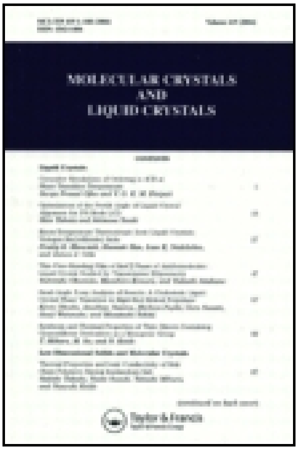

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Properties of Novel Liquid Crystalline Compounds Having Fluorinated Ring Systems

Koki Sago [a] & Atsuko Fujita [a]

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

To cite this article: Koki Sago & Atsuko Fujita (2007): Synthesis and Properties of Novel Liquid Crystalline Compounds Having Fluorinated Ring Systems, Molecular Crystals and Liquid Crystals, 479:1, 151/[1189]-160/[1198]

To link to this article: http://dx.doi.org/10.1080/15421400701732555

Mol. Cryst. Liq. Cryst., Vol. 479, pp. 151/[1189]–160/[1198], 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701732555

Synthesis and Properties of Novel Liquid Crystalline Compounds Having Fluorinated Ring Systems

Koki Sago
Atsuko Fujita
Chisso Petrochemical Corporation, Goi Research Center, Ichihara,
Chiba, Japan

To satisfy the current requirements for better quality of the liquid crystal displays (LCDs), the three series of liquid crystalline (LC) compounds having fluorine substituted chroman ring systems have been prepared and evaluated. These chroman compounds were synthesized through their individual ring closure reaction as a key step. All of the compounds show high dielectric anisotropy (Δε) and high birefringence (Δn), but the significant different solubility is shown between two similar compounds having two fluorine atoms on chroman ring system. The solubility to the base mixture consisted of fluorinated compounds depends on the position of fluorine atoms on the core structure. We suggest that the difference of the solubility is caused by the two parameters: the melting enthalpy and the structure.

Keywords: chroman; fused ring; high birefringence (Δn); solubility

INTRODUCTION

Nowadays, the active matrix liquid crystal displays (AM-LCDs) have been applied to various kinds of displays, such as PC monitors, cellular phones or TVs. The current major requirements for the AM-LCDs are, in particular, quick response, low driving voltage, and a wide viewing angle. To satisfy this requirement, the development of the liquid crystalline materials is still necessary. And the important parameters of LC materials are dielectric anisotropy (Δε), birefringence (Δn),

The authors acknowledge Professor Dietrich Demus (ISCO, International Scientific Consultant Office, Halle, Germany) suitable discussions.

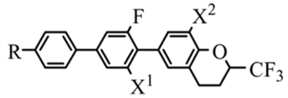
Address correspondence to Koki Sago, Chisso Petrochemical Corporation, Goi Research Center, 5-1 Goikaigan, Ichihara, Chiba 290-8551, Japan. E-mail: ksagou@chisso.co.jp

viscosity, transition temperature and so on [1–3]. Usually LC compounds are provided in the form of mixtures, because single compound cannot satisfy all the desired parameters. Therefore, solubility is also an important parameter.

To develop the new LC materials, we focused on fused ring systems with hetero atoms, because such LC compounds have not been studied extensively. We have designed three series of novel LC compounds having a chroman ring system (Compounds **1**–**3**) [4,5]. These compounds are introduced trifluoromethyl group, two fluorine atoms or 3,4,5-trifluorophenyl group into the fused ring, and introduced a few fluorine atoms into the core structure at the same time.

We could expect that compounds having these structures would show high Δε and high Δn, but we could not know the solubility of these compounds. Here we report the synthesis and the physical properties of Compounds **1**–**3**, and the discussion for the solubility consideration of Compounds **2**.

1



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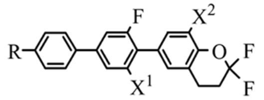

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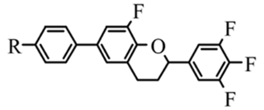
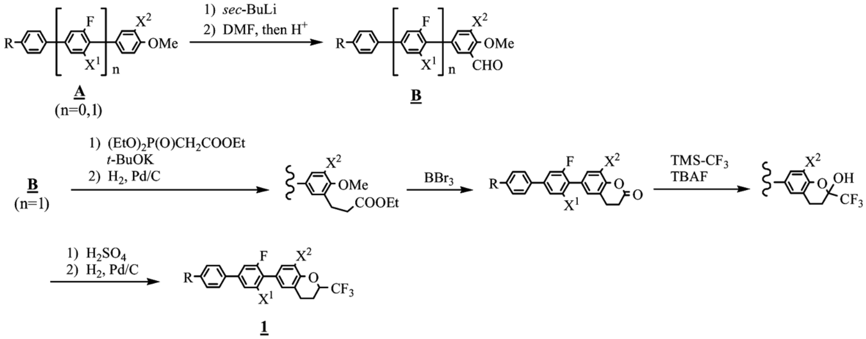


1a : R=C_5H_{11}, X^1=F, X^2=H
1b : R=C_5H_{11}, X^1=H, X^2=F
2a : R=C_5H_{11}, X^1=F, X^2=H
2b : R=C_5H_{11}, X^1=H, X^2=F
3 : R=C_3H_7

SYNTHESIS

The synthetic of Compounds **1** is shown in Scheme 1. The synthesis of all of the chroman compounds were started from the benzaldehyde derivatives **B** with a 25–40% yield. In the case of Compound **1**, Aldehyde **B** was converted into the dihydrocoumarine derivatives through Horner-Emons reaction, a hydrogenation with a palladium catalyst, and a deprotection with tribromoborane. Finally, Compounds **1** were obtained through the substitution reaction with Ruperts reagent, a dehydoration, and a hydrogenation.

The synthesis of compounds **2** is shown in Scheme 2. First, Aldehyde **B** was converted into difluorinated ethylene derivatives through the double use of Wittig type reactions and a deprotection.

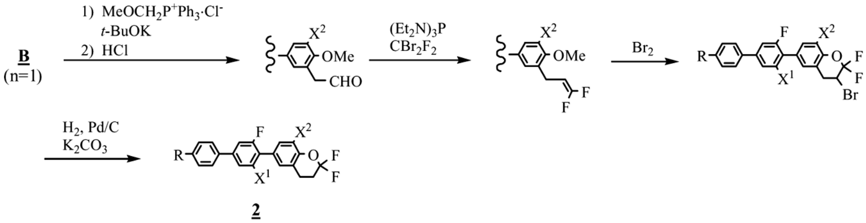


SCHEME 1 Synthesis of compounds **1**.

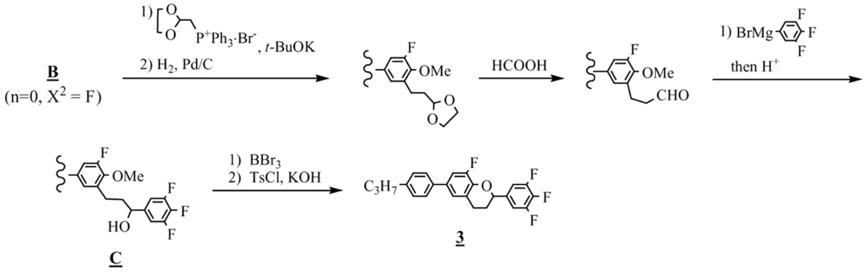
The obtained intermediate was converted into the precursor of the desired material with bromine. The bromine mediated addition and etherification took place at the same time. Lastly, the desired compounds were obtained by a hydrogenation with a palladium catalyst under a basic condition.

The synthesis of compound **3** is shown in Scheme 3. First, Aldehyde **B** was converted into the alcohol derivative **C** through the Wittig reaction, dehydrogenation with a palladium catalyst, a deprotection of the acetal, and Grignard reaction. Finally, the desired compound was obtained through an ether cleavage with tribromoborane, and a cyclization with tosyl chloride and potassium hydroxide as a base.

These chroman compounds synthesized through their individual ring closure reactions as key steps, were chemically and thermally stable. The transition temperatures of five chroman compounds are shown in Table 1. Compound **1a** and **1b** have a monotropic smectic phase and an enantiotropic smectic phase, respectively. On the other hand, compounds **2a**, **2b**, and **3** do not have any mesophase.



SCHEME 2 Synthesis of compounds **2**.



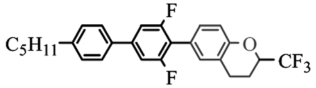
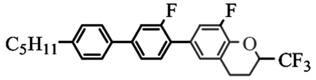
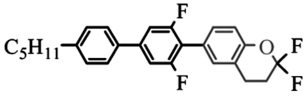
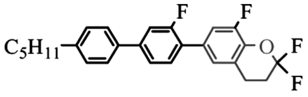
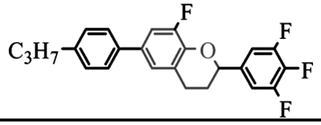
SCHEME 3 Synthesis of compounds **3**.

RESULTS AND DISCUSSIONS

Physical Properties

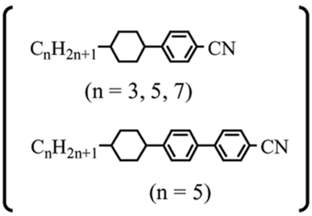
The physical properties of five chroman compounds are shown in Table 2. The value for T_{NI}, $\Delta\varepsilon$, and Δn are extrapolated data from the mixture, which consists of 10–15 wt% of chroman compounds and 85–90 wt% of a highly polar base mixture (Mix-01). Compounds

TABLE 1 Transition Temperatures of Compounds **1–3**

Structures		Transition temp. (°C)
1a		Cr · 111.5 (· SmA · 88.1) · I
1b		Cr · 104.0 · SmA · 128.9 · I
2a		Cr · 90.4 · I
2b		Cr · 91.9 · I
3		Cr · 91.5 · Cr · 95.9 · I

These temperatures were detected by DSC, and their phase type were determined by microscopic texture observation.

TABLE 2 Physical Properties of Compounds 1–3

	T_{NI}(°C)*	$\Delta\varepsilon$*	Δn*	Conc. (wt%)	
1a	65.7	17.4	0.184	15	Mix-01 : 
1b	79.7	16.9	0.190	15	
2a	43.7	18.6	0.177	10	
2b	41.7	18.3	0.164	15	
3	15.7	17.7	0.124	15	
Mix-01**	72.4	11.0	0.137	–	

*T_{NI}, $\Delta\varepsilon$ and Δn are extrapolated data at 25°C, 10–15 wt% of each compound in the base mixture, Mix-01.

**Mix-01 is a highly polar mixture, consisting of four benzonitrile compounds.

1 and **2** show high $\Delta\varepsilon$ and high Δn, on the other hand, Compound **3** shows a lower Δn, compared with Compounds **1** and **2**. We suggest that the reasons for the low Δn of Compound **3** are, namely, the T_{NI} is relatively low because the molecular is bent at the jointing point between the chroman ring and the phenyl group, and the phenyl chroman ring does not conjugate with the trifluorophenyl group. The relation between T_{NI} and $\Delta\varepsilon$, and the relation between T_{NI} and Δn are shown in Figure 1. In figures, Compounds **2** show higher $\Delta\varepsilon$ than Compounds **1**, on the other hand, Compounds **1** shows higher Δn and higher T_{NI} than Compounds **2**.

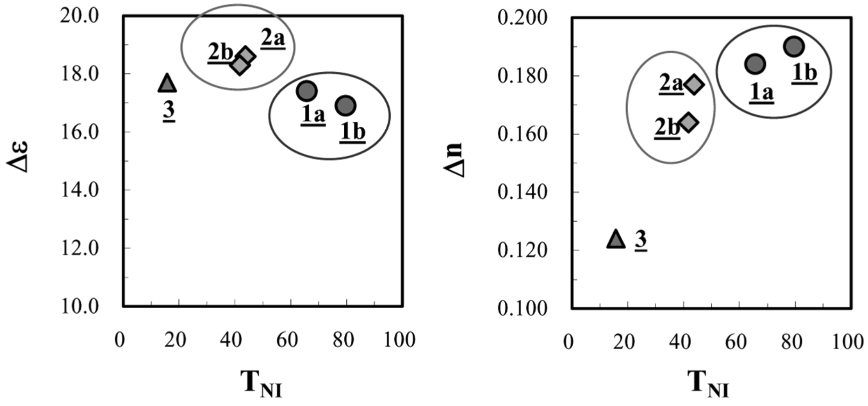


FIGURE 1 Relation of T_{NI} to $\Delta\varepsilon$, and T_{NI} to Δn.

Solubility

At first, we did the simple preservation tests in order to know the tendency of the solubility of chroman compound in the base mixture (Mix-02). Mix-02 consists of nine fluorinated compounds, and the composition of this mixture is close to the practical mixtures material. We prepared four samples with concentrations of 5, 10, 15, and 20 wt% of the chroman compound, respectively. These samples had been preserved at 20°C for 30 days. After that, we visually determined whether solid or smectic materials appeared in the samples. If no solid or smectic materials were observed in the 20 wt% sample, solubility was regarded to be over 20 wt%, and if solid or smectic materials were observed in the 20 wt% sample, solubility was regarded to be 15 wt%. In the same way, each solubility was estimated.

The results of the preservation tests are shown in Figure 2. The solubility of Compound **2b** was the highest, and surprisingly that of Compound **2a** was the lowest even though the structures of these two were very similar.

For further consideration about the significant difference of the solubility in Compound **2a** and **2b**, we have created the two phase diagrams of the individual substrate and the base mixture, Mix-02. The two phase diagrams for the mixtures are shown in Figure 3. Figure 3-(1) is the phase diagram of compound **2a** and Mix-02, and Figure 3-(2) is for **2b** and Mix-02, and x_i is the molar fraction of compound ***i*** in the mixture. In figures, there are two remarkable differences: First, a monotropic smectic phase appeared only in Figure 3-(2). And second, the transition temperature from C + N to

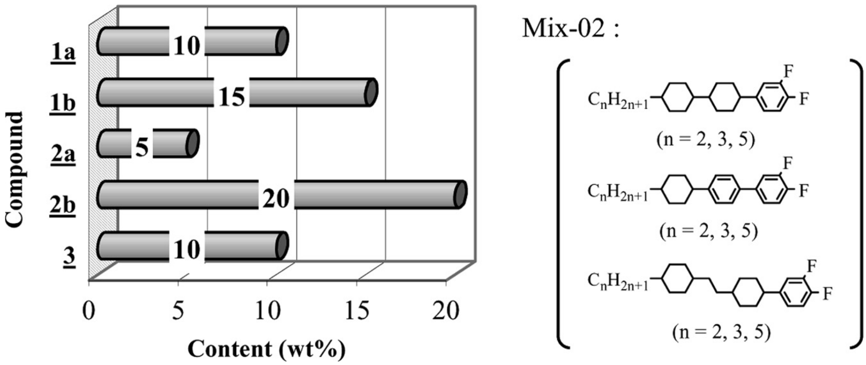


FIGURE 2 The results of preservation test in the mixture, Mix-02, consisting of nine fluorinated compounds.

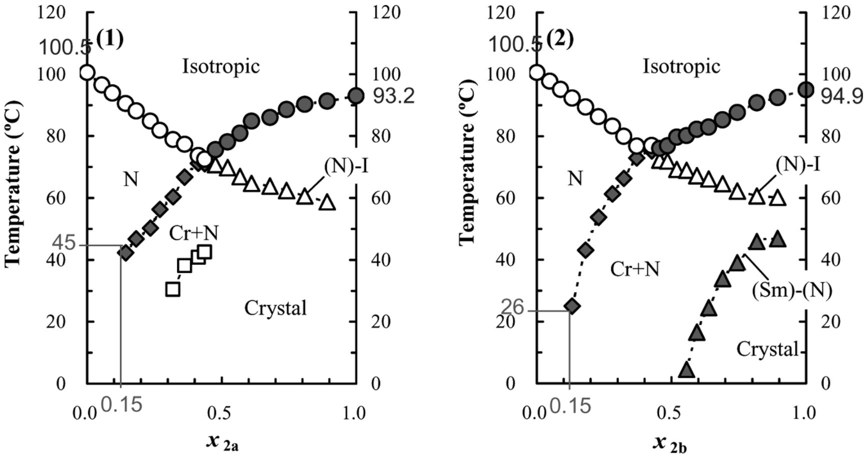


FIGURE 3 Phase diagrams for the mixtures of (**1**) Compound **2a** and Mix-02, (**2**) Compound **2b** and Mix-02. Mix-02 consists of nine fluorinated compounds. These data were determined based on observations with a microscope during heating. In figures, □ is the transition temperature from the monotropic Nematic to Iso, and ▲ is the transition temperature from monotropic smectic to monotropic Nematic.

nematic of **2b** is lower than **2a** in the low molar fraction range. For example, at around 15%, the transition temperature from C + N to nematic of **2a** is 45°C, on the other hand, for **2b**, it is 26°C. The difference between these two values is significant.

Calculated Melting Curves in an Ideal System

We calculated the melting curves in an ideal system (Fig. 4) with the Schröder-van Laar equation (1), which is usually adapted to estimate the melting temperature from solid to liquid in ideal solutions [6].

$$T_i = \frac{\Delta H_{0i}}{\frac{\Delta H_{0i}}{T_{0i}} - R\ln x_i} \tag{1}$$

where T_i is the temperature on the melting curve of compound i, and ΔH_{oi}, T_{oi} and x_i are respectively the melting enthalpy, the transition temperature, and the molar fraction of compound i. This equation suggests that with a higher melting enthalpy and a higher transition temperature, the melting temperature of the compound is higher. Experimental data of the transition temperature and the melting

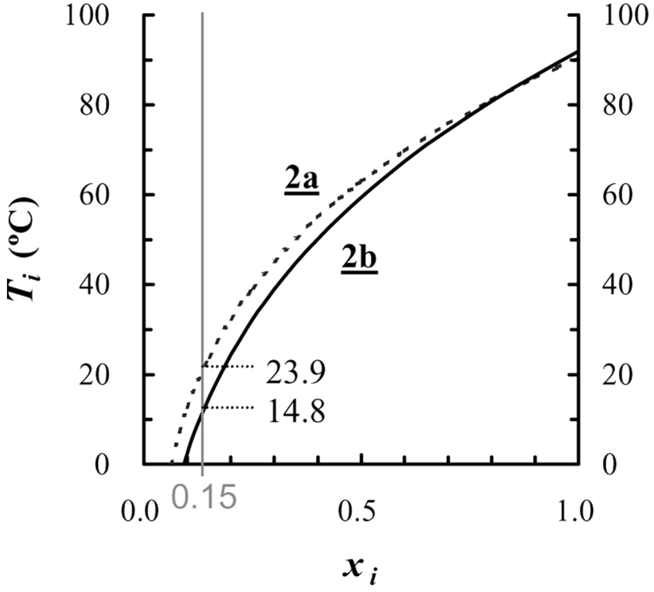


FIGURE 4 The calculated melting curves of **2a** and **2b**.

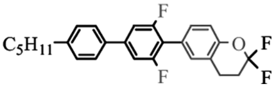
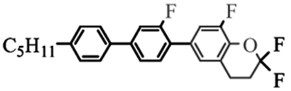
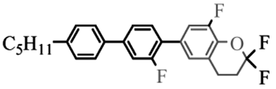
enthalpy of Compounds **2a** and **2b** are shown in Table 3. We see in this table that, the transition temperature of **2b** is slightly higher than that of **2b**, and melting enthalpy of **2b** is lower than that of **2a**.

The melting curves of **2a** and **2b** calculated from the Schröder-van Laar equation are shown in Figure 4. When x_i is 0.15, the melting temperatures of **2a** and **2b** are calculated to be 23.9, and 14.8°C, respectively. The difference of the solubility is just caused by the melting enthalpy of each compound in this case, because the transition temperature of each compound is not so different. However, the calculated difference of melting temperature between **2a** and **2b** does not match the experimental result. Therefore, we considered that there must be another parameter related to the solubility in this case.

TABLE 3 The Transition Temperature and the Melting Enthalpy (ΔH_0) of **2a** and **2b**

	Transition temp. (°C)	ΔH_0 (KJ/mol)
2a	90.4	25.6
2b	91.9	21.5

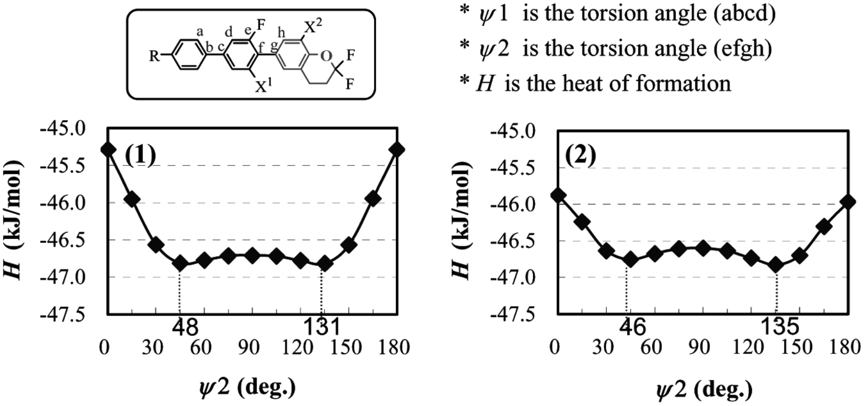
TABLE 4 The Calculated Data of Compound **2a**, **2b-1**, and **2b-2**

		$\psi 2$ (deg.)	H (Kcal/mol)	μ^* (debye)	β^* (deg.)	$\mu_y{}^*$ (debye)
2a		48.4	−196.19	5.142	30.56	2.475
2b-1		45.6	−196.00	6.575	47.49	4.839
2b-2		135.4	−196.21	5.277	27.87	2.408

*μ is a dipole moment, β is an angle between μ and a molecule long axis, and μ_y is a lateral dipole moment.

Stable Conformations

The relation between the heat of formation (H) and the torsion angle e-f-g-h (Ψ_2) is shown in Figure 5. The torsion angle a-b-c-d ($\Psi 1$) is fixed at 40 degree, and then the heat of formation was calculated the torsion angle e-f-g-h at each 15 degrees. All the calculations were carried out by the MOPAC AM-1 method [7]. As shown in this figure, both **2a** and **2b** have two local minimums at around 45 degrees and around 135



* $\psi 1$ is the torsion angle (abcd)
* $\psi 2$ is the torsion angle (efgh)
* H is the heat of formation

FIGURE 5 The relation between the heat of formation (H) and the torsion angle (Ψ_2).

degrees. Here, **2a** is symmetric, thus these two conformations are the same. On the other hand, **2b** is non-symmetric, thus **2b** has two stable conformations with two fluorine atoms at the same side (**2b-1**), and another with two fluorine atoms at opposite sides (**2b-2**). The calculated dipole moments of Compound **2a**, **2b-1** and **2b-2** are shown in Table 4. We can see the significant difference of the data, especially the lateral μ (μ_y), between **2b-1** and **2b-2**. Therefore, we consider that **2b** has two stable conformations with different properties, and behaves as if Compound **2b** is the mixture of two compounds. This result suggest that the better solubility **2b** compared with **2a**, is induced by the non-symmetric structure of **2b** as well as the lower melting enthalpy.

CONCLUSIONS

The three series of chroman compounds were synthesized from benzaldehyde derivatives through their individual ring closure reaction as key steps with 25 to 40% yield. These chroman compounds have high $\Delta\varepsilon$ and high Δn, especially Compounds **1** show higher $\Delta\varepsilon$ than Compounds **2**. Furthermore, we consider the better solubility of **2b** can be caused by two parameters. The first is the melting enthalpy, where that of **2b** is lower than **2a**. The second is the structure, where **2a** is symmetric, and **2b** is non-symmetric. According to the results of the empirical calculation, Compound **2b** has the two conformational isomers with quite different properties.

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