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Preliminary communication

Synthesis and mesomorphic properties of cholesteryl *p*-2,2,3,3,4,4,5,5-octafluoropentoxybenzoate

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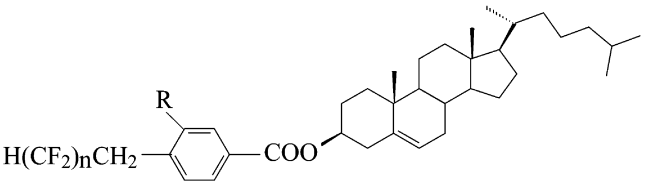
Cholesteryl *p*-2,2,3,3,4,4,5,5-octafluoropentoxybenzoate was synthesized and its phase transition behaviour studied by differential scanning calorimetry and thermal polarizing microscopy. The results show that the compound has SmA and monotropic SmE phases.

Ferroelectric liquid crystals (FLCs) have been intensively studied in recent years owing to their excellent memory effect and high response speed. These ferroelectric liquid crystalline compounds contain one or more chiral centres. The steroid group provides a cheap chiral resource: in 1992, Vill *et al.* reported that steroidal liquid crystals containing a long alkyl chain, e.g. cholesteryl *p*-hexadecylbenzoate and cholesteryl *p*-hexadecyloxyphenylcarbonate, display monotropic ferroelectric phases [1]. It is also known that liquid crystals containing highly fluorinated alkyl or alkoxy chains as terminal groups tend to form a smectic C phase with increasing temperature range [2–4]. 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 is notable for producing a smectic C phase [5]. Therefore the homologous cholesteryl 4-polyfluoroalkoxy-3-nitrobenzoate **1** was synthesized by our group (figure 1) [6]. In order to study the effect of the lateral nitro group on mesophase formation, cholesteryl 2,2,3,3,4,4,5,5-*p*-octafluoropentoxybenzoate **2** was synthesized (figure 1 and the scheme). However, the desired SmC* phase was not observed in these compounds. The SmE phase was found in compound **2**.

The mesophase behaviour of compound **2** was studied using polarizing optical microscopy (Amplival Pol U equipped with a Boetius hot stage). Differential scanning calorimetry was carried out with a Mettler DSC FP80HT. The sample was incorporated into a 4.7 μm thick, polyimide-coated ITO cell, purchased from Lincome Co. For electro-optical studies, a digital oscilloscope (DS 6612) and a function generator (Type TR-0463) were used. The results are summarized in the table.

From a comparison of the mesomorphic properties of compounds **1** and **2**, some interesting results have been obtained. Firstly, the clearing point was increased on eliminating the lateral nitro group, but the melting point was decreased. The mesomorphic range of non-nitro-substituted compound **2** becomes wider than that of the nitro derivative. Secondly, compound **2** shows no enantiotropic Ch phase but an enantiotropic SmA phase was observed. Nitro derivative **1** with $n=4$ exhibits both an enantiotropic Ch phase and a monotropic SmA phase. Compound **1** with $n=8$, like compound **2**, shows no enantiotropic Ch phase but



1 R = NO_2 n = 2, 4, 8.

2 R = H n = 4

Figure 1. The molecular structures of compounds **1** and **2**.

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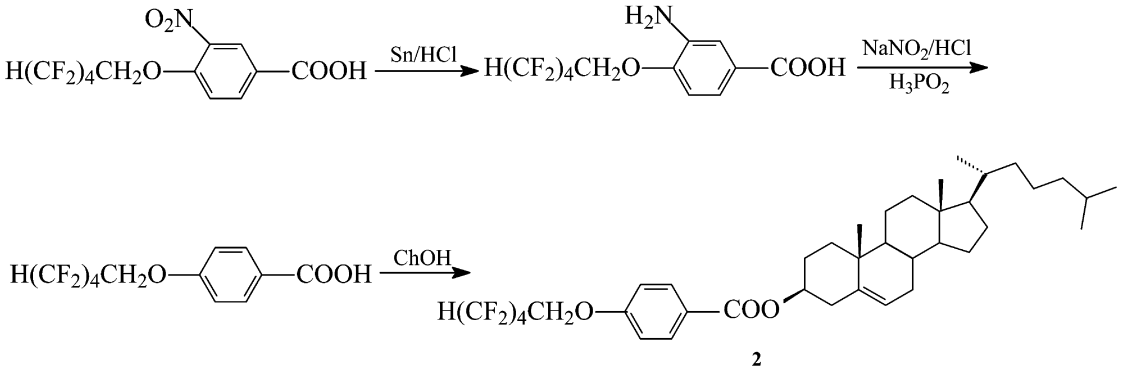

Scheme. The synthesis of cholesteryl 2,2,3,3,4,4,5,5-*p*-octafluoropentoxybenzoate **2**.

Table 1. The transition temperatures of the synthesized compounds. Cr = crystal; Ch = cholesteric phase; SmA = smectic A phase; I = isotropic phase; SmE = smectic E phase; Recr = recrystallization.

Compound	*n*	Transition temperatures/°C
1	2	Cr 179.0 Ch 183.8 I 179.9 Ch 121.9 Recr
	4	Cr 178.0 Ch 184.4 I 176.5 Ch 155.8 SmA137.3 Recr
	8	Cr 164.3 SmA 209.0 I 194.1 SmA 131.9 Recr
2	4	Cr 175.0 SmA 195-210 I 210-195 SmA 175 SmE 116 Recr

does exhibit an enantiotropic SmA phase. Thirdly, a highly ordered smectic SmE phase, which was not observed in the nitro derivative, was observed in the non-nitro compound **2** during cooling (figure 2). Thus the introduction of a long rigid fluorinated side chain and elimination of the nitro group suppress the cholesteric phase and increase the thermal stability and temperature range of the smectic phase. Eliminating the nitro group, although decreasing the molecular polarity, results in increased arrangement order, which favours the observed smectic ordering.

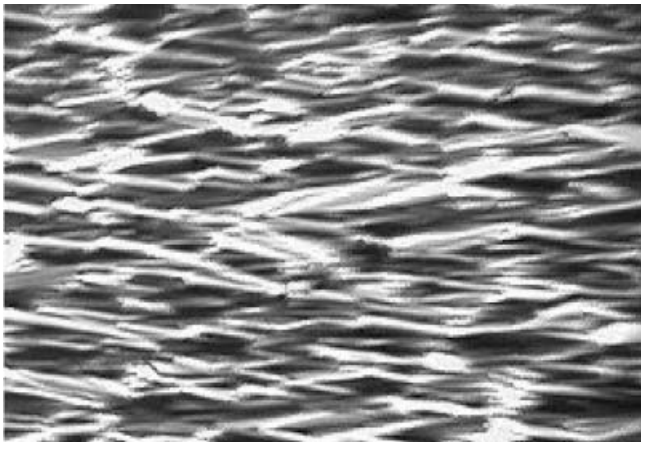

Figure 2. Optical polarizing micrograph of compound **2** smectic E phase (12.5 × 12.5).

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Appendix

Cholesteryl *p*-2,2,3,3,4,4,5,5-octafluoropentoxybenzoate **2** was synthesised according to the scheme. The structures of the final product and intermediates were elucidated by a variety of spectral methods. ^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer with TMS as internal standard. MS spectra were measured on a micromass GCT. IR spectra were recorded on a Nicolet FTIR 20sx spectrometer using solid KBr pellets.

The following are the results of identification analysis on the intermediate materials and the target compound cholesteryl *p*-octafluoropentoxybenzoate **2**.

4-(2,2,3,3,4,4,5,5)-Octafluoropentoxy-3-aminobenzoic acid. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.55 (t, 2H, $J = 12.70$ Hz, OCH_2CF_2), 6.08 (tt, 1H, $J_1 = 46.63$ Hz, $J_2 = 5.30$ Hz, HCF_2), 6.82 (d, 1H, $J = 8.49$ Hz, ArH), 7.27 (s, 1H, ArH), 7.47 (d, 1H, $J = 1.87$ Hz, ArH), 7.53 (dd, 1H, $J_1 = 6.57$ Hz, $J_2 = 1.90$ Hz, ArH). MS (*m*/*z*, %): 367.2 (M^+, 100.00), 350.2 (M^+–OH, 2.55), 322.2 (M^+–COOH, 1.23), 152.1 (M^+–$CH_2CF_2CF_2CF_2CF_2H$, 39.91).

p-2,2,3,3,4,4,5,5-Octafluoropentoxy benzoic acid. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.54 (t, 2H, $J = 12.84$ Hz, OCH_2CF_2), 6.08 (tt, 1H, $J_1 = 46.53$ Hz, $J_2 = 5.40$ Hz, HCF_2), 7.00 (dd, 2H, $J_1 = 6.90$ Hz, $J_2 = 2.48$ Hz, ArH), 8.12 (dd, 2H, $J_1 = 5.31$ Hz, $J_2 = 2.78$ Hz, ArH). MS (*m*/*z*, %): 352.0 (M^+, 100.00), 335.0 (M^+–OH, 29.54),

308.0 (M^+–COOH +1, 19.66), 151.0 (M^+–CF_2CF_2-CF_2CF_2H, 33.72).

Cholesteryl p-2,2,3,3,4,4,5,5-octafluoropentoxybenzoate **2**. ^1H NMR ($CDCl_3$) δ (ppm): 0.63 (s, 6H), 0.80–1.98 (m, 35H), 2.38 (d, 2H, $J=7.78$ Hz), 4.45 (t, 2H, $J=12.84$ Hz, OCH_2CF_2), 4.77 (m, 1H), 5.53 (d, 1H, $J=3.93$ Hz), 6.02 (tt, 1H, $J_1=41.13$ Hz, $J_2=5.40$ Hz, HCF_2), 6.88 (d, 2H, $J=8.88$ Hz, ArH), 7.97 (d, 2H, $J=8.88$ Hz, ArH). MS (*m*/*z*, %): 720.3 (M^+, 0.19), 368.3 (OCh^+, 78.46), 350.2 (M^+–OCh, 100). IR (KBr) cm^{-1}: 2950, 2850, 1712, 1614, 1520, 1472, 1370, 1320, 1280, 1250, 1170, 1120, 1080, 1050, 1000, 910, 870, 840, 800, 770, 750, 690, 630, 550.

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