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Synthesis and Mesomorphic Properties of Some Chiral Fluorinated Benzoates

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One series of chiral fluorinated benzoates have been synthesized. These compounds were characterized by IR, ^{1}H NMR, ^{19}F NMR, MS, and elemental analysis. Their phase transition behavior was investigated by DSC and polarizing optical microscopy. Generally, they show an enantiotropic SmA phase. The effect of lateral and terminal fluoro-substitution was studied in this series.

Keywords: chiral; fluorinated; liquid crystal

INTRODUCTION

Fluorinated liquid crystals (LCs) have received a great attention due to unique properties such as low viscosity, low birefringence, and low conductivity. They are suitable to be applied in the mixtures for liquid crystal displays [1–14]. Therefore, many fluorinated LCs have been prepared, and the fluoro-substitution effect has been well-studied, especially the LCs with fluorinated aromatic rings [15–17]. Generally, lateral fluoro-substitutions in the cores enhance the formation of the nematic phase and decrease clearing points; on the contrary, terminal fluoro-substitutions in the cores enhance the formation of smectic phases and increase clearing points [9–14]. However, in

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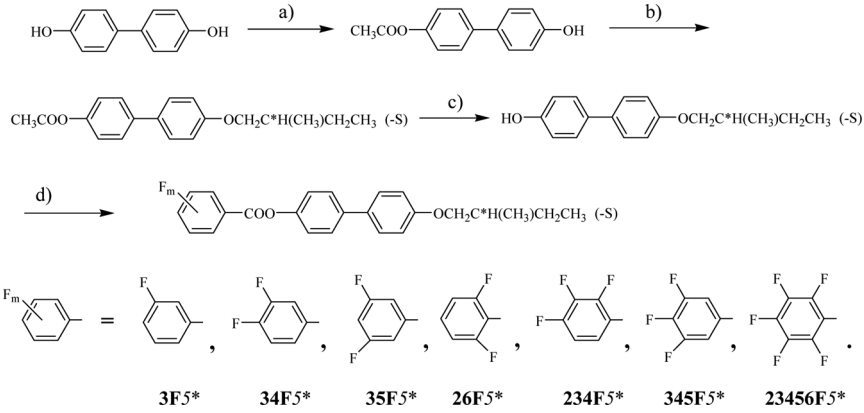
banana-shape liquid crystals, the lateral fluoro-substitutions in the cores enhance the formation of mesophases [18–19].

Because chiral LCs which show SmC* phase are suitable for ferroelectric liquid crystal display (FLCD) mixtures, many kinds of chiral LCs were designed and synthesized [20–31]. These FLCs also show other interesting physical properties, such as photorefractive properties [32]. To design chiral LCs, simple and cheap compounds are attractive. Several series of fluorinated benzoate LCs with achiral alkoxy chains have been synthesized by us [10]. These compounds show enantiotropic SmA and SmB phases. Herein, FLCD candidates were synthesized by changing the achiral alkoxy chains to chiral ones. The mesomorphic properties and the fluoro-substitution effect were studied.

RESULTS AND DISCUSSION

The compounds were obtained by routes depicted in Scheme 1. The intermediates and final compounds were synthesized according to literature methods [9–14]. The phase transition behaviors of the final compounds is summarized in the Table 1 and Figure 1 and were determined using differential scanning calorimetry.

The compounds shown here show only the enantiotropic SmA phase, except **26F*5***. Higher-order liquid crystalline phases were suppressed. Only a monotropic SmC* phase was identified from **3F*5*** at a cooling rate of 15°C/min. Although they do not show an enantiotropic



SCHEME 1 Synthesis of chiral fluorinated benzoates. a) CH_3COCl, Et_3N, CH_2Cl_2; b) DEAD/PPh_3, (S-) $C_2H_5C^*H(CH_3)CH_2OH$; c) NaOH aq.; d) fluorinated acids, DCC/DMAP, THF.

SmC* phase, because both fluorine atom and chiral alkoxy group are introduced to these compounds, they may be applied in the FLCD mixtures.

The effect of fluoro-substitution can be clearly found in these compounds. The *para*-fluoro-substitution effect was found from two pairs, **3F***5**/**34F***5** and **35F***5**/**345F***5**. With the introduction of a fluorine atom at the *para*-position of the fluorinated benzoates, both the polarity and the length-width ratio are increased. Compounds **34F***5** and **345F***5** show wider SmA phase temperature ranges and higher clearing points than **3F***5** and **35F***5**, respectively. For example, the SmA phase temperature range of **3F***5** is 3.6°C, however, that of **34F***5** is 45.8°C, an increase of more than 40°C. To the clearing points, those of **3F***5** and **34F***5** are 115.8 and 175.4°C, respectively. With a *para*-fluoro-substituent, the clearing point increases by nearly 60°C, and the melting point increases by 17.4°C. The polarity of fluorine atom at the *para*-position should play an important role on these phenomena.

If we consider **35F***5** to be the derivative of **3F***5** with a *meta*-fluoro-substituent, the length-width ratio is lower than **3F***5**, and the SmA phase temperature range became narrow. However, because the molecular symmetry is enhanced, the melting point is increased by 18.7°C. To the pair of **34F***5**/**345F***5**, both melting and clearing points are

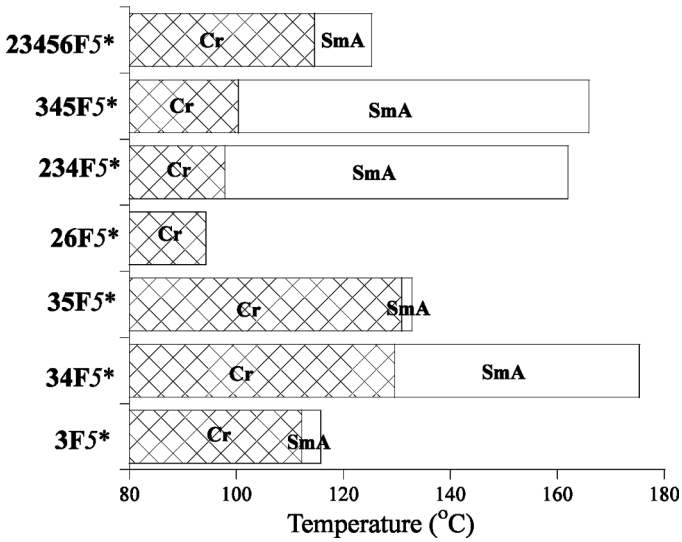


FIGURE 1 Comparison of the phase transition behavior of the obtained fluorinated liquid crystals.

TABLE 1 Transition Temperatures of Chiral Benzoates. Cr = crystal; SmA = smectic A phase; I = isotropic liquid; Recr = recrystallization

Compounds	Transition temperatures (°c)
3F*5**	Cr 112.2 SmA 115.8 I 114.1 SmA 95.5 Recr
34F*5**	Cr 129.6 SmA 175.4 I 173.6 SmA 108.1 Recr
35F*5**	Cr 130.9 SmA 132.9 I 130.7 SmA 108.9 Recr
26F*5**	Cr 94.3 I 64.3 Recr
234F*5**	Cr 97.9 SmA 162.0 I 160.0 SmA 80.7 Recr
345F*5**	Cr 100.4 SmA 165.9 I 164.0 SmA 92.0 Recr
23456F*5**	Cr 114.6 SmA 125.3 I 123.5 SmA 96.8 Recr

decreased with *meta*-fluoro-substitution. The melting and clearing points decrease by 29.2°C and by 9.5°C, respectively. Compared with these two pairs, the *meta*-fluoro-substitution shows reverse effect. It was thought that multi-fluoro-substitution at the terminal of aromatic rings may induce the aromatic ring to show fluorophilic properties, and the resulting microphase separation causes the melting point to decrease.

The *ortho*-fluoro-substitution effect can be found from **34F***5** and **234F***5**. Because of the interaction between carboxy group and fluoro-substituent, the thickness of molecule is increased. Therefore, the clearing point decreases by 13.4°C. Comparing **345F***5** with **23456F***5**, the two *ortho*-fluoro-substituents cause the clearing point to decrease by 40.6°C. Moreover, the SmA phase temperature range decreases by 54.8°C. Since the *ortho*-fluoro-substituents can increase both the width and thickness of molecules, compound **26F***5** is not liquid crystal.

In summary, one series of chiral fluorinated benzoates were synthesized. Generally, they show only enantiotropic SmA phase. The *para*-fluoro-subsitution can increase both the clearing point and the SmA phase temperature range. On the contrary, *ortho*-fluoro-substitution will decrease both the clearing point and the SmA phase temperature ranges. However, according to the presence or not of a fluorine atom at the *para*-position, the *meta*-fluoro-substitution shows the reverse effect.

EXPERIMENTAL

Characterization

The structures of the final products and intermediates were determined by a variety of spectral methods. IR spectra were taken

on a PE-983G spectrophotometer, using KBr pellets of the solids, or films of liquids. ^{1}H NMR spectra, with TMS as internal NMR standard were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q (90 MHz) instrument; ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz). For spectra spectrum ^{19}F NMR the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope.

The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (DSC, Shimidazu DSC-50 calorimeter with a data system, heating and cooling rate 5°C$\cdot$min^{-1}). The transition temperatures reported in this article were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature.

Synthesis

All of the obtained liquid crystals were purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent and then recrystallized from acetone/methanol.

Synthesis of 3F5*

A typical synthetic procedure was shown as follows. (S-) 4-(4′-(2-Methylbutoxy)phenyl)phenol (0.60 mmol), 3-fluorobenzoic acid (0.60 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.7 mmol), catalytic DMAP, and dry THF (10 mL) were stirred under N_2 at room temperature for 48 h. The mixture was filtered and the residue was washed with THF. The collected filtrates were evaporated on a rotary evaporator. The residue was purified by flash chromatography and recrystallized from acetone/methanol to give white solid. $[\alpha]_D^{20} = +8.45$ (25°C, $CHCl_3$). Mp. 112.2°C. IR (KBr) υ_{max}: 2920, 2874(s, C−H), 1726(vs, C=O), 1609(s, C_6H_4), 1498(vs, C_6H_4F), 1248, 1168(s, C−O−C) cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.96(d, 2H, ArH), 7.20–7.64(m, 8H, ArH), 7.85–8.05(m, 2H, ArH) ppm, ^{19}F NMR δ_F(56.4 MHz, $CDCl_3$, TFA): 34.5(m, F) ppm. MS m/z (rel. int.): 378(M^+, 39.77), 308($C_6H_4FCOOC_6H_4C_6H_4OH^+$, 36.57), 123 ($C_6H_4FCO^+$, 100.00). Elemental analysis: calculated (for $C_{24}H_{23}FO_3$), C, 76.17 H, 6.13; F, 5.02%, found, C, 76.26; H, 6.20; F, 4.90%.

Compound 34F*5**

$[\alpha]_D^{20} = +8.73$ (25°C, $CHCl_3$). Mp. 129.6°C. IR (KBr) υ_{max}: 2921, 2870(s, C−H), 1726(vs, C=O), 1610(s, C_6H_4), 1496(vs, $C_6H_3F_2$), 1249, 1168(s, C−O−C) cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.95(d, 2H, ArH), 7.18–7.28(m, 3H, ArH), 7.43–7.63(m, 4H, ArH), 7.93–8.13(m, 2H, ArH) ppm, ^{19}F NMR δ_F(56.4 MHz, $CDCl_3$, TFA): 52.85(m, F), 60.02(m, F) ppm. MS m/z (rel. int.): 396(M^+, 12.26), 326($C_6H_3F_2COOC_6H_4C_6H_4OH^+$, 45.62), 141($C_6H_3F_2CO^+$, 100.00). Elemental analysis: calculated (for $C_{24}H_{22}F_2O_3$), C, 72.71 H, 5.59; F, 9.58%, found, C, 73.05; H, 5.44; F, 9.55%.

Compound 35F*5**

$[\alpha]_D^{20} = +9.52$ (25°C, $CHCl_3$). Mp. 130.9°C. IR (KBr) υ_{max}: 2920, 2877(s, C−H), 1738(vs, C=O), 1600(s, C_6H_4), 1495(vs, $C_6H_3F_2$), 1271, 1169(s, C−O−C) cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.87–7.23(m, 5H, ArH), 7.40–7.77(m, 6H, ArH) ppm, ^{19}F NMR δ_F (56.4 MHz, MHz, $CDCl_3$, TFA): 31.11(s, F)ppm. MS m/z (rel. int.): 396(M^+, 41.85), 326($C_6H_3F_2-COO-C_6H_4C_6H_4OH^+$, 63.77), 141($C_6H_3F_2CO^+$, 100.00). Elemental analysis: calculated (for $C_{24}H_{22}F_2O_3$), C, 72.71; H, 5.59; F, 9.58%, found, C, 72.95; H, 5.61; F, 9.66%.

Compound 26F*5**

$[\alpha]_D^{20} = +11.84$ (25°C, $CHCl_3$). Mp. 94.3°C. IR (KBr) υ_{max}: 2920, 2875(s, C−H), 1752(vs, C=O), 1607, 1495(vs, ArH), 1258, 1169(s, C−O−C) cm^{-1}. ^1H NMR δ_H (60 MHz; $CDCl_3$; TMS): 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.88–7.67(m, 11H, ArH)ppm, ^{19}F NMR δ_F(56.4 MHz, $CDCl_3$, TFA): 42.89(s, F) ppm. MS m/z (rel. int.): 395($M^+ - 1$, 56.87), 325($C_6H_3F_2COOC_6H_4C_6H_4O^+$, 21.69), 141($C_6H_3F_2CO^+$, 100.00). Elemental analysis: calculated (for $C_{24}H_{22}F_2O_3$), C, 72.71 H, 5.59; F, 9.58%, found, C, 72.96; H, 5.55; F, 9.92%.

Compound 234F*5**

$[\alpha]_D^{20} = +8.05$ (25°C, $CHCl_3$). Mp 97.9°C, υ_{max} (KBr): 2916, 2877(s, C−H), 1739(vs, C=O), 1605(s, C_6H_4), 1481(vs, $C_6H_2F_3$), 1257, 1170(s, C−O−C) cm^{-1}. δ_H ($CDCl_3$), 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.80–8.10(m, 10H, ArH)ppm, δ_F($CDCl_3$): 47.95(m, F), 51.23(m, F), 81.92(m, F) ppm. m/z(%): 414(M^+, 41.54), 344($^+HOC_6H_4C_6H_4OCOC_6H_2F_3$, 63.42), 159($^+OCC_6H_2F_3$, 100.00). Elemental analysis: calculated (for $C_{24}H_{21}F_3O_3$), C, 69.56; H, 5.11; F, 13.75, found, C, 69.72; H, 5.14; F, 13.89.

Compound 345F*5**

$[\alpha]_D^{20} = +7.83$ (25°C, $CHCl_3$). Mp. 100.4°C, υ_{max} (KBr): 2920(s, C−H), 1739(vs, C=O), 1606(s, C_6H_4), 1496(vs, $C_6H_2F_3$), 1254, 1168(s, C−O−C) cm^{-1}. δ_H ($CDCl_3$), 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.80–8.13(m, 10H, ArH) ppm, $\delta_F(CDCl_3)$: 53.82(m, 2F), 73.50(m, F) ppm. m/z(%): 414(M^+, 30.65), 344($^+HOC_6H_4C_6H_4OCOC_6H_2F_3$, 45.61), 159($^+OCC_6H_2F_3$, 100.00). Elemental analysis: calculated (for $C_{24}H_{21}F_3O_3$), C, 69.56; H, 5.11; F, 13.75, found, C, 69.60; H, 5.01; F, 13.58.

Compound 23456F*5**

$[\alpha]_D^{20} = +8.05$ (25°C, $CHCl_3$). Mp 114.6°C, υ_{max} (KBr): 2964(s, C−H), 1742(vs, C=O), 1605(s, C_6H_4), 1491(vs, C_6F_5), 1225, 1170(s, C−O−C) cm^{-1}. δ_H ($CDCl_3$), 0.89–2.09(m, 9H, aliphatic hydrogens), 3.78–3.87(m, 2H, RCH_2O), 6.85–7.57(m, 8H, ArH) ppm, $\delta_F(CDCl_3)$: 59.40(m, 2F), 70.37(m, F), 83.28(m, 2F) ppm. m/z(%): 450(M^+, 68.70), 380($C_6F_5COOC_6H_4C_6H_4OH^+$, 75.97), 195($C_6F_5CO^+$, 100.00). Elemental analysis: calculated (for $C_{24}H_{19}F_5O_3$), C, 64.00; H, 4.25; F, 21.09, found, C, 63.97; H, 4.22; F, 21.46.

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REFERENCES

[1] Gray, G. W., Hird, M., Lacey, D., & Toyne, K. J. (1989). *J. Chem. Soc. Perkin II*, 2041.
[2] Fearon, J. E., Gray, G. W., Ifill, A. D., & Toyne, K. J. (1985). *Mol. Cryst. Liq. Cryst.*, *124*, 89.
[3] Gray, G. W., Lacey, D., Station, J. E., & Toyne, K. J. (1986). *Liq. Cryst.*, *1*, 407.
[4] Gray, G. W., Hird, M., Ifill, A. D., Smith, W. E., & Toyne, K. J. (1995). *Liq. Cryst.*, *19*, 77.
[5] Hird, M., Toyne, K. J., Gray, G. W., McDonnell, D. G., & Sage I. C. (1995). *Liq. Cryst.*, *28*, 1.
[6] Seed, A. J., Toyne, K. J., & Goodby, J. W. (1995). *J. Mater. Chem.*, *5*, 2201.
[7] Matharu, A. S., Wilson, R. C., & Byron, D. J. (1997). *Liq. Cryst.*, *23*, 575.
[8] Coates, D. (1987). *Liq. Cryst.*, *2*, 423.
[9] Yang, Y., Wang, K., & Wen, J. (2001). *Liq. Cryst.*, *28*, 1553.
[10] Yang, Y., Chen, H., Tang, G., & Wen, J. (2002). *Liq. Cryst.*, *29*, 255.
[11] Li, H., Yang, Y., & Wen, J. (2000). *Liq. Cryst.*, *27*, 1445.
[12] Yang, Y., Li, H., Wang, K., & Wen, J. (2001). *Liq. Cryst.*, *28*, 375.
[13] Yang, Y., Tang, G., & Wen, J. (2002). *Mol. Cryst. Liq. Cryst.*, *373*, 1.
[14] Tang, G., Wang, K., Yang, Y., & Wen, J. (2001). *Liq. Cryst.*, *28*, 1623.

[15] Haruyoshi, T., Sadao, T., Kiyofumi, T., & Yoshinori, I. (2002). *DIC Technical Review*, 33.
[16] Kirsch, P., Huber, F., Lenges, M., & Taugerbeck, A. (2001). *J. Fluorine Chem.*, *112*, 69.
[17] Catalano, D., Geppi, M., Marini, A., Veracini, C. A., Urban, S., Czub, J., Kuczyński, W., & Dabrowski, R. (2007). *J. Phys. Chem. C*, *111*, 5286.
[18] Lee, C.-K., Kwon, S.-S., Kim, T.-S., Shin, S.-T., Choi, H., Choi, E.-J., Kim, S. Y., Zin, W.-C., Kim, D.-C., & Chien, L.-C. (2004). *Bull. Korean Chem. Soc.*, *25*, 1171.
[19] Wang, K., Jàkli, A., Li, H., Yang, Y., & Wen, J. (2001). *Liq. Cryst.*, *28*, 1705.
[20] Wen, J., Tian, M., & Chen, Q. (1994). *Liq. Cryst.*, *16*, 445
[21] Xu, Y., Wang, W., Chen, Q., & Wen, J. (1996). *Liq. Cryst.*, *21*, 65.
[22] Yin, H. & Wen, J. (1996). *Liq. Cryst.*, *21*, 217.
[23] Cowling, S. J., Hall, A. W., & Goodby, J. W. (2005). *Liq. Cryst.*, *32*, 1483.
[24] Yang, Y. & Wen, J. (2002). *Liq. Cryst.*, *29*, 159.
[25] Yang, Y. & Wen, J. (2002). *Liq. Cryst.*, *29*, 161.
[26] Yang, Y., Li, H., & Wen, J. (2007). *Liq. Cryst.*, *34*, 1167.
[27] Yang, Y., Li, H., & Wen, J. (2007). *Liq. Cryst.*, *34*, 975.
[28] Kašpar, M., Bubnov, A., Hamplová, V., Málková, Z., Pirkl, S., & Glogarová, M. (2007). *Liq. Cryst.*, *34*, 1185.
[29] Wu, S.-L. & Lin, C.-Y. (2006). *Liq. Cryst.*, *33*, 537.
[30] Wu, S.-L. & Lai, F.-S. (2005). *Liq. Cryst.*, *32*, 1243.
[31] Wu, S.-L. & Lin, T.-C. (2005). *Liq. Cryst.*, *32*, 797.
[32] Sasaki, T. (2006). *The Chemical Record*, *6*, 43.