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# Synthesis and mesomorphic properties of cholesteryl *p*-polyfluoroalkoxy-*m*-nitrobenzoate

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**Abstract**

Homologous cholesteryl *p*-polyfluoroalkoxy-*m*-nitrobenzoate were synthesized and their phase transition behaviours were studied. Due to the activation of chlorine atom in aromatic ring by introducing *o*-nitro and *p*-trifluoromethyl groups, the fluoroalkoxylation can directly be processed using potassium carbonate as base. 

*Keywords:* Fluoroalkylation; Liquid crystals

## 1. Introduction

Owing to their excellent switching characteristics, ferroelectric liquid crystals have been intensely studied in recent years. These ferroelectric liquid crystalline (FLC) compounds consist of one or more chiral centres. Steriod, as we know, is a cheap chiral resource. Vill et al. reported that steroidal liquid crystals containing a long alkyl chain, e.g. cholesteryl *p*-hexdecyl benzoate and cholesteryl *p*-hexdecycloxyphenyl carbonate display a monotropic ferroelectric phase [1]. We also know liquid crystals containing highly fluorinated alkyl or alkoxy chain as terminal groups are intended to form smectic C phase and increase its temperature range [2–4]. So cholesteryl *p*-perfluoroalkyl benzoate and cholesteryl *p*-perfluoroalkyl phenyl carbonate were synthesized by our group [5], but no ferroelectric phase was observed. Janulis et al. have shown the influence of $(CH_2)_n$ as a spacer between the fluorinated tail and the rigid core on the nature of the mesomorphic phase notably for obtaining a smectic C phase [6]. So the synthesis of cholesteryl *p*-polyfluoroalkoxy benzoate was desired.

There are various methods which have been developed to synthesize fluoroalkyl aryl ethers [7]. Direct aromatic nucleophilic fluoroalkoxylation was used in some methods. These reactions can be carried out for activated aryl and heteroaryl halides [8–10]. Trifluoromethyl and nitro groups were considered as the activating substituents in aromatics and trifluromethyl benzene can be converted into benzoic acid easily. The direct aromatic nucleophilic fluoroalkoxylation can be carried out under the condition of weak base such as potassium carbonate. Strong base such as sodium hydride or potassium hydroxide is not needed.

In this paper, we describe a convenient method to prepare cholesteryl *p*-polyfluoroxy-*m*-nitrobenzoic acid using commercially available reagents and discuss the mesomorphic properties of these liquid crystals.

## 2. Results and discussion

In general, it is difficult to obtain 1H,1H-perfluoroalkoxybenzene by the direct etherification of the alcohols due to the activation of chlorine atom in aromatic ring. The fluoroalkoxylation can easily be carried out by introducing *o*-nitro and *p*-trifluoromethyl groups, using potassium carbonate as base.

Transition temperatures of liquid crystals were measured by DSC and phase identification was made by comparing the observed textures with those in the literature [11,12]. The results were summarized in Table 1.

From the observation of the mesomorphic properties of these compounds, some interesting results have been obtained. First, the clearing points were increased with increasing length of fluorocarbon chains, but the melting points were decreased with increasing length of fluorocarbon carbons. As a result of the two opposite trends,

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Table 1
The transition temperatures of the synthesized compounds[a]

| Compounds | $n$ | Transition temperature (°C) |
|---|---|---|
| **4a** | 2 | Cr 179.0 Ch 183.8 I 179.9 Ch 121.9 Recr |
| **4b** | 4 | Cr 178.0 Ch 184.4 I 176.5 Ch 155.8 SmA 137.3 Recr |
| **4c** | 8 | Cr 164.3 SmA 209.0 I 194.1 SmA 131.9 Recr |

[a] Cr: crystal; Ch: cholesteric phase; SmA: smectic A phase; I: isotropic liquid; Recr: recrystallization.

mesomorphic range becomes wider when the length of polyfluoroalkoxy chain increases. Secondly, the sample with $n = 2$ shows only a enantiotropic Ch phase, while the sample with $n = 4$ exhibits enantiotropic Ch phase and monotropic SmA phase. For the sample with $n = 8$, no Ch phase but enantiotropic SmA phase was observed. So it is worth noting that in these cases, the introduction of fluorine atoms induces the suppression of cholesteric phase and increases the thermal stability of the mesophases and temperature range of the smectic phase [13,14]. It is ascribed to the influence of introduction of perfluoroalkyl chain as there is a strong attractive interaction between perfluoroalkyl chains. When the length of perfluoroakyl chain is short, the lateral attractive interaction is weaker than that between terminal chains, which favours the formation of the Ch phase. With increasing length of perfluoroalkyl chain, the lateral attractive interaction which favours the stacking of molecules in the layer increases. Thus it is obvious that the smectic phase will appear.

Some high ordered smectic phases, such as SmB and SmE phases, which are observed in the cholesteryl *p*-perfluoroalkyl benzoate, were not observed in these compounds. Due to the perfluoroalkyl chains being more rigid than the corresponding alkyl chain, cholesteryl *p*-perfluoroalkyl benzoate are more rigid than the compounds with a soft –$OCH_2$– spacer which exhibit only Ch and SmA phases.

But it is regrettable that the $SmC^*$ phase which was desired was not observed in these compounds.

## 3. Experimental details

### 3.1. General techniques

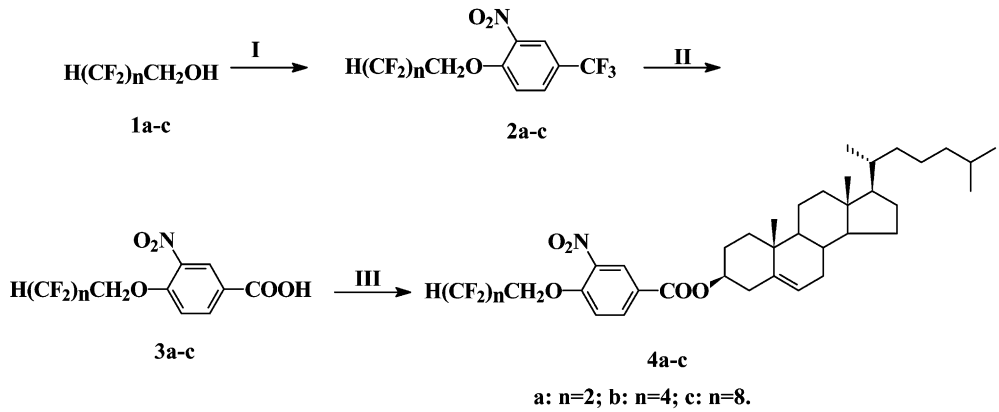
The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer using solid KBr pellets or liquid films. $^1$H NMR spectra with TMS as internal standard and $^{19}$F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Bruker300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q (90 MHz). For $^{19}$F NMR spectra, the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope. The phase transition temperatures of the target compounds were measured visually by optical polarizing microscope (Olympus PM-6) fitted with a heating stage (Metter FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min$^{-1}$). The transition temperatures reported in this paper were the peak values of the transition on DSC traces.

### 3.2. Synthesis

The mesogens are synthesized in four steps according to the following (Scheme 1).

#### 3.2.1. Preparation of p-2,2,3,3-tetrafluoropropoxy-m-nitro-trifluoromethylbenzene (*2a*)

To 4.554 g (0.033 mol) of potassium carbonate in a dried flask purged with nitrogen, a solution of 4.356 g (0.033 mol) 2,2,3,3-tetrafluoropropanol (**1a**) in dried DMF (30 ml) was added slowly at room temperature. Then 6.765 g (0.03 mol) *p*-chloro-*m*-nitro-trifluoromethylbenzene was added at room temperature. The reaction mixture was stirred for 10 h at 120°C, poured into 100 ml of diluted HCl after cooling and extracted by diethyl ether. The ether extracts are washed




Reagents and Conditions: **I**. *p*-chloro-*m*-trifluoromethylbenzene, $K_2CO_3$, DMF. **II**. fuming $H_2SO_4$. **III**. cholesterol, DCC, DMAP, THF.

Scheme 1.

neutral with brine, dried over anhydrous $MgSO_4$ and the solvent distilled off in vacuo. Purification was possible by column chromatography on silica gel using petroleum ether–ethyl acetate (20:1) as the eluent to give (**2a**) as a liquid 8.215 g, yield 85%.$^1$H NMR ($CDCl_3$) $\delta$ (ppm): 4.95 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 6.45 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.63 (d, 1H, $J = 9$ Hz, ArH), 8.33 (d, 1H, $J = 9$ Hz, ArH), 8.52 (s, 1H, ArH). $^{19}$F NMR ($CDCl_3$) $\delta$ (ppm): −13.7 (s, 3F, $CF_3$), 49 (m, 2F, $CF_2$), 63.9 (dtt, $J_1 = 56$ Hz, $J_2 = 28$ Hz, $J_3 = 4$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 321 ($M^+$, 44.87), 191 (*m*-$NO_2C_6H_3CF_3^+$, 100.00).

*p*-2,2,3,3,4,4,5,5-Octfluoropentoxy-*m*-nitro-trifluoromethylbenzene (**2b**): Yield 83%. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 4.90 (t, 2H, J=14Hz, $OCH_2CF_2$), 6.30 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.48 (d, 1H, $J = 9$ Hz, ArH), 8.12 (d, 1H, $J = 9$ Hz, ArH), 8.40 (s, 1H, ArH). $^{19}$F NMR ($CDCl_3$) $\delta$ (ppm): −14.7 (s, 3F, $CF_3$), 42.8 (m, 2F, $CF_2$), 48.5 (m, 2F, $CF_2$), 53.3 (m, 2F, $CF_2$), 60.8 (d, $J_1 = 56$ Hz, $HCF_2$). MS (*m*/*z*): 421 ($M^+$, 30.78), 191 (*m*-$NO_2C_6H_3CF_3^+$, 100.00).

*p*-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecfluorononoxy-*m*-nitro-trifluoromethylbenzene (**2c**): Yield 75%. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 4.76 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 6.26 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.38 (d, 1H, $J = 9$ Hz, ArH), 7.95 (d, 1H, $J = 9$ Hz, ArH), 8.25 (s, 1H, ArH). $^{19}$F NMR ($CDCl_3$) $\delta$ (ppm): −15.5 (s, 3F, $CF_3$), 41.4 (m, 2F, $CF_2$), 44.2 (m, 8F, $(CF_2)_4$), 45.5 (m, 2F, $CF_2$), 51.5 (m, 2F, $CF_2$), 59.0 (d, $J_1 = 56$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 621 ($M^+$, 27.79), 191 (*m*-$NO_2C_6H_3CF_3^+$, 100.00).

### 3.2.2. Preparation of p-2,2,3,3-tetrafluoropropoxy-m-nitrobenzoic acid (*3a*)

*p*-2,2,3,3-Tetrafluoropropoxy-*m*-nitro-trifluoromethylbenzene (**2a**) (6.42 g, 0.02 mol) was added to fuming sulfuric acid (5 ml), then heated to 120°C, stirred for 2 h, poured into 100 ml of ice water and filtered off. Then the pale yellow crystal was recrystallized from ethanol to yield (**3a**) as white flaky crystals 5.346 g. Yield 90%. $^1$H NMR ($CD_3COCD_3$) $\delta$ (ppm): 4.95 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 6.45 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.33 (d, 1H, $J = 9$ Hz, ArH), 8.03 (d, 1H, $J = 9$ Hz, ArH), 8.22 (s, 1H, ArH). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ (ppm): 49 (m, 2F, $CF_2$), 64.1 (dtt, $J_1 = 56$ Hz, $J_2 = 28$ Hz, $J_3 = 4$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 297 ($M^+$, 57.42), 167 (*m*-$NO_2C_6H_3COOH^+$, 96.76), 150 (*m*-$NO_2C_6H_3CO^+$, 100.00).

*p*-2,2,3,3,4,4,5,5-Octfluoropentoxy-*m*-nitrobenzoic acid (**3b**): Yield 84%. $^1$H NMR ($CD_3COCD_3$) $\delta$ (ppm): 4.74 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 6.40 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.29 (d, 1H, $J = 9$ Hz, ArH), 7.97 (d, 1H, $J = 9$ Hz, ArH), 8.10 (s, 1H, ArH). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ (ppm): 43.3 (m, 2F, $CF_2$), 48.6 (m, 2F, $CF_2$), 54.0 (m, 2F, $CF_2$), 61.5 (d, $J_1 = 56$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 397 ($M^+$, 40.77), 167 (*m*-$NO_2C_6H_3COOH^+$, 90.76), 150 (*m*-$NO_2C_6H_3CO^+$, 100.00).

*p*-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecfluorononoxy-*m*-nitrobenzoic acid (**3c**): Yield 70%. $^1$H NMR ($CD_3COCD_3$) $\delta$ (ppm): 4.75 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 6.40 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.30 (d, 1H, $J = 9$ Hz, ArH), 8.00 (d, 1H, $J = 9$ Hz, ArH), 8.12 (s, 1H, ArH). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ (ppm): 42.1 (m, 2F, $CF_2$), 45.0 (m, 8F, $(CF_2)_4$), 46.2 (m, 2F, $CF_2$), 52.3 (m, 2F, $CF_2$), 61.0 (d, $J_1 = 56$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 597 ($M^+$, 31.23), 167 (*m*-$NO_2C_6H_3COOH^+$, 89.06), 150 (*m*-$NO_2C_6H_3CO^+$, 100.00).

### 3.2.3. Preparation of cholesteryl p-2,2,3,3-tetrafluoropropoxy-m-nitrobenzoate (*4a*)

*p*-2,2,3,3-Tetrafluoropropoxy benzoic acid (**3a**) (500 mg, 1.68 mmol), dicyclohexylcarbodiimide (DCC) (347 mg, 1.68 mmol), cholesterol (650 mg, 1.68 mmol), *N*,*N*-dimethylaminopyridine (DMAP) as catalyst, in dry tetrahydrofuran (THF) (10 ml), stirred for 48 h at room temperature. Then added water and filtered off, extracted by diethyl ether, and the filtrate washed with water, dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (8:1) as eluent to give a white crystal which was recrystallized from acetone–methanol to give (**4a**) as white flaky crystals 980 mg, yield 88%. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.65–0.80 (s, 6H), 0.82–2.10 (m, 35H), 2.42–2.60 (m, 2H), 4.50–4.55 (m, 1H), 4.70 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 5.45 (m, 1H), 6.35 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.27 (d, 1H, $J = 9$ Hz, ArH), 8.40 (d, 1H, $J = 9$ Hz, ArH), 8.70 (s, 1H, ArH). $^{19}$F NMR ($CDCl_3$) $\delta$ (ppm): 47.8 (m, 2F, $CF_2$), 62.9 (d, $J_1 = 56$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 368 ($OCh^+$, 100.00), 280 (*p*-$HC_2F_4CH_2O$-*m*-$NO_2C_6H_3COOH^+$, 27.02). IR (KBr) $cm^{-1}$: 2934, 2866, 1715, 1616, 1534, 1355, 1322, 1295, 1248, 1131, 1051, 980, 953, 924, 839, 761, 723, 549. Anal. for $C_{37}H_{51}F_4NO_5$, calc. C: 66.75, H: 7.72, N: 2.10, F: 11.41%; found C: 66.60, H: 7.77, N: 2.24, F: 11.23%.

Cholesteryl *p*-2,2,3,3,4,4,5,5-octfluoropentoxy-*m*-nitrobenzoate (**4b**): Yield 85%. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.65–0.75 (s, 6H), 0.85–2.08 (m, 35H), 2.45–2.55 (m, 2H), 4.55–4.65 (m, 1H), 4.75 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 5.45 (m, 1H), 6.30 (tt, $J_1 = 52$ Hz, $J_2 = 6$ Hz, 1H, $HCF_2$), 7.35 (d, 1H, $J = 9$ Hz, ArH), 8.40 (d, 1H, $J = 9$ Hz, ArH), 8.60 (s, 1H, ArH). $^{19}$F NMR ($CDCl_3$) $\delta$ (ppm): 42.1 (m, 2F, $CF_2$), 47.4 (m, 2F, $CF_2$), 52.8 (m, 2F, $CF_2$), 60.3 (d, $J_1 = 56$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 765 ($M^+$, 1.43), 368 ($OCh^+$, 100.00). IR (KBr) $cm^{-1}$: 2954, 2866, 1710, 1616, 1533, 1358, 1323, 1292, 1253, 1177, 1133, 1090, 998, 923, 809, 760, 715, 541, 413. Anal. for $C_{39}H_{51}F_8NO_5$ calc. C: 61.17, H: 6.71, N: 1.83, F: 19.85%; found C: 61.28, H: 6.67, N: 1.81, F: 19.52%.

Cholesteryl *p*-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecfluorononoxy-*m*-nitrobenzoate (**4c**): Yield 87%. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.60–0.70 (s, 6H), 0.85–2.10 (m, 35H), 2.40–2.50 (m, 2H), 4.55–4.65 (m, 1H), 4.75 (t, 2H, $J = 14$ Hz, $OCH_2CF_2$), 5.38 (m, 1H), 6.30 (tt, $J_1 = 52$ Hz,

$J_2 = 6$ Hz, 1H, $HCF_2$), 7.35 (d, 1H, $J = 9$ Hz, ArH), 8.40 (d, 1H, $J = 9$ Hz, ArH), 8.60 (s, 1H, ArH). $^{19}F$ NMR ($CDCl_3$) $\delta$ (ppm): 41.5 (m, 2F, $CF_2$), 44.3 (m, 8F, $(CF_2)_4$), 45.7 (m, 2F, $CF_2$), 52.0 (m, 2F, $CF_2$), 59.5 (d, $J_1 = 56$ Hz, 2F, $HCF_2$). MS (*m*/*z*): 965 ($M^+$, 2.77), 368 ($OCh^+$, 100.00). IR (KBr) $cm^{-1}$: 2950, 1721, 1616, 1535, 1351, 1292, 1214, 1151, 1029, 836, 810, 761, 709, 655, 634, 535, 413. Anal. for $C_{43}H_{51}F_{16}NO_5$, calc. C: 53.47, H: 5.32, N: 1.46, F: 31.47%; found C: 53.61, H: 5.63, N: 1.46, F: 31.23%.

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