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Materials

Synthesis and mesomorphic properties of fluorinated Schiff's base liquid crystals containing vinyl end groups

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Abstract: Three kinds of fluorinated Schiff's base esters, 4-allyloxy-2-X-6-X-benzoic acid 4-[(2, 3, 4-trifluorophenylimino)-methyl]phenyl ester, where X=H or F, were synthesized and characterized. Their chemical structures were identified by Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance (^{1}H NMR). Their mesomorphic properties were studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). It was found that all the three compounds exhibited enantiotropic nematic phases only. And their clearing point temperature and thermal range of mesophase decreased with the number of fluorine atoms on the rigid core of the compounds; while their melting point temperature showed no distinct regularity.

Key words: synthesis; Schiff's base; fluorinated liquid crystal; vinyl end group

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1. Introduction

Schiff's base compounds are widely used in many fields, such as catalytic chemistry [1], organometallic chemistry [2], biochemistry [3], and photochemistry [4]. In 1969, Kelker and coworkers [5] reported for the first time that the Schiff's base liquid crystal compound 4-methoxybenzylidene-4'-butylaniline (MBBA), exhibited a room temperature nematic phase. Since then, Schiff's bases, especially Schiff's base esters have attracted much attention of liquid crystal researches. Over the past few decades, lots of low molar mass Schiff's base esters have been synthesized and investigated extensively for liquid crystalline applications [6-11]. It has been found that the terminal or lateral groups, such as –F, –Cl, –CN, –CH_3, and –OCH_3, had a significant influence on the liquid crystalline properties of the Schiff's base esters as well as other liquid crystals. The introduction of terminal or lateral polar groups into the molecular system will lead to a change in molecular polarizability as well to a change in the physical properties such as the clearing point [12]. Thus, by introduction of different groups, new Schiff's base liquid crystals with diverse mesomorphic properties can be obtained. Previous studies [13] have indicated that the replacement of one or several hydrogen atoms by fluorine confers to the resulting material unusual and peculiar properties, such as optical and chemical stability, wide mesomorphic temperature range, low melting point, low viscosity, and low conductivity. Therefore, the studies of fluorinated liquid crystals are of great importance, and many researchers [13-15] have devoted themselves to this field. And some studies have been made on fluorinated Schiff's base ester liquid crystals [6, 16]. However, to the best of one's knowledge, no study about Schiff's base ester liquid crystals that have an unsaturated carbon chain has been reported.

In this communication, the synthesis, characterization, and mesomorphic properties of three kinds of new fluorinated Schiff's base ester liquid crystals are reported, whose structure is indicated in Fig. 1. The effects of the lateral fluorinated ring on the mesomorphic properties with different lengths of unsaturated carbon chains are currently being examined. These results will be reported elsewhere.

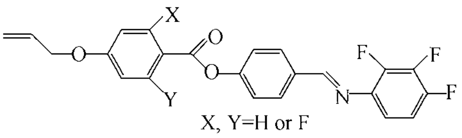

Fig. 1. Structure of the aim compounds.

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2. Experimental

All solvents were AR quality. All starting materials were commercially available reagents and used without further purification. The synthetic route of the aim structures is summarized in Fig. 2 and the procedures are summarized below.

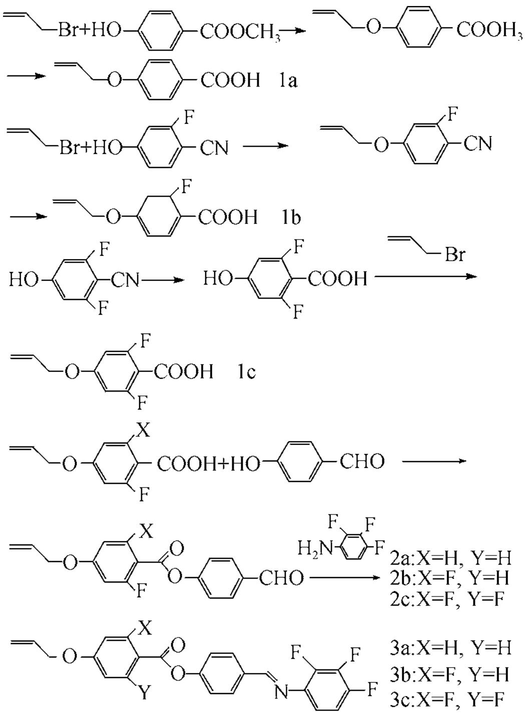

Fig. 2. Synthetic route of the aim compounds.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 510P instrument. ^{1}H nuclear magnetic resonance (^{1}H NMR) (300 MHz) spectra were obtained with a Bruker DMX-300 spectrometer, using CDCl$_3$ as solvent. The thermal phase transition temperature determinations and optical investigation of the liquid crystalline phase were carried out on the samples between ordinary glass slides, using an Olympus BX-51 polarizing microscope equipped with a Linkam Scientific LTS 350 heating/freezing stage. Differential scanning calorimeter (DSC) thermograms were obtained on a Perkin-Elmer DSC-6 system using 2-5 mg samples in sample pans at a scan rate of 10°C/min when heating and 5°C/min when cooling. A slow purge of nitrogen gas (5 mL/min) was maintained to prevent any possible oxidative degradation.

2.1. Synthesis of 4-allyloxybenzoic acid (1a)

The method in Ref. [17] was used to prepare 1a, and the yield was 85%. IR, ν/cm^{-1}: 2560-3088 (acidic −OH), 1680 (C=O), 1605, 1508 (aromatic C=C), 1251 (C−O−Ar). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.62 (d, 2H, −CH$_2$−O), 5.33 (d, H, HCH=), 5.44 (d, H, HCH=), 6.07 (m, H, =CH−), 6.96 (d, 2H, Ar−H), 8.06 (d, 2H, Ar−H).

2.2. Synthesis of 4-allyloxy-2-fluorobenzoic acid (1b)

The mixture of 2-fluoro-4-hydroxybenzonitrile 13.7 g (0.1 mol), NaOH 4.4 g (0.11 mol), allyl bromide 13.3 g (0.11 mol), and butanone 100 mL were heated to 60°C and stirred for 10 h. After cooling, the insolubles were filtrated off and the butanone in the filtrate removed through evaporation. The residues were mixed with 80 mL of 10wt% NaOH water solution, refluxed for 24 h, and then acidified with hydrochloric acid. The precipitate was collected by suction filtration, and recrystallized from ethanol. The yield was 72%. IR, ν/cm^{-1}: 2556-3083 (acidic −OH), 1688 (C=O), 1630 (C=C), 1508 (aromatic C=C), 1242 (C−O−Ar). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.60 (d, 2H, −CH$_2$−O), 5.34 (d, H, HCH=), 5.44 (d, H, HCH=), 6.04 (m, H, =CH−), 6.67 (d, H, Ar−H), 6.76 (d, H, Ar−H), 7.98 (m, H, Ar−H).

2.3. Synthesis of 4-allyloxy-2, 6-difluorobenzoic acid (1c)

2, 6-difluoro-4-hydroxybenzonitrile, 15.5 g (0.1 mol), was added to 100 mL of 10wt% NaOH water solution, refluxed for 24 h, and then acidified by hydrochloric acid. The precipitate was 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, 6.85 g (25 mmol), in ethanol (200 mL), and the mixture heated under reflux for 1 h. Allyl bromide, 9.1 g (75 mmol), was added and the mixture was refluxed for a further 12 h. KOH water solution (100 mL, 10wt%) was added and reflux continued for 2 h. After cooling, the mixture was acidified with hydrochloric acid and filtered. The crude product was recrystallized from ethanol giving a 70% yield of 1c. IR, ν/cm^{-1}: 2552-3118 (acidic −OH), 1692 (C=O), 1632 (C=C stretching), 1580 (aromatic C=C), 1247 (C−O−Ar), 1052 (C−F). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.59 (d, 2H, −CH$_2$−O), 5.37 (d, H, HCH=), 5.44 (d, H, HCH=), 6.03 (m, H, =CH−), 6.54 (d, H, Ar−H).

2.4. Synthesis of 4-allyloxybenzoic acid 4-formylphenyl ester (2a)

Dicyclohexylcarbodiimide 10.3 g (50 mmol) and *N*, *N*-dimethylaminopyridine 20 mg were added to a solution of 1a 8.9 g (50 mmol) and 4-hydroxybenzaldehyde 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). IR, ν/cm^{-1}: 2926, 2846 (–CH$_2$–), 1731 (C=O of ester), 1695 (C=O of aromatic aldehyde), 1605, 1515 (aromatic C=C), 1216 (C–O–Ar). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.64-4.65 (d, 2H, –CH$_2$–O), 5.33-5.36 (d, H, HCH=), 5.43-5.47 (d, H, HCH=), 6.05-6.12 (m, H, =CH–), 7.00-7.02 (d, 2H, Ar–H), 7.39-7.41 (d, 2H, Ar–H), 7.96-7.98 (d, 2H, Ar–H), 8.14-8.16 (d, 2H, Ar–H), 10.02 (s, H, Ar–CHO).

2.5. Synthesis of 4-allyloxy-2-fluorobenzoic acid 4-formylphenyl ester (2b)

The synthetic procedure was similar to 2a. IR, ν/cm^{-1}: 2926, 2840 (–CH$_2$–), 1743 (C=O of ester), 1697 (C=O of aromatic aldehyde), 1598, 1502 (aromatic C=C), 1213 (C–O–Ar). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.62-4.63 (d, 2H, –CH$_2$–O), 5.35-5.38 (d, H, HCH=), 5.43-5.47 (d, H, HCH=), 6.00-6.09 (m, H, =CH–), 6.71-6.75 (d, H, Ar–H), 6.81-6.83 (d, H, Ar–H), 7.40-7.42 (d, 2H, Ar–H), 7.95-7.97 (d, 2H, Ar–H), 8.03-8.07 (d, 2H, Ar–H), 10.02 (s, H, Ar–CHO).

2.6. Synthesis of 4-allyloxy-2, 6-difluorobenzoic acid 4-formylphenyl ester (2c)

The synthetic procedure was similar to 2a. IR, ν/cm^{-1}: 2930, 2841 (–CH$_2$–), 1740 (C=O of ester), 1695 (C=O of aromatic aldehyde), 1600, 1502 (aromatic C=C), 1220 (C–O–Ar). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.53-4.61 (d, 2H, –CH$_2$–O), 5.36-5.39 (d, H, HCH=), 5.42-5.47 (d, H, HCH=), 5.98-6.03 (m, H, =CH–), 6.56-6.59 (d, 2H, Ar–H), 7.42-7.45 (d, 2H, Ar–H), 7.96-7.98 (d, 2H, Ar–H), 10.03 (s, H, Ar–CHO).

2.7. Synthesis of 4-allyloxybenzoic acid 4-[(2,3,4-trifluorophenylimino)methyl]phenyl ester (3a)

1b 2.82 g (10 mmol) and 2, 3, 4-trifluorophenylamine 1.47 g (10 mmol) were 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 compound 3a at an 82% yield. IR, ν/cm^{-1}: 2928, 2863 (–CH$_2$–), 1725 (C=O), 1623 (C=N), 1604, 1505 (aromatic C=C), 1217 (C–O–Ar), 1046 (C–F). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.64 (d, 2H, –CH$_2$–O), 5.33-5.36 (d, H, HCH=), 5.43-5.47 (d, H, HCH=), 6.04-6.10 (m, H, =CH–), 6.44-6.45 (d, H, Ar–H), 6.75-6.77 (d, H, Ar–H), 7.00-7.03 (m, 2H, Ar–H), 7.36-7.41 (d, 4H, Ar–H), 7.96-8.00 (d, 2H, Ar–H), 8.14-8.16 (d, 2H, Ar–H), 8.51 (s, H, –CH=N).

2.8. Synthesis of 4-allyloxy-2-fluorobenzoic acid 4-[(2,3,4-trifluorophenylimino)methyl] phenyl ester (3b)

The synthetic procedure was similar to 3a. IR, ν/cm^{-1}: 2928, 2867 (–CH$_2$–), 1737 (C=O), 1624 (C=N), 1602, 1509 (aromatic C=C), 1208 (C–O–Ar), 1048 (C–F). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.62-4.63 (d, 2H, –CH$_2$–O), 5.38-5.43 (d, H, HCH=), 5.43-5.47 (d, H, HCH=), 6.03-6.07 (m, H, =CH–), 6.71-6.99 (m, 4H, Ar–H), 7.35-7.37 (d, 2H, Ar–H), 7.97-7.99 (d, 2H, Ar–H), 8.04-8.08 (m, H, Ar–H), 8.51 (s, H, –CH=N).

2.9. Synthesis of 4-allyloxy-2,6-difluorobenzoic acid 4-[(2,3,4-trifluorophenylimino) methyl]phenyl ester (3c)

The synthetic procedure was similar to 3a. IR, ν/cm^{-1}: 2930, 2850 (–CH$_2$–), 1727 (C=O), 1640 (C=N), 1600, 1505 (aromatic C=C), 1220 (C–O–Ar), 1045 (C–F). ^{1}H NMR (CDCl$_3$, 300 MHz): 4.60-4.61 (d, 2H, –CH$_2$–O), 5.36-5.39 (d, H, HCH=), 5.42-5.46 (d, H, HCH=), 6.00-6.06 (m, H, =CH–), 6.56-6.59 (m, H, Ar–H), 6.87-6.91 (m, H, Ar–H), 6.93-6.97 (m, H, Ar–H), 7.37-7.39 (d, 4H, Ar–H), 7.96-8.00 (d, 2H, Ar–H), 8.51 (s, H, –CH=N).

3. Results and discussion

DSC measurements and polarized optical microscopy (POM) observations performed on 3a, 3b, and 3c revealed that these compounds, containing allyloxy end groups and different numbers of fluorine atoms in their rigid core, formed only the enantiotropic nematic phase. Fig. 3 shows the polarizing optical micrograph of the nematic phases of compounds 3a, 3b, and 3c, formed from the isotropic liquid in the cooling process. Small droplets, followed on further cooling by the formation of Schlieren textures, typical of the nematic phase, were clearly observed.

The formation of the nematic phases of 3a, 3b, and 3c were also evidenced by DSC. Fig. 4 shows the DSC curves for compound 3a. When the crystalline sample of 3a is heated, an endothermic peak is observed at 130°C to give the nematic phase. On further heating, the transition from nematic phase to the isotropic liquid is observed at 212°C. When the isotropic liquid is cooled, the transition into a nematic phase is observed at approximately 206°C. The nematic phase crystallizes at 100°C. The trace is reproducible. Compound 3b and 3c exhibit similar DSC properties. The phase transition temperature and associated enthalpy changes of all the three compounds are listed in Table 1.

Data from DSC in Table 1 shows that all the three compounds exhibit only nematic phases. Their clearing point temperature and thermal range of mesophase decreases with the number of fluorine atoms on the rigid core, which can be attributed to the changes in slenderness ratio of these compounds. In these compounds, the difference in slenderness ratio mainly lies on the width of the ring of benzoic acid. With the data of bond lengths and bond angles of C–C, C=C, C–H and C–F bonds, it can be figured out that the widths of the benzoic acid moieties are 0.437 nm for 3a, 0.456 nm for 3b, for 3b, and 0.475 nm for 3c. The increased width of the benzoic acid moieties decreases the slenderness ratio of the compounds, which is usually considered a disadvantageous factor for the formation of mesophase. An interesting phenomenon is that compound 3b, which possesses of an asymmetric benzoic acid moiety, exhibits the highest melting point temperature among the three compounds.

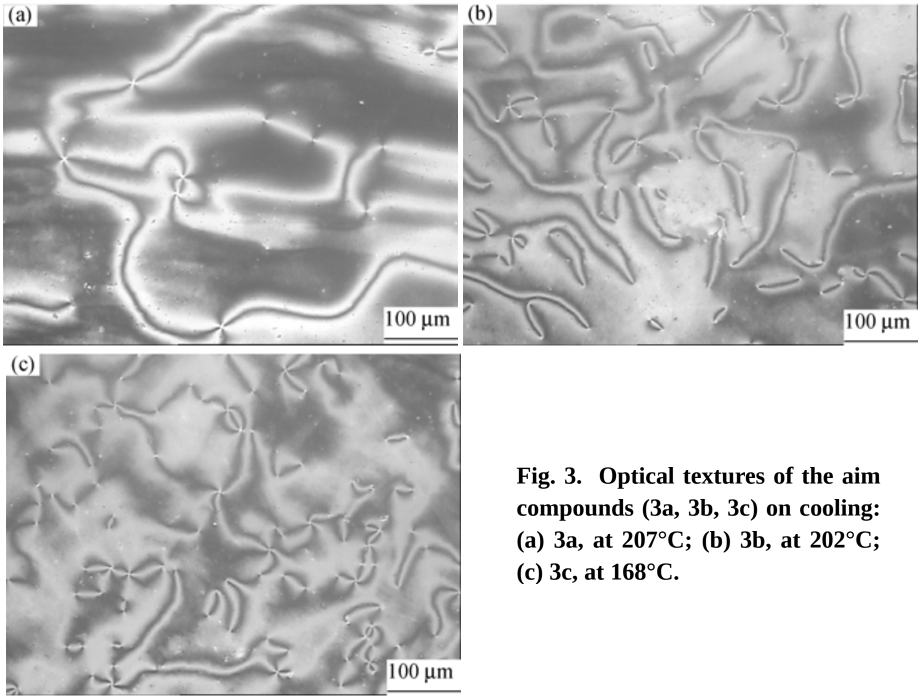

Fig. 3. Optical textures of the aim compounds (3a, 3b, 3c) on cooling: (a) 3a, at 207°C; (b) 3b, at 202°C; (c) 3c, at 168°C.

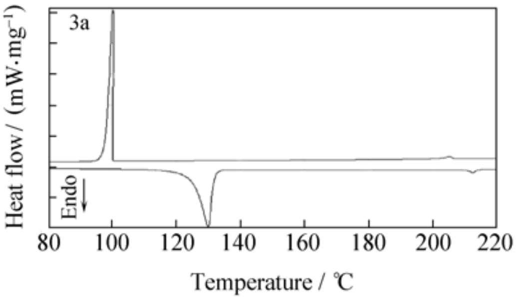

Fig. 4. DSC spectra of compound 3a.

Table 1. Phase transition temperature and associated enthalpy changes of compound 3

Compound	Phase transition temperature (°C) and enthalpy changes (J/g, in parentheses)
3a	$\mathrm{Cr} \underset{100}{\overset{130(72.29)}{\rightleftharpoons}} \mathrm{N} \underset{206}{\overset{212(1.18)}{\rightleftharpoons}} \mathrm{I}$
3b	$\mathrm{Cr} \underset{103}{\overset{143(105.85)}{\rightleftharpoons}} \mathrm{N} \underset{196}{\overset{201(1.38)}{\rightleftharpoons}} \mathrm{I}$
3c	$\mathrm{Cr} \underset{75}{\overset{121(89.54)}{\rightleftharpoons}} \mathrm{N} \underset{164}{\overset{167(0.99)}{\rightleftharpoons}} \mathrm{I}$

Note: Cr— crystal; N— nematic; I— isotropic.

4. Conclusions

Three kinds of fluorinated Schiff's base ester liquid crystals have been successfully synthesized and characterized. It is found that all the three compounds exhibit nematic phases only. Their clearing point temperature and thermal range of mesophase decreases with the number of fluorine atoms on the rigid core; while their melting point temperature shows no regularity.

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