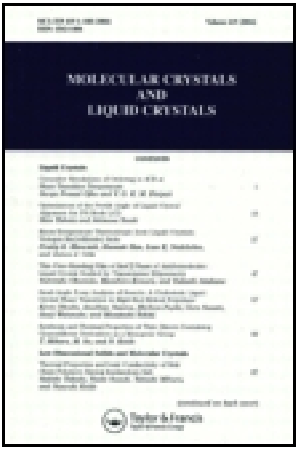

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Synthesis and Mesomorphic Properties of Fluorinated Schiff's Base Esters Containing Alkyl and Alkoxy End Groups

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Two series of fluorinated Schiff's base esters have been synthesized and characterized. Their chemical structures were identified by FTIR, ^1H NMR, and elemental analysis (EA). Their mesomorphic properties were studied by polarizing optical, microscopy (POM) and differential scanning calorimeter (DSC). It was found that most of the compounds with alkyl end group exhibited enantiotropic smectic A and nematic phase; while that with alkoxyl behaved differently, some exhibited enantiotropic smectic A and nematic phase; others exhibited monotropic smectic A and enantiotropic nematic phase or unique enantiotropic nematic phase. And for both series, their melting point and clearing point temperature decreased and thermal ranges of mesophase increased with the length of their end groups (n). Furthermore, it was also found that the increase of n was propitious to the stability of smectic phase but went against for that of nematic.

Keywords: fluorinated liquid crystal; mesomorphic property; Schiff's base; synthesis

INTRODUCTION

The mesomorphic behaviors of liquid crystals are basically dependent on their molecular structures in which a slight change in their molecular geometry may bring about considerable change in their mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules which included the effect of chemical constitution on the nematic and smectic mesophases [1]. Most of these studies have been focused on Schiff's bases ever since the discovery of 4-methoxybenzylidene-4′-butylaniline (MBBA) which exhibits a room temperature

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nematic phase [2]. Over the past few decades, many Schiff's base ester liquid crystals have been synthesized and investigated [1,3–8]. It is proved that the terminal or lateral groups, such as -F, -Cl, -CN, -CH_3, and -OCH_3, had significant influence on the liquid crystalline properties of the Schiff's base esters as well as in other liquid crystals. The introduction of terminal or lateral polar groups into the molecular system would lead to a change in molecular polarizability as well as to a change in the physical properties such as clearing point [9]. Thus, by introduction of different groups into the molecular system, new Schiff's base liquid crystals of diverse mesomorphic properties can be obtained. Previous studies [10] indicated that the replacement of one or several hydrogen atoms by fluorine confers to the resulting materials unusual and peculiar properties such as optical and chemical stability, wide mesomorphic temperature range, low melting point, low viscosity, and low conductivity. So the studies of fluorinated liquid crystals are of great importance, and many researchers [10–13] have devoted themselves into this field. And some studies have been made on fluorinated Schiff's base ester liquid crystals [3,13,14].

The aim of the present study was to synthesize and characterize two series of new fluorinated Schiff's base esters whose structure was indicated in Fig. 1, and to study their mesomorphic properties by using differential scanning calorimeter (DSC) and polarizing optical microscopy (POM). The effects of the "soft tail" with different length of alkyl or alkoxy carbon chains on the mesomorphic properties of the fluorinated Schiff's base esters were also to be examined.

EXPERIMENT

All solvents were AR quality. All starting materials were commercially available reagents and used without further purification. The

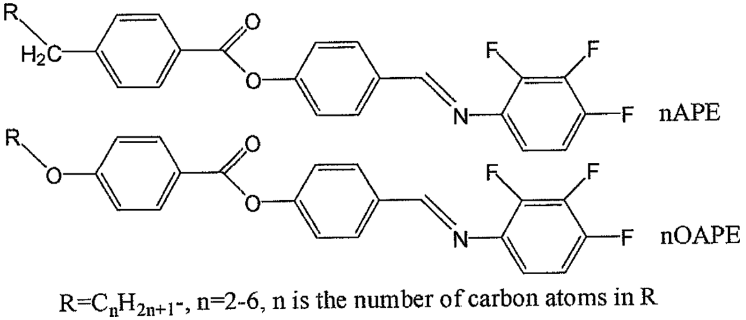

FIGURE 1 Structure of the aim compounds.

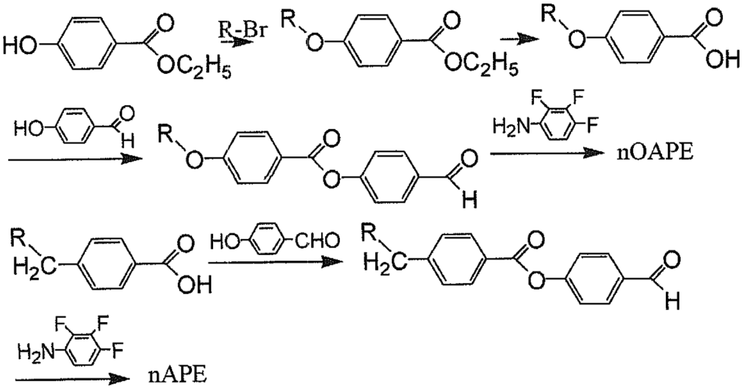

FIGURE 2 Synthetic routes of the aim compounds.

synthetic route to the aim structures was summarized in Fig. 2 and procedures were summarized below.

Infrared (IR) spectra were recorded on a Nicolet 510P instrument and ^{1}H NMR spectra on Bruker AV400 instrument in $CDCl_3$. EA measurements were carried out on a Thermo Finnigan Flash EA1112 elemental analyzer. The mesomorphic properties of the compounds and complexes were studied by an Olympus BX-51 polarizing microscope equipped wilh a Linkam Scientific LTS 350 heating/freezing stage. For 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. The smectic subphase was identified by POM observation by using homeotropic oriented liquid crystal cells.

Synthesis of 4-Hexyloxybenzoic Acid

Literature method [15] was used to prepare 4-hexyloxybenzoic acid. IR, ν/cm^{-1}: 2552–3075 (acidic -OH), 1682 (C=O), 1605, 1580, 1510 (aromatic C=C), 1251 (C-O-Ar). ^{1}H NMR ($CDC1_3$, δ ppm): 0.90–1.84 (m, 11H, alkyl protons), 4.01–4.04 (m, 2H, $J = 6.48$ Hz, -CH_2-O), 6.92–6.94 (d, 2H, $J = 7.48$ Hz, Ar-H), 8.04–8.06 (d, 2H, $J = 7.64$ Hz, Ar-H). Anal. Calcd. For $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found C, 70.32; H, 8.15.

Synthesis of 4-Hexyloxybenzoic Acid 4-Formylphenyl Ester

Dicyclohexylcarbodiimide 10.3 g (50 mmol) and N,N-dimethylaminopyridine 20 mg were added to a solution of 4-hexyloxybenzoic acid

11.1 g (50 mmol) and 4-hydroxylbenzaldehydc 6.1 g (50 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) and then evaporated at reduced pressure gave the white crystals at a yield of 76%. IR, ν/cm^{-1}: 2960, 2872, 2932, 2850 (aliphatic C-H), 1735 (C=O of ester), 1695 (C=O of aromatic aldehyde), 1605, 1579, 1510 (aromatic C=C), 1265 (C-O-Ar). ^{1}H NMR ($CDC1_3$, δ ppm): 0.92–1.85 (m, 11H, alkyl protons), 4.03–4.08 (m, 2H, $J = 6.30$ Hz, -CH_2-O), 6.97–7.00 (d, 2H, $J = 8.31$ Hz, Hz, Ar-H), 7.39–7.42 (d, 2H, $J = 7.98$ Hz, Ar-H), 7.96–7.98 (d, 2H, $J = 7.92$ Hz, Ar-H), 8.13–8.16 (d, 2H, $J = 8.34$ Hz Ar-H), 10.03 (s, H, Ar-CHO). Anal. Calcd. For $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found C, 73.46; H, 6.81.

Synthesis of Aim Compound 6OAPE

Several drops of acetic acid, 4-hexyloxybenzoic acid 4-formylphenyl ester 3.26 g (10 mmol) and 2,3,4-trifluorophenylaimne 1.47 g (10 mmol) was dissolved in 100 mL of absolute ethanol. The mixture was stirred under refluxing for 7 h, then cooled and left unstirred overnight. The crude product was collected and recrystallized from ethanol to give white crystals of the aim compound 6OAPE at an 82% yield. IR, ν/cm^{-1}: 2960, 2936, 2863 (CH_3-, -CH_2-), 1731 (C=O), 1628 (C=N), 1605, 1502 (aromatic C=C), 1264 (C-O-Ar). ^{1}H NMR ($CDC1_3$, δ ppm): 0.94–1.90 (m, 11H, alkyl protons), 4.07–4.10 (d, 2H, $J = 6.52$ Hz, -CH_2-O), 6.96–6.99 (d, H, $J = 10.36$ Hz, Ar-H), 7.01–7.03 (d, 3H, $J = 8.76$ Hz, Ar-H), 7.38–7.40 (d, 2H, $J = 8.36$ Hz, Ar-H), 8.02–8.04 (d, 2H, $J = 8.28$ Hz, Ar-H), 8.20–8.17 (d, 2H, $J = 8.72$ Hz, Ar-H), 8.55 (s, H, CH=N). Anal. Calcd. For $C_{26}H_{24}F_3NO_3$: C, 68.56; H, 5.31; N, 3.08. Found C, 68.67; H, 5.33, N, 3.09.

Synthesis of 4-Heptylbenzoic Acid 4-Formylphenyl Ester

Same synthetic procedure to 4-hexyloxybenzoic acid 4-formyl-phenyl ester was used to prepare 4-heptylbenzoic acid 4-formylphenyl ester that gave the white crystals at a yield of 82%. IR, ν/cm^{1}: 2957, 2922, 2850 (CH_3-, -CH_2-), 1738 (C=O of ester), 1696 (C=O of aromatic aldehyde), 1600, 1500 (aromatic C=C), 1262 (C-O-Ar). ^{1}H NMR ($CDCl_3$, δ ppm): 0.87–1.68 (m, 13H, alkyl protons), 2.69–2.73 (m, 2H, $J = 7.84$ Hz, Ar-CH_2), 7.32–7.34 (d, 2H, $J = 7.72$ Hz, Ar-H), 7.40–7.42 (d, 2H, $J = 8.12$ Hz, Ar-H), 7.96–7.98 (d, 2H, $J = 7.36$ Hz, Ar-H), 8.10–8.12 (d, 2H, $J = 7.76\,\mathrm{Hz}$, Ar-H), 10.03 (s, H, Ar-CHO). Anal. Calcd. For $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found C, 77.69; H, 7.48.

Synthesis of 6APE

The synthetic procedure was same to 6OAPE and the white crystals were got at a yield of 86%. IR, ν/cm^{-1}: 2960, 2932, 2854 (CH_3-, -CH_2-), 1735 (C=O), 1627 (C=N), 1601, 1502 (aromatic C=C). ^1H NMR ($CDCl_3$, δ ppm): 0.87–1.66 (m, 13H, alkyl protons), 2.69–2.74 (m, 2H, $J = 7.40\,\mathrm{Hz}$, Ar-CH), 6.90–7.03 (m, 2H, Ar-H), 7.32–7.37 (m, 4H, $J = 7.85\,\mathrm{Hz}$, Ar-H), 7.98–8.01 (d, 2H, $J = 8.16\,\mathrm{Hz}$, Ar-H), 8.11–8.14 (d, 2H, $J = 7.74\,\mathrm{Hz}$, Ar-H), 8.52 (s, H, CH=N). Anal. Calcd. For $C_{27}H_{26}F_3NO_2$: C, 71.51; H, 5.78; N, 3.09. Found C, 71.59; H, 5.79, N, 3.09.

TABLE 1 Phase Transition Temperature and Associated Enthalpy Changes of nAPE and nOAPE

Compound	Phase transition temperature (°C) and enthalpy changes (kJ/mol, in parentheses)*
6APE	$\mathrm{Cr}\underset{45}{\overset{81(52.0)}{\rightleftharpoons}}\mathrm{S_A}\underset{163}{\overset{165(1.9)}{\rightleftharpoons}}\mathrm{N}\underset{172}{\overset{173(0.3)}{\rightleftharpoons}}\mathrm{I}$
5APE	$\mathrm{Cr}\underset{39}{\overset{75(33.6)}{\rightleftharpoons}}\mathrm{S_A}\underset{156}{\overset{159(1.8)}{\rightleftharpoons}}\mathrm{N}\underset{176}{\overset{178(0.4)}{\rightleftharpoons}}\mathrm{I}$
4APE	$\mathrm{Cr}\underset{46}{\overset{82(28.6)}{\rightleftharpoons}}\mathrm{S_A}\underset{151}{\overset{155(1.1)}{\rightleftharpoons}}\mathrm{N}\underset{180}{\overset{182(0.5)}{\rightleftharpoons}}\mathrm{I}$
3APE	$\mathrm{Cr}\underset{46}{\overset{101(25.8)}{\rightleftharpoons}}\mathrm{S_A}\underset{142}{\overset{145(1.3)}{\rightleftharpoons}}\mathrm{N}\underset{178}{\overset{180(0.4)}{\rightleftharpoons}}\mathrm{I}$
2APE	$\mathrm{Cr}\underset{62}{\overset{114(22.7)}{\rightleftharpoons}}\mathrm{S_A}\underset{124}{\overset{126(0.5)}{\rightleftharpoons}}\mathrm{N}\underset{186}{\overset{189(0.5)}{\rightleftharpoons}}\mathrm{I}$
6OAPE	$\mathrm{Cr}\underset{43}{\overset{77(24.8)}{\rightleftharpoons}}\mathrm{S_A}\underset{167}{\overset{169(0.5)}{\rightleftharpoons}}\mathrm{N}\underset{197}{\overset{198(0.4)}{\rightleftharpoons}}\mathrm{I}$
5OAPE	$\mathrm{Cr}\underset{51}{\overset{91(29.8)}{\rightleftharpoons}}\mathrm{S_A}\underset{159}{\overset{161(0.4)}{\rightleftharpoons}}\mathrm{N}\underset{201}{\overset{203(0.5)}{\rightleftharpoons}}\mathrm{I}$
4OAPE	$\mathrm{Cr}\underset{51}{\overset{102(28.9)}{\rightleftharpoons}}\mathrm{S_A}\underset{140}{\overset{142(0.4)}{\rightleftharpoons}}\mathrm{N}\underset{209}{\overset{212(0.8)}{\rightleftharpoons}}\mathrm{I}$
3OAPE	$\mathrm{Cr}\underset{80}{\overset{120(33.0)}{\rightleftharpoons}}\mathrm{S_A}\underset{120(0.2)}{\rightleftharpoons}\mathrm{N}\underset{216}{\overset{218(0.7)}{\rightleftharpoons}}\mathrm{I}$
2OAPE	$\mathrm{Cr}\underset{102}{\overset{134(30.8)}{\rightleftharpoons}}\mathrm{N}\underset{233}{\overset{235(0.5)}{\rightleftharpoons}}\mathrm{I}$

*Cr: crystal; S_A: smectic A; N: nematic; I: isotropic.

RESULTS AND DISCUSSION

The liquid crystalline properties of the two series of aim compounds were studied by DSC and POM. Their optical textures were shown in Fig. 3. Their phase variants, transition temperatures, and associated enthalpy were listed in Table 1 and their phase transition data in heating scan were represented graphically in Fig. 4.

All the members of the two series were mesomorphic. Series nAPE (n = 2–6) exhibited similarly mesomorphic properties, they all showed enantiotropic smectic A and nematic phase with no respect to the length change of their alkyl chains, which indicated that the phase variant of this series were mainly depended on their core structure. As to series nOAPE, 6OAPE, 5OAPE, and 4OAPE showed enantiotropic smectic A and nematic phase, but 3OAPE exhibited a monotropic

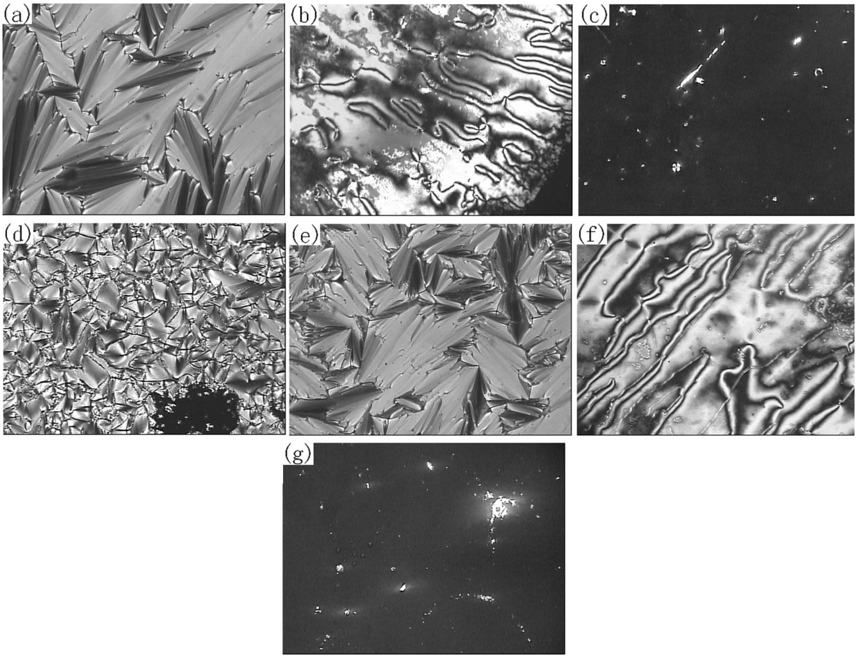

FIGURE 3 Optical textures of the aim compounds on cooling cycle. (a) Fan-shaped. texture 6APE. 162 °C, × 200: (b) Schlieren texture. 6APE. 169 °C. × 200: (c) Black field. 6APE. 160 °C homeotropic oriented. × 200: (d) Focal conic texture 6APE. 149 °C. homeotropic oriented. × 100: (e) Fan-shaped texture. 6OAPE. 163 °C × 100: (f) Schlieren texture. 6OAPE. 192 °C × 100: (g) Black field. 6OAPE. 154 °C. homeotropic oriented × 100.

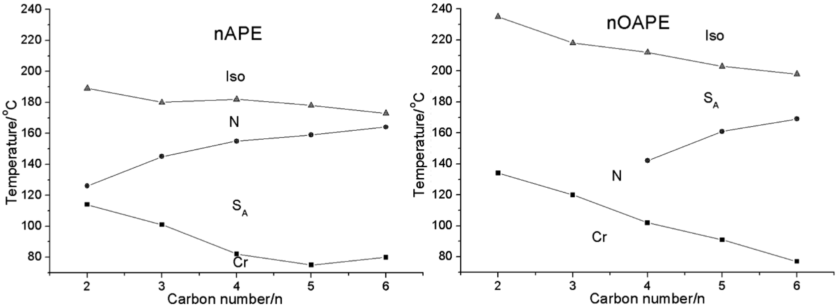

FIGURE 4 Effect of carbon atoms in the end groups on the phase transition properties.

smectic A and enantiotropic nematic phase, as for 2OAPE, only an enantiotropic nematic phase can be observed, which indicated that the length of alkoxy "tail" had more effect on the liquid crystal properties than of alkyl "tail" in these studied compounds. The typical optical textures of the two series were listed in Fig. 3.

The results shown in Fig. 4 revealed that series nAPE showed little and series nOAPE almost showed no even–odd effects. And on the whole, the melting point and clearing point temperature of both series decreased with the number of carbon atoms (n) in their end groups. These results also testified that the core structure of these studied compounds predominated in shaping their liquid crystal properties as compared to their alkyl or alkoxy chains which is considered the main reason of the even–odd effects. Furthermore, with the increase of n, the thermal range of smectic phase of both series broadened; and at the same time, their thermal range of nematic phase narrowed. When compared nAPE with nOAPE, it was found that the melting point and clearing point temperature of nAPE always lower than their corresponding compounds of nOAPE.

CONCLUSION

We have successfully synthesized and characterized two series of fluorinated Schiff's base ester liquid crystals. It was found that most of the compounds with alkyl end group exhibited enantiotropic smectic A and nematic phase; while that with alkoxyl behaved differently, some exhibited enantiotropic smectic A and nematic phase; others exhibited monotropic smectic A and enantiotropic nematic phase or unique enantiotropic nematic phase. And for both series their melting point and clearing point temperature decreased and thermal ranges of mesophase increased with the length of their end groups. Furthermore, it was also found that the increase of n was propitious to the stability of smectic phase but went against for that of nematic. Additionally, it was also found that the melting point and clearing point temperature of nAPE always lower than their corresponding compounds of nOAPE.

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