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Synthesis and Properties of Novel Liquid Crystalline Compounds having a Difluoromethyleneoxy Moiety as a Linkage Group

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SYNTHESIS AND PROPERTIES OF NOVEL LIQUID CRYSTALLINE COMPOUNDS HAVING A DIFLUOROMETHYLENEOXY MOIETY AS A LINKAGE GROUP

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Novel liquid crystal compounds having a difluoromethyleneoxy group as a linkage group have been prepared by the new synthetic method using dibromodifluoromethane in good yield. From the results of physical property measurements; i.e., transition temperature, dielectric anisotropy ($\Delta \varepsilon$), birefringence (Δn) and viscosity, it becomes obvious that the derivatives having 3,5-Difluorophenyl group at the carbon side of difluoromethyleneoxy group (1) have high dielectric anisotropy and low viscosity, and the derivatives having 1,4-cyclohexylene group at the carbon side of difluoromethyleneoxy group (2) have good balance of their physical properties. Moreover, 1 and 2 indicate high voltage holding ratio. Therefore, a novel series of the compounds having a difluoromethyleneoxy linkage group is an eminently suitable material that can lower driving voltage and achieve quicker response time of the AM-LCDs.

Keywords: active matrix LCD; dibromodifluoromethane; difluoromethyleneoxy; high dielectric anisotropy; low viscosity

INTRODUCTION

According to expansion in application of the AM-LCDs, e.g., PC-monitor, note PC, cellar phone or TV, required characteristics for liquid crystalline materials became very diverse. In particular, reduction of driving voltage and response time is the most important aim for any kind of driving mode, e.g., TN, IPS, VA or OCB. One of the common solutions to reduce driving voltage is to develop the compound with high dielectric anisotropy; thus, many liquid crystalline compounds have been investigated to meet this

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aim. To design a compound having high dielectric anisotropy, introduction of one or more fluorine atom at a ring structure or a side chain moiety according to a molecular long axis is well known method [1]. Nevertheless, this method normally causes nematic temperature range reduction and viscosity increase in proportion to rise of $\Delta \varepsilon$.

Although, as formerly described, there were many reports about introduction of the fluorine atom to a ring structure or a side chain moiety, research works of a compound having a fluorinated linkage group were quite limited [2]. Therefore, we focused on compounds having a fluorinate linkage group to increase $\Delta \varepsilon$ without rise of viscosity, especially compounds with a difluoromethyleneoxy group ($-CF_2O-$) [3]. Here we now report new synthetic methods and physical properties of compounds <u>1</u> and <u>2</u> which are relatively different from ordinal liquid crystalline compounds.



RESULT AND DISCUSSION

Synthesis

Preparation of Compound <u>1</u> (Scheme 1)

Previously, as preparation of a compound having phenyl group at a carbon side of a difluoromethyleneoxy linkage, A. Haas has been reported



SCHEME 1

a three steps route including photobromination of the difluoromethylbenzen that was derived from benzaldehyde and SF₄, following etherification [4]. However, this method is not applicable to practical scale production. We developed a new synthetic route to compound (1) involving direct difluorobromomethylation of 3,5-Difluorobenzen derivatives (A)[5a]. Compound <u>A</u> was treated by n-BuLi in THF below -70° C, and then generated phenyl lithium reacted with CF₂Br₂ to give an intermediate bromodifluoromethylbenzene (CF₂Br-form) derivative. The intermediate was converted into a desired material (1) by the Williamson etherification in DMF under K₂CO₃ basic condition with a halogenated phenol. The isolation yield of <u>1a</u> (X = L₁ = F) is 32% based on 4'-propyl-3,5-difluorobiphenyl. This synthetic process provides a convenient alternative to formerly known methods from both handling and yield.

This reaction also produced brominated derivatives (Br-form). The ratio of CF_2Br -form to Br-form is affected by a chemical structure of the substrate <u>A</u>. The correlation between selectivity of Br-form and the structure of <u>A</u> was shown in Table 1.

TABLE 1 Selectivity of Bromodifluoromethylation



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From Table 1, when the substrate having an electron withdrawing group, such as 5-alkyl-1,3-dioxane-2-yl or alkylated phenyl, bromodifluoromethylation selectivity is higher than the case of a substrate containing an electron donating group, such as alkyl or alkylated cyclohexyl. However, when 3-fluorophenyl or non fluorinated phenyl derivatives was used as a substrate, a bromodifluoromethylated product was not obtained.

Wakselman *et al.* reported two considerable mechanisms of the reaction between perhaloalkanes (CF_2X_2 , X = Cl or Br) and a phenoxide or a thiophenoxide as a nucleophile: 1) an ionic chain reaction mechanism which involves the difluorocarbene (: CF_2), 2) a radical mechanism [6]. In our case, since no difluoromethane product was observed, we assume that the newly developed method carried out in a different pathway from two mechanisms proposed by Wakselman *et al.*

NMR and GC-MS data of Compound $\underline{1a}(X = L_1 = F \text{ in general fournula } \underline{1})$

¹H-NMR: δ (ppm) 0.956–0.985(t,3H), 1.658–1.702(m,2H), 2.630–2.661(m,2H), 6.956–7.013(m,2H), 7.191–7.212(d,2H), 7.306–7.322(d,2H), 7.481–7.498(d,2H)

¹⁹F-NMR: δ (ppm) -62.00- -62.16(t,2F), -111.09- -111.22(m,2F), -133.97- -133.07(m,2F), -163.68- -163.79(m,1F)

$$\begin{split} & \text{EIMS}(\text{m/e}): \ 27(1.2\%), \ 41(1.1), \ 51(1.0), \ 69(1.4), \ 75(1.0), \ 81(1.5), \\ & 119(2.9), \ 126(6.1), \ 131(1.2), \ 147(1.4), \ 163(1.3), \ 170(1.2), \ 183(5.0), \\ & 187(1.3), \ 201(7.0), \ 232(1.9), \ 237(2.2), \ 252(36.4), \ 259(2.7), \ 265(1.8), \\ & 281(100), \ 428(1.4, \ \text{M}^+) \end{split}$$

Synthesis of Compound 2 (Scheme 2)

As synthetic method of difluoromethyleneoxy derivatives having an aliphatic group at the carbon side, it is generally known that fluorination



of the thioester by means of DAST [7] or $n-Bu_4^+H_2F_3^-$ with an oxidative condition using NBS and the like [8]. However, if an aromatic ester substituted by fluorine atoms, yield of thioester was very low (around 10%). It is difficult to apply these methods to our target compounds in practical production. Therefore, we have developed a novel synthetic method of compound 2 (Scheme 2) applicable to bulk scale [5b].

Referred to report of D. G. Naae *et al.* or N. Ishikawa *et al.* [9], we prepared a difluorovinyliden derivative **<u>B</u>** by means of dibromodifluoromethane and trisdiethyl aminophosphine. Addition of bromine to **<u>B</u>** gave an intermediate <u><u>C</u></u> which could be converted into an intermediate <u><u>D</u></u> by treatment with a phenol and K_2CO_3 owing to proceed both etherification and dehydrobromination at the same time. The intermediate <u><u>D</u> was hydrogenated under Pd/C cat. to give <u>2</u> in 22% isolated yield based on 4-(trans-4-propylcyclohexyl)cyclohexanone.</u>

This novel synthetic method is a useful and convenient introduction way of a difluoromethylene moiety not only for commercial production of $\underline{2}$ but also for a general synthetic technique.

NMR and GC-MS data of Compound $\underline{2b}(n = 1, X = L_1 = F$ in general formula $\underline{2}$)

¹H-NMR: δ (ppm) 0.858–0.887(m,5H), 0.991–1.054(m,7H), 1.131–1.154(t,3H), 1.297–1.340(m,4H), 1.700–1.745(m,3H), 1.770–1.780(d,2H), 1.996–2.019(m,3H), 6.820–6.847(m,2H),

¹⁹F-NMR: δ (ppm) -79.33- -79.34(d,2F), -133.76- -133.83(m,2F), -165.21- -165.31(m,1F)

EIMS(m/e): 29(5.9%), 41(34.1), 55(60.7), 69(93.3), 83(100), 97(41.5), 111(68.7), 123(22.2), 131(14.1), 148(17.8), 213(5.9), 256(45.9), 404(14.8, M^+)

PROPERTIES

The chemical structures and physical properties of $\underline{\mathbf{1a}} \sim \underline{\mathbf{1c}}$ are listed in Table 2. Further, 2D plot of $\Delta \varepsilon$ and rotational viscosity (γ_1) is shown in Figure 1. For comparison, physical properties measured in same condition of three compounds $\underline{\mathbf{3}} \sim \underline{\mathbf{5}}$ [1b, 10] which have analogous structures to $\underline{\mathbf{1}}$ are also shown. Where, physical properties of $\underline{\mathbf{5}}$ is measured as a 20 wt% mixture of three alkyl analogs of R in the formula ($C_2H_5 : C_3H_7 : C_5H_{11} = 6 : 8 : 6$) in FB-01 [1b]. From Figure 1, $\underline{\mathbf{1a}} \sim \underline{\mathbf{1c}}$ are higher $\Delta \varepsilon$ and lower viscosity compared with analogous compounds $\underline{\mathbf{3}}$ and $\underline{\mathbf{4}}$. In comparison with the ester $\underline{\mathbf{5}}$, $\underline{\mathbf{1a}}$ is almost the same $\Delta \varepsilon$, on the contrary, extremely low viscosity. It became obvious that $\underline{\mathbf{1a}}$ shows better balance of $\Delta \varepsilon -\gamma_1$ than $\underline{\mathbf{3}} \sim \underline{\mathbf{5}}$.

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No.	Chemical structures	Transition Temp. (°C)	$T_{NI}(^{\circ}C)$	$\Delta \epsilon$	Δn	γ ₁ (mPa⋅s)
<u>1a</u>	C ₃ H ₇ -	C 47.01	-16.4	22.3	0.125	63.3
<u>1b</u>	C ₃ H ₇ -	C 40.91	1.1	16.8	0.135	77.8
<u>1c</u>	C₃H ₇ -€ F F C₃H ₇ -€ F C₃H ₇ -€ F	C 38.71	14.6	19.3	0.135	108.8
	FB-01 [1b]		112.6	4.8	0.080	171.3

TABLE 2 Structure and Physical Properties of Compounds 1a-1c

Clearing points (T_{NI}) , dielectric anisotropy ($\Delta \epsilon$), birefringence (Δn), and rotational viscosity (γ_1) are extrapolated data at 20°C, 20 wt% of each compound in the liquid crystal mixture FB-01 (Chisso Corp.).



FIGURE 1 Relation of rotational viscosity (γ_1) to dielectric anisotropy $(\Delta \varepsilon)$.

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Moreover, in comparison with $\underline{4}$ having no fluorine atom at the linkage group, significant difference was observed on balance of $\Delta \varepsilon - \gamma_1$. It is usually understood that the introduction of an oxygen atom or substitution of a fluorine atom at a side chain or a ring structure constructing molecular framework causes increase of viscosity. However, viscosity of $\underline{1}$ indicates unusual tendency to generally known liquid crystalline compounds. The study for these unusual tendencies of some physical properties possessed by this series are still under working, it would contribute to design and develop of new liquid crystalline materials.

The quantum chemical calculation (MOPAC Ver.6 AM1) results of the compound <u>1a</u>, <u>1d</u> and <u>2b</u> are shown in Figure 2. For the reason of predominantly high $\Delta \varepsilon$ of <u>1a</u>, the calculation resulted that <u>1a</u> has large dipole moment (μ) and comparatively small angle (β) between the μ and a molecular long axis (principal moment of inertia).

Structures and physical properties of $\underline{2a} \sim \underline{2d}$ are listed in Table 3.

These compounds have high extrapolated $\Delta \varepsilon$ for Δn . Additionally, <u>**2b**</u> and <u>**2c**</u> have very wide nematic temperature range. To compare to <u>**6**</u> ~ <u>**9**</u>[1b, 10], their 2D plot of $\Delta \varepsilon - \gamma_1$ and $T_{NI} - \Delta \varepsilon$ are also shown in Figure 3. The $\Delta \varepsilon - \gamma_1$ plot shows that <u>**2b**</u> has higher $\Delta \varepsilon$ than the other compound except the ester (**8**). Concerning viscosity, <u>**2b** has almost the same as directly connected <u>**6**</u> and lower than compounds with the other linkage groups. In the plot of $T_{NI} - \Delta \varepsilon$, <u>**2b**</u> shows good balance of properties compare to the other compounds **6** ~ **9**.</u>

Therefore, we conclude compound $\underline{2}$ is a practical material with good balance of physical properties required to AM-LCDs, excel especially in $\Delta \varepsilon - \gamma_1$ balance. Here, to consider the fluorine introduction effect on the linkage group, we paid notice to difference of physical properties between



FIGURE 2 Dipole moment μ /DEBYE and angle between molecule long axis and dipole moment β /DEG by MOPAC Ver.6 AM-1.

No.	Chemical structures	Transition temp. (°C)	$T_{\rm NI}(^\circ\!{\rm C})$	Δε	Δn	γ ₁ (mPa⋅s)
<u>2a</u>	C ₅ H ₁₁	C - 0.6 I	-63.9	7.8	0.035	-94.2
<u>2b</u>	C ₃ H ₇ -	C 42.9 N 105.5 I	99.6	9.8	0.070	184.8
<u>2c</u>	C ₃ H ₇	C 35.6 N 129.0 I	125.6	6.3	0.070	212.3
<u>2d</u>	C ₃ H ₇ F _F	C 32.0 N 136.5 I	125.1	8.3	0.080	242.8

TABLE 3 Structure and Physical Properties of Compounds 2a-2c

Clearing points (T_{NI}) , dielectric anisotropy $(\Delta \epsilon)$, birefringence (Δn) , and rotational viscosity (γ_1) are extrapolated data at 20°C, 20 wt% each compound in the liquid crystal mixture FB-01 (Chisso Corp.).



FIGURE 3 Physical properties of compound $\underline{2b}$ and relative compounds $\underline{6-9}$.

the compound with a methyleneoxy linkage group (7) and 2b. Figure 3 indicates that introduction of two fluorine atoms into the methyleneoxy group induced a rise of $T_{\rm NI}$, increase of $\Delta \varepsilon$ and decrease of viscosity.

One of the most important factor for the AM-LCDs materials is reliability, i.e. voltage holding ratio (VHR) and specific resistance. Figure 4 shows VHR dependence on temperature of the mixtures comprising each 20wt% of <u>1a</u> and <u>2b</u>, and 80wt% of FB-01. The existing AM-LCDs materials, <u>3</u>, <u>6</u> and <u>8</u>, are also shown for reference in the same figure.

The mixtures including <u>**1a**</u> and <u>**2b**</u> indicated the same level of VHR as common AM-LCDs materials not only at ambient temperature but also at high temperature. It is proven that a series of compound having diffuoromethyleneoxy as a linkage group has very high reliability.

To develop low driving voltage LC mixture, we prepared some new LC mixtures including compound <u>1</u> and <u>2</u>. The threshold voltage-viscosity correlation of prepared mixtures and common low driving voltage mixtures are shown in Figure 5. The new LC mixture was able to reduce 20% of viscosity from the referred common LC-mixture when both were compared at same threshold voltage.

In order to lower viscosity, LC mixture is usually controlled their viscosity by mixing a high $\Delta \varepsilon$ material which usually has relatively high viscosity and low viscosity material without effective dipole moment (neutral material)[11]. Since the compound <u>1</u> and <u>2</u> had both high $\Delta \varepsilon$ and low viscosity, it became clear that these compounds are eminently suitable for the component of mixture aiming quick response.



Voltage holding ratio was measured for 20wt% of each compound in the liquid crystal mixture FB-01 (f=30Hz).

FIGURE 4 Voltage holding ratio(%) of compounds <u>**1a**</u>, <u>**2b**</u> and relative compounds <u>**3**</u>, <u>**6**</u>, and <u>**8**.</u>



FIGURE 5 Characteristic the new LC mixture comprise compound <u>1a</u> and <u>2b</u>

CONCLUSIONS

Novel liquid crystal compound $\underline{1}$ and $\underline{2}$ having a difluoromethyleneoxy group as a linkage group have been prepared in good yield by the new synthetic methods with reactions using dibromodifluoromethane as a key step. From the result of physical properties measurement of $\underline{1}$ and $\underline{2}$, it becomes obvious that $\underline{1}$ has high dielectric anisotropy and low viscosity, and $\underline{2}$ has good balance of their physical properties in comparison with the compounds having non or the other known linkage groups. Moreover, $\underline{1}$ and $\underline{2}$ indicate high voltage holding ratio owing to their high stability. Therefore, this series is eminently suitable materials, which can achieve lower driving voltage and quicker response time of AM-LCDs.

To consider the Fluorine introduction effect on linkage group, we compared physical properties of the compound with a methyleneoxy and a difluoromethyleneoxy linkage group. As a result, introduction of two Fluorine atoms into the methyleneoxy group induces a rise of $T_{\rm NI}$, increase of $\Delta \varepsilon$ and decrease of viscosity.

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