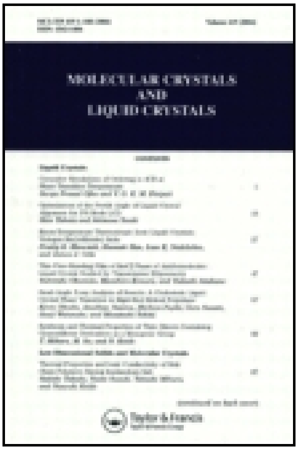

Molecular Crystals and Liquid Crystals

Nematic Liquid Crystal Compounds with Five-Ring Framework

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Nematic Liquid Crystal Compounds with Five-Ring Framework

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A series of novel liquid crystal compounds with five-ring framework having a –CF_2O- *linkage group (***1a**–**1e***) has been synthesized and their physical properties were measured. These compounds are characterized to have higher nematic-isotropic liquid transition temperatures and broader mesophase temperature range. As for the anisotropic properties, this series is categorized as compounds having large* $\Delta\varepsilon$ *and* Δn*. Although these compounds possess five rings in their structures, they exhibit high miscibility caused by the rotately non-symmetric structures including the lateral fluorine substituted phenylene rings. One of the novel compounds exhibits SmF phase and shows the second-order phase transition of SmA to SmC. The compounds are effective to improve the response property of the mixtures due to their high elastic constants. These five-ring compounds possess diversified properties and of high potential materials for improving the LCD performances.*

Keywords: difluoromethyleneoxy; five-ring framework; nematic liquid crystal compound; nematic mixtures

INTRODUCTION

Nowadays, the active matrix liquid crystal displays (AM-LCDs) are used to the various kinds of applications, such as PC monitors, TVs, and cellular phones. With the recent progress of the technology, the requirements for characteristics of AM-LCDs are increasing and diversifying, for example, the quicker response, the lower driving voltage and the higher contrast ratio. In order to adapt to these diversified

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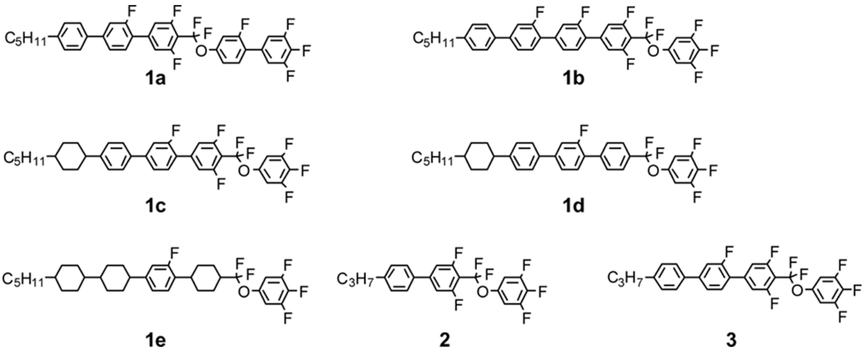


FIGURE 1 Chemical structures of compounds **1a**–**1e**, **2**, and **3**.

requirements, liquid crystal compounds that fulfill the physical properties i.e., higher nematic-isotropic liquid transition temperature, higher dielectric anisotropy ($\Delta\varepsilon$), higher optical anisotropy (Δn), simultaneously are essentially demanded. As well as the physical properties, miscibility is also considerable issue in the practical application.

In order to fulfill the requirements, the practically optimized nematic liquid crystal mixtures are designed as the combination of the polar compounds and the lower viscous non-polar compounds. In particular, the characteristics of the polar compounds relate to the response time and the driving voltage of LCDs, therefore, it is important to develop novel polar liquid crystal compounds with improved properties. To find out the high potential liquid crystal compounds, we have designed the compounds **1a**–**1e** possessing the five-ring framework, and their properties were verified and compared with those of the analogous three- and four-ring compounds **2** [1] and **3** [2] (Fig. 1).

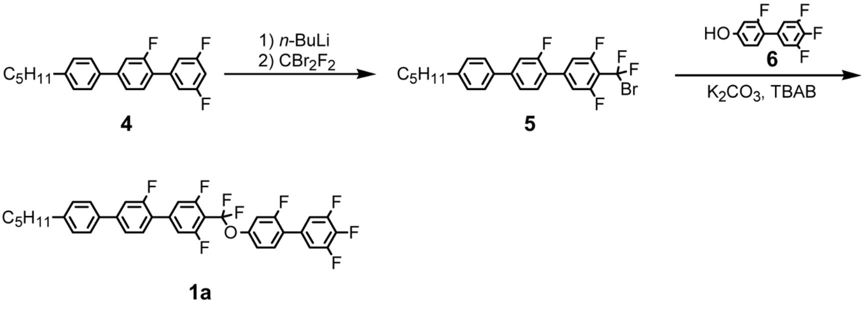


FIGURE 2 Synthetic route of compound **1a**.

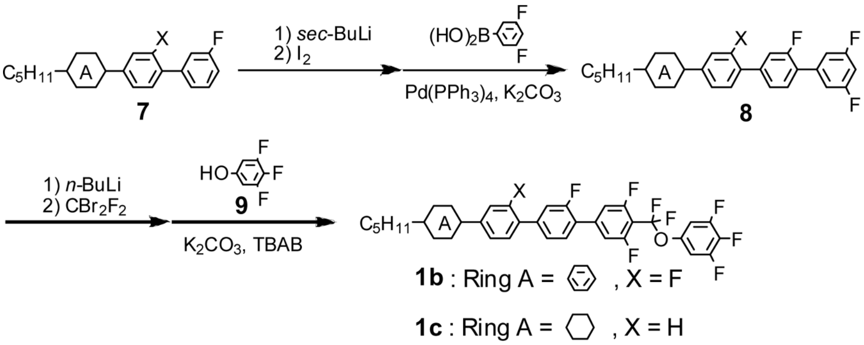


FIGURE 3 Synthetic route of compounds **1b** and **1c**.

EXPERIMENTAL SECTION

Synthesis

The five-ring compound **1a** was synthesized according to the scheme shown in Figure 2. The compound **4** was prepared by Suzuki cross-coupling reaction [3] of 3,5-difluorophenylboronic acid and the corresponding halide. The compound **4** was converted to the bromodifluoromethyl derivative **5** with *n*-BuLi followed by CBr_2F_2. The etherification of the compound **5** with the phenol derivative **6** resulted in the desired compound **1a**.

The compounds **1b** and **1c** were synthesized as shown in Figure 3. The compounds **7** were converted to the four-ring compounds **8** through the iodination and Suzuki cross-coupling reaction. The desired compounds **1b** and **1c** were obtained with the same manner as described in Figure 2.

The synthetic route of the compound **1d** is shown in Figure 4. The compound **10** was prepared from 4-bromobenzoic acid according to the literature [4]. The desired compound **1d** was obtained by Suzuki cross-coupling reaction of the bromide **10** and the corresponding boronic acid **11** [5].

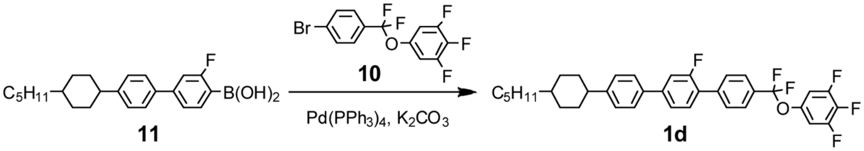


FIGURE 4 Synthetic route of compound **1d**.

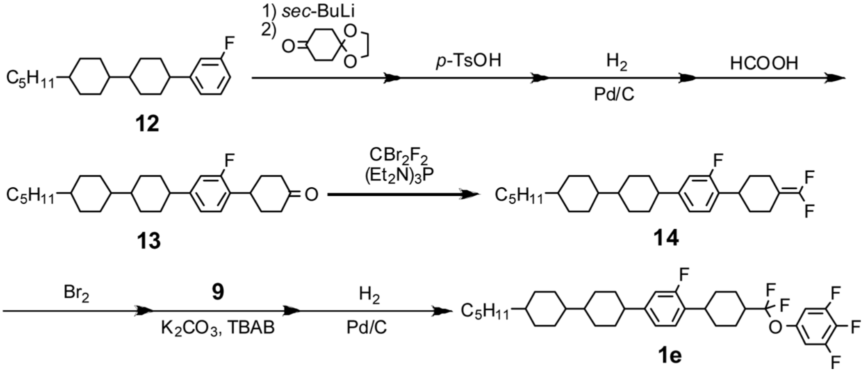


FIGURE 5 Synthetic route of compound **1e**.

The compound **1e** was synthesized according to the synthetic route shown in Figure 5. First, the compound **12** was converted to the cyclohexanone **13** through the nucleophilic addition, the dehydration, the hydrogenation and the deprotection. The compound **13** was converted to the difluorinated methylenecyclohexane **14** with a Wittig type reaction [6]. The compound **14** was converted to the desired compound **1e** through the bromination, the etherification and the hydrogenation [1a].

RESULTS AND DISCUSSIONS

Measurement Conditions and Instruments

^{1}H-NMR: Bruker DRX 500 (500 MHz); δ (ppm) = 7.26 for chloroform. ^{19}F-NMR: Bruker DRX 500 (470 MHz); $CFCl_3$ as internal reference. Transition temperature: Perkin Elmer Diamond DSC differential scanning calorimetry and Nikon Optiphot polarizing microscopy with a Mettler Toledo FP82HT hot stage. X-ray diffraction (XRD): Bruker D8 Discover diffractometer with a CuKα source (Cu-Kα, $\lambda = 1.54$ Å). Quantum chemical calculation was carried out by MOPAC AM-1 method [7]. Dielectric anisotropy ($\Delta\varepsilon$) and Elastic constants at 25°C: Hewlett Packard 4284A LCR meter. Optical anisotropy (Δn) at 25°C: Atago 4 T and 2 T Abbe refractometer. Rotational viscosity (γ1) at 25°C: TOYO Corporation TCM-1. Response time at 25°C: Otsuka Electronics LCD-5100WT.

Phase Sequences

Transition temperatures of the five-ring compounds **1a–1e** are shown in Table 1 together with those of the reference compounds **2** and **3**.

TABLE 1 Transition Temperatures of Compounds **1a**–**1e**, **2**, and **3**

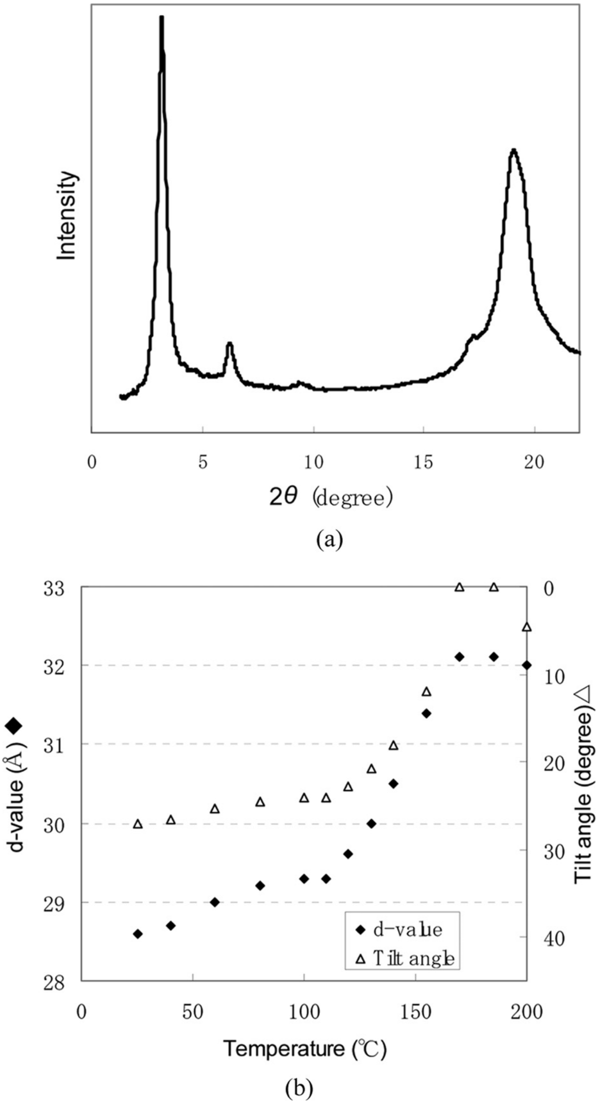
Compound	Transition Temperature (°C)[a]
1a	C 79.4 SmA 138 N 223 Iso
1b	C 87.1 SmA 181 N 255 Iso
1c	C 87.5 N 271 Iso
1d	C 76.9 SmF 114 SmC 143 SmA 215 N 305 Iso
1e	C 70.1 SmA 194 N 330 Iso
2	C 46.1 Iso
3	C 86.8 N 129 Iso

[a] The temperatures were detected by DSC analyses, and the mesophase types were determined by microscopic texture observations.

As shown in Table 1, the compounds **1a**–**1e** have the higher nematic-isotropic liquid transition temperatures and the wider range of the mesophases in compared to the three- and the four-ring compounds **2** and **3**. The wide mesophases temperature ranges of the compounds **1a**–**1e** are resulted by the high N-I temperatures (>223°C) accompanied with the moderate melting temperatures (70.1–87.5°C) that are comparable to that of the compound **3** (86.8°C). It should be noteworthy that such large molecules containing five rings exhibit their melting temperatures at such lower temperature region (<90°C).

XRD study, namely the measurements of the temperature dependences of the layer space (d-value) and the molecular tilt angle in the smectic phase of the compound **1d** has been carried out to investigate the polymorphism more in detail. Figure 6a shows the diffractogram measured at 25°C of a super-cooled smectic phase of the compound **1d**. The diffractogram shows the first-order reflection peak in the small angle region that corresponds to the d-value 28.5 Å, and shows the strong hollow peak that is typically observed in highly ordered smectic phases. The molecular length of the compound **1d** was estimated to be 31.9 Å by a molecular orbital calculation (MOPAC AM-1 method). From this result, the molecules in the smectic phase can be assumed to be tilted to the layer normal for 27.0 degrees.

The temperature dependences of the d-value and the molecular tilt angle of the compound **1d** are shown in Figure 6b. The d-value (32.1 Å) measured at 160–200°C fits with the calculated molecular length (31.9 Å), which represents that the smectic phase over this temperature range is a non-tilted phase. The continuous decrease of the d-value at 110–160°C (32.1 Å → 29.3 Å) could indicate that



(a)

(b)

FIGURE 6 (a) XRD pattern of the compound **1d** measured at 25°C; (b) Temperature dependence of d-value and molecular tilt angle.

these is a second-order transition of smectic A to smectic C. This result might also be reasonably understood from the DSC analysis (Figure 7), that no exothermic peak is found over 110–160°C.

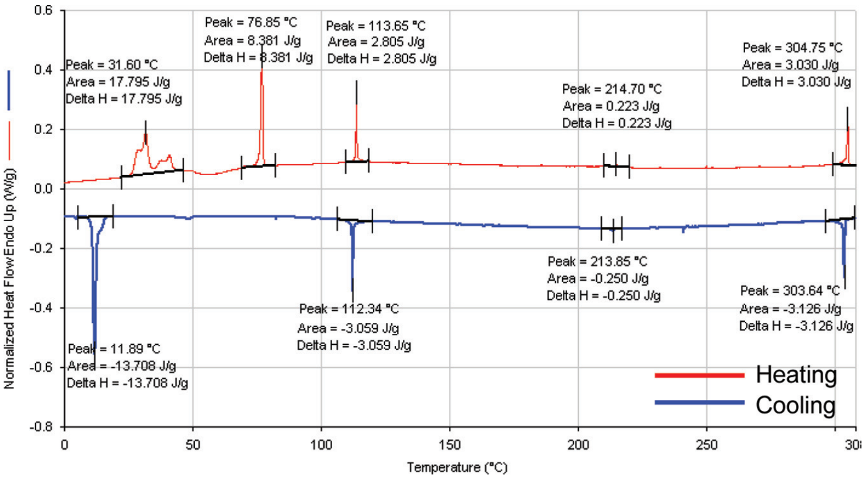


FIGURE 7 DSC chart of the compound **1d**.

Physical Properties

The physical properties of the five-ring compounds **1a–1e** are shown in Table 2. The value for $T_{N\text{-}I}$, $\Delta\varepsilon$, and Δn were extrapolated from mixtures that respectively consist of 15 wt% of the five-ring compounds and 85% of a high polar base mixture Mix-01 ($T_{N\text{-}I}$: 72.4°C, $\Delta\varepsilon$: 11.0, Δn: 0.137) containing the four benzonitrile derivatives. The value for rotational viscosity ($\gamma 1$) was extrapolated from mixtures that respectively consist of 20 wt% of the five-ring compounds and 80% of a base mixture Mix-02 ($\gamma 1$: 166 mPa · S) containing the nine fluorinated compounds. The compositions of the base mixtures Mix-01 and Mix-02 are shown in Figure 8.

TABLE 2 Physical Properties of Compounds **1a**–**1e**, **2**, and **3**

Compound	$T_{N\text{-}I}$ (°C)	$\Delta\varepsilon$	Δn	$\gamma 1$ (mPa · S)
1a	146	39.0	0.237	730
1b	169	36.7	0.257	699[a]
1c	189	22.9	0.210	706
1d	218	11.7	0.224	530
1e	216	6.77	0.130	548
2	−3.60	27.7	0.110	95.6
3	96.4	34.0	0.210	378

[a] Extrapolated from 10 wt% of the compound in the base mixture Mix-02.

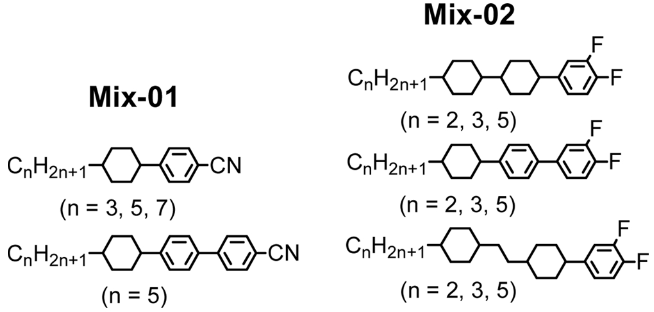


FIGURE 8 Compositions of Mix-01 and Mix-02.

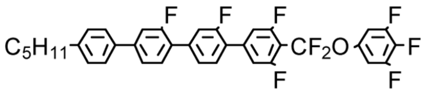
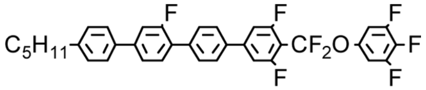
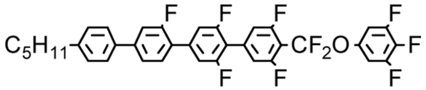
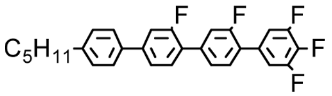
As clearly figured in Table 2, the compounds **1a–1e** have higher $T_{N\text{-}I}$ (146–218°C) in comparison to those of the compounds **2**(−3.6°C) and **3** (96.4°C). The extrapolated $\Delta\varepsilon$ and Δn of the compounds **1a–1e** spread widely, depending on the position and the number of the fluorine substituents and the ring structures. The compounds **1a–1c** with the higher π-conjugated and fluorinated structures exhibit higher $\Delta\varepsilon$ and Δn simultaneously. The replacement of the benzene ring into the cyclohexane ring, and the decrease of the number of the fluorine substituents induce the decrease in the $\Delta\varepsilon$ value and the depress of the Δn magnitude, respectively, as displayed in the properties of the compounds **1d** and **1e**. As for the viscosity, the compounds **1d** and **1e** have relatively lower $\gamma 1$ compared to the other five-ring compounds **1a–1c**. It suggests that the viscosity is specifically influenced by the existence of the two fluorine substituents on the benzene ring of the α,α-difluorobezyloxy moiety (−Ar-CF2O−).

These five-ring compounds possess diversified $T_{N\text{-}I}$, $\Delta\varepsilon$, Δn, and $\gamma 1$ according to the position of the $-CF_2O$- moiety, the number of the fluorine atoms, and the ring structures. Therefore, it will be possible to provide the mixtures having diverse characteristics that are suitable to fulfilling the requirements by the appropriate selections of the structures of the five-ring compounds.

Miscibility

The miscibility of the compounds **1b**, **1f**, and **1g** into the base mixture Mix-01 are displayed in Table 3 with that of the compound **15** as the reference. The compounds **1f** and **1g** were prepared according to the scheme in Figure 3, and the compound **15** was synthesized by the procedures reported in the literature [8]. The miscibility

TABLE 3 Difference in Miscibility of Compounds **1b**, **1f**, **1g**, and **15**

	Compound	Transition temperature (°C)	$\Delta H_{\text{C-SmA}}$ (kJ/mol)	Miscibility in mix-01 (%)
1b		C 87.1 SmA 181 N 255 I	22.4	15
1f		C124 SmA 206 N 270 I	24.4	5
1g		C125 SmA 167 N 240 I	34.0	5
15		C106 SmA 169 N 200 I	33.5	5

has been estimated as followings. We prepared three samples with concentrations of 5%, 10%, and 15% of compounds, respectively. These samples were preserved at 20°C for 30 days. After that, we visually determined whether solid or smectic phase separation appeared in the samples. If no solid or smectic phase separation was observed in the 15% sample, its miscibility was regarded to be over 15%, and if solid or smectic phase separation was observed in the 15% sample, the miscibility was regarded to be lower than 10%. In the same way, each miscibility was estimated.

The transition temperatures and the melting enthalpies of the compounds **1b**, **1f**, **1g**, and **15** are also summarized in Table 3, because the miscibility of liquid crystal compounds is intimately related to melting points and melting enthalpy [9].

As shown in Table 3, the miscibility of the compound **1b** is significantly high among the tested five-ring compounds and the reference four-ring compound **15**. Even though the melting enthalpies of the compounds **1b** (22.4 kJ/mol) and **1f** (24.4 kJ/mol) are similar, the miscibilities of the compounds **1b** (15%) and **1f** (5%) are notably different. It suggests that the differences of the miscibilities of the compounds are strongly influenced by the melting temperatures of the compounds, as observed in **1b** (87.1°C) and **1f** (124°C).

Molecular Conformations

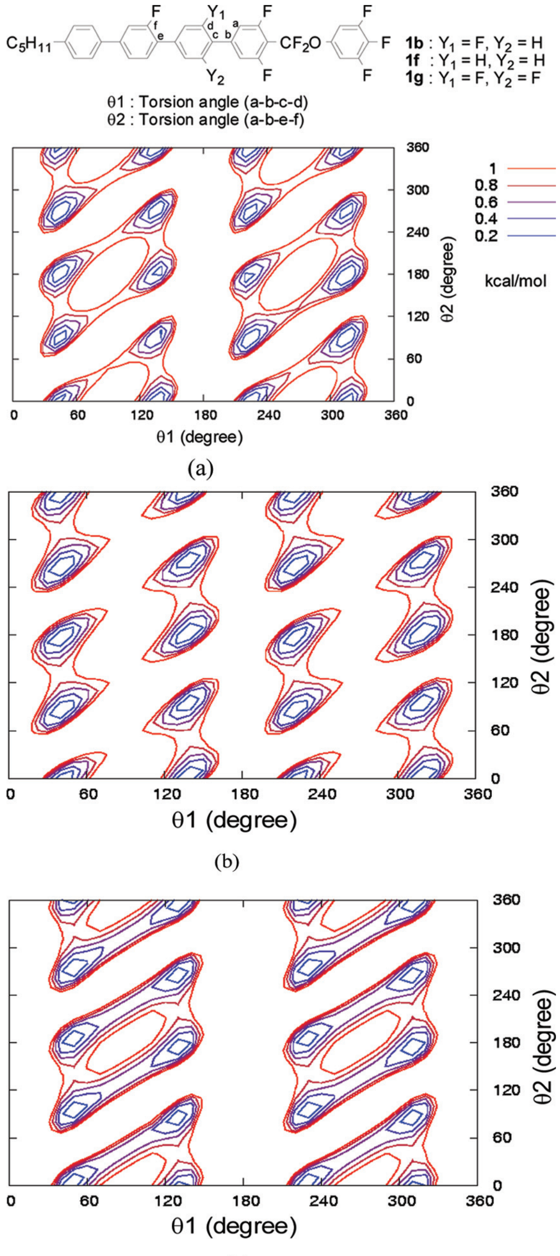
For further investigation about the significant differences in miscibilities and the melting temperatures of the compounds **1b**, **1f**, and **1g**, the distribution of the conformations of **1b** was calculated and the results are displayed in Figure 9a, as the relationship of the heat of formations to the torsion angle a-b-c-d ($\theta 1$) and the angle a-b-e-f ($\theta 2$), where the heat of formation of the most stable conformation is indicated as 0 kcal/mol. The calculations were carried out by the MOPAC AM-1 method. As shown in Figure 9a, the compound **1b** has a number of stable conformations, in which the connecting benzene rings have the torsion angles of 45 degrees one to another. This result means that the compound **1b** is able to exist stable in many conformational states in liquid crystal mixtures.

The distributions of the conformations of the compounds **1f** and **1g** are shown in Figures 9b and c, respectively. While the distributions of the stable conformations of the compounds **1f** and **1g** are similar to that of **1b**, their conformations in 180–360 degrees of $\theta 1$ exhibit as the same conformations in 0–180 degrees of $\theta 1$, so that the number of the stable conformations of the compounds **1f** and **1g** is limited by half.

The results suggest that the better miscibility of the compound **1b** (15%) is induced by the less-symmetric structure of the compound **1b** introduced by the existence of the two mono-fluorinated phenylene rings in compared to the compounds **1f** (5%) and **1g** (5%), and by the existence of the –CF_2O- moiety in compared to the four-ring compound **15**. From the results of the miscibility investigations and the molecular orbital calculations, it might be assumed that the non-symmetric structures inducing the diversified distribution of the molecular conformers as the compound **1b** have a tendency to be prevented in forming ordered structures, which may help to decrease a growth of the crystalline structures and, as a result of this, to sustain the high miscibility.

Response Property

With the recent progress of LCD technology, the most important requirement in terms of characteristics of the liquid crystal mixtures is quick response. The response property of the TN mode LCDs is



(a)

(b)

(c)

FIGURE 9 (a) Conformational distribution of **1b**; (b) Conformational distribution of **1f**; (c) Conformational distribution of **1g**.

described as the following two formulas (1) and (2) [10].

$$T_{rise} = \gamma 1 d^2/\pi^2 K(V^2/V_c^2 - 1) = \gamma 1 d^2/\varepsilon_0 \Delta\varepsilon (V^2 - V_c^2) \tag{1}$$

$$T_{decay} = \gamma 1 d^2/\pi^2 K \tag{2}$$

(T_{rise}: Rise time, T_{decay}: Decay time, d: Cell thickness, K: Elastic constant, V: Applied voltage, V_c: Threshold voltage, ε_0: Dielectric constant of a vacuum).

As shown in the formulas (1) and (2), the total response time ($T_{rise} + T_{decay}$) is proportional to $\gamma 1$ and K, so that enlargement of K without increasing $\gamma 1$ is essentially important for the improvement of the response property. The elastic constant is represented as

$$K = K_{11} + (K_{33} - 2K_{22})/4 \tag{3}$$

where K_{11}, K_{22}, and K_{33} are the splay, twist and bend elastic constants, respectively. As for the relationship between the elastic constants and the molecular structure, K_{33} is known to be proportional to the molecular length (L) [11], and the elastic constant ratio (K_{33}/K_{11}) is roughly correlated to the molecular length and width ratio (L/D) [12].

The L/D ratio of the compound **1a** (3.39) has been estimated with the molecular orbital calculation applying MOPAC AM-1 method and is listed in Table 4 together with those of the reference compounds **2** (2.23) and **3** (2.98). As clearly seen in Table 4, the compound **1a** has the longest molecular length among the compounds estimated, which may suggests that the five-ring compounds are expected to have larger K_{33} and K_{33}/K_{11} ratios, which would work in the right direction into reducing the response time.

For further investigation of the elastic constants of the five-ring compounds, the following three mixtures (*Mixture A–Mixture C*) were prepared. The properties of the mixtures containing 10% each of the compound **1a**, the three-ring compound **2** and the four-ring compound **3**, respectively, as their high polar components, are shown in Table 5. The other components in the three mixtures were adjusted to settle their $T_{N\text{-}I}$, $\Delta\varepsilon$, Δn and $\gamma 1$ in the same ranges.

TABLE 4 Results of Molecular Orbital Calculations

	L (Å)	D (Å)	L/D
1a	32.4	9.57	3.39
2	21.6	9.70	2.23
3	25.9	8.67	2.98

TABLE 5 Properties of *Mixture A–Mixture C*

	Mixture A	*Mixture B*	*Mixture C*
Property			
$T_{N\text{-}I}$ (°C)	106	106	107
$\Delta\varepsilon$	5.8	5.6	5.5
Δn	0.101	0.100	0.101
$\gamma 1$ (mPa · S)	109	106	108
Composition (wt%)			
1a	10	–	–
2	–	10	–
3	–	–	10

The elastic constants and the elastic constant ratio (K_{33}/K_{11}) of *Mixture A–Mixture C* are measured and shown in Table 6. As expected from the calculated large value of L and L/D ratio of the compound **1a**, the *Mixture A* shows the significantly large K_{33} and K_{33}/K_{11} ratio that are greater than those of the other two mixtures.

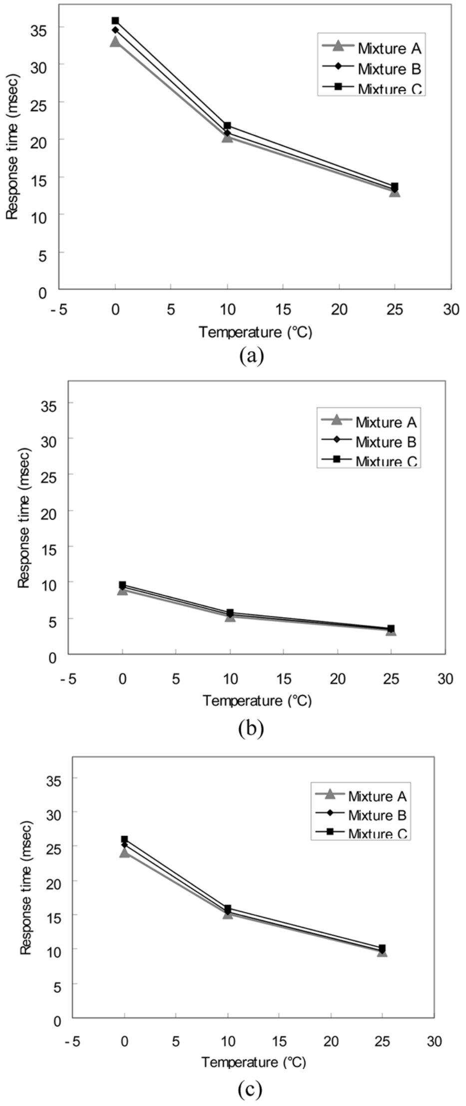
The temperature dependence of the response time and $\gamma 1$ of *Mixture A–Mixture C* were measured, and the influence of the elastic constants onto the response property has been studied (Figures 10 and 11).

The total response time (T_{all}) of *Mixture A* is the shortest among those of the investigated three mixtures and the difference is wider at the lower temperature region (Figure 10a). This difference in the T_{all} is derived mainly from the T_{decay} characteristics (Figure 10b, Figure 10c). In contrast to the response time, the viscosity of *Mixture A* was found to be larger than those of the other two mixtures, in which the gap becomes larger according to the decrease of the temperature.

The shorter response time of *Mixture A* at low temperature, even though the viscosity is larger than the other mixtures, indicates that the temperature dependence of the elastic constant of *Mixture A* is smaller than that of the other mixture. From the effect notably observed, the five-ring compounds will be effective for improvement

TABLE 6 Elastic Constants of *Mixture A–Mixture C*

	K_{11} (pN)	K_{22} (pN)	K_{33} (pN)	K_{33}/K_{11}
Mixture A	12.8	12.4	28.1	2.20
Mixture B	12.6	11.0	25.7	2.04
Mixture C	13.0	11.6	23.5	1.81



(a)

(b)

(c)

FIGURE 10 (a) Temperature dependence of T_{all}; (b) Temperature dependence of T_{rise}; (c) Temperature dependence of T_{decay}.

of the response property of the current liquid crystal mixture, especially at low temperature, and the result suggests that the use of the five-ring compounds reported in this paper will provide a favorable improvement in elastic constants of liquid crystal mixtures.

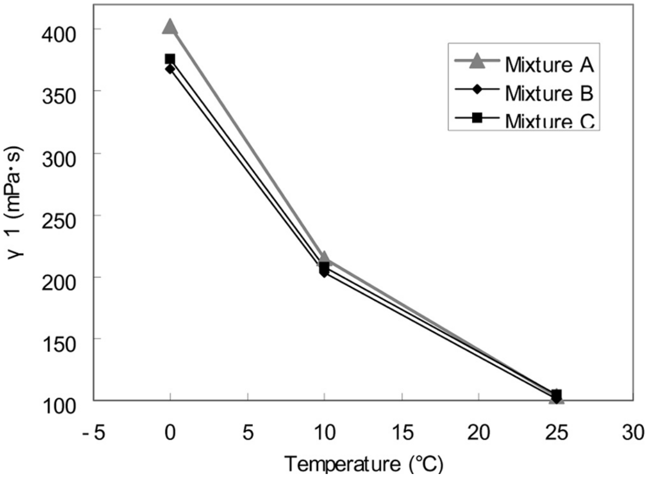


FIGURE 11 Temperature dependence of $\gamma 1$.

CONCLUSIONS

A series of novel liquid crystal compounds with five-ring framework having a $-CF_2O$- linkage group has been synthesized and their physical properties were measured. These compounds are characterized to have higher nematic-isotropic liquid transition temperatures, broader mesophase, large $\Delta\varepsilon$ and large Δn. Although the novel compounds possess five rings in their structures, they exhibit remarkably high miscibility caused by the rotately non-symmetric structures and the lateral fluorine substituted phenylene rings. The high elastic constants of the compounds allow the mixtures containing them to provide the reduction of the response time especially at the low temperature region. These five-ring compounds possess diversified properties and they are potential materials for the improvement of the LCD performances.

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