Molecular Crystals and Liquid Crystals

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

SYNTHESIS AND PROPERTIES OF FLUORO- SUBSTITUTED FERROELECTRIC LIQUID CRYSTALS HAVING A 2-(BIPHENYL-4′-YL)-1,3-DIOXANE MESOGENIC CORE

Riswoko Asep [a] & Hiroyuki Nohira [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-Ohkubo, Saitama 338-8570, Japan

Version of record first published: 15 Jul 2010

To cite this article: Riswoko Asep & Hiroyuki Nohira (2003): SYNTHESIS AND PROPERTIES OF FLUORO- SUBSTITUTED FERROELECTRIC LIQUID CRYSTALS HAVING A 2-(BIPHENYL-4′-YL)-1,3-DIOXANE MESOGENIC CORE, Molecular Crystals and Liquid Crystals, 400:1, 31-37

To link to this article: http://dx.doi.org/10.1080/15421400390242959

Mol. Cryst. Liq. Cryst., Vol. 400, pp. 31–37, 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390242959

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND PROPERTIES OF FLUORO-SUBSTITUTED FERROELECTRIC LIQUID CRYSTALS HAVING A 2-(BIPHENYL-4′-YL)-1,3-DIOXANE MESOGENIC CORE

Riswoko Asep and Hiroyuki Nohira
Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-Ohkubo, Saitama 338–8570, Japan

Ferroelectric liquid crystals (FLCs) showing a short response time have been investigated with respect to their application for high resolution graphic displays addressed by thin film transistors. It is found that the introduction of fluoro substituents in the molecule at a suitable position such as the core and theasymmetric tail allowed the compounds to have a short response time. Here, in order to obtain further information about the fluorination effect on the structure, a new series of ferroelectric liquid crystals having a 2-(biphenyl-4′-yl)-1,3-dioxanyl group as the core has been synthesised. Their mesomorphic and physical properties have been measured, and the correlation between the structures and the properties is discussed.

Keywords: fluorination effect; 2-(biphenyl-4′-yl)-1,3-dioxane; response time; ferroelectric liquid crystal

INTRODUCTION

Numerous investigations have been carried out in order to obtain ferroelectric liquid crystals (FLCs) having a short response time because of their rapid switching for display applications [1]. However, the relationship between the structure of the FLC and the property is complicated. Hence, it is hard to obtain a FLC with a short response time without experiments, including the development in design and synthesis.

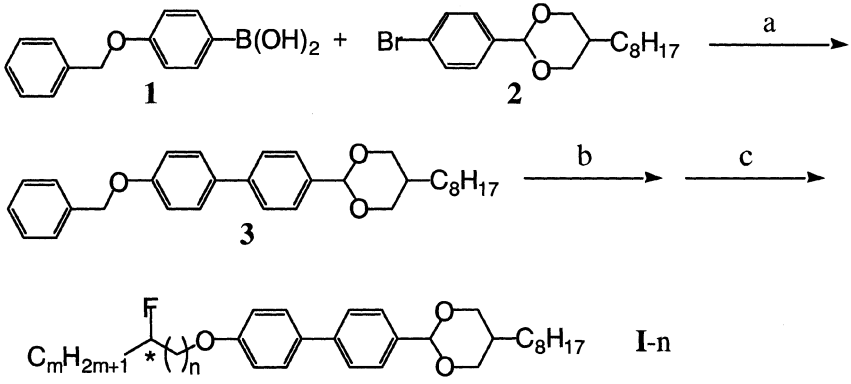
Recently, FLCs have been actively developed for active matrix display applications [2,3]. It is known that introduction of fluoro substituents into the molecule allows the compounds to have lower viscosities [4]. However, developments using FLC having fluoro substituents are very few. In our previous work it was reported that the fluoro-substituted FLC which had been developed for active matrix display applications have a short response

time (of the order of 10 μμs) [5]. Furthermore a tendency was found for this series that when the the fluoro-substituted chiral centre was positioned close to a laterally fluoro-substituted core, the shorter the response time. This suggests that the introduction of fluoro substituents in the materials in an appropriate position is effective in reducing their response times. Therefore, in order to develop the FLC, investigations focused on the tendency just described, are necessary.

There are a number of studies which have been carried out to understand the effects of lateral fluoro substitution of liquid crystals on their behaviour [6-9]. However, the relationship between the lateral fluoro substitution and the response time has not been investigated to any significant extent [12]. From this fact, a new FLC that can be used for active matrix display applications and consists of a similar mesogenic core without the lateral fluoro substituents is required to understand, the effect of fluorination on their electrooptical properties. Here, a new series of FLCs having a 2-(biphenyl-4′-yl)-1,3-dioxanyl mesogenic core, which was expected to exhibit the phase sequence SmC^*-N^* [10], have been synthesized. The properties of the FLCs have been measured and the extent of the FLC properties will be discussed.

SYNTHESIS

Scheme 1 shows a synthetic procedure for ferroelectric liquid crystals having a fluoro-substituted asymmetric frame and a 2-(biphenyl-4′-yl)-1,3-



a) $Pd(PPh_3)_4$, 5%wt Na_2CO_3 aq., dry DME b) 5% Pd-C, H_2, dry CH_2Cl_2

c) $C_mH_{2m+1}CH^*F(CH_2)_nOTs$, NaH, dry DMF.

SCHEME 1 Synthesis of the fluoro-substituted FLCs, **I**-n.

dioxanyl group as a core. The reaction of the aryl boronic acid **1** with **2**, obtained from 2-octyl-1,3-propandiol [11], catalysed by $Pd(0)(PPh_3)_4$ afforded the benzyl protected core, **3**, in good yield. After the hydrogenation of **3** catalysed with 5%Pd-C in dry methylene dichloride, the product was attached to an optically active fluoro substituted alkyl tosylate, derived from a corresponding 1,2-epoxide [12] or 5-alkyl-δ-lactone [12,13], to give the FLCs, **I**-n.

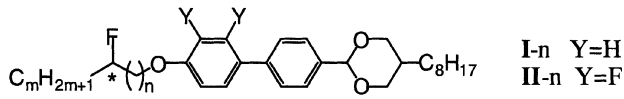
RESULT AND DISCUSSION

Mesomorphic Properties

Table 1 shows the mesomorphic behaviour of the liquid crystals synthesised. Compounds **I** and **II** [cited from our previous work, 5] are different in the existence of lateral fluoro substituents in the core, and compounds **I**-1 and **I**-4 are different in the position of the fluoro- substituted chiral centre relative to the core.

From Table 1, the absence of the lateral fluoro substituents in the core can be seen to cause the FLCs to have melting and liquid crystal–isotropic transitions at higher temperatures than those of the FLCs **II**. Compounds **I** exhibit a SmA phase between the N* and SmC* phase and additionally a SmB phase for the compound with the chiral centre in the 5-position. In contrast, compounds **II** show only the N* and SmC* phases [5]. These results suggest that, as a consequence of π-π stacking of the biphenyl part, the fluoro substituents act to disrupt the lamellar packing of compounds **I**

TABLE 1 Phase Transition Temperatures of FLCs



				Temperature*)/ °C											
Compounds	m	m	Y	Cr		SmB		SmC*		SmA		N*		Iso	
I-1	6	1	H	•	98	–		•	111	•	141	•	161	•	
I-4	3	4	H	•	63	•	109	•	128	•	132	•	162	•	
II-1	6	1	F	•	39	–		•	103	–		•	115	•	
II-2	5	2	F	•	42	–		•	98	–		•	123	•	
II-3	4	3	F	•	27	–		•	94	–		•	111	•	
II-4	3	4	F	•	23	–		•	67	–		•	103	•	

)Cr: crystallization temperature, SmB: smectic B phase, SmC: chiral smectic C phase, SmA: smectic A phase, N*: chiral nematic phase, I: isotropic liquid.

more than **II**. In other words the lateral fluoro substituents tend to destabilise the mesomorphic behaviour. However, due to the lateral fluoro substituents the biphenyl-1,3-dioxane mesogenic core of the FLCs (**II)** possesses two sites of high electron density, this is conducive to the formation of the SmC phase [11]. Therefore, the widest temperature range of the SmC*phase (64 K) for **II-**1 must be due to its packing behaviour. Compounds **I**-n which have a fluoro-substituted asymmetric frame show a slightly different mesomorphic behaviour to that of the materials without the asymmetric frame [10]. Introduction of a fluoro substituent in the alkyl chain causes compounds **I**-n to exhibit the SmA phase and lowers the nematic-isotropic transition by about 10 K. It was also shown that the temperature range of the N* phase was almost unchanged, however the range of the SmC* phase for compounds **I**-n was appreciably narrowed.

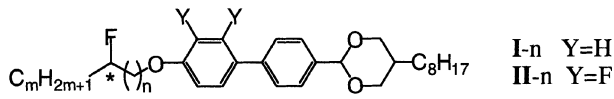
Electro-optical Properties

The physical properties of the FLCs such as the tilt angle, θ, response time, τ, and spontaneous polarization, P_S, were measured and the results are described in Table 2. Compounds **I**-n with the SmC* phase, because of the second order SmC*-SmA transition, showed generally a smaller tilt angle than compounds **II**-n.

It was found that compounds **I** with the fluoro-substituted chiral centre in the 2-position showed a longer response time than that with the chiral centre in 5-position. Although the P_S of **I**-1 is higher than that of **I**-4. For compounds **II**-n, the tendency was found to be the opposite [5]. The tendency of compounds **I** was similar to that of the FLCs with a phenylpyrimidinyl group in the core [12].

Since the fluoro substitutions act to disrupt the lamellar packing of the core and to reduce the interaction of the fluorinated aromatic part with the

TABLE 2 Physical Properties of FLCs



Compounds	m	n	Y	θ/°	τ/μs	P_S/nC.cm^{-2}	T (Tc-T)/°C
I-1	6	1	H	9	940	108	101 (10)
I-4	3	4	H	12	34	32	118 (10)
II-1	6	1	F	23	13	8	93 (10)
II-2	5	2	F	35	53	28	88 (10)
II-3	4	3	F	31	49	42	84 (10)
II-4	3	4	F	34	163	17	57 (10)

other hydrocarbon parts, the extent of local fluorination within the molecule is used to decrease the viscosity [4]. On the other hand, as a consequence of the π-π stacking of the biphenyl part and of the dipole moment from the fluorinated chiral centre and alkoxy chain, the more ordered lamellar packing of compounds **I** than **II** has been achieved. Therefore, in terms of the absence of the fluoro substitution on the mesogenic core, the FLC **I**-1 exhibits a longer response time than that of **II**-1.

These facts suggest that fluorination of the mesogenic core plays an important role in characterizing the FLC properties, especially the response time for compounds having a fluoro-substituted chiral centre.

CONCLUSION

Two new series of FLCs (**I**-n and **II**-n) were synthesized and their physical properties were measured. Effects of fluoro substitution in the core and the asymmetric frame on the FLC properties have been investigated. It appears that the response time depends on the position of the fluoro-substituted chiral centre and on the existence of the fluoro substituents in the mesogenic core.

EXPERIMENTAL

The structures of the intermediates and products were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy (Bruker AM400). Mesomorphic behaviour was investigated using a differential scanning calorimeter (Mac Science DSC3100), and a Nikon Optiphot2-POL polarizing microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 thermal controller. The magnitudes of P_S and τ were measured using the triangular-wave method and the field-reversal method, respectively, under a field of ± 10 $V_{p\text{-}p}\,\mu m^{-1}$ in a 2 μm thick cell (KSRO02B111P1NSS cell produced by EHC Co.).

Synthesis of 2-(4-benzyloxybiphenyl-4′-yl)-5-octyl-1, 3-dioxane (3)

A mixed solution of tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (36 mg, 0.031 mmol), 2-(4-bromophenyl)-5-octyl-1,3-dioxane (**2**) [8] (250 mg, 0.70 mmol), 2 M aqueous sodium carbonate (0.8 ml), and 4-benzyloxyphenylboronic acid (**1**) (160 mg, 0.70 mmol) in dry dimethoxyethane (DME) (5 ml) was stirred at 95°C for 25 h. To the mixture, 30% hydrogen peroxide was added slowly at room temperature. The organic layer was shaken with diethyl ether, and the extract was dried over anhydrous

magnesium sulphate. The solvent was evaporated from the extract, and the remaining product purified by thin layer chromatography twice (ethyl acetate:hexane = 1:12, and dichloromethane:hexane = 1 : 2) to yield a white powder. The powder was recrystallized from hexane to yield **3** (145 mg, 0.32 mmol, 45%). ^{1}H NMR ($CDCl_3$): 0.87–0.89(t, 3H, CH_3), 1.09–1.11(m, 2H, CH_2), 1.25–1.37(m, 12H, $6CH_2$), 2.10–2.19(m, 1H, CH), 3.52–3.617(t, 2H, 2CH), 4.22–4.29(dd, 2H, 2CH), 5.11(sm 2H, CH_2O), 5.44(s, 1H, CHO_2), 7.02–7.04, 7.37–7.54(d, 2H; m, 11H, $C_{18}H_{13}$) ;^{13}C NMR ($CDCl_3$): 14.1(CH_3), 22.7–34.2($8CH_2$), 70.1, 72.7($3CH_2O$), 101.4, 115.1, 126.5–136.9, ($C_{18}H_{13}$), 196.1(CHO_2).

Synthesis of (S)-(+)-2-[4-(2-fluorooctyloxy)-biphenyl-4′-yl]-5-octyl- 1,3-dioxane (*I*-1)

To a solution of 2-(4-hydroxybiphenyl-4′-yl)-5-octyl-1,3-dioxane obtained by deprotection of **3** (26 mg, 0.07 mmol) and sodium hydride (NaH) (60% wt, 8 mg, 0.2 mmol) in dry *N*, *N*-dimethylformamide (DMF) (2 ml), a solution of (*S*)-(+)-2-fluorooctyl *p*-toluenesulfonate [4] (21 mg, 0.07 mmol) in dry DMF (1 ml) was added at 25°C under a nitrogen atmosphere. The mixture was heated for 10 h at 70°C. Saturated aqueous sodium chloride was added, and the organic matter was extracted into diethyl ether. The extract was washed with distilled water and dried over anhydrous magnesium sulphate. After concentration, the product was purified by thin layer chromatography (ethyl acetate: hexane = 1:12) and was recrystallized from hexane to yield white crystals (17 mg, 0.034 mmol, 50 %). ^{1}H NMR ($CDCl_3$): 0.87–0.89(t, 6H, $2CH_3$), 1.09–1.10(m, 2H, CH_2), 1.28–1.82(m, 22H, $11CH_2$), 2.11–2.17(m, 1H, CH), 3.52–3.57(t, 2H, CH_2O), 4.04–4.16(m, 2H, CH_2O), 4.22–4.26(m, 2H, CH_2O), 4.78–4.91(dm, 1H, CHF, $J = 52$Hz), 5.44(s, 1H, CHO_2), 6.96–6.98(d, 2H, $C_{12}H_8$), 7.49–7.56(m, 6H, $C_{12}H_8$);^{13}C NMR ($CDCl_3$): 13.8,14.0($2CH_3$), 24.8–40.9($13CH_2$), 69.4, 72.6($3CH_2O$), 90.9–92.8(d, CHF, $J = 191.2$ Hz), 114.9, 123.5, 126.4, 128.5, 128.6, 135.3, 135.7, 143.1, 147.6 ($C_{12}H_8$).

REFERENCES

[1] Schadt, M., 1994, *Liquid Crystals: Topics in Physical Chemistry*, Vol. 3, edited by H. Stegemeyer (Darmstadt: Steinkoft; New York: Springer), pp. 215.
[2] Nonaka, T., Li, J., Ogawa, A., Hornung, B., Schmidt, W., Wingen, R., and Dubai, H. (1999). *Liq. Cryst., 26*, 1599.
[3] See, for example, Chang, J.K., Yu, J.K., Long, M.W., and Kyuk, S.K., in Proceedings of the 8th International Conference on Ferroelectric Liquid Crystals, pp. 175.
[4] Collings, P.J., and Hird, M. (1997). *Introduction to Liquid Crystals* (London: Taylor & Francis), pp. 70.

[5] Asep, R., Aoki, Y., Hirose, T., and Nohira, H. (2001). *Liq. Cryst., 28*, 785.
[6] Nagle, J.K. (1990). *J. Am. Chem. Soc., 112*, 4741.
[7] Hird, M., and Toyne, K.J. (1998). *Mol. Cryst. Liq. Cryst., 323*, 1.
[8] Petrov, V.F., Tasaka, T., Okamoto, H., and Takanaka, S. (2000). *Mol. Cryst. Liq. Cryst., 338*, 11.
[9] Okamoto, H., Petrov, V.F., and Takenaka, S. (1999). *Liq. Cryst., 26*, 691.
[10] Villiger, A., and Leenhouts, F, (1991). *Mol. Cryst. Liq. Cryst., 209*, 297.
[11] Dong, C.C., Styring, P., Goodby, J.W., and Chan, L.K.M. (1999). *J. Mater. Chem.*, *9*, 1669.
[12] Nagashima, Y., Ichihashi, T., Noguchi, K., Iwamoto, M., Aoki, Y., and Nohira, H. (1997). *Liq. Cryst., 23*, 537.
[13] Asep, R., Aoki, Y., Hirose, T., and Nohira, H. (2000). *Mol. Cryst. Liq. Cryst., 346*, 51.