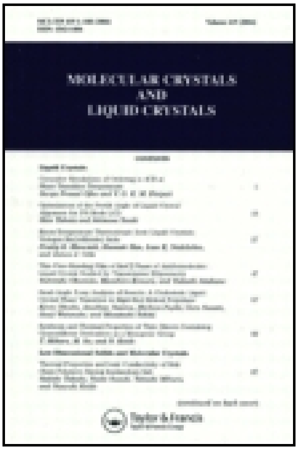


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation and Mesomorphic Properties of Highly Fluorinated Materials Incorporating S-Ethyl-Lactate

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

[a] Laboratoire de Chimie des Matériaux Organiques et Métalliques, Université de Nice, Pare Valrose, F-06108, Nice cedex 2, France

To cite this article: Elisabeth Taffin De Givenchy, Frederic Guittard & Serge Geribaldi (2001): Preparation and Mesomorphic Properties of Highly Fluorinated Materials Incorporating S-Ethyl-Lactate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 91-98

To link to this article: http://dx.doi.org/10.1080/10587250108025285

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 91-98
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Preparation and Mesomorphic Properties of Highly Fluorinated Materials Incorporating S-Ethyl-Lactate

ELISABETH TAFFIN DE GIVENCHY, FREDERIC GUITTARD* and SERGE GERIBALDI

Laboratoire de Chimie des Matériaux Organiques et Métalliques,
Université de Nice, Parc Valrose, F-06108 Nice cedex 2 – France

The synthesis of three different chiral short molecular weight compounds have been reported. The overall compounds incorporate a linear perfluorinated tail and S-ethyl-lactate as chiral moiety. Each compound differ to the other by one molecular parameter: a spacer carbonyloxy or oxycarbonylmethoxy or by the presence or not of an ester function between the two aromatic rings of the mesogenic core. The synthesis have been carried out from 2-*F*-hexylethyl-iodide or 2-*F*-hexylethanol. The mesomorphic properties have been characterized by light microscopy and by differential thermal analysis showing the peculiar effect of the spacer. The two biphenyl derivatives exhibit liquid crystal properties over a wide temperature range. The mesophase for both compounds is smectic of type A. However, the introduction of an ester function in the core contribute to enhance the melting temperature and suppress the liquid crystal behavior.

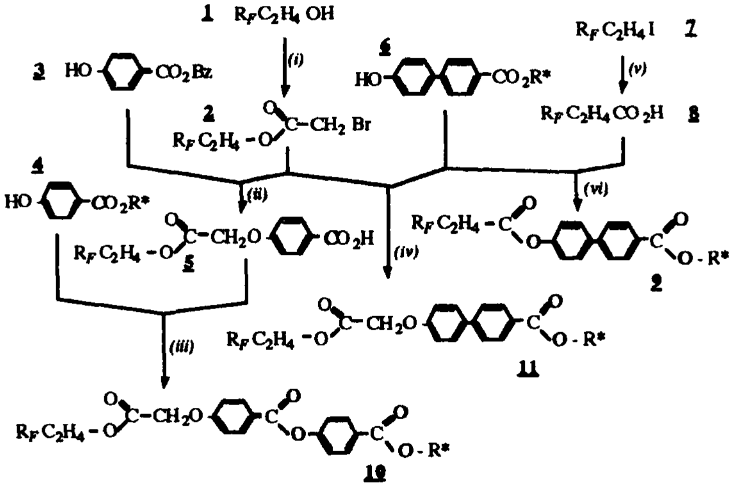
Keywords: fluorinated; smectic phase; (S)-ethyl-lactate; chiral

---

* Corresponding author: (email: guittard@unice.fr)

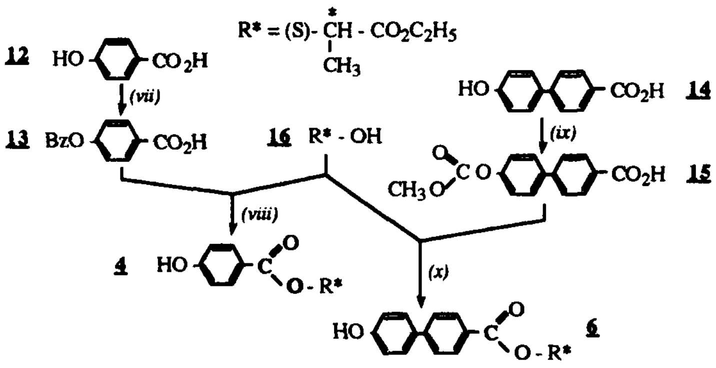
INTRODUCTION

For reach ferroelectric liquid crystal materials, highly fluorinated part could be introduced[1-3] in order to strongly enhances smectic phases with regard to their hydrocarbon homologues[4,5]. Furthermore, the use of this kind of tail give to the resulting system the intrinsic properties of the perfluorinated part : low viscosity, thermal stability, chemical inertia but also low surface properties[6]. Thus the association of *F*-alkylated moiety with a chiral center offer a further alternative[7,8]. In the present study, three different low molecular weight compounds (**9**,**10**,**11**) within fluorinated series have been synthesized according to the reaction pathway described in figure 1 and 2. Their liquid crystalline behavior were investigated in order to evaluate the impact of molecular parameters on the stability of the mesophase.



Reagents and conditions: (i)BrC(O)CH$_2$Br, 60°C; (ii) K$_2$CO$_3$/acetone/60°C; H$_2$/Pd/AcOEt; (iii) DCC/DMAP/CH$_2$Cl$_2$ rt; (iv) K$_2$CO$_3$/acetone/60°C; (v) Mg/CO$_2$; H$_3$O$^+$/Et$_2$O; (vi) DCC/DMAP/CH$_2$Cl$_2$ rt.

FIGURE 1 Synthetic route to compounds **9**-**11**.



Reagents and conditions: (vii) KOH/H_2O/EtOH; B_zBr reflux, recrist. CH_3CO_2H; (viii) DCC/DMAP/CH_2Cl_2 rt; (ix) $CH_3OC(O)Cl$, NaOH $_{aq}$; (x) DEAD/TPP, NH_3aq.

FIGURE 2. Synthetic route to the chiral moities **4** and **6**.

EXPERIMENTAL

The liquid crystalline textures were observed with an Olympus BH-2 polarizing microscope equipped with a set of cross-polarizers and a Mettler model FP-52 hot stage apparatus. The phase transition temperatures (clearing temperatures and smectic transitions) were determined with a Perkin Elmer differential scanning calorimeter DSC 7 equipped with a thermal analysis controller TAC 7/DX and also by a polarizing microscope described above. The heating and cooling curves were collected at rates of 2 and 10°C/min, in a nitrogen atmosphere. ^1H-NMR (chemical shifts measured in deuterated solvents are given in ppm from TMS) and ^{19}F- NMR ($CFCl_3$ as internal reference) spectra were recorded at room temperature with a Bruker AC 200 MHz spectrometer, using $CDCl_3$ and CD_3COCD_3 solutions (5-10 wt%). Mass spectra were run on a Finnigan Mat INCOS 500 E mass spectrometer coupled with a gas chromatography (Varian 3400). Distillations were performed owing to a Kugelrohr Aldrich with an Alcatel pump 2004 A. All final compounds give satisfactory elemental analysis. All reagents were purchased from Aldrich and were used without further purification.

1-ethyloxycarbonyl-1-methyl-(S)-methyl-4-(4-*F*-hexylethyl carbonyloxyphenyl)benzoate (9)

A solution of 3-*F*-hexylpropanoic acid ($1.0\ 10^{-2}$ mol.) previously prepared[9], dicyclohexylcarbodiimide (DCC) ($1.0\ 10^{-2}$ mol.), 4-(N,N-dimethylamino)pyridine (DMAP) ($1.0\ 10^{-3}$ mol.) and compound **6** ($1.0\ 10^{-2}$ mol.) in dry dichloromethane (25 ml) was stirred for 12 h at room temperature. The reaction mixture was then filtered and the solvent was removed under vacuum to give a colorless solid. The residue was purified by column chromatography on silica gel with chloroform as eluent to yield the pure compound **9** as a white solid (table 1). ^{1}H NMR ($CDCl_3$ / TMS) δ (ppm) : 1.19 (t, 3H, $^{3}J_{HH}$=7.4Hz); 1.61 (d, 3H, $^{3}J_{HH}$=6.7Hz); 2.61 (tt, 2H, $^{3}J_{HH}$=6.3Hz, $^{3}J_{HF}$=18.6Hz); 2.97 (t, 2H, $^{3}J_{HH}$=6.3Hz); 4.19 (q, 2H, $^{3}J_{HH}$=7.4Hz); 4.81 (q, 1H, $^{3}J_{HH}$=6.7 Hz); 7.10 (d, 2H, $^{3}J_{HH}$=8.7Hz); 7.51 (m, 4H); 8.11 (d, 2H, $^{3}J_{HH}$=8.7Hz); ^{19}F NMR (CDC13): -81.3 (m, CF_3); -114.6 (m, CF_2); -122.4 (m, CF_2); -123.3 to -124.0 (m, 4F, CF_2); -126.6 (m, CF_2); MS (70 eV); m/z (%) : 688 (1.3).

1-ethyloxycarbonyl-1-methyl-(S)-methyl-4-(4-*F*-hexylethyl oxycarbonylmethoxyphenylcarbonyloxy)benzoate (10)

A solution of 4-*F*-hexylethyloxycarbonylmethoxybenzoic acid ($1.2\ 10^{-2}$ mol.) previously prepared from standard procedures, dicyclohexyl carbodiimide ($1.2\ 10^{-2}$ mol.), 4-(N,N-dimethylamino)pyridine ($1.2\ 10^{-3}$ mol.) and compound **4** ($1.2\ 10^{-2}$ mol.) in dry dichloromethane (25 ml) was stirred for 12 h at room temperature. The reaction mixture was then filtered and the solvent was removed under vacuum to give a colorless solid. The residue was purified by column chromatography on silica gel with dichloromethane as eluent to yield the pure compound **10** as a white solid (table 1). ^1H NMR ($CDCl_3$ / TMS) δ (ppm) : 1.19 (t, 3H, $^3J_{HH}$=7.4Hz); 1.61 (d, 3H, $^3J_{HH}$=6.7Hz); 2.41 (tt, 2H, $^3J_{HH}$=6.6Hz, $^3J_{HF}$= 18.8Hz); 4.19 (q, 2H, $^3J_{HH}$=7.4Hz); 4.48 (t, 2H, $^3J_{HH}$=6.6Hz); 4.65 (s, 2H); 6.85 (d, 2H, $^3J_{HH}$=8.4Hz); 7.53 (m, 4H); 8.11 (d, 2H, $^3J_{HH}$=8.7Hz); ^{19}F NMR (CDCl3): -81.3 (m, CF_3); -114.5 (m, CF_2); -122.4 (m, CF_2); -123.3 to -124.0 (m, 4F, CF_2); -126.6 (m, CF_2); MS (70 eV); m/z (%) : 718 (3.0).

1-ethyloxycarbonyl-1-methyl-(S)-methyl-4-(4-F-hexylethyl oxycarbonylmethoxyphenyl)benzoate (11)

2-*F*-hexylethylbromoacetate (2.0 10^{-3} mol.), previously prepared[10,11] from the reaction of 2-*F*-alkylethanol with bromoacetylbromide, in acetone was added to compound **6** (2.0 10^{-3} mol.) in a dilute suspension of potassium carbonate (4.0 10^{-3} mol.) in acetone. The reaction mixture was boiled for 12 hours, then filtered, and the solide 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 **11** as a white solid (table 1). ^1H NMR ($CDCl_3$ / TMS) δ (ppm) : 1.19 (t, 3H, $^3J_{HH}$=7.4Hz); 1.61 (d, 3H, $^3J_{HH}$=6.7Hz); 2.41 (tt, 2H, $^3J_{HH}$=6.6Hz, $^3J_{HF}$= 18.8Hz); 4.19 (q, 2H, $^3J_{HH}$=7.4Hz); 4.48 (t, 2H, $^3J_{HH}$=6.6Hz); 4.65 (s, 2H); 6.91 (d, 2H, $^3J_{HH}$=8.6Hz); 7.29 (d, 2H, $^3J_{HH}$=8.5Hz); 8.11 (d, 2H, $^3J_{HH}$=8.5Hz); 8.26 (d, 2H, $^3J_{HH}$=8.6Hz); ^{19}F NMR ($CDCl_3$): -81.3 (m, CF_3); -114.6 (m, CF_2); -122.4 (m, CF_2); -123.4 to -124.0 (m, 4F, CF_2); -126.6 (m, CF_2); m/z (%) : 762 (4.1).

RESULTS AND DISCUSSIONS

The yields for the final compounds (**9-11**) are reported in table 1. Intermediates were prepared according to standard procedures described in figures 1 and 2. The synthetic route envisioned allows us to have high global yields.

TABLE 1 Yields for preparation of compounds **9**-**11**.

Cpd N°	*R_F value*	*yield %*		*mp (°C)±1°C†*
		final step	*global‡*	
9	C_6F_{13}	88	62	60
10	C_6F_{13}	91	57	104
11	C_6F_{13}	96	67	43

(†) from Bucchi-Tottoli apparatus; (‡) from raw fluorinated materials (iodide or alcohol).

The thermic data (temperatures and enthalpies) recorded from differential scanning calorimetry and thermal microscopy analysis for these new materials are summarized in Table 2. Comparison of the liquid crystal behavior of the synthesized compounds allowed us to evaluate the impact of the nature of molecular parameters. The biphenyl core affect in favorable manner the mesomorphic range. In both cases, for compounds **9** and **11** which differ by the nature of the spacer bounding the fluorinated tail to the rigid core, we observe a smectogenic behavior over a wide temperature range. The spacer of ester type (**9**) generate the widest mesomorphic behavior (74°C) while the oxycarbonylmethoxy (**11**) contribute to decrease both melting and clearing temperature. The great influence of these spacers (oxycarbonylmethoxy and carbonyloxy) is in good agreement with previous results[12,13]. For compound **10** no liquid crystal behavior was observed. The formal introduction, in compound **11**, of an ester function, between the two aromatic rings leading to compound **10**, increase the melting point above 100°C which could contribute to mask the liquid crystalline mesophase observed below 100°C for compound **11**.

TABLE 2 Phase transition temperatures obtained from compounds **9**-**11**.

Cpd N°	R_F value	C	transition temperatures (°C)†	S_A		I
9	C_6F_{13}	•	59.6 [27.95]	•	130.7 [9.03]	•
10	C_6F_{13}	•	103.3 [26.80]	-		•
11	C_6F_{13}	•	42.5 [15.90]	•	95.1 [10.77]	•

(†) from heating; figures in square brackets denote enthalpies of transition (kJ.g^{-1})

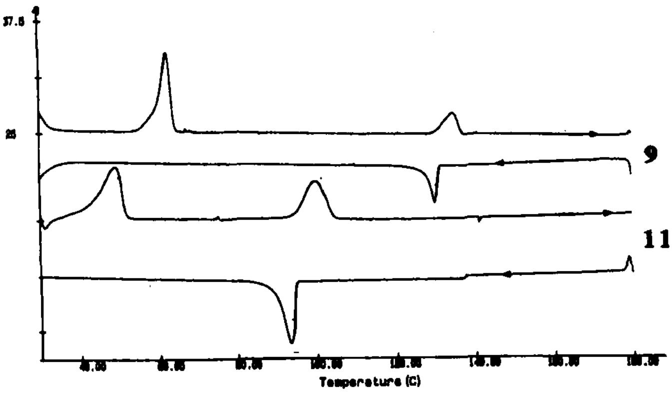


FIGURE 3 DSC curves for compounds **9** and **11** (heating and cooling rates : 10°C.min^{-1})

By optical observation, the mesophases of these two compounds (**9**,**11**) appear as rods on cooling from the isotropic melt and they coalesce to make well-developed fan shaped textures with focal conic domains that are characteristic of the layer structure of smectic mesophases. The miscibility studies carried out from standard materials show that the mesophases observed are of type smectic A.

Acknowledgments

The authors thank Atochem for the gift of 2-(*F*-hexyl)ethyl iodide and 2-(*F*-hexyl)ethanol.

References

[1] F. Guittard, E. Taffin de Givenchy, S. Geribaldi, A. Cambon, *J Fluorine Chem* **100**, 85 (1999) and references therein.
[2] S. Sarmento, P. Simeao Carvalho, M. Glogarova, M.R. Chaves, H.T. Nguyen, M.J. Ribeiro, *Liq Cryst* **25**, 375 (1998).
[3] E. Taffin de Givenchy, F. Guittard, S. Geribaldi, A. Cambon, *Mol Cryst Liq Cryst* **332**, 9 (1999).
[4] F. Guittard, P. Sixou, A. Cambon, *Mol Cryst liq Cryst* **308**, 83 (1997).
[5] S. Diele, D. Lose, H. Kruth, G. Pelzl, F. Guittard, A. Cambon, *Liq Cryst* **21**, 603 (1996).
[6] F. Guittard, S. Geribaldi, in "Anisotropic Organic Materials", ACS, (2000), in press.
[7] H. Liu, H. Nohira, *Liq Cryst* **24**, 719 (1998) and references therein.
[8] W.J. Cumming, R.A. Gaudiana, *Liq Cryst* **20**, 283 (1996).
[9] M.A. Jouani, F. Szonyi, A. Cambon, *J. Fluorine Chem* **56**, 85 (1992).
[10] A. Sismondi, P.S. Abenin, A. Cambon, (Atochem), Fr. pat. 88 17240 (1988).
[11] A. Sismondi, L. Joncheray, P.S. Abenin, A. Cambon, *J Fluorine Chem* **59**, 127 (1992).
[12] E. Taffin de Givenchy, F. Guittard, F. Bracon, A. Cambon, *Liq Cryst* **26**, 1371 (1999).
[13] E. Taffin de Givenchy, F. Guittard, F. Bracon, A. Cambon, *Liq Cryst* **26**, 1163 (1999).