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Synthesis and Mesomorphic Properties of Two Series of Laterally Fluorinated Symmetric Ester Liquid Crystals

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Two series of symmetric ester liquid crystals (nAFBHQ and nADFBHQ) with lateral fluorine atoms have been synthesized. Their chemical structures were measured by FTIR, ^{1}H NMR, and elemental analysis (EA). Their mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). It was found that both series showed nematic phase only. And their melting point and clearing point decreased with the number of carbon atoms in alkoxy group. It can also be found that nAFBHQ have approximately the same temperatures of melting point but much higher temperatures of clearing point than their corresponding compound in nADFBHQ series.

Keywords: ester; fluorinated liquid crystal; mesomorphic property; synthesis

INTRODUCTION

Ester liquid crystals are considered as one of the important components of high-grade liquid crystal mixtures for their favorable advantages such as high clearing point and large birefringence [1]. Thereinto ester liquid crystals with hydroquinone moieties attracted more attention for their scientific and practical applications. Many works [2–8] have been done on the synthesis and mesomorphic properties of these ester compounds with different substituent groups.

Recently fluorinated liquid crystals become a hot field because the replacement of one or several hydrogen atoms by fluorine atoms confers to the resulting materials unusual and peculiar properties [9]. Particularly, liquid crystals with lateral fluoro-substituents are

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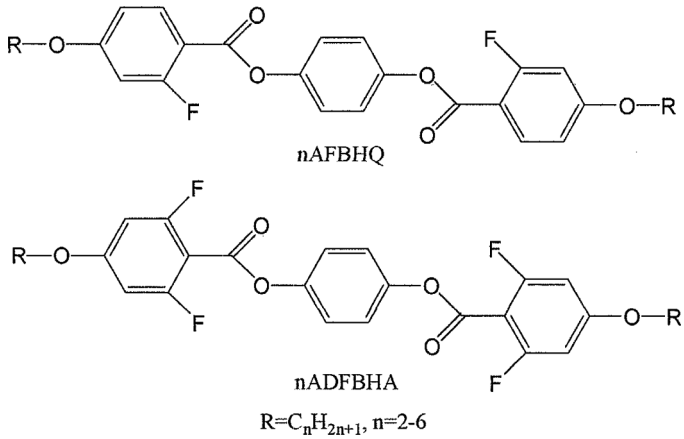

FIGURE 1 Aim structure of the laterally fluorinated ester compounds.

of more importance and attracted much more attention [10–14]. The advantage of these laterally fluorinated materials is that they may exhibit many attractive properties such as negative dielectric anisotropy, low viscosities, optical and chemical stability, low melting point, and low conductivity.

In order to obtain liquid crystal materials with broad nematic temperature ranges and low viscosity, and to establish the relationships between structures and properties of laterally fluorinated materials, we synthesized and characterized two kinds of novel laterally fluorinated ester liquid crystals with hydroquinone moiety. The general structures of these compounds are indicated in Fig. 1 (series nAFBHQ and nADFBHQ).

EXPERIMENT

Characterization

IR spectra were recorded on a Nicolet 510P instrument and ^{1}H NMR spectra on Bruker DMX-400 instrument in $CDCl_3$. EA measurements were carried out on a Thermo Finnigan Flash EA1112 elemental analyzer. The mesomorphic properties of the compounds were studied by an Olympus BX-51 polarizing microscope equipped with hot stage. For differential scanning calorimeter (DSC), a Perkin-Elmer DSC-6 instrument was used, the scanning rate was 10°C/min, the samples were sealed in aluminum capsules, and the holder atmosphere was dry nitrogen.

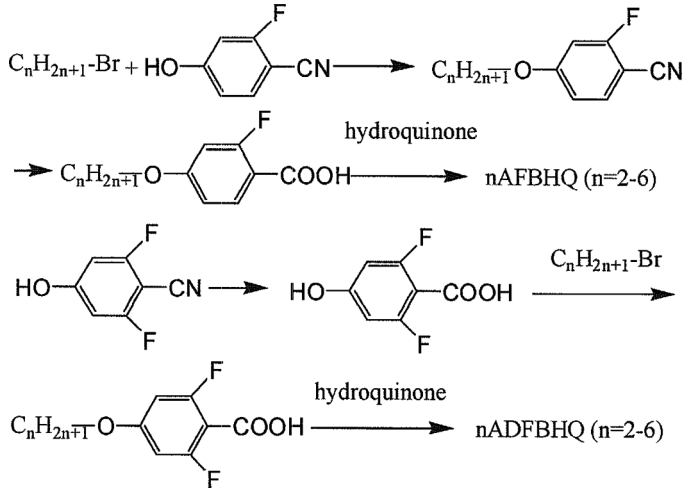

FIGURE 2 Synthesis routes of the aim structures.

Synthesis

The synthetic routes to these compounds were shown in Fig. 2, procedures were summarized below. Both series dealt with in this study were prepared similarly and the whole process for the preparation of 6AFBHQ and 6ADFBHQ was described as examples.

Synthesis of 2-Fluoro-4-hexyloxybenzoic Acid (6AFBA)

The mixture of 13.7 g (0.1 mol) 2-fluoro-4-hydroxybenzonitrile, 4.4 g (0.11 mol) NaOH, 4 g anhydrous KI, 0.11 mol hexyl bromide and 100 mL butanone were heated to 60°C for 10 hr. After cooling, the insolubles were removed and the filtrate was washed with 10% NaOH water solution for 2 times. The butanone was then removed through evaporation and the residues were mixed with 80 mL 10% NaOH water solution, refluxing for 24 hr. After cooling, the mixture was acidified with hydrochloric acid, and the precipitate was collect by suction filtration, recrystallized from 95% ethanol. The yield was 72%. FTIR, ν/cm^{-1}: 2552–3170 (acidic −OH stretching), 1684 (C=O stretching), 1575, 1508 (aromatic C=C stretching), 1242 (C-O stretching). ^{1}H NMR: δ 0.92–1.86 (m, 11H, alkyl protons), δ4.01–4.04 (m, 2H, $J = 6.48$ Hz, $-CH_2$-O), δ6.65–6.68 (d, H, $J_{HF} = 12.90$ Hz, Ar-H), 6.74–6.76 (d, H, $J = 8.94$ Hz, Ar-H), δ7.96–8.01 (m, 1H, $J = 8.70$ Hz, $^2J_{HF} = -8.74$ Hz, Ar-H). Anal. Calcd. For $C_{13}H_{17}FO_3$: C, 64.98; H, 7.13. Found C, 64.72; H, 7.1.5.

Synthesis of 2,6-Difluoro-4-hexyloxybenzoic Acid (6ADFBA)

2,6-difluoro-4-hydroxybenzonitrile 15.5 g (0.1 mol) was added to 100 mL of 10% NaOH water solution, refluxing for 24 hr, and then acidified by hydrochloric acid, the precipitate collected and recrystallized from alcohol. A 92% yield of 2,6-difluoro-4-hydroxybenzoic acid was obtained.

KOH 2.8 g (50 mmol) in 50 mL of distilled water was added to a slurry of 2, 6-difluoro-4-hydroxybenzoic acid (25 mmol) in ethanol (200 mL), and the mixture heated under reflux for 1 hr, hexyl bromide (75 mmol) was added and the mixture was heated a further 12 hr. KOH water solution (100 mL, 10%) was added and reflux continued for 2 hr. After cooling, the mixture was acidified by hydrochloric acid and filtered. The crude product was recrystallized from ethanol giving a 70% yield of 6DFABA. IR, ν/cm^{-1}: 2530–3118 (acidic -OH), 1692 (C=O), 1575, 1450 (aromatic C=C), 1277 (C-O-Ar). ^{1}H NMR: δ0.90–1.81 (m, 11H, alkyl protons), δ3.96–3.99 (m, 2H, $J = 6.45$ Hz, -CH_2-O), δ6.48–6.50 (d, 2H, $J_{HF} = 11.47$ Hz, Ar-H). Anal. Calcd. For $C_{13}H_{16}F_2O_3$: C, 60.46; H, 6.24. Found C, 60.29; H, 6.25.

Synthesis of Aim Compounds nAFBHQ and nADFBHQ

Dicyclohexylcarbodiimide 10.3 g (50 mmol) and N,N-dimethylaminopyridine 20 mg were added to a solution of 50 mmol substituted alkoxybenzoic acid (nAFBA or nADFBA) and hydroquinone 2.75 g (25 mmol) in 120 mL of dichloromethane (DCM). The mixture was stirred for 12 h. The dicyclohexylurea was filtered off and the solvent from the filtrate was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM) giving a 69% yield of 6AFBHQ and a 83% yield of 6ADFBHQ. 6AFBHQ: IR, ν/cm^{-1}: 2967, 2920, 2876, 2854 (aliphatic C-H), 1718 (C=O), 1618, 1575, 1510 (aromatic C=C), 1264 (C-O-Ar). ^{1}H NMR: δ0.94–1.87 (m, 11H, alkyl protons), δ4.04–4.07 (m, 2H, $J = 6.52$ Hz, -C$\underline{H}_2$-O), δ6.71–6.74 (d, H, $^1J_{HF} = 12.72$ Hz, Ar-H), δ6.80–6.82 (d, H, $J = 8.88$ Hz, Ar-H), δ7.28–7.30 (d, 2H, Ar-H), δ8.06–8.10 (m, 1H, $J = 8.68$ Hz, $^2J_{HF} = -8.60$ Hz, Ar-H). Anal. Calcd. For $C_{32}H_{36}F_2O_6$: C, 69.30; H, 6.54. Found C, 69.12; H, 6.55. 6ADFBHQ: IR, ν/cm^{-1}: 2963, 2932, 2870 (aliphatic C-H), 1744 (C=O), 1575, 1502, 1450 (aromatic C=C), 1256 (C-O-Ar). ^{1}H NMR; δ0.94–1.87 (m, 11H, alkyl protons), δ4.01–4.04 (m. 2H, $J = 6.51$ Hz, -C$\underline{H}_2$-O), δ6.55–6.58 (d, 2H. $^1J_{HF} = 10.55$ Hz, Ar-H), δ7.29–7.33 (d, 2H, Ar-H). Anal. Calcd. For $C_{32}H_{34}F_4O_6$: C, 65.08; H, 5.80. Found C, 64.82; H, 5.81.

RESULTS AND DISCUSSION

By using POM and DSC, the liquid crystalline properties of the two series of compounds were measured carefully. It was found that all aim compounds showed similar mesomorphic properties. The DSC spectra scanned in heating and cooling cycles of the typical aim compounds 6AFBHQ and 6ADFBHQ were shown in Fig. 3. In the heating scan, the POM observation indicated that 6AFBHQ and 6ADFBHQ only showed nematic properties. On cooling, the formation of the nematic phase beginning as small droplets, followed on further cooling by the formation of a schlieren texture (Fig. 4a, b), was observed in the melts of 6AFBHQ and 6ADFBHQ, respectively. The detailed data of phase variant, transition temperature, and associated enthalpy changes of all the members of the two series were summarized in Table 1.

The results in Table 1 revealed that the number of fluorine atoms introduced into the aim compounds and the number of carbon atoms in alkoxy chains had significant effect on the thermal stability of the

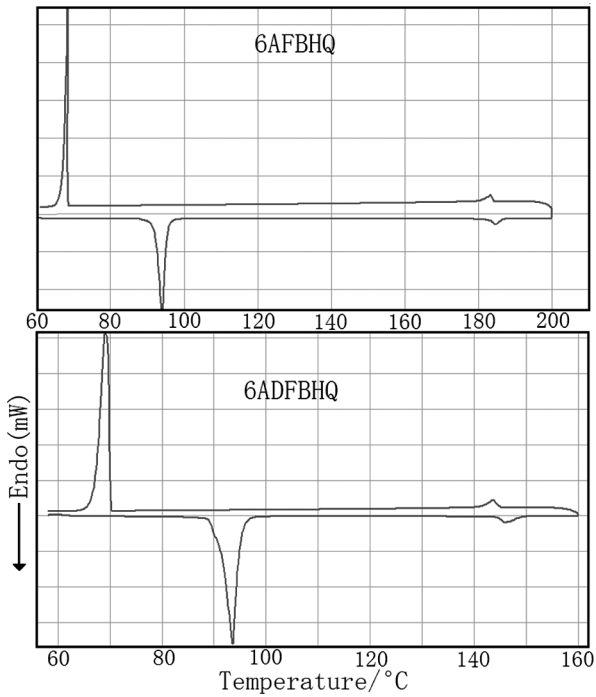

FIGURE 3 DSC spectra of 6AFBHQ and 6ADFBHQ.

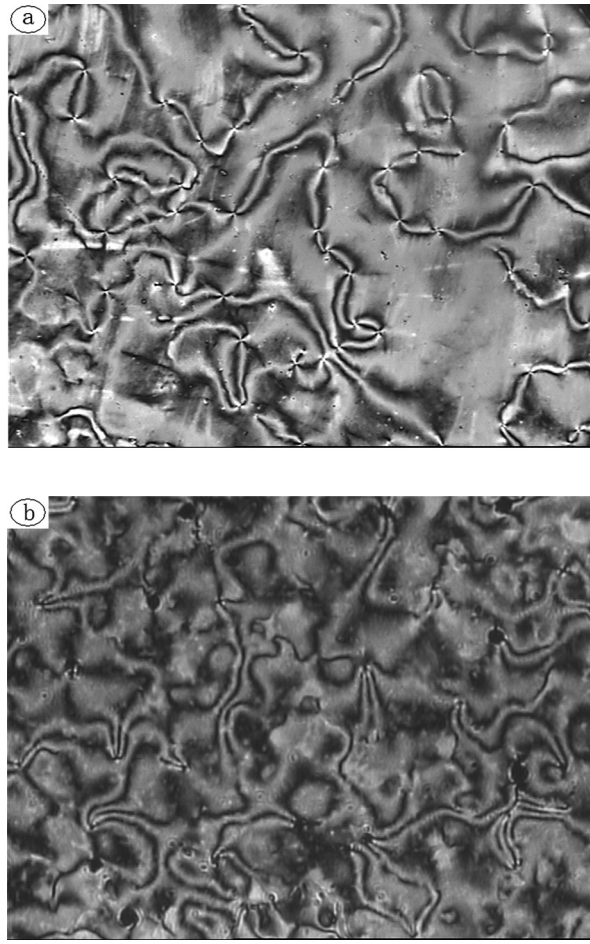

FIGURE 4 Textures of the aim structures on cooling cycle.

aim compounds' mesophase. The melting point and clearing point temperatures of the two series show no clear even-odd effects and they all decreased with the number of carbon atoms in their alkoxy chains, which is similar to their non-fluorinated analogs (here we designated them as nABHQ) as described in Ref. [8]. Furthermore, because the introduction of lateral fluorine atoms debased the symmetry and lowered the slenderness ratio of the molecules, so the melting point and clearing point temperatures of nAFBHQ and nADFBHQ was always lower than their corresponding analogs in non-fluorinated series nABHQ.

TABLE 1 Phase Transition Temperature and Associated Enthalpy Changes of nAFBHQ and nADFBHQ

Compound	Phase transition temperature (°C) and enthalpy changes (kJ/mol, in parantheses)*
6AFBHQ	$\mathrm{Cr} \underset{58.5}{\overset{94.0(29.1)}{\rightleftharpoons}} \mathrm{N} \underset{183.1}{\overset{184.6(1.9)}{\rightleftharpoons}} \mathrm{I}$
5AFBHQ	$\mathrm{Cr} \underset{82.5}{\overset{116.8(34.8)}{\rightleftharpoons}} \mathrm{N} \underset{190.5}{\overset{193.3(1.4)}{\rightleftharpoons}} \mathrm{I}$
4AFBHQ	$\mathrm{Cr1} \overset{106.1(1.7)}{\longrightarrow} \mathrm{Cr2} \underset{100}{\overset{121.7(26.1)}{\rightleftharpoons}} \mathrm{N} \underset{213}{\overset{217.8(1.8)}{\rightleftharpoons}} \mathrm{I}$
3AFBHQ	$\mathrm{Cr1} \underset{130.2}{\overset{105.3(7.1)}{\rightleftharpoons}} \mathrm{Cr2} \underset{138.1}{\overset{150.8(32.4)}{\rightleftharpoons}} \mathrm{N} \underset{227.0}{\overset{229.1(2.2)}{\rightleftharpoons}} \mathrm{I}$
2AFBHQ	$\mathrm{Cr} \underset{156.4}{\overset{166.2(39.1)}{\rightleftharpoons}} \mathrm{N} \underset{267.7}{\overset{269.9(2.7)}{\rightleftharpoons}} \mathrm{I}$
6ADFBHQ	$\mathrm{Cr} \underset{68.5}{\overset{93.6(45.4)}{\rightleftharpoons}} \mathrm{N} \underset{143.1}{\overset{146.0(2.0)}{\rightleftharpoons}} \mathrm{I}$
5ADFBHQ	$\mathrm{Cr} \underset{101.7}{\overset{116.7(58.8)}{\rightleftharpoons}} \mathrm{N} \underset{151.5}{\overset{153.4(1.8)}{\rightleftharpoons}} \mathrm{I}$
4ADFBHQ	$\mathrm{Cr} \underset{98.3}{\overset{138.1(54.8)}{\rightleftharpoons}} \mathrm{N} \underset{174.1}{\overset{176.2(2.44)}{\rightleftharpoons}} \mathrm{I}$
3ADFBHQ	$\mathrm{Cr} \underset{117.0}{\overset{151.3(31.2)}{\rightleftharpoons}} \mathrm{N} \underset{181.1}{\overset{183.01.74)}{\rightleftharpoons}} \mathrm{I}$
2ADFBHQ	$\mathrm{Cr} \underset{120.9}{\overset{160.1(45.4)}{\rightleftharpoons}} \mathrm{N} \underset{220.0}{\overset{221.9(2.6)}{\rightleftharpoons}} \mathrm{I}$

*Cr: crystal; N: nematic; I: isotropic.

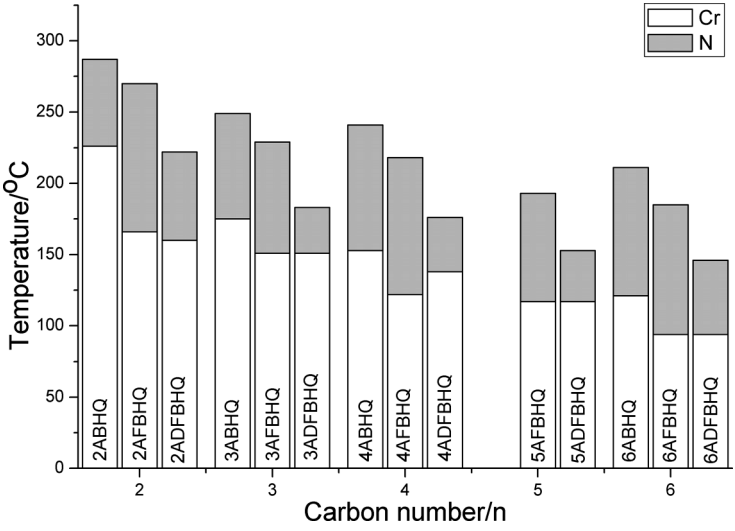

FIGURE 5 Effect of lateral fluorine atoms on the phase transition properties.

To make the effect of the introduced fluorines at the lateral positions clearer, the transition temperatures for the two series together with their non-fluorinated analogs nABHQ were plotted against the carbon number in their alkoxy chains and shown in Fig. 5.

It could be seen from Fig. 5 that nAFBHQ had much lower melting point temperatures and slightly lower clearing point temperatures than nABHQ and so the thermal range of mesophase of nAFBHQ was broader than their corresponding analogs in nABHQ. But as to the series with two lateral fluorine atoms (nADFBHQ), their melting and clearing point temperatures were both greatly lowered and exhibited narrower thermal range of mesophase than nABHQ. When compared nAFBHQ with nADFBHQ, it could be found that nAFBHQ had approximately the same temperatures of melting point but much higher temperatures of clearing point than their corresponding compound in nADFBHQ series. From these results it can be concluded that one lateral fluorine atom was propitious to the preparation of promising liquid crystals.

CONCLUSIONS

We have successfully synthesized and characterized two series of laterally fluorinated symmetric liquid crystal compounds. It was found that both series showed nematic phase only. And their melting point and clearing point all decreased with the number of carbon atoms in their alkoxy chains. It also can be found when compared nAFBHQ with nADFBHQ that the former had approximately the same temperatures of melting point but much higher temperatures of clearing point than their corresponding compound in nADFBHQ series.

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REFERENCES

[1] Shen, N. & Gao, A. A. (2002). *Chinese J. Synth. Chem.*, *10*, 228.
[2] Schoreder, J. P. (1980). *Mol. Cryst. Liq. Cryst.*, *61*, 229.
[3] Kossmehl, G., Gerecke, B., Harmsen, N., Schrocder, F., & Vieth, H. M. (1995). *Mol. Cryst. Liq. Cryst. Sci. Techn. Sect A: Mol Cryst. Liq. Cryst.*, *269*, 39.
[4] Kossmehl, G., Gerecke, B., Harmsen, N., Vieth, H. M., & Wolff, D. (1998). *Mol. Cryst. Liq. Cryst. Sci. Techn. Sect. A: Mol. Cryst Liq. Cryst.*, *317*, 1.

[5] Mundhe, P. G. (1999). *Asian J. Chem.*, *11*, 130.
[6] Small, A. C. & Pugh, C. (2002). *Macromolecules*, *35*, 2105.
[7] Hu, J. S., Zhang, B. Y., Sun, K., & Li, Q. Y. (2003). *Liq. Cryst.*, *30*, 1267.
[8] Michael, J. S. D. & Ronald, S. G. (1970). *J. Am. Chem. Soc.*, *92*, 1582.
[9] Guittard, F., Taffin de Givenchy, E., Geribaldi, S., & Cambon, A. (1999). *J. Fluorine Chem.*, *100*, 85.
[10] Lee, C. K., Kim, J. H., Choi, E. J., Zin, W. C., & Chien, L. C. (2001). *Liq. Cryst.*, *28*, 1749.
[11] Lee, C. K., Kwon, S. S., Zin, W. C., Kim, D. C., Slim, S. T., Song, J. H., Choi, E. J., & Chien, L. C. *Liq. Cryst.*, *30*, 415.
[12] Murthy, S. H. N. & Sadashiva, B. K. (2004). *Liq. Cryst.*, *31*, 1337.
[13] Sun, G. X., Chen, B., Tang, H., & Xu, S. Y. (2003). *J. Mater. Chem.*, *13*, 742.
[14] Sun, G., Chen, B., Tang, H., Shi, G., & Xu, S. (2004). *Liq. Cryst.*, *31*, 1151.