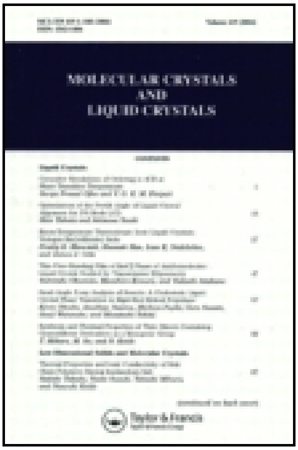

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Synthesis and Mesomorphic Behavior of Chiral Partially Fluorinated Liquid Crystal Incorporating S-2-Methylbutyl

Elisabeth De Givenchy [a], Frederic Guittard [a], Serge Geribaldi [a] & Aime Cambon [a]

[a] Laboratoire de Chimie Organique du Fluor, Université de Nice—Sophia Antipolis, Faculté des sciences, Parc Valrose, 06108, Nice, Cedex 2, France

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Synthesis and Mesomorphic Behavior of Chiral Partially Fluorinated Liquid Crystal Incorporating S-2-Methylbutyl

ELISABETH TAFFIN DE GIVENCHY, FREDERIC GUITTARD*, SERGE GERIBALDI and AIME CAMBON

Laboratoire de Chimie Organique du Fluor, Université de Nice – Sophia Antipolis, Faculté des sciences, Parc Valrose, 06108 Nice Cedex 2, France

Three different smectic liquid-crystalline 4,4'-biphenyl derivatives within the fluorinated series and incorporating S-2-methylbutyl moiety have been prepared and their mesomorphic properties investigated. The synthesis of these compounds have been carried out from 2-*F*-hexylethyl iodide or 2-*F*-hexylethanol. The spacer linking the fluorinated tail to the mesogenic core was a carboxylate, an ether or an oxycarbonylmethoxy function. The ether function lead to an increase of the melting and clearing temperatures with a reducing of the span of the mesophase. The physical properties of these novel fluorinated materials are commented and illustrated by the study realized from the differential thermal analysis and the light microscopy.

Keywords: 2-*F*-alkylethyl; chiral LC; smectic phase

INTRODUCTION

The discovery of ferroelectricity in the chiral smectic C (S_C*) phase by R. Meyer in 1975[1] and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980[2], have generated a great deal of interest in academic and industrial research laboratories. Since, extensive

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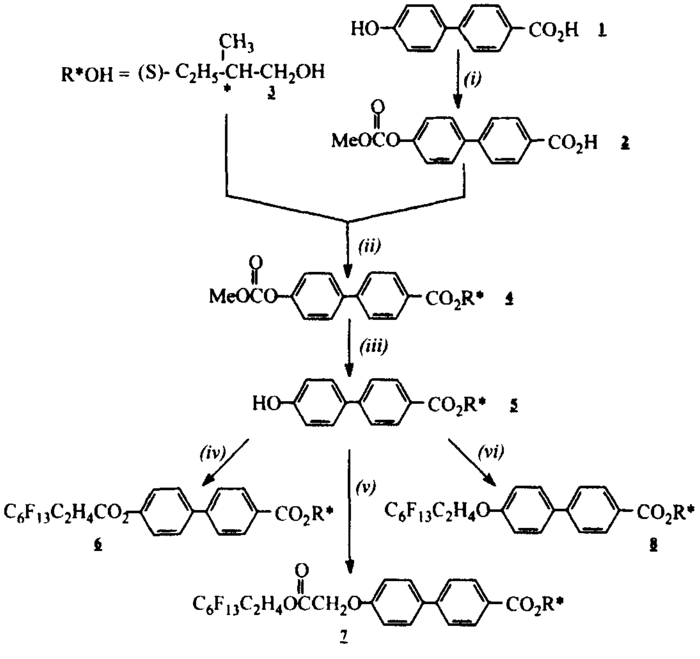
* (email : guittard@unice.fr).

studies have been done on ferroelectric liquid crystal materials and their applications. Recent studies show that the perfluoroalkylated tails strongly enhances smectic phases with regard to their hydrocarbon homologues[3,4]. Thus, association of a *F*-alkylated moieties with a chiral unit via a mesogen connector appeared to offer a further attractive alternative[5-10]. In the present study, three different 4,4'-biphenyl derivatives (compounds **6**, **7** and **8**) within the fluorinated series were prepared as shown in figure 1 and their liquid crystalline properties were investigated in order to study the correlation between the molecular structure and the stability of the smectic phase.



Reagents and conditions: (i) $CH_3OC(O)Cl$, NaOHaq., 0°C (ii) DEAD, TPP, THF, rt (iii) NH_3aq., CH_2Cl_2, EtOH, rt (iv) $R_FC_2H_4COOH$, DCC, DMAP, CH_2Cl_2, rt (v) $R_FC_2H_4OC(O)CH_2Br$, K_2CO_3, acetone, reflux (vi) $R_FC_2H_4OH$,, DEAD, TPP, THF, rt.

FIGURE 1 Reaction pathway to synthesize the 6, 7 and 8 derivatives

RESULTS AND DISCUSSION

All compounds show a liquid crystalline behavior. The phase behavior and transition temperatures of the series were determined both by thermal microscopy and by differential scanning calorimetry. The liquid crystal transition temperatures and enthalpies for these new materials are summarized in Table 1. The miscibility studies carried out from standard materials show that the mesophases observed are of the smectic A type.

TABLE 1 Phase transition temperatures obtained from compounds **6**, **7** and **8**.

Cpd N°	*spacer*	*Transition temperatures (°C) ‡*				
		C		*S_A*		*I*
6	$C_2H_4CO_2$	•	89.8 [31.0]	•	100.1 [3.1]	•
7	$C_2H_4OCOCH_2O$	•	79.5 [40.6]	•	107.3 [1.9]	•
8	C_2H_4O	•	109.5 [37.0]	•	122.0 [3.8]	•

(‡) figures in square brackets denote enthalpies of transition (kJ.g^{-1}).

The comparison of liquid crystal behavior of the synthesized compounds allow us to evaluate the impact of the nature of the spacer according to the figure 2 and 3.

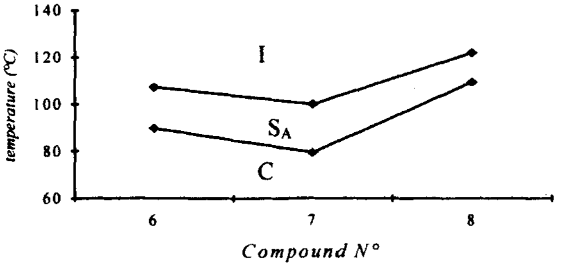


FIGURE 2 Phase diagram of compounds 6, 7 and 8.

For the spacers of ester type (6) and oxycarbonylmethoxy (7), the mesomorphic behavior are closely the same : the range of the liquid crystal domain is identical. However, the phase transition temperature are slightly lower for the compound 7. For the spacer of ether type (8) the mesomorphic behaviour is comparatively less important and the phase transition temperatures are more exalted.

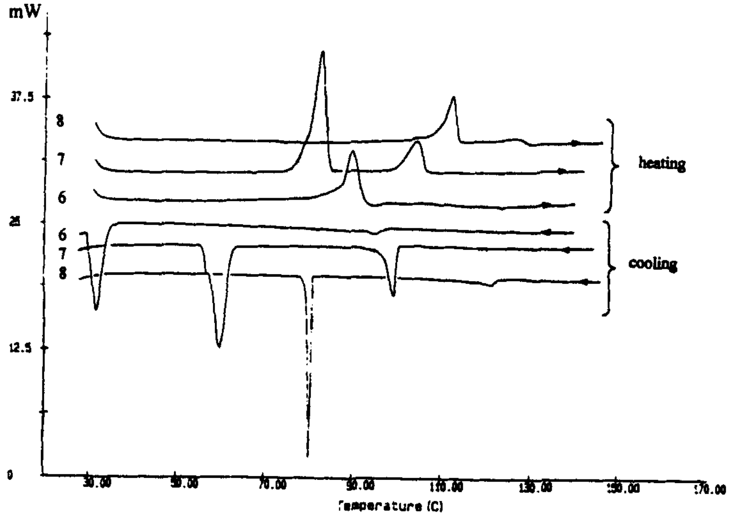


FIGURE 3 DSC curve for compounds 6,7,8 (heating and cooling rate : 10°C min^{-1}).

EXPERIMENTAL

The initial phase assignments and corresponding transition temperatures were determined with an Olympus BH-2 polarizing microscope equipped with crossed polarizers and using a Mettler model FP-52 hot stage. Temperatures and enthalpies of transitions were investigated by differential scanning calorimetry (DSC) using a Perkin Elmer PC series DSC7 calorimeter. The heating and cooling curves were obtained at rates of 10°C, in a nitrogen atmosphere. Mass spectrometry (MS) was carried out using a Finnigan Matt

INCOS 500E mass spectrometer coupled with a gas chromatograph (Varian 3400). Nuclear Magnetic Resonance (NMR) spectroscopy was carried out using a Brucker AC 200 MHz spectrometer. All spectra were recorded with $CFCl_3$ for ^{19}F NMR and TMS as internal reference for ^1H NMR. All finals compounds give satisfactory elemental analysis.

4-(4'-Methoxycarbonyloxyphenyl)benzoic acid (2)

Methyl chloroformate (4.10^{-2} mol) was added to a stirred mixture of 4-(4'-hydroxyphenyl)benzoic acid (2.10^{-2} mol), ground sodium hydroxyde (6.10^{-2} mol) and water (60 ml) at such a rate as to maintain the temperature between 0 and 2°C. The resulting turbid solution was left to stir at 0°C for further 12h, before being acidified with a 1:1 solution of concentrated hydrochloric acid-water. The resulting precipitate was then collected by filtration and washed thoroughly with cold water, recrystallized (ethanol) before being dried in a vacuum oven to give the acid **2** as a white solid. Yield = 85%. NMR ^1H (DMSO / TMS) δ (ppm) : 3.95 (s, 3H); 7.38 - 8.03 (3d, $8H_{arom.}$).

(S)-2-Methylbutyl-4-(4'-methoxycarbonyloxyphenyl)benzoate (4)

A solution of triphenylphosphine (1.10^{-2} mol) and (S)-2-methylbutan-1-ol (1.10^{-2} mol) in dry tetrahydrofuran (25ml) was added dropwise to a stirred solution of compound **2** (1.10^{-2} mol) and diethyl azodicarboxylate (1.10^{-2} mol) in dry tetrahydrofuran (25ml) at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred for 18h. The solvent was removed in vacuum and the crude product was diluted with diethyl ether and filtered through a pad of 'Hyflosupercel'. The filtrate was then dried over sodium sulfate, filtered and evaporated to give a white solid. The product was purified by column chromatography on silica gel using chloroform as eluent to yield the pure compound 4. Yield = 75%; ^1H NMR ($CDCl_3$ / TMS) δ (ppm):

0.97 (m, 6H); 1.29 (m, 1H); 1.51 (m, 1H); 1.86 (m, 1H); 3.95 (s, 3H); 4.18 (m, 2H); 7.18-8.2 (3d, 8H arom.).

(S)-2-Methylbutyl-4-(4'-hydroxyphenyl)benzoate (5)

A solution of **4** (3.10^{-3} mol) dissolved in a mixture of ethanol (20ml) and dichloromethane (20ml) was added to an aqueous solution of ammonia (40ml; 40%), at room temperature. The reaction mixture was stirred for a further 4h until TLC showed the complete reaction. The solvents were removed under vacuum and the product was dried in a vacuum oven to give the phenol **5** as a white solid. The solid could be used without further purification for the end of the synthesis. Yield = 95%; 0.97 (m, 6H); 1.29 (m, 1H); 1.51 (m, 1H); 1.86 (m, 1H); 4.18 (m, 2H); 5.75 (m, 1H); 6.91-8.2 (4d, 8H arom.).

(S)-2-Methylbutyl-4-(4'-*F*-hexylethylcarbonyloxyphenyl)benzoate (6)

A solution of 3-*F*-hexylpropanoic acid (1.10^{-2} mol) previously prepare[11], dicyclohexylcarbodiimide (DCC) (1.10^{-2} mol), 4-(N,N-dimethylamino) pyridine (DMAP) (1.10^{-3} mol) and compound **5** (1.10^{-2} mol) in dry dichloromethane (25ml) was stirred for a further 12h at room temperature. The reaction mixture was then filtered and the filtrate was dried over sodium sulfate; then filtered and evaporated to give a colorless solid. The residue was purified by column chromatography on silica gel with chloroform as eluent. Yield = 90%. ^{1}H NMR ($CDCl_3$ / TMS) δ (ppm) : 0.97 (m, 6H); 1.21 (m, 1H); 1.51 (m, 1H); 1.81 (m, 1H); 2.61 (Tt, 2H, $^3J_{H-H}$=6.3Hz, $^3J_{H-F}$=18.6Hz); 3.71 (m, 2H); 4.51 (t, 2H, ^3J=6.3 Hz); 7.92-8.02 (4d, 8H arom); ^{19}F NMR ($CDCl_3$) -81.2 ppm (m) [CF_3]; -113.5 ppm (m) [$(CF_2)_\alpha$]; -121.2 ppm (m) [$(CF_2)_\beta$]; -122.0 to -123.8 ppm (m) [$2(CF_2)_\gamma$], -126.4 ppm (m) [$(CF_2)_\omega$]; MS (70 eV); m/z (%): 658 (32.4), 571 (100), 543 (7.4), 375 (2.5), 197 (10.3), 169 (12.5), 131 (<1), 119 (1.8), 71 (5.2), 69 (7.4), 57 (8.9).

(S)-2-Methylbutyl-4-(4'-*F*-hexylethyloxycarbonylmethoxyphenyl) benzoate(7)

2-*F*-hexylethylbromoacetate (2.10^{-3} mol.), previously prepared [12,13] from the reaction of 2-*F*-alkylethanol with bromoacetyl bromide, in acetone was added to compound **5** (2.10^{-3} mol.) in a dilute suspension of potassium carbonate (4.10^{-3} mol.) in acetone. The reaction mixture was boiled for 12 hours, then filtered, and the solid washed with acetone. The acetone layer was evaporated and the residue purified by column chromatography on silica gel using chloroform as eluent to yield the pure compound **7** as a white solid (table 1). ^{1}H NMR ($CDCl_3$ / TMS) δ (ppm) : 0.97 (m, 6H); 1.21 (m, 1H); 1.51 (m, 1H); 1.81 (m, 1H); 2.41 (m, 2H); 4.12 (m, 2H); 4.48 (t, 2H, ^{3}J=6.6Hz); 4.65 (s, 2H); 6.91-8.0 (4d, 8H arom). MS (70 eV); m/z (%): 688 (46.4), 631 (1.3, 601 (100), 197 (9.9), 169 (4.1), 131 (1.8), 119 (2.0), 71 (8.2), 69 (15.7), 57 (3.4).

(S)-2-Methylbutyl-4-(4'-*F*-hexylethyloxyphenyl)benzoate(8)

A solution of triphenylphosphine (1.10^{-2} mol) and 2-*F*-hexylethanol (1.10^{-2} mol) in dry tetrahydrofuran (25ml) was added dropwise to a stirred solution of compound **5** (1.10^{-2} mol) and diethyl azodicarboxylate (1.10^{-2} mol) in dry tetrahydrofuran (25ml) at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred for 18h. The solvent was removed under vacuum and the crude product was diluted with diethyl ether and filtered through a pad of 'Hyflosupercel'. The filtrate was then dried over Na_2SO_4, filtered and evaporated to give a white solid. The product was purified by column chromatography on silica gel using chloroform as eluent to yield the pure compound **8**. Yield = 13%; ^{1}H NMR ($CDCl_3$ / TMS) δ (ppm) : 0.97 (m, 6H); 1.21 (m, 1H); 1.51 (m, 1H); 1.81 (m, 1H); 2.51 (Tt, 2H, $^3J_{H\text{-}H}$=6.4Hz, $^3J_{H\text{-}F}$=18.6Hz); 4.12 (m, 2H); 4.22 (t, 2H, ^{3}J=6.4Hz); 6.85-811 (4d, 8H arom.).

^{19}F NMR (CDCl$_3$/CFCl$_3$), δ(ppm); -81.6 (C$\underline{F_3}$), -114.8 (C$\underline{F_2}$α), -124.9 (C$\underline{F_2}$β), -126.6 (C$\underline{F_2}$ω); MS (70 eV); m/z (%): 630 (55.4), 543 (100), 515 (3.2), 297 (5.2), 197 (11.6), 169 (15.4), 131 (1.7), 119 (1.9), 71 (3.4), 69 (6.5), 57 (7.6).

Acknowledgments

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