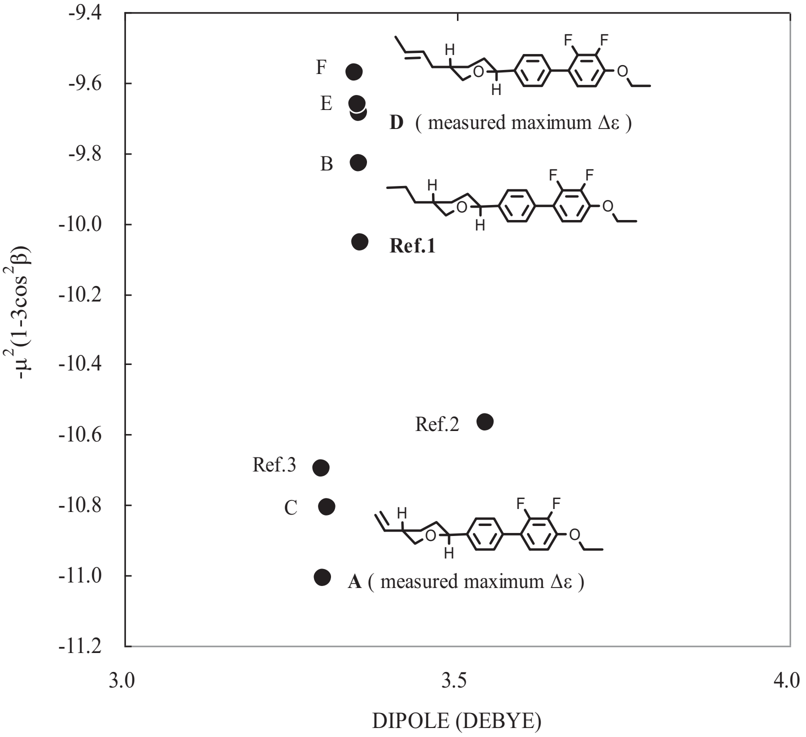
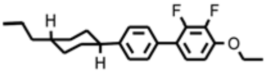
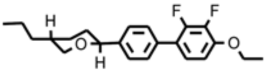
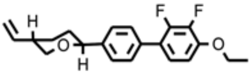


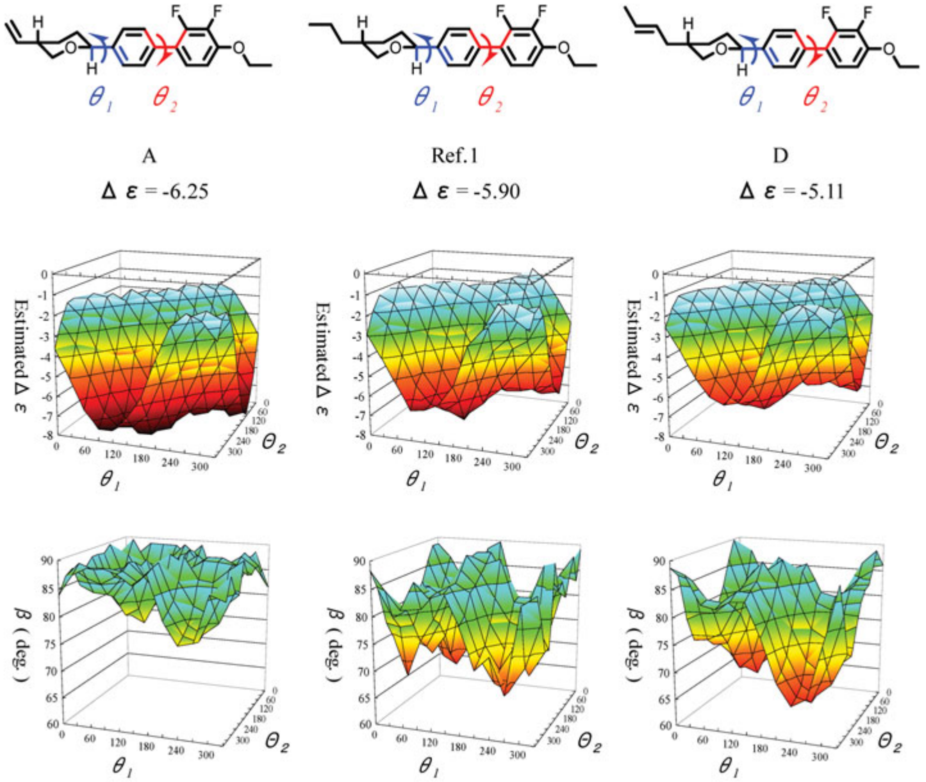
Figure 2. Side-chain length dependency of $-\mu^2(1 - 3\cos^2\beta)$ for each LC compound.

well as a model mixture containing 15 wt% Ref.1 and another containing 15 wt% Ref.2. Then, their physicochemical properties were compared, as shown in Table 4. It was shown that rotational viscosity, which has a large effect on response speed, can be improved by about 5%, without impairing any other properties, through the use of compound A.

Further, to prevent display defects at low temperatures, low temperature stability (LTS) is a stringent requirement for LC mixtures. Thus, it is crucial that no specific structural component is crystallized, and that no smectic phase is shown. We prepared nine kinds of

Table 4. Physicochemical properties of model mixtures consisting of an alkenyltetrahydopyran derivative and references

Physico-chemical properties	Ref.3 	Ref.1 	Mixture A 
NI (°C)	83.3	82.5	82.7
γ_1 (mPa·sec)	101.6	104.1	98.7
Δ n	0.105	0.104	0.104
$\Delta\ \varepsilon$	−2.8	−2.8	−2.8
K_{11}/K_{33}	14.8/15.1	14.5/14.5	13.7/14.0
V_c (V)	2.5	2.4	2.3



Difference in β distribution causes difference in Δ ε .

Figure 3. Comparison in distribution of estimated Δ ε, existence probability, and β for each conformer.

mixtures in total, by varying the content of each of the three different compounds used in Table 4 at three levels. Sample glass tubes were then filled with these mixtures, which were then left in a −20°C low temperature environment for 30 days. After the 30-day period, we visually checked the condition of mixtures. When a mixture exhibited a nematic state, it was described as “N” and a mixture exhibiting a smectic state, “S.” When crystal was deposited, the mixture was described as “C.” The results are given in Table 5, and show that compared to other compounds, the mixtures with a superior LTS performance in a low-temperature environment can be adjusted more easily by adopting newly synthesized compound A. These results are consistent with the results that compound A, when compared

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

Concentration of Ref. 3		Concentration of Ref. 1		Concentration of compound A	
10 (wt%)	N	10 (wt%)	N	10 (wt%)	N
15 (wt%)	C	15 (wt%)	N	15 (wt%)	N
20 (wt%)	C	20 (wt%)	S	20 (wt%)	N

with compounds Ref.1 and Ref.3, has the lowest melting point, and also has the smallest transition enthalpy of the three compounds.

Conclusion

JNC has developed novel LC compounds with alkenyl substituents as side chains with a tetrahydropyran ring. By introducing side-chain alkenyl substituents, a rise in the NI point as well as an increase in nematic temperature range has been successfully enabled. It was revealed that calculation of $\Delta\varepsilon$ using the Maier-Meier Theory is applicable not only to LC compounds with positive $\Delta\varepsilon$, but also to those with negative $\Delta\varepsilon$ by incorporating each conformer existence probability into such calculations. Further, it was found that the introduction of $-\mu^2(1-3\cos^2\beta)$ obtained through calculations was particularly useful as a guideline in designing compounds. It was understood from this study that the LC mixtures containing compounds newly developed by JNC exhibited favorable properties as LC mixtures for VA-LCD and PSA-LCD.

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