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Mayumi Goto [a], Tokifumi Masukawa [a], Tomoyuki Kondo [a] & Atsuko Fujita [a]

[a] Chisso Petrochemical Corporation, Goi Research Center, Chiba, Japan

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Novel Nematic Liquid Crystalline Compounds Having A Tetrahydropyrane Ring

Mayumi Goto, Tokifumi Masukawa, Tomoyuki Kondo, and Atsuko Fujita
Chisso Petrochemical Corporation, Goi Research Center, Chiba, Japan

A series of novel liquid crystalline compounds with a tetrahydropyrane ring were synthesized, and the physical properties have been measured. The compounds showed peculiar dependency of the dielectric anisotropy value on the connecting position of the tetrahydropyrane ring. This positional dependency is discussed with the measurement of the temperature dependency of the dielectric constants, and the semi empirical quantum calculation. In accordance with the experimental result, it was found that the difference of the dielectric anisotropy value is influenced by the difference of the dipole moment value and the direction of the dipole at the most stable conformation.

Keywords: negative dielectric anisotropy; structural dependency; tetrahydropyrane derivatives; VA-LCDS

INTRODUCTION

Active matrix liquid crystal displays (AM-LCDs) have been applied to various kinds of display, such as PC monitors, TVs, and cellular phones. The required characteristics for liquid crystalline materials are low driving voltage and quick response, and wide viewing angle. The viewing-angle dependency has been significantly improved through new display technologies, namely the vertical alignment (VA) modes [1–3], applying liquid crystalline materials with large negative dielectric anisotropy ($\Delta\varepsilon$).

Usually, the nematic liquid crystal compounds are made up of a benzene ring, a cyclohexane ring, a dioxane ring, and a pyrimidine

Address correspondence to Mayumi Goto, Chisso Petrochemical Corporation, Goi Research Center I, 5-1 Goikaigan Ichihara, Chiba 290-8551, Japan. E-mail: m.furuya@chisso.co.jp

ring, etc. However, since dioxane and pyrimidine rings have the polarity along the molecule long axis, these heterocyclic rings are not suitable as a structural fragment for the negative $\Delta\varepsilon$ materials. To expand the possibility of the combination of the kind of the ring systems, a heterocyclic ring which can be applied for negative compounds has been demanded. Here, we took notice of a tetrahydropyrane ring, which has a polarity along the vertical direction to the molecule long axis.

Liquid crystalline compounds with a tetrahydropyrane ring and their preparation have been reported recently [4–8]. However, negative $\Delta\varepsilon$-type tetrahydropyrane compounds have not been reported up to now. Here we report the first synthesis of negative $\Delta\varepsilon$-type compounds having a tetrahydropyrane ring system (compounds **1**–**4**), and their physical properties. These compounds show peculiar dependency of $\Delta\varepsilon$ values on the substitution position of the tetrahydropyrane ring. In addition, we have investigated temperature dependency of the dielectric constants, and calculated rotational barrier, dipole moment and the angle of dipole moment by utilizing the semi-empirical quantum calculation method.

SYNTHESIS

Compounds **1** and **3** have been prepared as shown in Figure 1. Aldehyde **A** was converted into Lactone **B** through the protection with the amine, Michael addition, deprotection, reduction of the formyl moiety, and cyclization. Compounds **1** and **3** were finally obtained through coupling reaction with the lithium reagent and reduction, with a $10 \sim 15\%$ yield (6 steps).

The synthetic method of compound **2** is shown in Figure 2. Lactone **C** was prepared in the same manner as described in Figure 1. Compound **2** was obtained through coupling reaction with pentynyl lithium, dehydration, and hydrogenation, with a 48% yield (3 steps).

Compound **4** was synthesized as shown in Figure 3. Oxetane **D** was converted into Lactone **E** through the coupling reaction, and hydrolysis, then cyclization. After this, compound **4** was obtained through two fold reductions, with a 10% yield (4 steps).

The NMR spectra is identical to the compounds **1**–**4**.

1: ^{1}H-NMR: δ(ppm, $CDCl_3$) 0.89 (t, $J = 7.2$ Hz, 3H), 1.09–1.68 (m, 12H), 1.83–1.87 (m, 2H), 1.95–1.99 (m, 2H), 3.22 (t, $J = 11.1$ Hz, 1H), 4.04–4.07 (m, 1H), 4.11 (q, $J = 7.0$ Hz, 2H), 4.51 (d, $J = 9.8$ Hz, 1H), 6.72 (td, $J = 9.0$ Hz, $^4J_{HF} = 1.8$ Hz, 1H), 7.10 (td, $J = 9.0$ Hz, $^4J_{HF} = 2.2$ Hz, 1H).

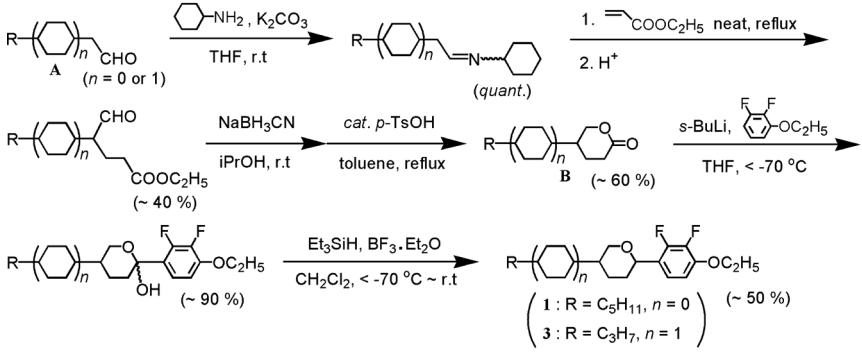


FIGURE 1 Synthetic route of compounds **1** and **3**.

^{19}F-NMR: δ(ppm, $CFCl_3$)–144.05 (dd, $^4J_{HF} = 7.6$ Hz, $^3J_{FF} = 19.4$ Hz, 1 F), −160.50 (dd, $^4J_{HF} = 7.6$ Hz, $^3J_{FF} = 19.8$ Hz, 1 F). MS (EI): 151 (100%), 171 (30%), 186 (60%), 312 (70%) [M^+].

2: ^{1}H-NMR: δ(ppm, $CDCl_3$) 0.89 (t, $J = 7.0$ Hz, 3H), 0.90–1.53 (m, 9H), 1.71–1.79 (m, 4H), 1.94–2.00 (m, 2H), 3.03–3.11 (m, 1H), 3.28–3.36 (m, 1H), 3.39 (t, $J = 11.1$ Hz, 1H), 3.98–4.01 (m, 1H), 4.07–4.11 (q, $J = 7.0$ Hz, 2H), 6.67 (td, $J = 9.0$ Hz, $^4J_{HF} = 1.8$ Hz, 1H), 6.81 (td, $J = 9.0$ Hz, $^4J_{HF} = 1.8$ Hz, 1H).

^{19}F-NMR: δ(ppm, $CFCl_3$)–142.36 (dd, $^4J_{HF} = 7.4$ Hz, $^3J_{FF} = 19.8$ Hz, 1 F), −159.56 (dd, $^4J_{HF} = 7.6$ Hz, $^3J_{FF} = 19.9$ Hz, 1 F).

MS (EI): 156 (100%), 184 (50%), 197 (40%), 241 (25%), 312 (20%) [M^+].

3: ^{1}H-NMR: δ(ppm, $CDCl_3$) 0.87 (t, $J = 7.3$ Hz, 3H), 0.95–1.58 (m, 16H), 1.71–1.79 (m, 4H), 1.86–1.99 (m, 2H), 3.34 (t, $J = 11.1$ Hz, 1H), 4.10 (q, $J = 7.0$ Hz, 2H), 4.13–4.17 (m, 1H), 4.48 (d, $J = 11.2$ Hz, 1H), 6.71 (td, $J = 8.9$ Hz, $^4J_{HF} = 1.5$ Hz, 1H), 7.10 (td, $J = 9.4$ Hz, $^4J_{HF} = 2.1$ Hz, 1H).

^{19}F-NMR: δ(ppm, $CFCl_3$)–144.11 (dd, $^4J_{HF} = 7.5$ Hz, $^3J_{FF} = 19.8$ Hz, 1 F), −160.55 (dd, $^4J_{HF} = 8.0$ Hz, $^3J_{FF} = 20.2$ Hz, 1 F).

MS (EI): 156 (30%), 184 (15%), 366 (100%) [M^+].

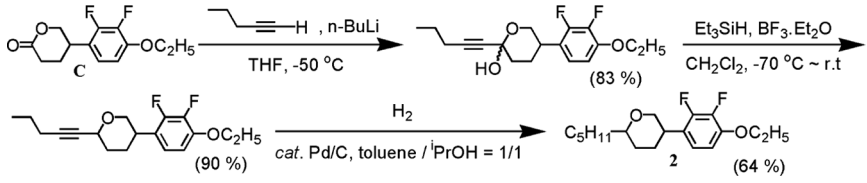


FIGURE 2 Synthetic route of compound **2**.

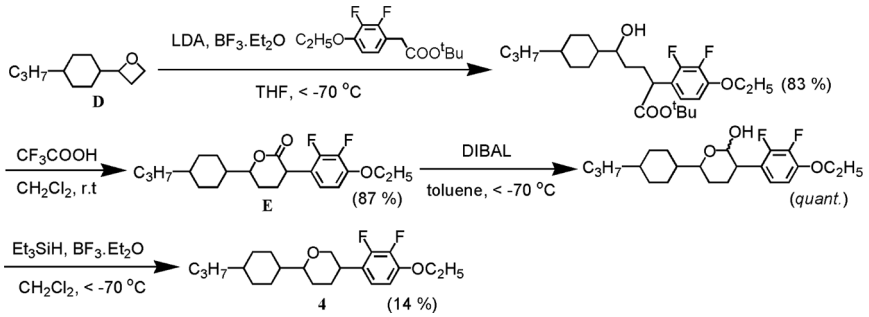


FIGURE 3 Synthetic route of compound **4**.

4: ^{1}H-NMR: δ(ppm, $CDCl_3$) 0.88 (t, $J = 7.2$ Hz, 3H), 0.90–1.53 (m, 16H), 1.71–1.79 (m, 4H), 1.94–2.00 (m, 2H), 3.05–3.09 (m, 1H), 3.37 (t, $J = 11.0$ Hz, 1H), 3.98–4.02 (m, 1H), 4.08 (q, $J = 7.0$ Hz, 2H), 6.67 (td, $J = 8.9$ Hz, $^4J_{HF} = 1.8$ Hz, 1H), 6.81 (td, $J = 9.3$ Hz, $^4J_{HF} = 2.2$ Hz, 1H).
^{19}F-NMR: δ(ppm, $CFCl_3$)–142.35 (dd, $^4J_{HF} = 7.3$ Hz, $^3J_{FF} = 19.9$ Hz, 1 F), −159.55 (dd, $^4J_{HF} = 7.6$ Hz, $^3J_{FF} = 19.9$ Hz, 1 F).
MS (EI): 184 (30%), 197 (100%), 241 (80%), 366 (20%) [M^+].

RESULTS AND DISCUSSION

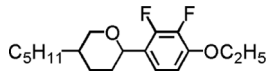
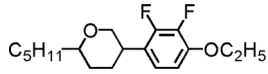
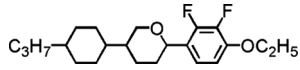
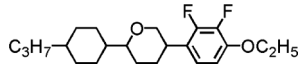
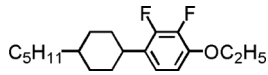
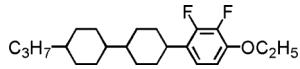
Physical Properties

Transition temperatures of compounds **1–4** are shown in Table 1 together with those of reference compounds **ref. 1** and **ref. 2**. As shown in Table 1, compounds **3** and **4** have a nematic phase, moreover, compound **3** also has a monotropic smectic phase. On the other hand, compounds **1** and **2** don't have any mesophase.

Table 2 shows the nematic-isotropic transition temperature (T_{NI}), $\Delta\varepsilon$, and optical anisotropy (Δn) of the synthesized compounds along with the reference compounds **ref. 1** and **ref. 2**, which were estimated by the linear extrapolation method using a nematic mixture (Host Mixture), consisting of phenyl cyclohexylcarboxylates. (Most compounds don't exhibit nematic phase at room temperature, so the linear extrapolation method is available for comparison [9].)

The T_{NI} values of compounds **1** and **2** are lower than that of compound **ref. 1**. Interestingly, compound **1** showed a lower magnitude of $\Delta\varepsilon$ and compound **2** showed a higher magnitude of $\Delta\varepsilon$, than that of compound **ref. 1**. A similar tendency was observed in the comparison of the three ring compounds **3**, **4**, and **ref. 2**. The synthesized compounds exhibit

TABLE 1 Transition Temperatures of the compounds **1–4**, **ref. 1**, and **ref. 2**

		Transition temperature (°C)
1		Cr · 56.4 · Iso
2		Cr · 50.6 · Iso
3		Cr · 107.7 (· SmB · 94.6) · N · 164.0 · Iso
4		Cr · 65.5 · N · 139.7 · Iso
ref. 1		Cr · 51.6 · Iso
ref. 2		Cr · 66.9 · SmB · 79.9 · N · 185.1 · Iso

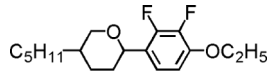
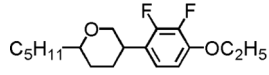
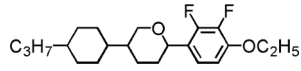
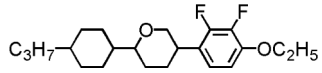
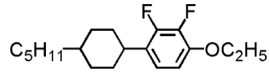
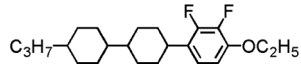
slightly lower Δn values than those of the cyclohexane derivatives **ref. 1**, **ref. 2**, which would indicate that the tetrahydropyrane ring works in the direction to decrease the optical anisotropy of the molecules.

Temperature Dependency of the Dielectric Constants $\varepsilon_\perp$ and $\varepsilon_{//}$

For meaningful comparison of the $\Delta\varepsilon$ values of compounds **1**, **2**, and **ref. 1**, as well as compounds **3**, **4**, and **ref. 2** possessing the different nematic-isotropic transition temperatures, we examined the temperature dependency of the dielectric constants.

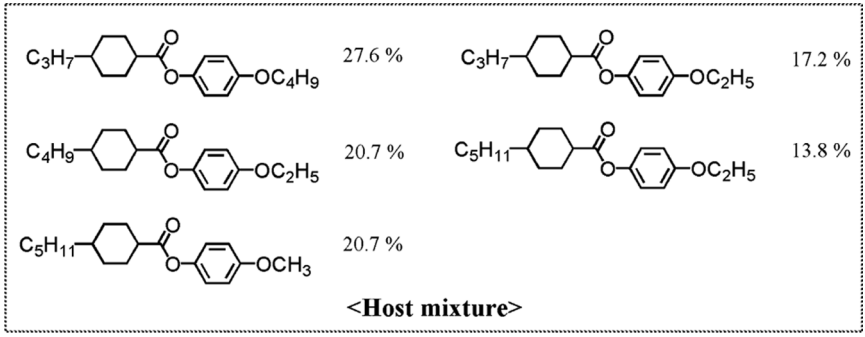
The temperature dependency of the dielectric constants $\varepsilon_\perp$ and $\varepsilon_\parallel$ were examined with the following methods ($\varepsilon_\parallel$ and $\varepsilon_\perp$ are the respective dielectric constants parallel and perpendicular to the nematic direction). The dielectric constants $\varepsilon_\perp$and $\varepsilon_\parallel$ of the samples each containing 15 wt% of compounds **1–4**, **ref. 1**, **ref. 2**, and 85 wt% of the Host Mixture, were measured at various temperatures. The graphs of the temperature dependence of $\varepsilon_\perp$ and $\varepsilon_\parallel$ were made by utilizing the extrapolated data based on the measured data and the constant reduced temperature T/Tc (Tc: nematic-isotropic

TABLE 2 Physical properties of the compounds **1**–**4**, **ref. 1**, and **ref. 2**

		T_{NI} (°C)	$\Delta\varepsilon$	Δn
1		4.6	− 3.3	0.067
2		−14.7	−8.3	0.063
3		138.6	−3.8	0.112
4		121.3	−7.3	0.107
ref. 1		17.3	−6.3	0.074
ref. 2		158.7	−5.4	0.114
Host Mixture		74.6	−1.3	0.087

i) Extrapolated data from mixtures containing 15 wt% of the synthesized compounds in Host Mixture 85 wt%.

ii) Measurement temperature of $\Delta\varepsilon$ and Δn; 25°C.



transition temperature) [10]. Two graphs for the compounds **1**, **2**, and **ref. 1**, and the compounds **3**, **4**, and **ref. 2** are shown as 4-1 and 4-2 in Figure 4.

As shown in Figure 4, the $\varepsilon_{\parallel}$ values for all of the samples are temperature independent, while the $\varepsilon_{\perp}$ values are greater in the lower

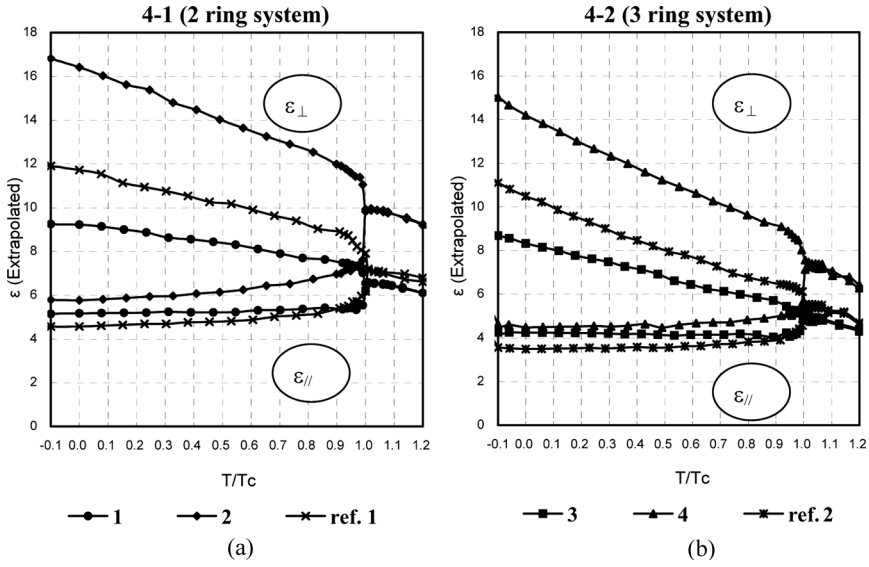


FIGURE 4 Temperature dependence of the dielectric constants $\varepsilon_{\perp}$ and $\varepsilon_{//}$.

temperature region, and decrease gradually with increasing temperature. This means that the $\Delta\varepsilon$ values greatly depend on the $\varepsilon_{\perp}$ values.

By comparison of the $\varepsilon_{\perp}$ curves of compounds **1**, **2**, and **ref. 1**, compound **2** exhibited higher $\varepsilon_{\perp}$ values over the entire temperature region. The same tendency was found in the case of compounds **3**, **4**, and **ref. 2**.

The Calculation of the Comformations

The interesting observed relationship between the $\Delta\varepsilon$ values and the structure of the synthesized compounds was studied applying a computer-aided calculation. It was presumed that the position of the oxygen atom in the tetrahydropyrane ring greatly influences the stable conformation of each compound. To examine the conformations of compounds **1**–**4**, the rotational barrier has been calculated by utilizing the semi-empirical quantum calculation method MOPAC/AM1 [11]. The calculated heat of formation at each 30 degree of $0 \sim 360$ degree dihedral angle (a, b, c, d) is shown in Figure 5.

As shown in Figure 5, the ΔH depends on the dihedral angle, and the conformations of compounds **1**-**4** were most stabilized at around $0 \sim 60$ degrees. In Figure 5-2 and 5-4, the conformations of compounds **2**, **4** were also stabilized at 180 degree. On the other hand, in Figures 5-1 and 5-3, compounds **1**, **3** exhibited unstable conformations

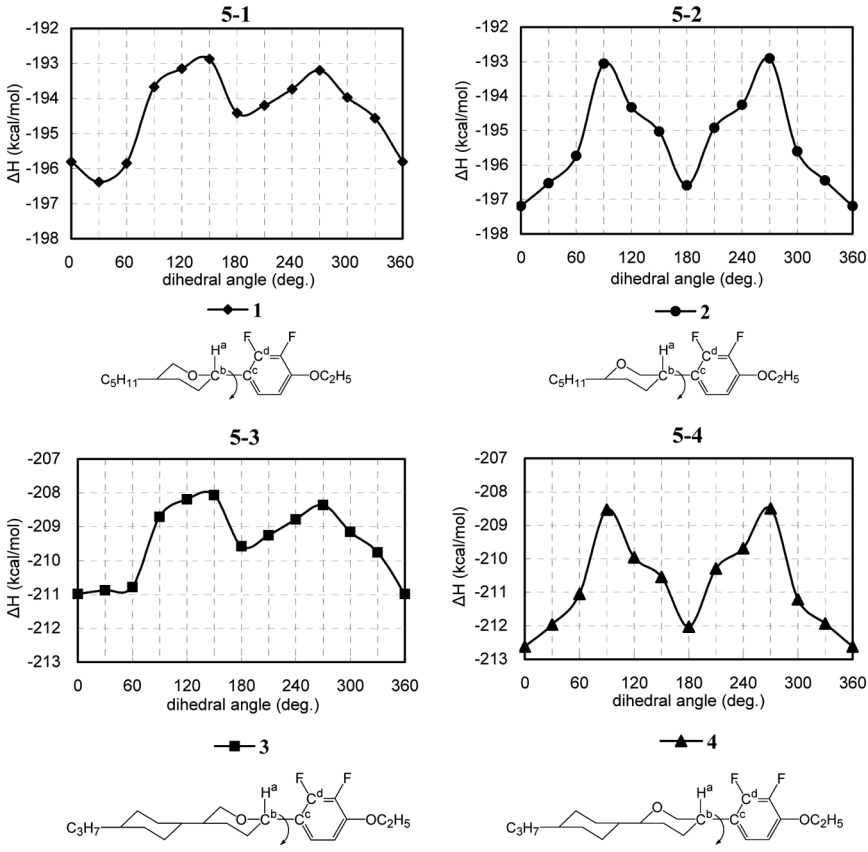


FIGURE 5 Rotational barrier in different conformations.

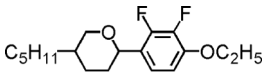
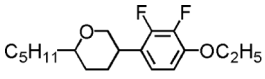
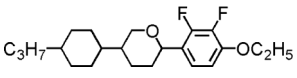
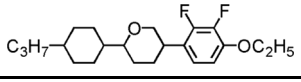
at 180 degrees. It is expected that the electric repulsion between the oxygen atom and the fluorine atom influences the stability of the corresponding conformations of compounds **1** and **3** at 180 degrees.

The Calculation of the Dipole Moment and the Angle of the Dipole Moment

The values of the dipole moment μ and the angle of the dipole moment β at the most stable formations have been calculated. The results are shown in Table 3.

Maximum β (90 degrees) indicates that the dipole moment is exactly parallel to the molecular short axis. Compounds having β close to 90 degrees and larger dipole moment μ exhibit greater negative Δε [12].

TABLE 3 The calculated data of ΔH, μ, β at the most stable formation

		Dihedral angle (degree)	ΔH (kcal/mol)	μ (Debye)	β (degree)
1		30	− 196.38	3.50	61.3
2		0	−197.19	4.50	89.0
3		0 ∼ 60	−210.88 (average*)	3.50 (average*)	63.0 (average*)
4		0	−212.62	4.49	89.4

*These are mean values of three points at 0, 30, and 60 degree.

As shown in Table 3, the significant differences between compounds **1, 3** and **2**, **4** were observed. Since the μ and β values of compounds **1** and **3** were smaller, they should exhibit lower negative Δε. On the other hand, compounds **2** and **4** showed larger values of μ and β, that can induce greater negative Δε.

The 3D models of compounds **3** and **4** at their most stable conformation are shown in Figure 6. As shown in Table 3 and Figure 6, there is a close relation between the μ and β values, and the molecular structure. In compounds **1** and **3**, since the lone-pair electron of the oxygen atom faces to the different direction of the fluorine atoms, it causes the decrease of the total dipole and the total angle of the dipole moment. On the other hand, as to compounds **2** and **4**, the direction of the lone-pair electron of the oxygen atom is on the same side as the

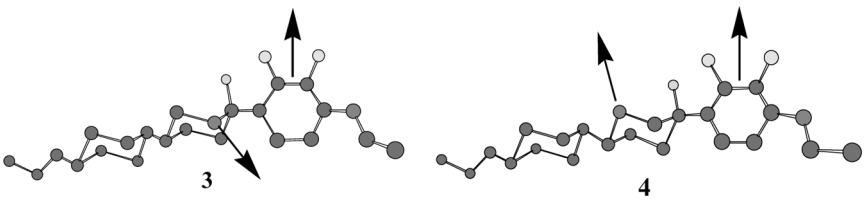


FIGURE 6 The 3D models of the compounds **3** and **4** at the most stable conformation.

fluorine atoms, inducing the greater μ and β values. We considered that this is caused by the difference of the position of the oxygen atom in the tetrahydropyrane ring.

CONCLUSIONS

A series of novel liquid crystalline compounds with a tetrahydropyrane ring has been synthesized. These compounds showed the peculiar dependency of the dielectric anisotropy ($\Delta\varepsilon$) values on the substitution position of the tetrahydropyrane ring. The same result was found when measuring the temperature dependency of the dielectric anisotropy constants $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$, and the reason of the peculiar dependency of the $\Delta\varepsilon$ values has been considered based on the result of the semi-empirical quantum calculations. Compounds **2** and **4**, exhibiting larger negative $\Delta\varepsilon$, are suitable for the vertical alignment (VA) mode LCDs.

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