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Synthesis and mesomorphic properties of 4-(1,1,7-trihydroperfluoroheptyloxycarbonyl)phenyl 4′-*n*-alkoxybiphenyl-4-carboxylate

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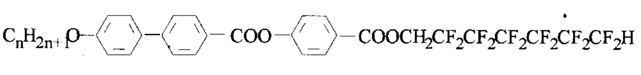
A family of 4-(1,1,7-trihydroperfluoroheptyloxycarbonyl)phenyl 4′-*n*-alkoxybiphenyl-4-carboxylates has been synthesized. The compounds show the smectic A phase while the mesogens with intermediate terminal alkyl chain ($n=7$–12) also exhibit a broad smectic C phase.

1. Introduction

Because the study of new liquid crystal compounds can bring about further development in the scientific understanding of liquid crystals (LCs) and their device applications, increasing research attention has been paid to lateral fluorinated LCs [1–11]. These are of great interest because varying the position and number of substitutions allows one to modify the range of mesophase, as well as other physical properties such as, chemical and thermal stability; low viscosity and lower birefringence may also be realized [12–15]. Up to now, hundreds of liquid crystalline molecules with fluoro-substituted phenyls have been prepared. Nevertheless, fluorine is rarely used as a substituent for replacing hydrogen in the flexible hydrocarbon tails of mesogens except for some ferroelectric LCs with a trifluoromethyl group or a fluoride bonding to a chiral carbon [16–19]. Earlier limited study on the effect of incorporating perfluoroalkyl or highly fluorinated alkyl tail groups into liquid crystals indicated that smectic character was enhanced in such fluorinated LC systems [20–26]. In this paper, we report the synthesis and observation of the mesomorphic properties of a class of novel mesogens containing a highly fluorinated tail group. The mesogens have the following structure.

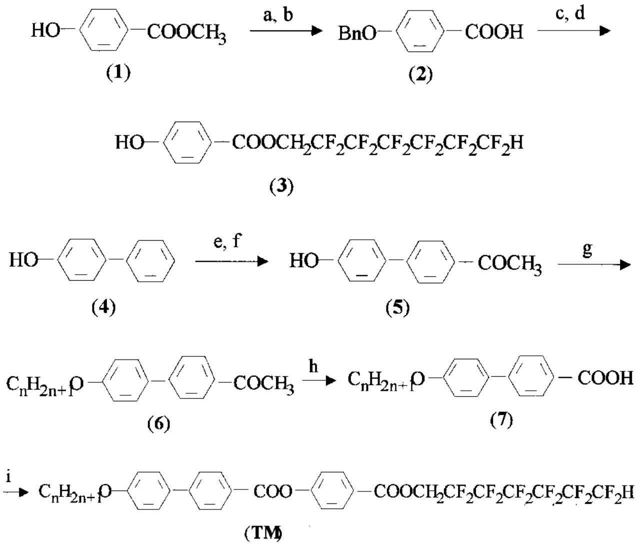


(TM)

2. Experimental

2.1. *Synthesis route*

The synthesis of the target molecules bearing a highly fluorinated tail chain (the 1,1,7-trihydroperfluoroheptyl group) is outlined in the scheme.



($n=3$ **TM1**; $n=4$ **TM2**, $n=5$ **TM3**, $n=6$ **TM4**, $n=7$ **TM5**, $n=8$ **TM6**, $n=9$ **TM7**, $n=10$ **TM8**, $n=11$ **TM9**, $n=12$ **TM10**, $n=16$ **TM11**)

Reagents and conditions: (a) Na, BnCl,C_2H_5OH, r.t.→ reflux; (b) NaOH, C_2H_5OH/H_2O; (c) $HOCH_2CF_2CF_2CF_2CF_2CF_2CF_2H$, DCC, DMAP, THF, 0°C→r.t.; (d) Pd/C, ethyl acetate; (e) CH_3COCl, CS_2, $AlCl_3$, reflux; (f) NaOH, C_2H_5OH/H_2O; (g) NaH, n-$C_nH_{2n+1}Br$, DMF, 110°C; (h) NaOBr, dioxane/water; (i) **3**, DCC, DMAP, THF.

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The hydroxyl group of methyl 4-hydroxybenzoate was protected with benzyl chloride and the methyl ester was hydrolysed to give the benzoic acid. The protected acid was then esterified with the appropriate alcohol using dicyclohexylcarbodiimide (DCC) as dehydrating agent and *N*,*N*-dimethylaminopyridine as catalyst, in dry tetrahydrofuran solution. The benzyl ether produced was then converted to the corresponding phenol ester by removal of the benzyl protecting group which was achieved by stirring at room temperature in a H_2 atmosphere in the presence of palladium on active carbon in ethyl acetate. The 4-*n*-alkoxybiphenyl-4′-carboxylic acid (7) was prepared in four steps using a slight modification of the procedure first reported by Gray *et al.* [27, 28]; it was then esterified with the previously prepared ester phenol **3**, again using the DCC/DMAP system. Details of the preparation of compound **TM4** are given in § 2.3 and 2.4, below.

2.2. *Analysis*

The structures of all intermediates and final products were determined by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrometer using a KBr disc. ^{1}H NMR spectra, with TMS as the internal standard, and ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard in $CDCl_3$ as the solvent, were run on a Fx-90Q (90 MHz) spectrometer or a Bruker 300AM instrument. 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 microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler 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 are the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature [29, 30].

2.3. *4-Benzyloxylbenzoic acid (**2**)*

Sodium chips (6·9 g) were added to 100 ml of dried alcohol cooled in an ice bath, and under a flow of nitrogen. After the disappearance of the sodium, methyl 4-hydroxybenzoate (45·6 g) in alcohol (150 ml) was added; benzyl chloride (37·8 g) was then added dropwise during 1 h while cooling in the ice bath. The resulting mixture was stirred at room temperature for 1 h and heated under for reflux for 5·5 h. After cooling to room temperature, 70 ml of water and 16 g of sodium hydroxide were added. The mixture was stirred at room temperature overnight; it was then acidified, diluted with water (300 ml) and filtered to give a white powder. The crude product was recrystallized from ethanol/water to give white crystals (**2**). Yield 56 g (81·3%). ^{1}H NMR (90 MHz, acetone-D_6) δ: 4·36 (s, 2H), 5·33 (s, 1H), 7·18 (d, 2H), 7·53 (m, 5H), 8·07 (d, 2H) ppm.

2.4. *1,1,7-Trihydroperfluoroheptyl 4-hydroxybenzoate (**3**)*

To a mixture of compound **2** (2·77 g, 12·1 mmol) and 1,1,7-trihydroperfluoroheptanol (2·86 g, 8·6 mmol) in THF (30 ml), cooled in an ice bath, DCC (3·17 g, 15 mmol) was added, followed by DMAP (0·02 g). The resulting mixture was stirred under dry conditions while warming to room temperature. After two days, precipitated dicyclohexylurea (DCU) was filtered off and the solvent was evaporated. The syrupy residue was filtered again and washed with petroleum ether (b.p. 60–90°C). After removal of the solvent, the product was purified by flash chromatography over silica gel using petroleum ether/ethyl acetate (20/1) as the eluent, and was recrystallized from methanol to give 3·96 g of white crystals. These were dissolved in ethyl acetate (50 ml) containing 0·03 g of palladium on carbon and stirred under a H_2 atmosphere at room temperature for 12 h to remove the benzyl group. This gave a colourless liquid which crystallized on standing at room temperature. Yield 3·3 g (85% from 1,1,7-trihydroperfluoroheptanol). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 4·82 (t, $J = 17$ Hz, 2H), 6·02 (m, 1H), 6·9 (s, $J = 7$ Hz, 2H), 7·97 (s, $J = 8$ Hz, 2H), 7·23 (m, H) ppm.

2.5. *4-(1,1,7-Trihydroperfluoroheptyloxycarbonyl)phenyl 4′-n-hexyloxylbiphenyl-4-carboxylate (**TM4**)*

Compound **TM4** was prepared by a procedure similar to that described for compound **3** from 4-*n*-hexyloxybiphenyl-4′-carboxylic acid and intermediate **3**. Yield 67%, m.p. 106·6°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm. ^{19}F NMR (300 MHz, $CDCl_3$), δ 42·3 (t, $J = 12·8$, 2F), 45·2 (m, 2F), 46·4 (m, 4F), 52·4 (m, 2F), 60·0 (d, $J = 51·7$, 2F) ppm. IR (KBr): ν 2938, 2865, 1604, 1508, 1276, 1199, 1072, 1014, 888, 828, 765, 717, 689 cm^{-1}. MS (*m/z*): 732 (M^+, 0·98), 281 (100·00), Elemental analysis: found, C 53·67, H 3·42, F 30·92; calculated (for $C_{33}H_{28}F_{12}O_5$), C 54·11 H 3·85, F 31·12%.

3. Results and discussion

The phase transition temperatures of **TM1–11** were determined by DSC and the mesomorphic textures were observed on the polarizing optical microscope (POM). The transition temperatures for compounds **TM1–11**, determined by DSC, are summarized in the table and plotted in the figure.

As shown in the table, all 11 compounds have liquid crystallinity. The mesogens with a short terminal hydrocarbon chain, $n = 3$ and 4, possess a wide mesomorphic

Table. Transition temperatures of LCs **TM1–11**. Cr = crystal; SmA = smectic A; SmC = smectic C; I = isotropic phase. Recr = recrystallization.

Compound	*n*	Transition temperatures/°C
TM1	3	Cr 160·3 SmA 248·4 I 245 SmA 147·1 Recr
TM2	4	Cr 137 SmA 240·5 I 237 SmA 116·9 Recr
TM3	5	Cr 129·5 SmA 232·2 I 228·8 SmA 110·3 SmC 102·6 Recr
TM4	6	Cr 106·6 Sc 113·2 SmA 220·6 I 218·1 SmA 103 Sc 90·2 Recr
TM5	7	Cr 121·6 Sc 187·6 SmA 212·8 I 210·4 SmA 186·2 Sc 102·3 Recr
TM6	8	Cr 120·1 Sc 187·3 SmA 203·3 I 201 SmA 185·2 Sc 99·7 Recr
TM7	9	Cr 115·5 Sc 176·3 SmA 189·3 I 187·0 SmA 174·3 Sc 98·1 Recr
TM8	10	Cr 113 Sc 182·2 SmA 190·5 I 188·1 SmA 180·0 Sc 97·6 Recr
TM9	11	Cr 117·3 Sc 175·2 SmA 182·3 I 179·8 SmA 172·9 Sc 103·1 Recr
TM10	12	Cr 116 Sc 171·3 SmA 177·8 I 175·1 SmA 169·4 Sc 95·5 Recr
TM11	16	Cr 98·1 SmA 144·8 I 142·4 SmA 86·5 Recr

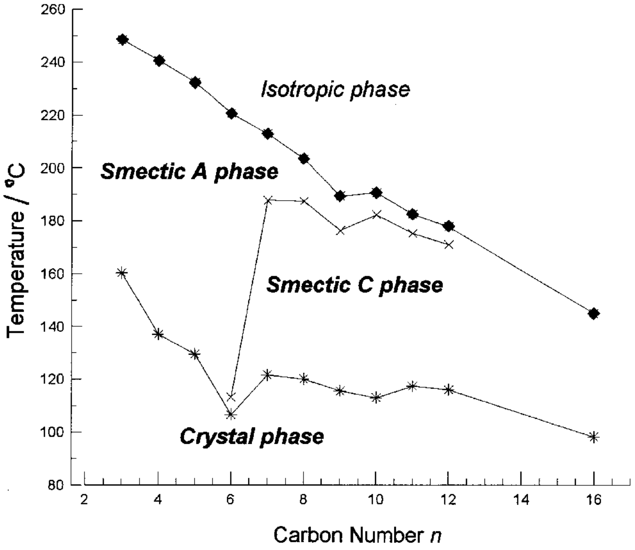

Figure. The number of carbon atoms in the alkoxyl chain versus the transition temperatures of the mesogens **TM1–11**.

range and a simple mesophase sequence, i.e. the mesogens TM1 and TM2 only show an enantiotropic smectic A (SmA) phase. When $n = 5$, the mesogen TM3 shows enantiotropic SmA and monotropic smectic C (SmC) phases. For $n = 6$–12, the mesogens **TM4–10** show enantiotropic SmA and SmC phases. Among these, the mesogens with $n = 7$–12 show a wide SmC phase with a relatively narrow SmA phase. With further lengthening of the hydrocarbon end tail, the mesogen **TM11** ($n = 16$) shows only the SmA phase, and the mesophase range shrinks to 46·7°C, the lowest in this series. On POM, the samples show typical focal-conic textures in the SmA phase, and broken focal-conic textures in the SmC phase. It is noteworthy that none of 11 mesogens show the nematic mesophase.

In the figure, transition temperatures are plotted against the number, *n*, of carbon atoms in the hydrocarbon chain. In these fluorinated mesogens, the melting and clearing temperatures decrease with the growing alkyl chain, with the exception for $n = 6$. At first a purity problem was suspected but repeated careful purifications led to the same transition temperatures. The mesophase range shrinks with increasing alkyl chain length, hence the stability of the mesophase decreases with lengthening terminal hydrocarbon chain. Mesogens with a long hydrocarbon tail chain ($n > 7$) prefer showing a SmC phase rather than a SmA phase.

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