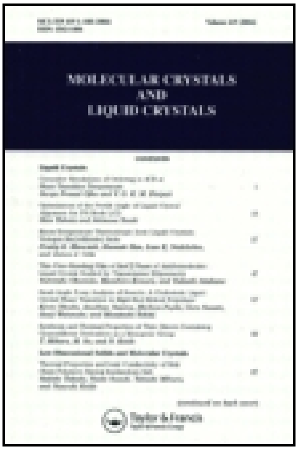

Molecular Crystals and Liquid Crystals

Synthesis and Mesomorphic Properties of Some Liquid Crystals with 2,3,5,6-Tetrafluorophenylene Unit

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Synthesis and Mesomorphic Properties of Some Liquid Crystals with 2,3,5,6-Tetrafluorophenylene Unit

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Nine fluorosubstituted liquid crystals have been synthesized and their mesomorphic properties have been studied by texture observation in a polarizing microscope and confirmed by DSC. They show enantiotropic smectic A and nematic phases. The effect of terminal and lateral fluorosubstitution is also discussed.

Keywords: Fluorinated, liquid crystal, mesomorphic

INTRODUCTION

The development of TFT LCD is the main trend in the LCD market. The introduction of fluorine atoms into LC molecules can usually lower the melting point and viscosity of the molecular system [1–6], and because of this fluorinated liquid crystals are widely used in TFT LCD. Thus it is quite important to study the effect of fluorosubstitution on the liquid crystal properties. It was found that smectic properties were enhanced with the introduction of a *meta*-fluorosubstituent in the terminal aromatic ring [7]. The reason for this is that the fluorine atom is shielded by the other part of the core. This phenomenon was also found in our group [8]. Furthermore, it was found in the series **I** that not only the *meta*-fluorosubstitutent but also the *para*-fluorosubstitutent of the terminal phenyl group enhanced the formation of SmA phase [9]. These phenomena may result from the existence of

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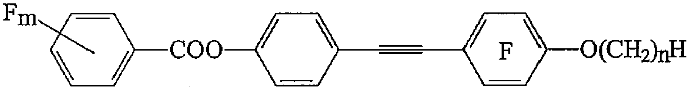
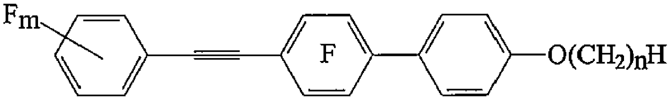
microphase separation when the number of the fluorine atoms increased to some degree [10].


n = 5-10. **(I)**

To further study whether a second *meta*-fluorosubstitution will promote the formation of smectic A phase in other groups, a class of novel, highly fluorinated mesogens were synthesized (see Scheme 1). The formulae were shown as below.


(II)

Series **A**: F_m, 3,4,5-trifluoro-; $n = 8$–10. Series **B**: F_m, 3,4-difluoro-; $n = 7$–10
Series **C**: F_m, 2,3,4-trifluoro-; $n = 8$. Series **D**: F_m, 3,4-difluoro-; $n = 7$

RESULT AND DISCUSSION

The phase transition temperatures of the four series are listed in Table 1 below.

As shown in Table 1, it is found that series **A** shows both smectic A and nematic phases; **D7** is not liquid crystal, and the others show only nematic phases during the process of heating and cooling.

Among these compounds, when $n = 8$ the clearing point of **C8** is the highest and that of **A8** is the lowest. With the introduction of an *ortho*-fluorosubstituent in compound **B8**, the polarizability and dipolarity were

TABLE 1 Phase transition temperatures of the compounds

Compounds	*n*	*Transition temperatures/°C*
A8	8	Cr 84.6 SmA 97.5 N 102.3 I 101.4 N 96.3 SmA 63.7 Recr
A9	9	Cr 96.7 N 98.3 I 97.9 N 95.7 SmA 80.6 Recr
A10	10	Cr 86.8 SmA 95.0 N 97.7 I 96.6 N 94.7 SmA 67.5 Recr
B7	7	Cr 98.4 N 113.0 I 111.6 N 75.6 Recr
B8	8	Cr 86.4 N 112.2 I 110.4 N 72.0 Recr
B9	9	Cr 97.2 N 106.4 I 104.5 N 78.2 Recr
B10	10	Cr 92.0 N 107.5 I 106.1 N 75.3 Recr
C8	8	Cr 88.4 N 121.9 I 120.9 N 85.0 Recr
D7	7	Cr 96.9 I 77.5 Recr

Cr, Crystal; SmA, Smectic A phase; N, Nematic phase; I, Isotropic phase; Recr, Recrystallization.

both increased. Then the clearing point of **C8** is higher than that of **B8**. But a second *meta*-fluorosubstituent is introduced to the compound **A8**, and due to the existence of conjugation of the triple bond the two fluorosubstituted aromatic rings are not in the same plane. Then the lateral fluorosubstituents in the terminal aromatic ring will not be shielded by those in the central one, which will broaden the molecule and lower the clearing point. Finally, **A8** shows the lowest clearing point in these three compounds.

Compound **D7** is the compound like series **A** without *para*-fluorosubstituent. It is not liquid crystal. The reason should not be the ratio of molecular length/width rather it should be that the hydrogen substituent offers little in the way of both conjugative and dipolar attractions [11].

It is also found that series **A** is more favorable to form smectic A phases than series **B**, although the compound of series **A** is broader than the corresponding one of series **B**. As we have discussed before, this phenomenon may be due to the existence of microphase separation when the number of fluorine atoms in the terminal aromatic ring is increased to some degree [10]. This means that the fluorocarbon parts stick together and the other parts also stick together. Then the strong fluorine-fluorine interactions tend to form smectic A phase [12–14].

It can also be explained in this way, considering that the radius of fluorine atom is very small but the electronegativity is the highest. The fluoro-contained compounds show low cohesive energy density and low surface free energy. With the increasing of the number of fluorosubstitutions, the polarity along the axis is increased, but because of the high electronegativity, the end-to-end distance increased too, which will decrease the terminal-terminal interaction. Then smectic phase emerged.

But compound **C8**, although it has the same degree of fluorosubstitution in the terminal phenyl group as **A8**, does not show a smectic phase. This seems that the *ortho*-fluorosubstituent may suffer electrostatic repulsion by the carbonyl oxygen atom, which will exert a twisting effect. Thus, the compound **C8** does not form smectic phase.

EXPERIMENTAL

The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrometer, using KBr pellets of solids or films of liquids. ^{1}H NMR spectra, with TMS as internal standard and $CDCl_3$ as the solvent, were run in FX-90Q (90 MHz) or Bruker 300 (300 MHz) spectrometer. ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard and $CDCl_3$ as the solvent, were recorded on a Varian EM 360L spectrometer (60 MHz; high field positive). MS spectra were measured by 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 a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system and heating and cooling rate of 5°C min^{-1}). The transition temperatures reported in this paper were the peak values of the transition on DSC traces.

The liquid crystal molecules studied were synthesized following the route as shown below.

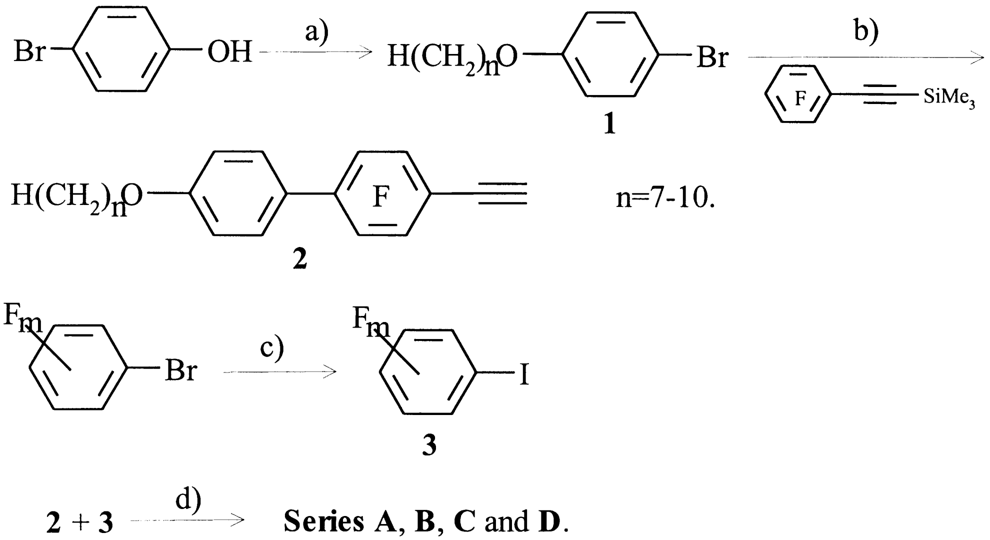
The important intermediates **2** was prepared by the method reported previously [9]. The iodocompounds were prepared via the bromocompounds. The target molecules were prepared via the couple reaction between **2** and **3** under $[Pd(OAc)_2]_3$ and PPh_3.

2,3,5,6-tetrafluoro-4-[(3″,4″-Difluorophenyl) acetylenyl] 4′-n-Octyloxybiphenyl (B8)

A typical procedure: under nitrogen, 20 ml of dried triethylamine was added to a mixture of compound 3,4-trifluoro-1-iodobenzene (75 mg, 0.31 mmol), n-octyloxyphenylacetylene, $[Pd(OAc)_2]_3$ (3 mg, 0.01 mol Pd) and PPh_3 (7 mg, 0.03 mmol). The resulting mixture was refluxed while stirring until analysis by TLC revealed a complete reaction. The cooled mixture was filtered and the filtrate was washed with anhydrous ether. The solvent was removed under vacuum and residue was purified by column chromatography on silica gel using petroleum ether(b.p. 60–90°C) and ethyl acetate (50:1) as eluent to give paleyellow crystals, which were then recrystallized from acetone-methanol to yield white crystals of compound **B8**. Yield: 102 mg (68.4%). Mp 86.4°C. ν_{max}(KBr): 2923, 2854, 1599, 1518, 1425, 1290, 1147, 1254, 1025 cm^{-1}. δ_H ($CDCl_3$): 0.87–0.92 (t, 3H), 1.30–1.86 (m, 12H), 4.02 (t, 2H, J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.15–7.46 (m, 5H) ppm. δ_F ($CDCl_3$): 57.70 (m, 1F), 60.00–62.00 (m, 3F), 68.40 (m, 1F) ppm. m/z (%): 490 (100.00), 378 (75.99). Anal. $C_{28}H_{24}OF_6$. Calcd: C, 68.59; H, 4.89; F, 23.25. Found: C, 68.48; H, 4.97; F, 23.27.

2,3,5,6-tetrafluoro-4-[(3″,4″-Difluorophenyl) acetylenyl] 4′-n-Heptyloxybiphenyl (B7)

Mp 98.4°C. ν_{max}(KBr): 2923, 2854, 1599, 1518, 1425, 1292, 1147, 1254, 1025 cm^{-1}. δ_H ($CDCl_3$): 0.88–0.92 (t, 3H), 1.26–1.86 (m, 10H), 4.02 (t, 2H,



SCHEME 1 (a) $H(CH_2)_nBr$/DMF, NaOH. (b) Mg/THF; NaOH, acetont. (c) Mg/THF, I_2. (d) $Pd(OAc)_2$, Ph_3P, NEt_3.

J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.18–7.46 (m, 5H) ppm. δ_F ($CDCl_3$): 57.70 (m, 1F), 60.00–62.00 (m, 3F), 68.40 (m, 1F) ppm. *m/z* (%): 377 (100.00), 476 (20.16). Anal. $C_{27}H_{22}OF_6$. Calcd: C, 68.09; H, 4.62; F, 23.93. Found: C, 67.72; H, 4.45; F, 23.79.

2,3,5,6-tetrafiuoro-4-(3″,4″-Difluorophenyl) acetylenyl] 4′-n-Nonyloxybiphenyl (B9)

Mp 97.2°C. ν_{max}(KBr): 2923, 2854, 1599, 1518, 1425, 1292, 1147, 1254, 1025 cm^{-1}. δ_H ($CDCl_3$): 0.87–0.91 (t, 3H), 1.29–1.82 (m, 14H), 4.02 (t, 2H, J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.18–7.43 (m, 5H) ppm. δ_F ($CDCl_3$): 57.70 (m, 1F), 60.00–62.00 (m, 3F), 68.40 (m, 1F) ppm. *m/z* (%): 504 (100.00), 378 (37.71). Anal. $C_{29}H_{26}OF_6$. Calcd: C, 69.07; H, 5.15; F, 22.60. Found: C, 69.09; H, 5.20; F, 22.81.

2,3,5,6-tetrafluoro-4-[(3″,4″-Difluorophenyl) acetylenyl] 4′-n-Decyloxybiphenyl (B10)

Mp 92.0°C. ν_{max}(KBr): 2923, 2854, 1599, 1518, 1425, 1292, 1147, 1254, 1025 cm^{-1}. δ_H ($CDCl_3$): 0.86–0.91 (t, 3H), 1.30–1.88 (m, 16H), 4.02 (t, 2H, J = 6.5 Hz), 6.99–7.04 (m, 2H), 7.15–7.46 (m, 5H) ppm. δ_F ($CDCl_3$): 57.70 (m, 1F), 60.00–62.00 (m, 3F), 68.40 (m, 1F) ppm. *m/z* (%): 518 (23.02), 378 (100.00). Anal. $C_{30}H_{28}OF_6$. Calcd: C, 69.52; H, 5.40; F, 21.99. Found: C, 69.28; H, 5.21; F, 21.95.

2,3,5,6-tetrafluoro-4-[(3″,4″,5″-trifluorophenyl) acetylenyl] 4′-n-Octyloxybiphenyl (A8)

Mp 84.6°C. ν_{max}(KBr): 2922, 2854, 1612, 1523, 1474, 1293, 1140, 1247, 1046 cm^{-1}. δ_H ($CDCl_3$): 0.87–0.92 (t, 3H), 1.28–1.86 (m, 12H), 4.02 (t, 2H, J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.21–7.26 (m, 2H) 7.40–7.43 (m, 2H) ppm. δ_F ($CDCl_3$): 52.92 (m, 2F), 56.03 (m, 2F), 63.03 (m, 2F), 74.91 (m, 1F) ppm. *m/z* (%): 508 (18.28), 395 (100.00). Anal. $C_{28}H_{23}OF_7$. Calcd: C, 66.16; H, 4.52; F, 26.17. Found: C, 65.87; H, 4.44; F, 26.35.

2,3,5,6-tetrafluoro-4-[(3″,4″,5″-trifluorophenyl) acetylenyl] 4′-n-Nonyloxybiphenyl (A9)

Mp 96.7°C. ν_{max}(KBr): 2922, 2854, 1612, 1523, 1473, 1293, 1140, 1247, 1046 cm^{-1}. δ_H ($CDCl_3$): 0.87–0.91 (t, 3H), 1.29–1.86 (m, 14H), 4.02 (t, 2H, J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.21–7.26 (m, 2H) 7.40–7.43 (m, 2H) ppm. δ_F ($CDCl_3$): 52.92 (m, 2F), 56.03 (m, 2F), 63.03 (m, 2F), 74.91 (m, 1F) ppm. m/z (%): 522 (27.14), 395 (100.00). Anal. $C_{29}H_{25}OF_7$. Calcd: C, 66.68; H, 4.79; F, 25.46. Found: C, 66.70; H, 4.85; F, 25.27.

2,3,5,6-tetrafluroro-4-[(3″, 4″, 5″-tripfluorophenyl)acetylenyl] 4′-n-Decyloxybiphenyl (A10)

Mp 86.8°C. ν_{max}(KBr): 2922, 2854, 1612, 1523, 1474, 1293, 1140, 1247, 1053 cm^{-1}. δ_H ($CDCl_3$): 0.87–0.91 (t, 3H), 1.28–1.88 (m, 16H), 4.02 (t, 2H, J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.20–7.29 (m, 2H) 7.40–7.43 (m, 2H) ppm. δ_I ($CDCl_3$): 52.92 (m, 2F), 56.03 (m, 2F), 63.03 (m, 2F), 74.91 (m, 1F) ppm. m/z (%): 536 (27.14), 395 (100.00). Anal. $C_{30}H_{27}OF_7$. Calcd: C, 67.18; H, 5.03; F, 24.80. Found: C, 66.95; H, 5.08; F, 25.10.

2,3,5,6-tetrafluroro-4-[(2″, 3″, 4″-tripfluorophenyl)acetylenyl] 4′-n-Octyloxybiphenyl (C8)

Mp 88.4°C. ν_{max}(KBr): 2927, 2854, 1610, 1491, 1414, 1261, 1188, 1067 cm^{-1}. δ_H ($CDCl_3$): 0.87–0.92 (t, J = 6.4 Hz, 3H), 1.28–1.84 (m, 12H), 4.02 (t, 2H, J = 6.5 Hz), 7.00–7.03 (m, 2H), 7.26–7.44 (m, 4H) ppm. m/z (%): 508 (38.41), 395 (100.00). Anal. $C_{28}H_{23}OF_7$. Calcd: C, 66.16; H, 4.52; F, 26.17. Found: C, 65.83; H, 4.84; F, 26.02.

2,3,5,6-tetrafluroro-4-[(3″, 5″-difluorophenyl)acetylenyl] 4′-n-Heptyloxybiphenyl (D7)

Mp 96.9°C. ν_{max}(KBr): 2923, 2856, 1612, 1481, 1416 cm^{-1}. δ_H ($CDCl_3$): 0.91–0.96 (t, J = 7.1 Hz, 3H), 1.35–1.84 (m, 10H), 4.28 (t, 2H, I = 6.6 Hz), 7.23–7.26 (m, 2H), 7.64–7.67 (m, 2H), 7.84–7.88 (m, 2H) ppm. δ_F ($CDCl_3$): 54.80 (m, 2F), 60.90 (m, 2F), 74.00 (m, 1F), 80.50 (m, 2F) ppm. m/z (%): 378 (100.00), 476 (31.54). Anal. $C_{27}H_{22}OF_6$. Calcd: C, 68.09; H, 4.62; F, 23.93. Found: C, 67.72; H, 4.45; F, 23.79.

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