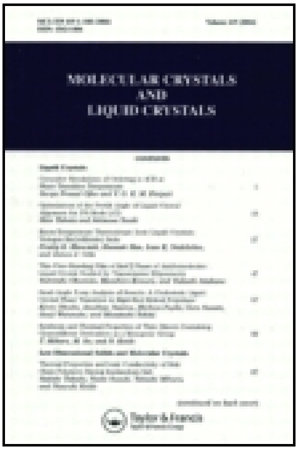

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# Novel Liquid Crystalline Four Ring Chain Difluoromethyleneoxy Compounds for Quicker Response LC Mixtures

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# Novel Liquid Crystalline Four Ring Chain Difluoromethyleneoxy Compounds for Quicker Response LC Mixtures

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*A series of chemically stable novel liquid crystalline four ring chain compounds (**1a**–**1c**) having a difluoromethyleneoxy ($CF_2O$) linkage moiety have been designed and prepared, and their properties have been thoroughly investigated. The novel compounds intrinsically possess much higher positive $\Delta\varepsilon$ (>32) and $\Delta n$ (>0.190), relatively low viscosity, wider nematic phase temperature ranges and significantly higher clearing temperatures in comparison to the analogous three ring chain $CF_2O$ compound (**2**) that is currently applied in almost all the latest TN-TFT monitors, notebook PCs and IPS-TVs.*

**Keywords:** difluoromethyleneoxy; four ring chain; nematic mixtures

## INTRODUCTON

The vastly expanding market and the leap of the LC display (LCD) performance, continuously and endlessly require property improvement of liquid crystalline materials. In particular, liquid crystalline materials exhibiting much quicker response characteristics and better performances in stability and reliability, that are directly proportional to the LCD quality, have strongly been demanded. In order to fulfill the requirements, the practically applied optimized nematic liquid crystal mixtures are designed as a combination of polar compounds

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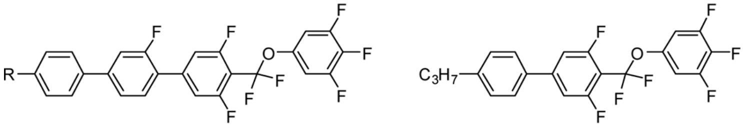


**1a**: R = $^nC_3H_7$
**1b**: R = $^nC_4H_9$
**1c**: R = $^nC_5H_{11}$

**2**

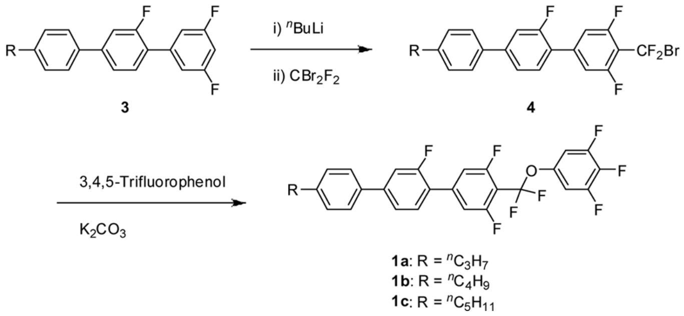
**FIGURE 1** Chemical structures of compounds **1a**–**1c** and **2**.

and lower viscous non-polar compounds. In particular, the characteristics of the polar compounds relate to the response time and the driving voltage of the LCDs, therefore, it is important to develop novel polar liquid crystal materials with better properties. We have designed and prepared the three ring chain compound (**2**) with a $CF_2O$ linkage moiety as a high performance polar liquid crystal compound [1]. The compound shows high $\Delta\varepsilon$ and low rotational viscosity ($\gamma 1$) and therefore it can contribute to low voltage driving and quick response. However, the compound **2** has no nematic phase and exhibits the low melting temperature (49.1°C), which results the significant decrease of the clearing point ($T_{NI}$) when doped in the lower viscous non-polar compounds. To overcome these difficulties, we have designed and synthesized the novel $CF_2O$ compounds containing the four ring chain structure (**1a**–**1c**) [Fig. 1].

# EXPERIMENTAL SECTION

## Materials

The compounds **1a**–**1c**, were synthesized according to the synthetic scheme shown in Scheme 1. The compounds (**3**) ($R = {}^nC_3H_7$, $^nC_4H_9$,



**SCHEME 1** Synthetic scheme of compounds **1a**–**1c**.

$^{n}C_5H_{11}$) were prepared by Suzuki cross-coupling reaction of 3,5-difluorophenylboronic acid and the corresponding 4-(4-alklylphenyl)-2-fluorophenyl iodides according to the literature [2]. The compounds **3** were treated with $^{n}$BuLi in tetrahydrofurane at −70°C, followed with $CBr_2F_2$ to give the difluoromethylbromides (**4**). The etherification of the compounds **4** with 3,4,5-trifluorophenol in a basic condition ($K_2CO_3$ in $H_2O$ at 100°C) resulted in the desired compounds **1a**−**1c**.

## RESULTS AND DISCUSSIONS

### Measurement Conditions and Instruments

$^1$H-NMR: Bruker DRX 500 (500 MHz); $\delta$ (ppm) = 7.26 for chloroform. $^{19}$F-NMR: Bruker DRX 500 (470 MHz); $CFCl_3$ as internal reference. Transition temperature: Perkin Elmer DSC 7 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 CuK$\alpha$ source (Cu-K$\alpha$, $\lambda = 1.54$ Å). Quantum chemical calculation was carried out by MOPAC AM-1 method [3]. Dielectric anisotropy ($\Delta\varepsilon$) at 25°C: Hewlett Packard 4284A LCR meter. Optical anisotropy ($\Delta$n) at 25°C: Atago 4 T and 2 T Abbe refractometers. Rotational viscosity ($\gamma$1) at 25°C: TOYO Corporation TCM-1. Response time (RT) at 25°C: Otsuka Electronics LCD-5100WT. Voltage holding ratio and specific resistivity were measured according to the literature [4].

### Mesomorphism

The phase transition temperatures of the synthesized compounds **1a**−**1c** obtained by the DSC measurements with 3°C/min of the heat rate are summarized in Table 1 with those of the compound **2** as references. Surprisingly, inserting one benzene ring into the

**TABLE 1** Phase Sequences and Transition Temperatures

| Compound | Transition temperature [°C] |
|---|---|
| **1a** | Cr 86.8 N 128.7 Iso |
| **1b** | Cr 78.1 (SmA 59.3) N 118.4 Iso |
| **1c**[a] | Cr 64.1 (SmA 65.1) N 122.9 Iso |
| **2** | Cr 49.1 Iso |

[a] Found to have at least two crystal structures. The melting point in the second heating was 10°C lower than that in the first heating.

molecular structure of the compound **2** induces the significant increase of the liquid crystalline potential. The compounds **1a**–**1c** exhibit the wide nematic temperature ranges with the high nematic-isotorpic liquid transition temperatures of greater than 118.4°C, most probably due to their larger molecular length and width ratio (L/D ratio). The L/D ratios of the compounds **1a**–**1c** and **2** have been estimated with the semi-empirical molecular orbital calculation applying MOPAC AM-1 method and are listed in Table 2. All the four compounds **1a**–**1c** and **2** possess their widths of the molecular rods in the range of 8.67–9.76 Å, while the molecular lengths are widely distributed as 25.9–28.2 Å for the compounds **1a**–**1c** and 21.6 Å for the compound **2**, resulting in the significant difference in the L/D ratios of the four- and the three-ring chain compounds.

As shown in Table 1, the compounds **1b** and **1c** possessing the longer alkyl chains i.e., butyl and pentyl have the higher ordered mesophase smectic A incorporating nematic phase. XRD study of the compound **1c** has been performed and the results are displayed in Figure 2A. The X-ray diffractogram of the compound **1c** at 62°C exhibiting SmA shows the sharp reflection in the small angle region that corresponds to the layer space of d (spacing)-value 26.6 Å. There is a reasonable fit of the layer space value (26.6 Å) obtained with the XRD measurement and 28.2 Å that has been estimated by the MOPAC calculation as the molecular length of the compound **1c**. The weak and broad hollow peak, which is typically observed in XRD of nematic phase [5], was found in the X-ray diffractogram of compound **1c** measured at 70°C.

The compound **1c** was found to have at least two different crystal structures. The melting point during the 2nd heating process was lower than that in the 1st heating process for 10°C. As shown in Figure 2B, two diffraction patterns of the virgin crystal and the crystal obtained through the crystallization after the melt are quite different in the small angle and the 15–20 degree regions. More detailed discussions will be reported separately in elsewhere.

**TABLE 2** Results of Molecular Orbital Calculations

| | Length (L) [Å] | Width (D) [Å] | L/D |
|---|---|---|---|
| **1a** | 25.9 | 8.67 | 2.98 |
| **1b** | 27.2 | 8.80 | 3.09 |
| **1c** | 28.2 | 9.76 | 2.89 |
| **2** | 21.6 | 9.70 | 2.23 |

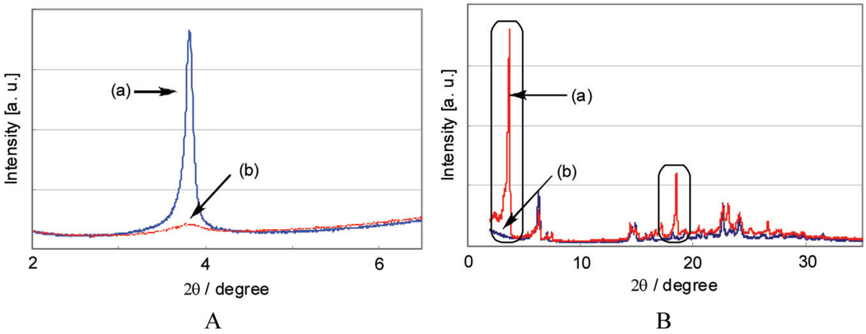


**FIGURE 2** X-ray diffractograms of compound **1c** obtained in A. (a) SmA (62°C) and (b) nematic phase (70°C); B. (a) before melting, and (b) crystallized after melting.

## Physical Properties

Physical properties of the compounds **1a**–**1c**, namely $T_{NI}$, $\Delta\varepsilon$, $\Delta n$, and $\gamma 1$, that have been estimated as extrapolated values from mixtures of the compounds **1a**–**1c** (15%) and 85% of a polar base nematic mixture ($T_{NI}$: 72.4°C, $\Delta\varepsilon$: 11.0, $\Delta n$: 0.137, $\gamma 1$: 166.0 mPa · S) comprising of liquid crystalline benzonitrile derivatives, are summarized in Table 3 with those of the compound **2** as references. As clearly displayed in Table 3, the compounds **1a**–**1c** exhibit the significantly high $T_{NI}$ that are approximately 90°C–100°C higher in comparison to that of the compound **2**. As well as the $T_{NI}$, the extrapolated $\Delta\varepsilon$ and $\Delta n$ of the compounds **1a**–**1c** are significantly larger than those of the reference, due to the extended $\pi$-electron conjugation incorporating the additional fluorine substituents on the benzene rings. The highly conjugated molecular structures of the compounds **1a**–**1c** induce the 20–25% greater $\Delta\varepsilon$ and the $\Delta n$ of two fold magnitude. The reasonable increase in the $\gamma 1$ has been observed in the compounds **1a**–**1c**.

It has also been found that the compounds **1a**–**1c** are reasonably highly stable against UV irradiation and high temperature. As shown

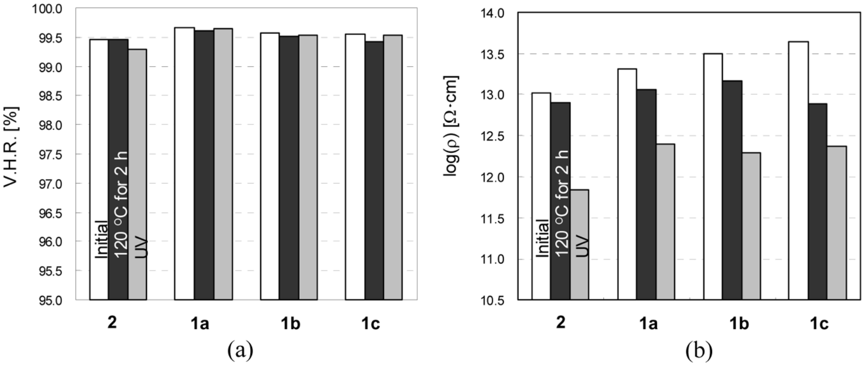
**TABLE 3** Extrapolated Physical Properties

| Compound | $T_{NI}$ [°C] | $\Delta\varepsilon$ | $\Delta n$ | $\gamma 1$ [mPa · S] |
|---|---|---|---|---|
| **1a** | 96.4 | 34.0 | 0.210 | 378.1 |
| **1b** | 89.7 | 32.7 | 0.190 | 374.2 |
| **1c** | 96.4 | 32.1 | 0.197 | 411.6 |
| **2** | –3.6 | 27.7 | 0.110 | 95.6 |

in Figure 3, the voltage holding ratio (V.H.R.) and the specific resistivity ($\rho$) of the compounds **1a**–**1c** after 2 hours storage at 120°C and UV irradiation (3,000 mJ/cm$^2$) have been estimated and found to be in the same level as or even better than those of the compound **2** that is already and widely applied for AM-LCDs.

## Representative Nematic Mixtures for Application

Quicker response liquid crystal mixtures that are in demand for AM-LCDs, can essentially be achieved by lowering $\gamma 1$ of the mixtures. In the mixture design principle, lowering $\gamma 1$ is the most effective approach for increasing the contents of the lower viscous non-polar compounds in the liquid crystal mixtures. Accordingly, the replacement of the compound **2** by the compounds **1a**–**1c** allows increase of the non-polar compounds contents in the mixtures, which enables $\gamma 1$ of the mixtures reduced without depressing other properties, namely decreasing the $T_{NI}$ or increasing the crystallizing temperature. Two representative mixtures *Composition 1* and *Composition 2* containing the compounds **1b** and **2**, respectively, are listed in Table 4. Substituting the polar component in the mixture from compound **2** (*Composition 2*) to compound **1b** (*Composition 1*), that allows the increase of the non-polar low viscous compounds, resulted in the significant reduction in the response time of 15% with sustaining other properties, namely $T_{NI}$, $\Delta\varepsilon$, and $\Delta n$. The nematic phase of both mixtures prepared are stable even at a low temperature (−20°C) and can be sustained for a long period (>10 days) without spontaneous crystallization.



(a) (b)

**FIGURE 3** V.H.R. and specific resistivity of compounds **1a**–**1c** and **2**; (a) V.H.R. (30 Hz, 25°C) of compounds **1a**–**1c**, and **2**; (b) Specific resistivity (25°C) of compounds **1a**–**1c**, and **2**.

**TABLE 4** Properties of Representative Liquid Crystal Mixtures

| Mixture | $T_{NI}$ [°C] | $\Delta\varepsilon$ | $\Delta n$ | RT [m sec] |
|---|---|---|---|---|
| COMPOSITION 1 | 74.4 | 8.9 | 0.100 | 8.42 |
| COMPOSITION 2 | 74.4 | 8.9 | 0.100 | 9.92 |

## CONCLUSIONS

A series of chemically stable novel liquid crystalline four ring chain compounds having a $CF_2O$ moiety have been synthesized. The novel compounds possess much higher $\Delta\varepsilon$ and $\Delta n$, and additionally the wider nematic phase temperature ranges in comparison to the three ring chain $CF_2O$ compound. The addition of the novel compounds in the liquid crystal mixtures allows the increase in the content of the lower viscous non-polar compounds. As the result of this approach, the significant response time reduction of the liquid crystal mixtures has been realized.

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